

Anthony W. Addison

Professor Emeritus (Inorganic) Email: addisona@drexel.edu, Tel: 215-895-2646, <http://www.drexel.edu/coas/faculty-research/faculty-directory/addison-anthony/> B.Sc. (Hons-I), 1968, Univ. of New South Wales; Ph.D., 1971, U. of Kent at Canterbury; Postdoctoral Fellow, 1970-72, Northwestern U.; Assistant Professor, 1972-78, U. of British Columbia; Associate Prof., 1978-1991, Drexel U.; Professor, 1991–2017; Professor Emeritus, 2017-present.



• Prof. Tony Addison, Drexel's token Australian, is a C. & M. Lindback Distinguished Teaching Awardee, the recipient of the 2016 ACS Philadelphia Section Research Award, a *Fellow* of the Royal Society of Chemistry (2008), of the American Chemical Society (2012) and of the Royal Australian Chemical Institute (2016). He is a past Chairman of the ACS Philadelphia Section, and also a member of the Canadian Society for Chemistry and the International EPR Society. He is lead author of the most-cited article published by the RSC in the field of Inorganic Chemistry in the last 120+ years, as well as of several other highly-cited papers, including the most-cited one ever published in *Inorganica Chimica Acta*. His 140+ articles have garnered over 16,000 citations in the research literature, a Hirsch Index of $h=44$, an Egghe g -index of 130, a Google $i99$ of 17, and a Google $i10$ of 101. He is the coauthor of three books, co-editor of another, coauthor of six editions of a 1st-year lab manual and 134 conference presentations.

Recent Main Collaborators:

Prof. Vitaly V. Pavlishchuk (Pisarzhevskii Institute, Kyiv); Dr. Anya V. Pavlishchuk (Shevchenko State U. & Purdue U.); Prof. Raymond J. Butcher (Howard U.); Prof. GorDan T. Reeves (Stockton State U.); Prof. Mark M. Turnbull (Clark U.); Dr. Lena A. Mikhalyova (Pisarzhevskii Institute & U. of Giessen); Dr. Matt Zeller (Purdue U.); Prof. H-f. Ji (Drexel U.); Dr. Molly A. O'Connor (Community College of Philadelphia); Prof. E. Rentschler (Gutenberg U. of Mainz); Prof. Naresh A. Dalal (Florida State U.); Dr. Mohammad Nozari (Toronto, Ont.); Dr. Pedro E. Martins Amaral (Drexel U.: DUCoM).

Courses taught: CHEM774 *Electrochemistry for Chemists*; CHEM862 *Magnetism & Magnetic Resonance*; Chem101-2 First year Chemistry; CHEM421 *Inorganic-I*; CHEM420 *Molecular Symmetry & Group Theory*; CHEM422 *Inorganic-II*; CHEM521 *Inorganic-I*; CHEM522 *Inorganic-II*; CHEM523 *Inorganic-III*.

• Research Interests

Design, synthesis and properties of novel chelating agents and of macrocyclic and oligonuclear metal complexes. Bioinorganic chemistry of metalloproteins, models for various properties of Fe, Cu, Ni and V centres in O₂-transporting and redox proteins. Electrochemistry, CD, EPR and magnetic properties of extended and molecular systems for thermal & photostimulated energy- and electron-transfer.

Recent Papers:

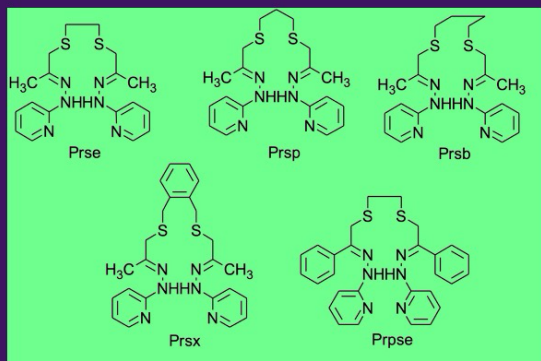
144. V.V. Pavlishchuk*, M.A. O'Connor, M. Zeller, R.J. Butcher & A.W. Addison, "A New Class of Hexadentate Thioether-Containing Ligands and Their Complexes with Nickel(II)" *Polyhedron* (2024) **256**, 116960.

A New Class of Hexadentate Thioether-Containing Ligands and Their Complexes with Nickel(II)

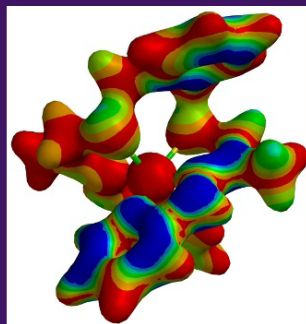
V.V. Pavlishchuk*, M.A. O'Connor, M. Zeller, R.J. Butcher & A.W. Addison

Polyhedron April 2024; doi: 10.16/j.poly.2024.116960

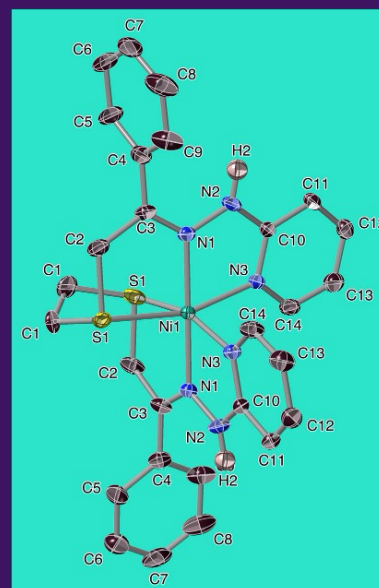
These light violet hexacoordinate, thioether/pyridyl-hydrazone ligated, high-spin, dicationic complexes of Ni(II) possess slightly distorted pseudo-octahedral geometries. DFT results indicate that the two SOMOs have mainly ligand character, associated with the delocalising imine and thioether moieties. Reduction to Jahn-Teller distorted Ni(I) occurs irreversibly at *ca.* -1 V vs. the APE, along with catalytic H₂ production arising from the hydrazone N-H units.



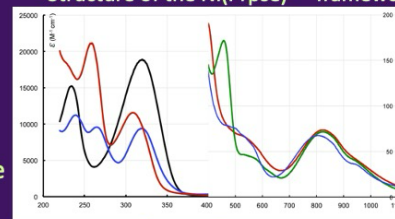
The dithioether-bis(pyridyl)hydrazone ligands



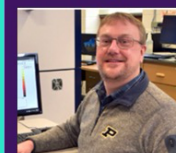
Upper SOMO density for Ni(Prsx)²⁺. Note the low density (red) on the central Ni



Structure of the Ni(Prpse)²⁺ framework



Electronic spectra



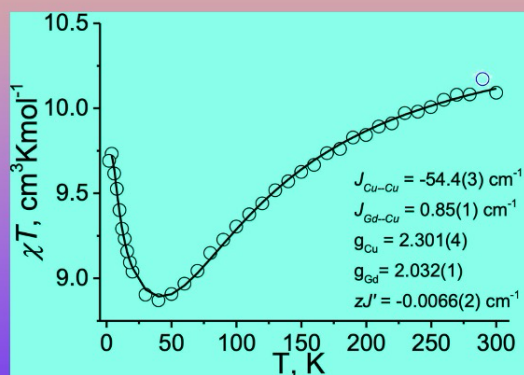
143. A.V. Pavlishchuk*, M. Zeller, L.M. Carrella, E. Rentschler, J. Kaur, N.S. Dalal, J. Kinyon, K. Perera, V.V. Pavlishchuk & A.W. Addison. "Structural and Magnetic Properties of a $\{GdCu_5\}_2$ Metallacrown Dimer with a Disulfonate Linker" *European Journal of Inorganic Chemistry* (2024) **27**, e202300544.

Structural and Magnetic Properties of a $\{GdCu_5\}_2$ Metallacrown Dimer with a Disulfonate Linker

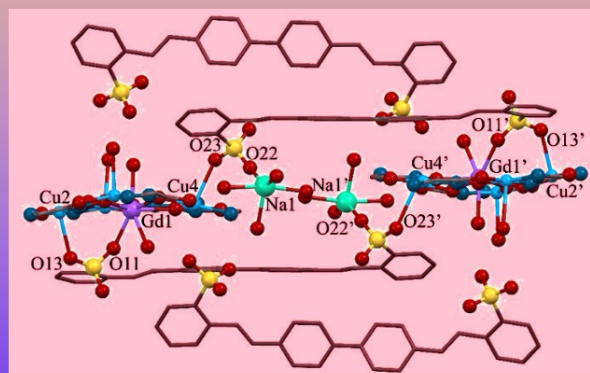
A.V. Pavlishchuk, M.Zeller, L.M. Carrella, E. Rentschler, J.K. Bindra, N.S. Dalal, J. Kinyon, K. Perera, V.V. Pavlishchuk & A.W. Addison
A collaboration involving seven laboratories in the U.S., Ukraine and Germany

European Journal of Inorganic Chemistry (2023) doi: 10.1002/ejic.202300544

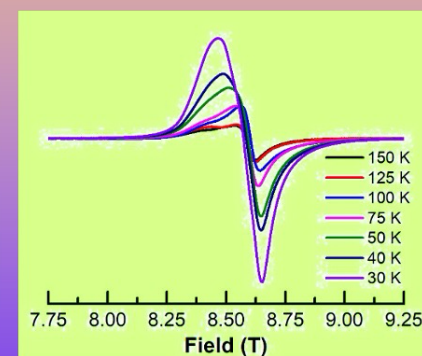
The Cu_5 glycinehydroxamate metallacrown unit binds a central gadolinium(III) ion. Waters and sulfonate O-donors from bis(2-sulfonatostyryl)biphenyl anions coordinate to the Gd. Within the resulting digadolinium assembly, the $Cu(II)_5$ are strongly antiferromagnetically coupled, while each octacoordinate Gd is weakly ferromagnetically coupled to the Cu_5 unit, yielding an $S=8/2$ ground state. This serves as a reference system for other lanthanide complexes in which the $Ln(III)$, unlike the Gd, also possess *orbital* contributions to their magnetism.



Variable-T magnetic properties (χT)



The 'side-by-side' sulfonate-bridged dinuclear system.



240 GHz EPR spectrum at various temperatures.

142. A.W. Addison, R.J. Butcher & M.M. Turnbull*, "A copper(II) coordination polymer of formate-bridged dimers: an alternating $S = \frac{1}{2}$ antiferromagnetic chain". *Journal of Coordination Chemistry* (2023), [doi: 10.1080/00958972.2023.2176227]

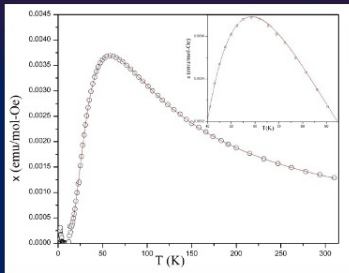
A copper(II) coordination polymer of formate-bridged dimers: an alternating $S = \frac{1}{2}$ antiferromagnetic chain

A.W. Addison, R.J. Butcher & M.M. Turnbull*

Journal of Coordination Chemistry (2023) 76(3–4), 403–413

With 1,3-diaminopropane in basic solution in the presence of *o*-iodophenol and the dehydrant trimethyl orthoformate, copper(II) perchlorate adventitiously formed the sodium salt of a formate-bridged copper polymer, rather than the intended phenolate complex. The formate anions bridge between coppers in two fashions.

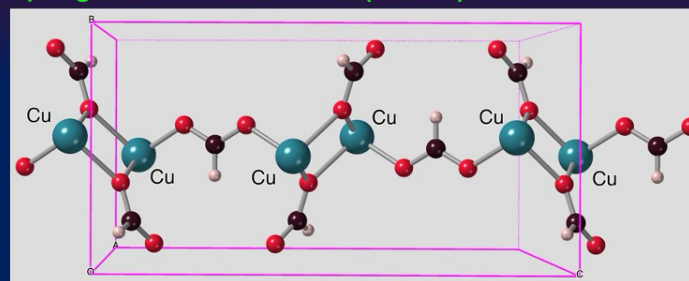
Magnetic measurements down to 1.8 K show the presence of strong antiferromagnetic coupling, especially through the monoatomic formate O-bridges. The data were modeled equally well by an alternating chain model or a dimer model with a term for weak inter-dimer interactions, yielding a major coupling of $J = -66(6) \text{ cm}^{-1}$ and a minor one of $J' = -2(1) \text{ cm}^{-1}$, using a "1J" coupling Hamiltonian $\mathcal{H} = -J(S_1.S_2)$.



The plunge to low susceptibility near 2 K betokens the antiferromagnetism.



This what the crystals look like !



The Cu(II) polymer chain snaking along the *c*-direction through the lattice. Note the two different types of formate bridges.

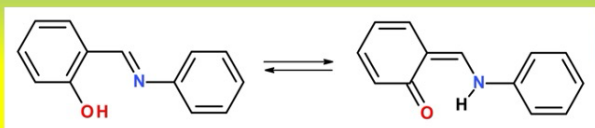
141. A. Mikhalyova*, K.V. Borysova, E.A. Goreshnik & A.W. Addison "Spectral and Luminescence Properties of Mixed-Ligand Eu^{3+} and Tb^{3+} complexes with Tris(3-[2'pyridyl]pyrazolyl)borate and Carboxylates Containing a Salicylideneimine Fragment", *Theoretical and Experimental Chemistry* (2023), 58(6) 409-416 (doi [10.1007/s11237-023-09756-7](https://doi.org/10.1007/s11237-023-09756-7)) *Teoretychna ta Eksperymentalna Khimiya* (2022), 58(6).

Spectral and Luminescence Properties of Mixed-Ligand Eu^{3+} and Tb^{3+} complexes with Tris(3-[2'pyridyl]pyrazolyl)borate and Carboxylates Containing a Salicylideneimine Fragment

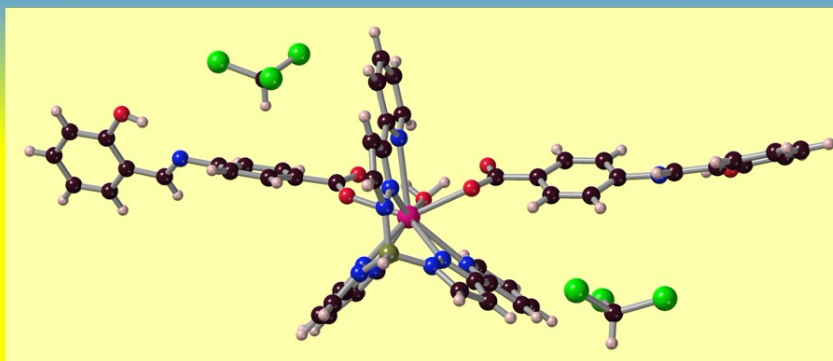
Elena A. Mikhalyova*, K.V. Borysova, E.A. Goreshnik & A.W. Addison

Theoretical & Experimental Chemistry (2023) 58(6) 409-416

Designing of controllable luminescent materials led us to europium(III) & terbium(III) ternary complexes, made by using the tris(3-[2'-pyridyl]pyrazolyl)borate "tripod" ligand and carboxylate Schiff base imines, prepared by the reaction of 4- or 3-aminobenzoic acids with salicylaldehyde. The complexes exhibit both broad ligand-centred and narrow metal-centred emission, with energy transfer from ligand to metal occurring. Under UV-irradiation, the ligands exhibit *photochromism* – their spectra change over several minutes of time. These changes are quasi-reversible, and are attributed to tautomerisation of the salicylidene fragments.



The known imine-phenol \rightleftharpoons amine-quinone phototautomerism for the organic moieties which are part of the ligands.



Structure of the chloroform-solvated europium(III) complex. The "wings" are the phenolic iminobenzoate ligands.

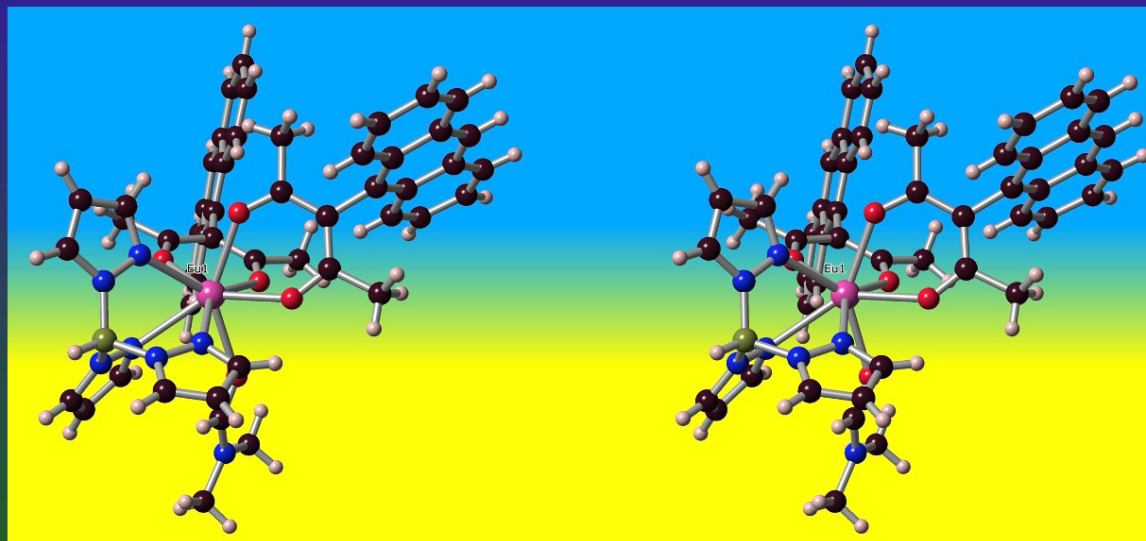
140. E.A. Mikhalyova*, M. Zeller, J.P. Jasinski, M. Kaur, & A.W. Addison, "Bis(3-(9'-anthracenyl)pentane-2,4-dionato)(*N,N*-dimethylformamide-*O*)(tris[pyrazol-1-yl- κ N(2)]hydroborato)europium(III)", *Acta Crystallographica* (2022) **E78**(2), 103-107. [doi: [10.1107/S2056989022000676](https://doi.org/10.1107/S2056989022000676)] *J. Jasinski Tribute issue*.

*Bis(3-(9'-anthracenyl)pentane-2,4-dionato)(*N,N*-dimethylformamide-*O*)- (tris[pyrazol-1-yl- κ N²]hydroborato)europium(III)*

E.A. Mikhalyova, M. Zeller, J.P. Jasinski, M. Kaur & A.W. Addison*

Acta Crystallographica (2022) **E78**, 103-107 doi: [10.1107/S2056989022000676](https://doi.org/10.1107/S2056989022000676) (*Jasinski tribute issue*)

The title compound was prepared by reaction of a tris(pyrazolyl)borate Eu³⁺-complex with an anthracene-substituted β -diketone anion. The eventual interest here is in the luminescence properties of this molecule, with its potentially efficient anthracene 'antenna' design - a pursuit interrupted by Goatshagger Putin on Feb. 24th. The Eu³⁺ has octavertex square-pyramidal eight-coordination. As we anticipated, there are parallel alignments of the large aromatic groups in the lattice, but for the most part, actual intermolecular π - π^* stacking interactions are limited to the edges of two anthracene rings. Intramolecularly, the anthracenes and nearly planar acetylacetonate fragments are all roughly mutually orthogonal.



Structure of the Eu(III) molecule (inverse stereoview).

EA. Mikhalyova*, M. Zeller, E.A. Goreshnik, J.P. Jasinski, R.J. Butcher, Y.V. Nelyubina, J.L. Hunter, A.E. Sedykh, S.V. Shishkina, K. Müller-Buschbaum, I.L. Eremenko, A.W. Addison, & V.V. Pavlishchuk*, "Lanthanide complexes with 4,4'-bis(2-sulfonatostyryl)-biphenyl: crystal structures and luminescence properties". *European Journal of Inorganic Chemistry* (2021) 22(4). [doi: [10.1002/ejic.202100941](https://doi.org/10.1002/ejic.202100941)]

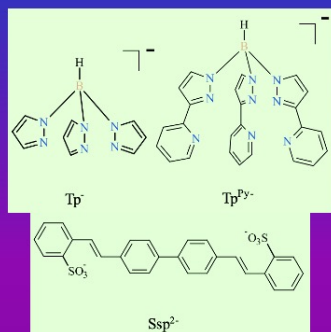
Lanthanide complexes with 4,4'-bis(2-sulfonatostyryl)-biphenyl: crystal structures and luminescence properties: Where will excitation and emission occur ?

E.A. Mikhalyova*, M. Zeller, E.A. Goreshnik, J.P. Jasinski, R.J. Butcher, Y.V. Nelyubina, J.L. Hunter, A.E. Sedykh, S.V. Shishkina, K. Müller-Buschbaum, I.L. Eremenko, A.W. Addison, & V.V. Pavlishchuk*

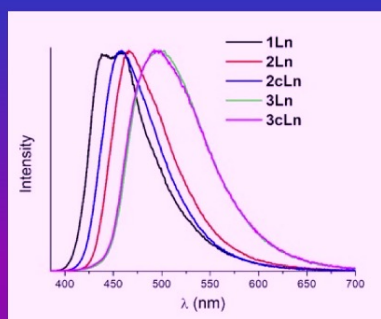
An international collaboration involving eleven laboratories.

The European Journal of Inorganic Chemistry (2021) 22(4); doi: 10.1002/ejic.202100941

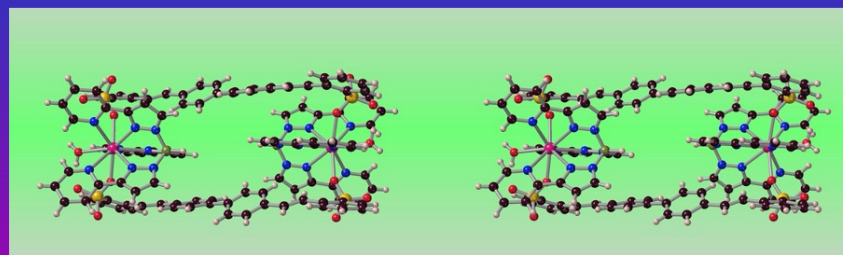
A series of new tris(pyrazolyl)borate (Tp^-) and tris(2-pyridylpyrazolyl)borate (TpPy) Eu^{3+} , Gd^{3+} , Tb^{3+} and Dy^{3+} complexes with the dianionic ligand 4,4'-bis(2-sulfonatostyryl)biphenyl (Ssp^{2-} , a widely used whitening agent) were synthesized and their luminescence properties were studied. The Gd^{3+} , Tb^{3+} and Dy^{3+} compounds possess only Ssp -ligand-centered emission, with high quantum yields, up to 60%. The emission quantum yields and lifetimes change in the order $[(\text{Tp}_2\text{Ln})_2\text{Ssp}] < [(\text{TpPyLnSsp})_2] < [\text{Ln}_2\text{Ssp}_3]_n$. Ln^{3+} -centered emission was observed for only $[(\text{Tp}_2\text{Eu})_2\text{Ssp}]$, in which Tp^- plays the role of an "antenna" ligand.



The ligands



The "organic"-shaped emission spectra



The adequately complicated structure of the dinuclear terbium complex

A.W. Addison*, S.J. Jaworski, J.P. Jasinski, M.M. Turnbull, F. Xiao, M. Zeller, M.A. O'Connor & E.A. Brayman, "Chlorocobalt(II) complexes with pyridylethyl-derived diazacycloalkanes". *Acta Crystallographica* (2022) **E78(3)**, 000-000. [[doi: 10.1107/S2056989022001220](https://doi.org/10.1107/S2056989022001220)] *J. Jasinski Tribute issue.*

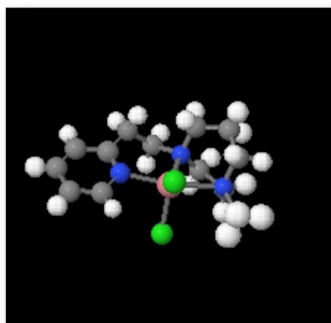
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March 2022 issue



A.W.A.



S.J.J.



M.M.T.



M.Z.



M.A.O.

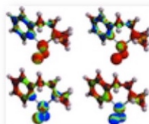


E.A.B.

Cover illustration: This issue contains an article that highlights just two of the things for which former *Acta E* Co-Editor Jerry P. Jasinski will always be remembered by the crystallographic community: his love for teaching and for scientific collaboration. In the paper by Addison *et al.*, the structures of four Co complexes with pyridylethyl-derived diazacycloalkanes are presented. The Co atoms display tetrahedral and trigonal-bipyramidal coordination. The use of Vis and NIR electronic spectra to differentiate these coordination geometries is presented. Solvophobicity of the Cl atoms present in the coordination sphere of Co plays a role in the different coordination geometries. The structures are sustained by weak, non-bonding interactions. Mono and di-nuclearity are also displayed by these compounds and the magnetic behaviour is attributed to zero-field splitting of the Co ion since there is no evidence of SMM behaviour. See: Addison, Jaworski, Jasinski, Turnbull, Xiao, Zeller, O'Connor & Brayman [*Acta Cryst.* (2022). **E78**, 235–243].

Jerry P. Jasinski tribute

Acta Cryst. (2022). **E78**, 235–243
<https://doi.org/10.1107/S2056989022001220>



Chlorocobalt complexes with pyridylethyl-derived diazacycloalkanes

A. W. Addison, S. J. Jaworski, J. P. Jasinski, M. M. Turnbull, F. Xiao, M. Zeller, M. A. O'Connor and E. A. Brayman

With cobalt(II) chloride, some piperazine- and homo-piperazine-derived ligands yield tetra- or pentacoordinate complexes. Observed variations in coordination number are ascribed as being related to chloride solvophobicity. Optical spectra are presented, while magnetism measurements indicate governance of the magnetism by zero-field splitting of the cobalt ion.

CCDC references: 2111922; 2111921; 2111920; 2111919

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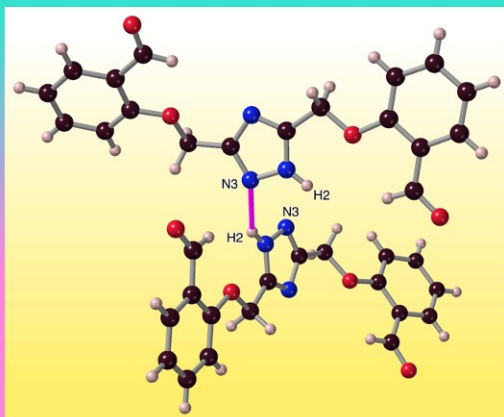
S. Elshani, J.P. Jasinski, A.W. Addison* and G.T. Reeves, "Two Bifunctionalised Derivatives of 1,2,4-Triazole". *Journal of Chemical Crystallography* (2022). [doi: [10.1007/s10870-021-00916-y](https://doi.org/10.1007/s10870-021-00916-y)] *J. Jasinski Tribute issue*.

Two Bifunctionalised Derivatives of 1,2,4-Triazole

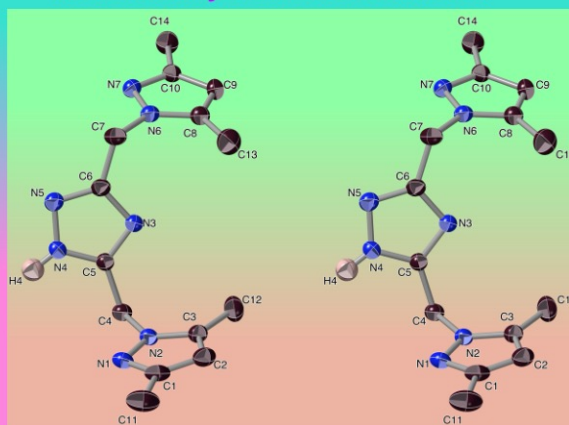
S. Elshani, J.P. Jasinski, A.W. Addison* & G.T. Reeves

Journal of Chemical Crystallography (2022) [doi: [10.1007/s10870-021-00916-y](https://doi.org/10.1007/s10870-021-00916-y)] *J.P. Jasinski Tribute issue*.

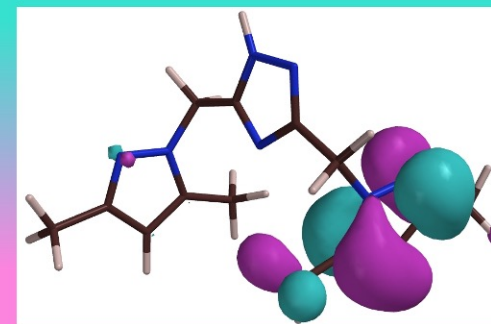
In the aldehyde 3,5-bis[2-(2'-formylphenoxy)methyl]-1,2,4-triazole and the pyrazole 3,5-bis[(3',5'-dimethyl)methylpyrazol-1'-N-yl]-1,2,4-triazole, the triazole N-H moiety forms hydrogen bonds, and is not disordered, so that individually chiral conformations are molecularly twisted. The H-bonding leads to noteworthy self-associations.



Aldehyde H-bonded dimer



The dipyrazole
(inverse stereoview)



The dipyrazole's HOMO –
note its confinement.

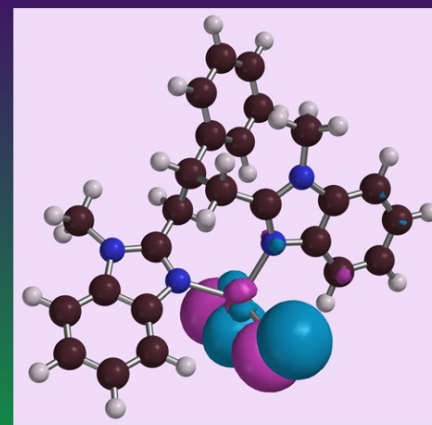
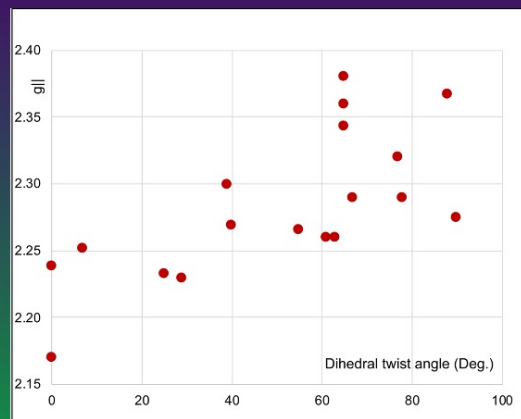
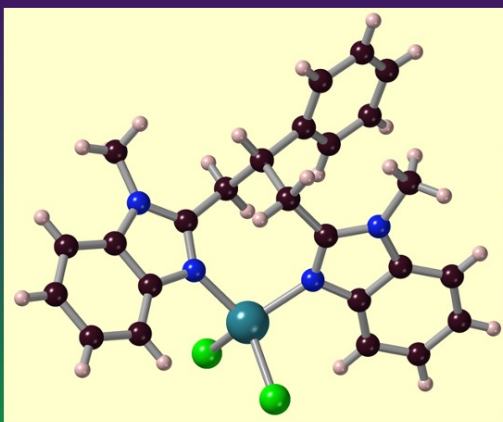
P.E.M. Amaral, M. Zeller, M. Nozari, & A.W. Addison*, "1,3-Bis(*N*-methylbenzimidazol-2'-yl)-2-phenylpropanedichloridocopper(II)" *Journal of Chemical Crystallography* (2022) [doi: [10.1007/s10870-021-00914-0](https://doi.org/10.1007/s10870-021-00914-0)] *J. Jasinski Tribute issue*.

1,3-bis(*N*-methylbenzimidazol-2'-yl)-2-phenylpropanedichloridocopper(II)

P.E.M. Amaral, M. Zeller, M. Nozari & A.W. Addison*

Journal of Chemical Crystallography (2022) doi.org/10.1007/s10870-021-00914-0

This orange complex of copper(II) chloride with a bidentate bis(*N*-methylbenzimidazole) ligand crystallises racemically. The CuN_2Cl_2 coordination core has flattened tetrahedral geometry, with the ligand forming an eight-membered chelate ring. We show that EPR g_{\parallel} -values for such CuN_2Cl_2 centres increase with increasing coordination core twist angle. The absorption spectrum displays visible-region bands which DFT calculations suggest are combinations of d-d, LMCT and MLCT components.



The SOMO

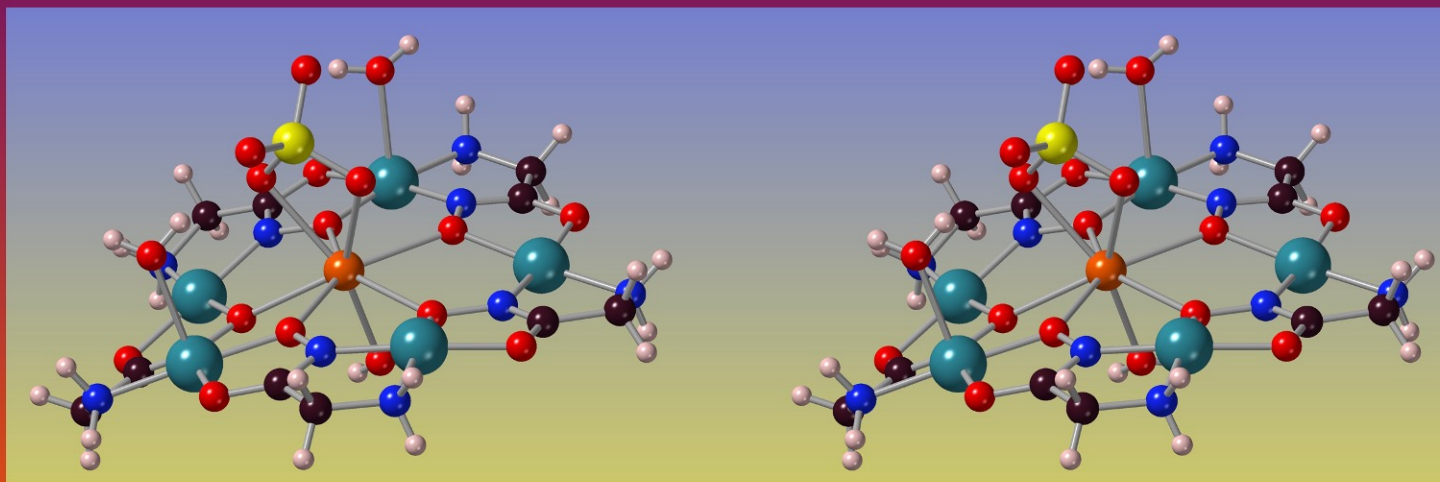
A.V. Pavlishchuk*, I.V. Vasylenko, M. Zeller & A.W. Addison, "Crystal structure of a Tb(III)-Cu(II) glycinehydroxamate 15-metallacrown-5 sulphate complex" *Acta Crystallographica* (2021) E77, 1197-1202. [doi: [10.1107/S2056989021011464](https://doi.org/10.1107/S2056989021011464)] *J.P. Jasinski Tribute Issue*.

Crystal structure of a Tb(III)-Cu(II) glycinehydroxamate 15-metallacrown-5 sulphate complex

A.V. Pavlishchuk*, I.V. Vasylenko, M. Zeller & A.W. Addison

Acta Crystallographica (2021) E77, 1197-1202; *J.P. Jasinski Tribute Issue*

The core of the complex consists of five glycinehydroxamate dianions (GlyHA²⁻) and five Cu(II) ions linked together in a metallamacrocyclic moiety. In [TbCu₅(SO₄)(GlyHA)₅(H₂O)_{6.5}]₂(SO₄).6H₂O, terbium(III) is bound to the centre of the structure through five hydroxamate oxygens. The Tb³⁺ is square-antiprismatic octacoordinate, via the additional apical O-atoms of a bidentate sulfate and a water molecule, while the Cu(II) ions are square, penta- or hexacoordinate via apical water coordination. The positive charge of each pair of [TbCu₅(GlyHA)₅(H₂O)(SO₄)]²⁺ fragments is compensated by a non-coordinated sulfate anion. The complex is isomorphous with the known analogues with Pr, Nd, Sm, Eu, Gd, Dy and Ho.



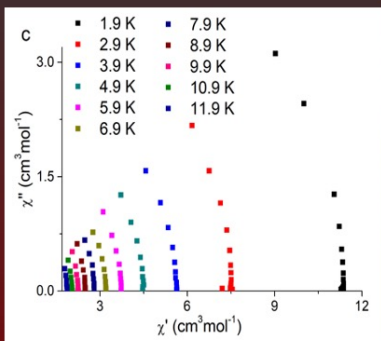
E.A.Mikhalyova, M.Zeller, J.P.Jasinski, R.J.Butcher, L.M.Carrella, A.E.Sedykh,, K.S.Gavrilenko, S.S.Smola, M.Frasso, S.C.Cazorla, K.Perera, A.Shi, H.G.Ranjbar, C.Smith, A.Deac, Y.Liu, S.M.McGee, V.P.Dotsenko, M.U.Kumke, K.Müller-Buschbaum, E.Rentschler, A.W.Addison* & V.V.Pavlishchuk*, "Combination of single-molecule magnet behaviour and luminescence properties in a new series of lanthanide complexes with tris(pyrazolyl)borate and oligo(β -diketonate) ligands" *RSC Dalton Transactions* (2020) [doi: 10.1039/D0DT00600A]

Combination of single-molecule magnet behaviour and luminescence properties in a new series of lanthanide complexes with tris(pyrazolyl)borate and oligo(β -diketonate) ligands

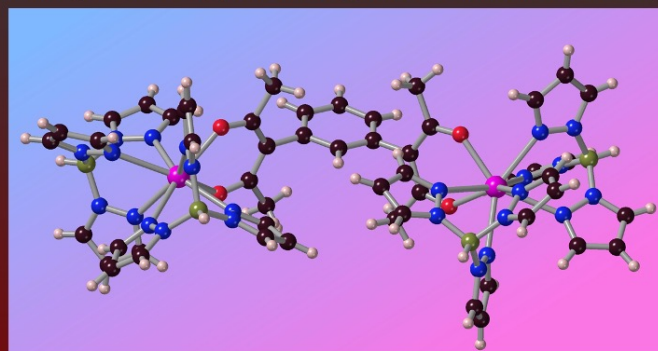
E.A.Mikhalyova, M.Zeller, J.P.Jasinski, R.J.Butcher, L.M.Carrella, A.E.Sedykh,, K.S.Gavrilenko, S.S.Smola, M.Frasso, S.C.Cazorla, K.Perera, A.Shi, H.G.Ranjbar, C.Smith, A.Deac, Y.Liu, S.M.McGee, V.P.Dotsenko, M.U.Kumke, K.Müller-Buschbaum, E.Rentschler, A.W.Addison* & V.V.Pavlishchuk*
A collaboration involving ten laboratories in the U.S., Ukraine and Germany

Dalton Transactions (2020) doi: 10.1039/D0DT00600A

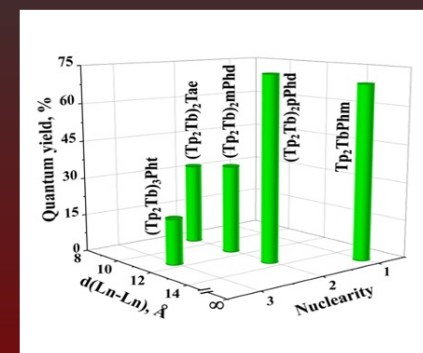
These ternary complexes, incorporating mono-, bis- & tris- β -diketonates with Eu^{3+} , Tb^{3+} and Dy^{3+} are luminescent, with quantum yields up to 73% for Tb^{3+} . The Dy^{3+} & Tb^{3+} complexes are also SMM's at low T. Having these two behaviours incorporated in the same molecule is an unusual situation. The octacoordinate bis-diketonate and tris-diketonate complexes are dinuclear and trinuclear respectively. Longer intramolecular metal-metal distances are advantageous for generating this combination of phenomena.



Out-of-phase vs in-phase ac hysteresis for a Dy-Dy complex.



The m -phenylene-bridged dinuclear terbium complex



Quantum yields summary for the Tb^{3+} systems

- G.T. Reeves*, A.W. Addison & M. Zeller, "Ruthenium(II) Complexes of the Tetradentate Polypyridyl Thioether 1,2-Bis[3'-(2''-pyridyl)-1'-thiopropyl]benzene", *Polyhedron* (2020) Article-114367 [<https://doi.org/10.1016/j.poly.2020.114367>].

Ruthenium(II) Complexes of the Tetradentate Polypyridyl Thioether 1,2-Bis[3'-(2''-pyridyl)-1'-thiopropyl]benzene

G.T. Reeves, A.W. Addison and M. Zeller

Polyhedron (2020) — <https://doi.org/10.1016/j.poly.2020.114367>

Reaction of the above novel tetradentate thioether, Ppes, with simple Ru(II) starting materials yields chloro-bridged dinuclear $[\{Ru(Ppes)\}_2(\mu-Cl)_2]^{2+}$ salts. In turn, their reaction with various bidentate diimines leads to mononuclear complexes of the form $[Ru(Ppes)(L)]^{2+}$, where L is the bidentate diimine, some of which are themselves novel. The dinuclear molecule below is dissymmetric and thus chiral.

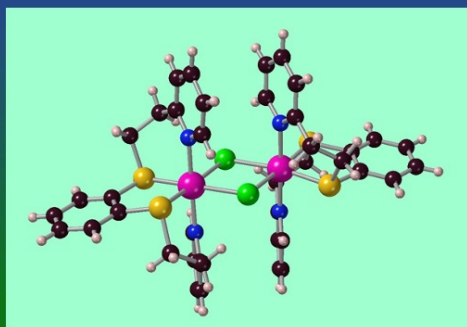
Electrochemistry reveals one-electron Ru(II)→Ru(III) oxidations over a wide range of potentials.



G.T.R.



A.W.A.



The RuPpes chloride dimer.



The mononuclear complex with the novel heterocycle 2-(2'-pyridyl)-1-methylindazole.

A plethora of outcomes for these molecules includes selective isomer formation, chiral molecules in racemic unit cells, the application of electrochemical $i:Q$ plots and redox potential vs. MLCT energy correlation.

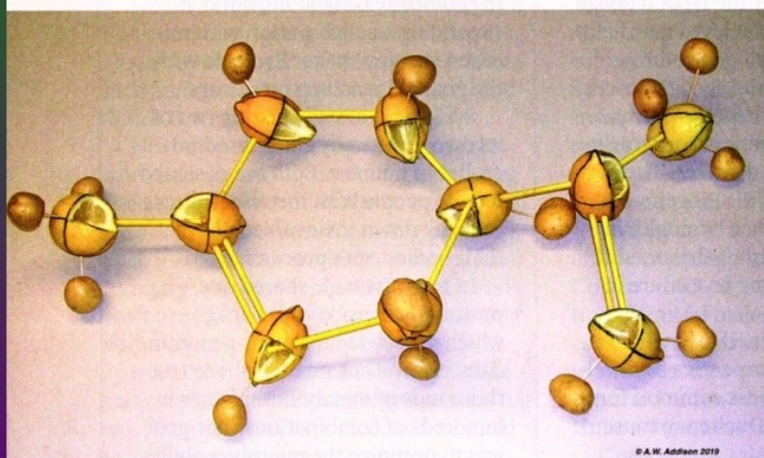
But before we go too much further:

Winner of the C&E News June 2019 Photo Contest.

CHEMISTRY IN PICTURES

Selections from cen.chempics.org,
where C&EN showcases the beauty of chemistry

Do science, take
pictures, win money.
Enter our photo contest at
cen.chempics.org or email
cenchempics@acs.org.



Structure refinement *in fructo*

Presenting the first almost*-all-natural 3-D structure of D-(+)-limonene. Mai-vy Nguyen assembled this thematic representation of the dominant component of citrus oil while a student in the Drexel University lab of Anthony Addison. For the structure, Nguyen used lemons as the carbons and potatoes as the hydrogens. Why potatoes? The team wanted something pale because crystal structures normally depict hydrogen atoms as white spheres. "Another reason is that the potatoes are firmer, whereas berries are softer and wouldn't hold as well," Addison says. "They were also more expensive."—CRAIG BETTENHAUSEN

*Save for some yellow paint on the bond sticks.

**Submitted by Mai-vy Nguyen and Anthony Addison,
Drexel University**

Maybe this is becoming a Drexel tradition ?

• J. Smith, P. Martins Amaral, D. Hagaman, A.W. Addison & H-F. Ji*, “Attaining Fine Hexagonal Nanostructures of SnP”, *Frontiers in Nanoscience & Nanotechnology* (2019) **5**, [doi: 10.15761/FNN.1000185]. (Note: the publisher failed to incorporate the corrections made on the galley proofs !)

• E.A. Mikhalyova, O.V. Khomenko, K.S. Gavrilenko, V.P. Dotsenko, A.W. Addison* & V.V. Pavlishchuk*, "Absorption- and excitation-modulated luminescence of Pr³⁺, Nd³⁺ and Lu³⁺ compounds with dianions of tetrafluoroterephthalic and camphoric acids" *ACS Omega* (Feb. 2019) [<http://dx.doi.org/10.1021/acsomega.8b02388>]

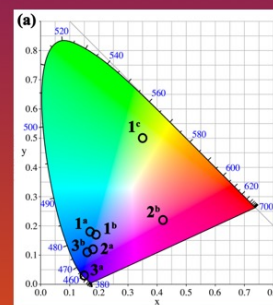
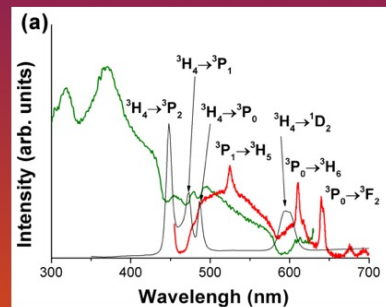
Absorption- and excitation-modulated luminescence of Pr³⁺, Nd³⁺ and Lu³⁺ compounds with dianions of tetrafluoroterephthalic and camphoric acids

E.A. Mikhalyova, O.V. Khomenko, K.S. Gavrilenko, V.P. Dotsenko, A.W. Addison* & V.V. Pavlishchuk*
ACS Omega (Feb. 2019) **4**(2), 2669-2675.

After previously describing some remarkable photon 'superantenna' capabilities of complexes of Eu³⁺ or Tb³⁺, we've now described the exact opposite - highly *ineffective* ligand 'antennæ'. Coordination polymers of Pr³⁺, Nd³⁺ and Lu³⁺ with tetrafluoroterephthalate and camphorate, Ln₂(Fbdc)₃(DMF)₂(H₂O)₂ and Ln₂(Camph)₂(NO₃)₂(MeOH)₄ display unconnected ligand-centred and metal-centred luminescence emission which depends on the excitation wavelength. A result is that the emitted light colour can be controlled. Pr³⁺ absorption exerts a *primary filtering effect* on the ligand-centred excitation, while a *secondary inner filter effect* changes the shape of the emission band, allowing observation of an unique purple emission, which is not normally seen.



E.A.M.



A.W.A. & V.V.P.

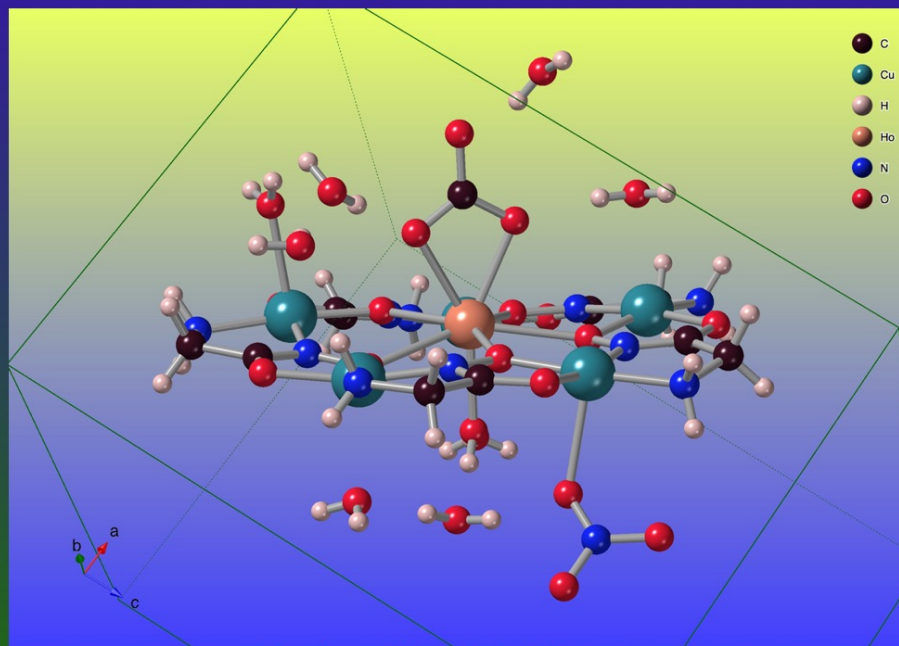
Note the emission (green) dip near 450 nm, due to Ln³⁺ absorption of ligand emission.

- A. Pavlishchuk*, D. Naumova, M. Zeller, S. Calderon Cazorla & A.W. Addison. "The crystal structures of $\{\text{LnCu}_5\}^{3+}$ (Ln = Gd, Dy and Ho) 15-metallacrown-5 complexes and a reevaluation of the isotypic Eu(III) analogue" *Acta Crystallographica* (2019) **E75**, 1215-1223 [[doi: 10.1107/S205698901900999X](https://doi.org/10.1107/S205698901900999X)] (Cover article)

The crystal structures of $\{\text{LnCu}_5\}^{3+}$ (Ln = Gd, Dy and Ho) 15-metallacrown-5 complexes and a reevaluation of the isotypic Eu(III) analogue

Anya V. Pavlishchuk, D. Naumova, M. Zeller, S. Calderon Cazorla and A.W. Addison
Acta Crystallographica (2019) **E75**, 1215-1223 (Issue cover article!)

Lanthanide(III) nitrates combine with the pentacopper metallacrown from glycinehydroxamate monoanion. Here, Gd^{3+} , Dy^{3+} or Ho^{3+} are bound by the crown O-donor groups in the centre of the macrocycle. In 1999, workers at the U. of Michigan indicated that for the isomorphous Eu^{3+} complex, the remaining anionic charges were provided by nitrate plus a coordinated hydroxide. However, recent experience at Drexel and our 'sister university' University in Kiev showed that the reaction media readily absorb atmospheric CO_2 , to yield carbonato-complexes. We see that there is a nitrate bound to one of the Cu^{2+} (front right), but that the previously supposed nitrate bound to Ln^{3+} is most likely a carbonate, and the "hydroxide" a water.



Anya P.



Matt Z.

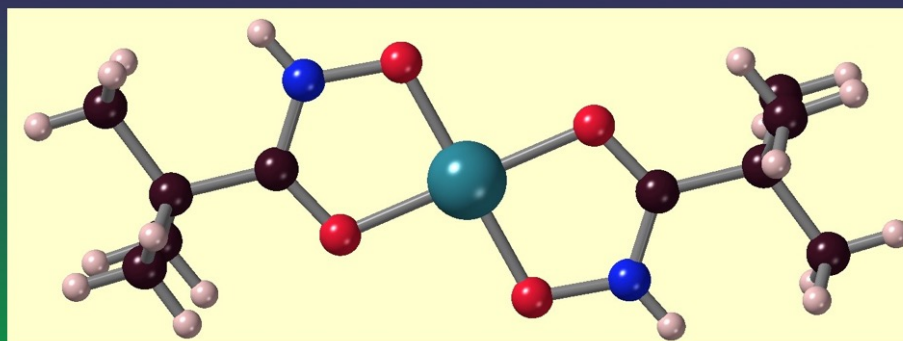
- K. Goleva, D. Naumova, A.V. Pavlishchuk*, M. Zeller & A.W. Addison*, “Crystal structure of bis-pivaloylhydroxamato-O,O'-copper(II)”. *Acta Crystallographica* (Sept. 2018) **E74**, 1384-1387 [<https://doi.org/10.1107/S2056989018012227>]

Crystal structure of bis(pivaloylhydroxamato- κ^2O,O')copper(II)

K.Goleva, D. Naumova, Anya V. Pavlishchuk,* M. Zeller & A.W. Addison*

Acta Crystallographica (2018) **74E**, 1384-1387

The now well-appreciated construction of metallacrown molecules from simple hydroxamate ligands such as glycinehydroxamate leads to questions about the effects of peripheral substitutions on their structures. For introduction of *t*-butyl substituents, reaction of copper(II) nitrate with pivaloylhydroxamic acid yielded the title compound, [Cu(pivHA)₂] (pivHA⁻ = (CH₃)₃C.CO.NH.O⁻). The centrosymmetric mononuclear complex consists of a Cu(II) ion coordinated by two hydroxamate monoanions, forming two O,O'-containing five-membered chelate rings. The copper(II) ion geometry is square-planar with the pivHA⁻ anions bound mutually *trans*. Hence, at this level of deprotonation, the otherwise typical tetra/pentacopper oligomerisation does not occur with R.CO.NH.O⁻ when R = *t*Bu



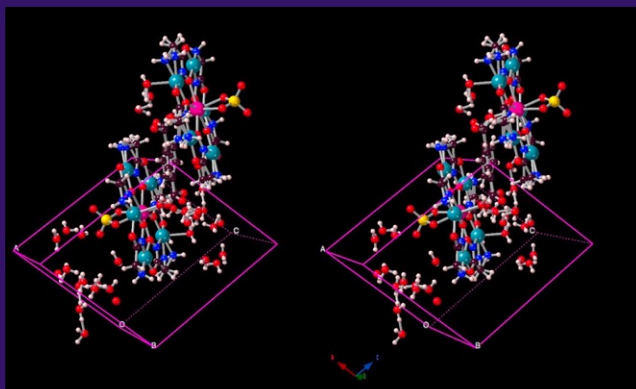
- A.V. Pavlishchuk*, S.V. Kolotilov, M. Zeller, S.E. Lofland & A.W. Addison,* "Magnetic Properties of Ln(III)-Cu(II) 15-Metallacrown-5 Dimers with Terephthalate (LnIII = Pr, Nd, Sm, Eu)", *The European Journal of Inorganic Chemistry* (May 2018), 3504-3511 [doi: [10.1002/ejic.201800461](https://doi.org/10.1002/ejic.201800461)]

Magnetic Properties of Ln(III)-Cu(II) 15-Metallacrown-5 Dimers with Terephthalate (Ln = Pr, Nd, Sm, Eu)

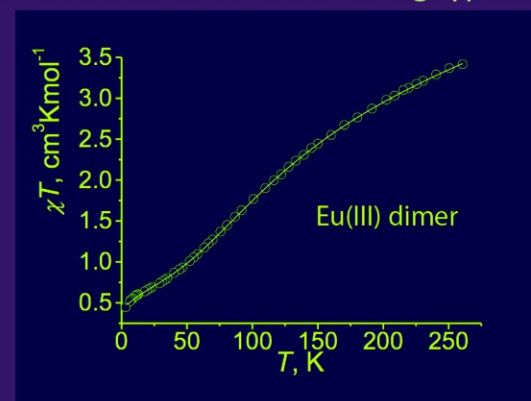
Anya V. Pavlishchuk,* S.V. Kolotilov, M. Zeller, S.E. Lofland & A.W. Addison*

The European Journal of Inorganic Chemistry (2018) doi: 10.1002/ejic.201800461

This represents another of our advances in the quantitative parameterisation of the magnetic properties of such Ln/Cu systems – a so far rare occurrence. The complexes are discrete dimers with two glycinehydroxamate 15-metallacrown-5 blocks $\{\text{LnCu}_5\}^{3+}$, a bridging terephthalate and an anion cap (CO_3^{2-} or SO_4^{2-}) on each Ln^{3+} . Intrametallacycle antiferromagnetism amongst the Cu^{2+} dominate the magnetic properties: $-2J_{\text{Cu-Cu}} = 88\text{--}120\text{ cm}^{-1}$. For the Ln^{3+} , SOC and crystal field effects are prominent, the g -factors, SOC λ - and axial CF Δ -values being typical.



Inverse stereo diagram of the Eu molecular cell



Antiferromagnetism of the di-crown Eu(III) dimer.

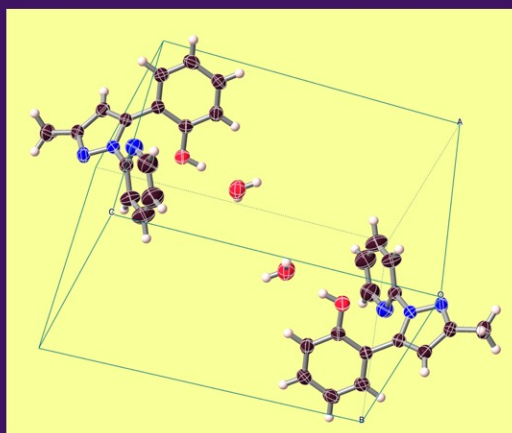
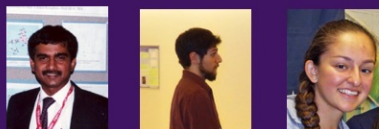
- M. Nozari, A.W. Addison*, G.T. Reeves, M. Zeller, J.P. Jasinski, M. Kaur, J.G. Gilbert, C.R. Hamilton, J.M. Popovitch, L.M. Wolf, L.E. Crist & N. Bastida, “New Pyrazole and Benzimidazole-Derived Ligand Systems”; *The Journal of Heterocyclic Chemistry* (2018), **55**(6), 1291-1307 [doi: [10.1002/jhet.3155](https://doi.org/10.1002/jhet.3155)]

New Pyrazole- and Benzimidazole-Derived Ligand Systems

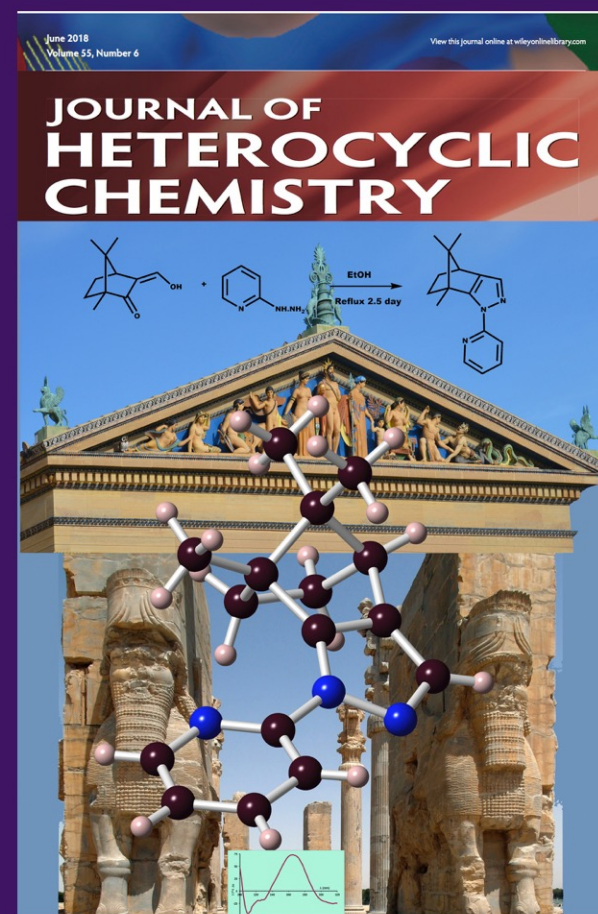
M. Nozari, A.W. Addison*, G.T. Reeves, M. Zeller, J.P. Jasinski, M. Kaur, J.G. Gilbert, C.R. Hamilton, J.M. Popovitch[†], L.M. Wolf[†], L.E. Crist[†] & N. Bastida[†]

JHC (2018) 55(6) 1291-1307 – doi: [10.1002/jhet.3155](https://doi.org/10.1002/jhet.3155) † Drexel undergrads.

This describes chelating agents of interest to Inorganic Chemists - our fourth paper in a series which has been cited >430 times so far. These compounds include pyridyl and phenolic molecules and several which are luminescent and/or conformationally or intrinsically chiral.



An enantiomeric pair of phenolic ligand molecules.



The cover Wiley asked for

Highly-Cited Papers:

- A.W. Addison*, T.N. Rao, J. Reedijk*, J. van Rijn and G.C. Verschoor, "Synthesis, Structure and Spectroscopic Properties of Copper(II) Compounds Containing Nitrogen-Sulphur Donor Ligands; the Crystal and Molecular Structure of Aqua[1,7-bis(*N*-methylbenzimidazol-2-yl)-2,6-dithiaheptane]-copper(II) Perchlorate", *The Journal of the Chemical Society, Dalton Transactions*, 1349-1356 (1984) [DOI: [10.1039/DT9840001349](https://doi.org/10.1039/DT9840001349)] *Over 9,400 citations.*

Synthesis, Structure, and Spectroscopic Properties of Copper(II) Compounds containing Nitrogen-Sulphur Donor Ligands; the Crystal and Molecular Structure of Aqua[1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) Perchlorate †

Anthony W. Addison* and T. Nageswara Rao

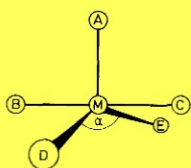
Department of Chemistry, Drexel University, Philadelphia, PA 19104, U.S.A.

Jan Reedijk,* Jacobus van Rijn, and Gerrit C. Verschoor

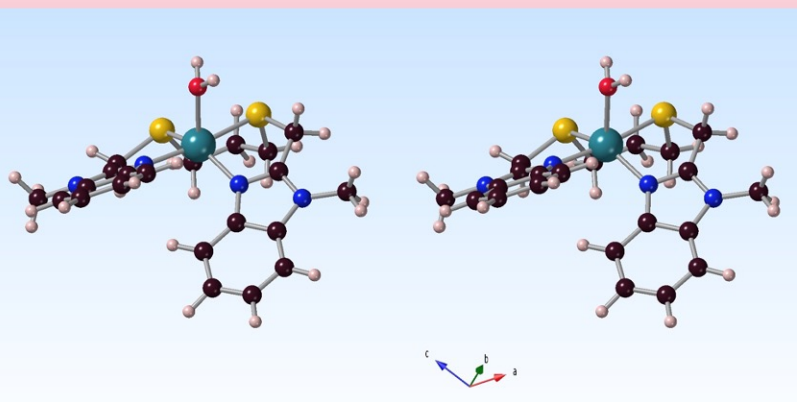
Department of Chemistry, State University of Leiden, 2300 RA Leiden, The Netherlands

The title compound served as a model for the copper(II) centre in the Type-I cuproprotein azurin, but a greater impact derived from our introduction of the structural index parameter τ , which describes the geometry of pentacoordinate centres.

In a five-co-ordinate system such as that represented below, ideally square-pyramidal geometry is associated with $\alpha = \beta = 180^\circ$, for A as the axial ligand (β is the greater of the basal angles, BMC). For perfectly trigonal-



bipyramidal geometry, α becomes 120° and BMC the principal axis. In the great majority of real square-pyramidal systems M is displaced out of the BCDE plane²⁷ toward A, so that these C_{4v} geometries usually have $\alpha = \beta < 180^\circ$, and can be characterised by the value of $(\beta - \alpha)$, which is 0° for a C_{4v} , and 60° for a D_{3h} co-ordination polyhedron. We thus define the geometric parameter $\tau = (\beta - \alpha)/60$ which is applicable to five-co-ordinate structures as an index of the degree of trigonality, within the structural continuum between trigonal bipyramidal and rectangular pyramidal. For a perfectly tetragonal geometry τ is equal to zero, while it becomes unity for a perfectly trigonal-bipyramidal geometry.



Right-handed enantiomer of the title complex

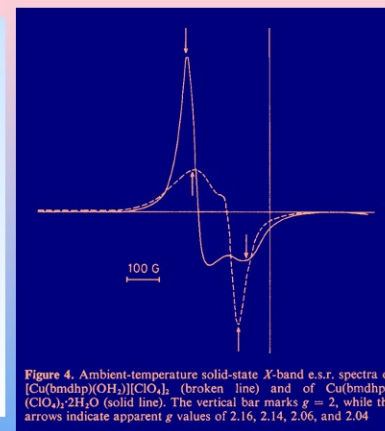


Figure 4. Ambient-temperature solid-state X-band e.s.r. spectra of $[\text{Cu}(\text{omdhp})(\text{OH}_2)](\text{ClO}_4)_2$ (broken line) and of $\text{Cu}(\text{omdhp})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (solid line). The vertical bar marks $g = 2$, while the arrows indicate apparent g values of 2.16, 2.14, 2.06, and 2.04

EPR spectra of the two subtly different forms

- V. V. Pavlishchuk and A. W. Addison, "Conversion Constants for Redox Potentials Measured vs. Different Reference Electrodes in Acetonitrile Solutions at 25 °C", *Inorganica Chimica Acta*, **298**, 97-102 (2000) [DOI: [10.1016/S0020-1693\(99\)00407-7](https://doi.org/10.1016/S0020-1693(99)00407-7)] *Over 1,200 citations; the most highly-cited paper ever published in this journal.*

Conversion constants for redox potentials measured versus different reference electrodes in acetonitrile solutions at 25°C

Vitaly V. Pavlishchuk ^a, Anthony W. Addison ^{b,*}

Inorganica Chimica Acta (2000) **298**, 97

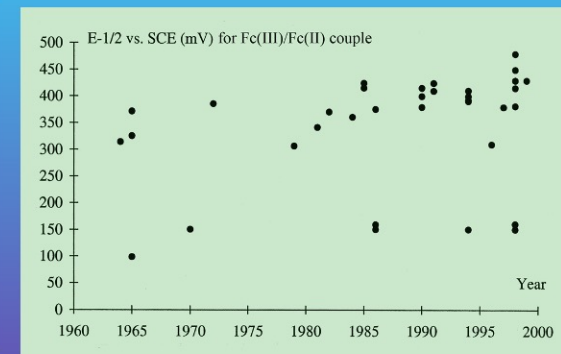
The use by different labs, of different reference electrodes for measuring the redox potentials of molecules makes data intercomparison fraught. Our work enables this to be done correctly. We also uncovered some erroneous beliefs in the literature of this field.



The authors, fabricating an electrode

Table 1
Conversion constants between different reference electrodes in CH₃CN at 25°C

↓From\to→	ANE1	ANE2	ANE3	APE	Fe ³⁺ /Fe	NHE	SCE	SSCE	SHE
ANE1	0	+45	+97	+47	-37	+593	+343	+347	+587
ANE2	-45	0	+52	+2	-87	+548	+298	+302	+542
ANE3	-97	-52	0	-50	-133	+496	+246	+250	+490
APE	-47	-2	+50	0	-83	+546	+296	+300	+540
Fe ³⁺ /Fe	+37	+87	+133	+83	0	+630	+380	+384	+624
NHE	-593	-548	-496	-546	-630	0	-250	-246	-6
SCE	-343	-298	-246	-296	-380	+250	0	+4	+244
SSCE	-347	-302	-250	-300	-384	+246	-4	0	+235
SHE	-587	-542	-490	-540	-624	+6	-244	-240	0



The guts of it – how to convert data vs. one reference electrode, to another one.

A modern scientific folly: literature misuseage of the ferrocenium/ferrocene redox potential

- A.W. Addison* and P.J. Burke, "Synthesis of Some Imidazole- and Pyrazole-Derived Chelating Agents", *The Journal of Heterocyclic Chemistry*, **18**, 803-805 (1981) [DOI: 10.1002/jhet.5570180436] *Over 350 citations; the fourth most highly cited paper published in this journal*

Synthesis of Some Imidazole- and Pyrazole- Derived Chelating Agents

Anthony W. Addison* and Philip J. Burke

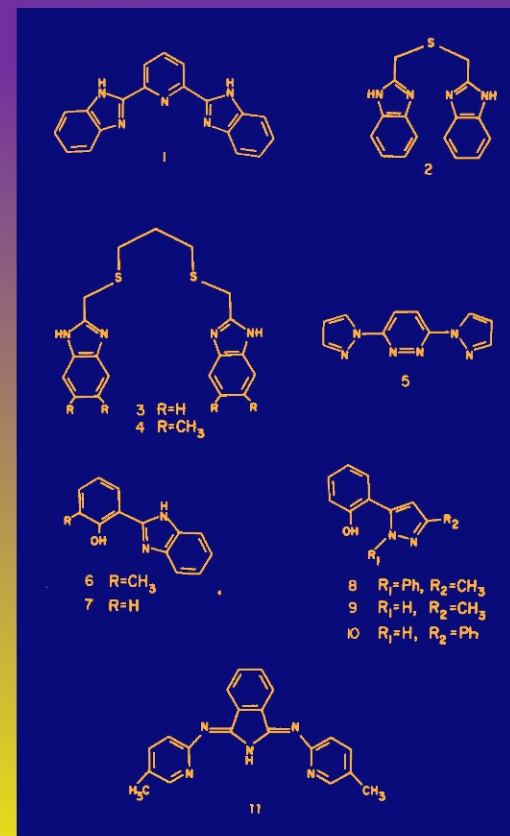
Department of Chemistry, Drexel University, Philadelphia, PA 19104, U.S.A.

Received January 5, 1981

Procedures involving condensation of *o*-phenylenediamines with carboxylic acids, and reaction of bifunctional alkyl halides with bifunctional nucleophiles are described. Syntheses are reported of 2,6-bis(2-benzimidazolyl)pyridine, 1,3-bis(2-benzimidazolyl)-2-thiopropane, 1,7-bis(2-benzimidazolyl)-2,6-dithiaheptane, 2-hydroxymethyl-5,6-dimethylbenzimidazole, 2-chloromethyl-5,6-dimethylbenzimidazole hydrochloride, 1,7-bis(5,6-dimethyl-2-benzimidazolyl)-2,6-dithiaheptane, 3,6-bis(1-pyrazolyl)pyridazine, 2-(2-hydroxy-3-methylphenyl)benzimidazole, 2-(2-hydroxyphenyl)benzimidazole, 5-(2-hydroxyphenyl)-3-methyl-1-phenylpyrazole, 3(5)-(2-hydroxyphenyl)-5(3)-methylpyrazole, 3(5)-(2-hydroxyphenyl)-5(3)-phenylpyrazole, and 1,3-bis((5-methylpyridyl)imino)isoindoline.

The Journal of Heterocyclic Chemistry (1981) **18**, 803.

This paper described some new heterocyclic nitrogen ligands, and improved syntheses for some known ones. In particular, the benzimidazole #1 has now been widely studied; authors of some more recent papers often seem to 'reinvent' our synthesis ! In addition, our convenient and solventless preparation of #11 is an early example of "green" chemistry, and greatly improves on another method published in the same year.



The ligands for which the syntheses were described

- U. Sakaguchi and A.W. Addison* "Spectroscopic and Redox Studies of Some Copper(II) Complexes with Biomimetic Donor Atoms: Implications for Protein Copper Centres", *The Journal of the Chemical Society, Dalton Transactions*, 600-608 (1979) [DOI: [10.1039/DT9790000600](https://doi.org/10.1039/DT9790000600)] *Over 640 citations.*

Spectroscopic and Redox Studies of Some Copper(II) Complexes with Biomimetic Donor Atoms: Implications for Protein Copper Centres

By Ushio Sakaguchi and Anthony W. Addison,*† Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada V6T 1W5

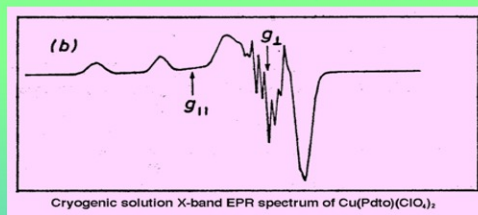
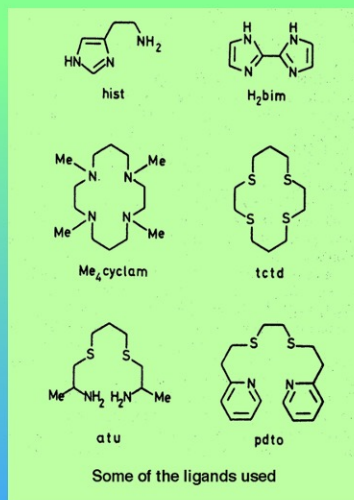
The redox chemistry and e.s.r. spectra of a number of copper(II) complexes with nitrogen- and sulphur-donor ligands have been examined, including complexes with 2,2'-bi-imidazole, histamine, and cyclic and acyclic saturated amine and thioether ligands. The tetrahedral Cu^{II}S_4 centre generated by γ -irradiation of single crystals of a thioacetamide complex of Cu^2+ has a low value of $|A_{||}|$. Tetrahedral distortion of otherwise tetragonal copper(II) centres increases $g_{||}$ and decreases $|A_{||}|$ for N-, S-, and O-donor ligands, and is a more effective source of reduction of $|A_{||}|$ than charge effects. The quotient $g_{||}/|A_{||}|$ appears to be a convenient empirical index of distortion of the donor set from planar toward tetrahedral, indicating that most type I copper in proteins is tetrahedrally, rather than tetragonally, co-ordinated.

*The Journal of the Chemical Society,
Dalton Transactions (1979) 600-608*



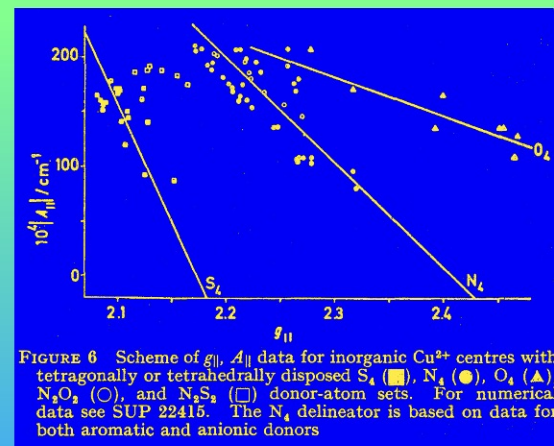
Dr. Ushio Sakaguchi;
believed to have been lost
in the Fukushima disaster.

This paper expanded on previous work, giving highly-sought insights into the effects of endogenous sulfur donor ligands in Type-1 copper proteins, and defined what became an often-used ESR parameter for geometric distortion of Cu(II) complexes.



Species	g_{\perp}	$g_{ }$	$g_{\perp}(g_{\perp})$	A_{\perp}	$A_{ }$	$A_{\perp}(A_{\perp})$	A_{\parallel}	g_{\parallel}
$[\text{Cu}(\text{ta})]^{2+}$	2.027	2.027	2.152	24	24	87*		
Major	2.034	2.034	2.080	35	35	69*		
Minor								
$[\text{Cu}(\text{tctd})][\text{PF}_6]_2$	Solution*	2.032	2.099	37	35	161		
$[\text{Cu}(\text{tctd})][\text{ClO}_4]_2$	Solution*	2.037	2.085	36		165	79	1.053
$[\text{Cu}(\text{dth})][\text{BF}_4]$	Powder	2.029	2.041	2.099				
Solution*	2.031	2.122	2.122	33		154	73	2.061
$[\text{Cu}(\text{atu})][\text{ClO}_4]_2$	Solution*	2.042†	2.155	35		183	84	2.078
$[\text{Cu}(\text{pdto})][\text{ClO}_4]_2$	Solution*	2.052†	2.164	24		174	74	2.087
$[\text{Cu}_4(\text{H}_2\text{bim})_4][\text{ClO}_4]_4$	Solution**	2.060†	2.262	13		176	67	2.129
$[\text{Cu}(\text{min})_4][\text{ClO}_4]_4$	Solution*	2.065	2.256	35		192	87	2.122
$[\text{Cu}(\text{hist})_2][\text{ClO}_4]_2$	Solution*	2.048	2.227	23		195	78	2.114
$[\text{Cu}(\text{en})_2][\text{ClO}_4]_2$	Solution*	2.047	2.206	30		205	88	2.100
$[\text{Cu}(\text{Me}_2\text{cyclam})][\text{PF}_6]_2$	Solution*	2.049	2.215	25		175	75	2.104

* Via simple first-order spectral analysis. † h.f. coupling constants in 10^4 cm^{-1} , all as $|A_{\perp}|$. * The g_{\perp} and A_{\perp} axes coincide with crystal c axis. † Two sites: the crystal c axis coincides with g_{\perp} and A_{\perp} and $g_{||}$ coincide for both sites, while the a and b axes coincide with g_{\parallel} and g_{\perp} or g_{\parallel} and g_{\perp} , respectively. * In MeNO_2 at 77 and ca. 300 K. A_{\perp} , g_{\perp} estimated via $2A_{\perp} = 2A_{\parallel}$ and $3g_{\perp} = 2g_{\parallel} + g_{\perp}$ using g_{\parallel} , A_{\parallel} at 77 K and g_{\perp} , A_{\perp} at 300 K, except when otherwise noted. $A_{\perp} \pm 0.001 \text{ cm}^{-1}$, $g_{\perp} \pm 0.002$. † g_{\perp} estimated from central feature of superhyperfine structure at 77 K. * Containing 10% MeOH. † W. R. McWhinnie, *J. Inorg. Nuclear Chem.*, 1964, 26, 21.



- H. Yokoi and A.W. Addison*, "Spectroscopic and Redox Properties of Pseudotetrahedral Copper(II) Complexes. Their Relationship to Copper Proteins." *Inorganic Chemistry*, **16**, 1341-1349 (1977) [DOI: [10.1021/ic50172a018](https://doi.org/10.1021/ic50172a018)] *Over 460 citations*.

Spectroscopic and Redox Properties of Pseudotetrahedral Copper(II) Complexes. Their Relationship to Copper Proteins

H. YOKOI¹ and A. W. ADDISON*

Inorganic Chemistry (1977) **16**, 1341

This paper used simple CuN₄-core chelates to establish the definitive model for relationships amongst structure, EPR spectroscopic parameters and redox potentials and molecular structure for copper(II) complexes, including copper proteins.

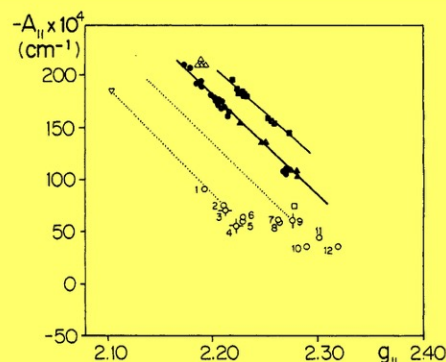
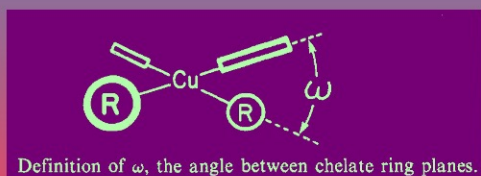
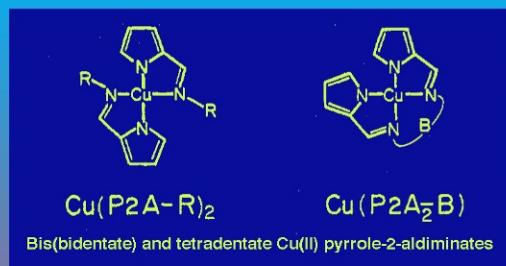


Figure 4. Relationships between $A_{||}$ and $g_{||}$ for copper(II) complexes with (●) pyrrole-2-carboxaldehydes, (▲) dipyrromethenes,¹⁴ (Δ) tetraphenylporphyrins,³⁰ and (■) salicylaldehydes.¹⁵ The points ○ are for selected copper proteins:⁶ 1, *P. versicolor* laccase; 2, human ceruloplasmin; 3, *R. succedanea* laccase; 4, *C. sativus* ascorbate oxidase; 5, zucchini ascorbate oxidase; 6, spinach plastocyanin; 7, *P. denitrificans* azurin; 8, *P. fluorescens* azurin; 9, *B. pertussis* azurin; 10, *R. vernicifera* stellacyanin; 11, *R. vernicifera* laccase; 12, horseradish uceyanin. The point ▽ is for a CuN_2S_2 species (see text); □ is for $\text{Cu}(\text{P2A-}i\text{Bu})_2$ doped into the Zn(II) lattice.

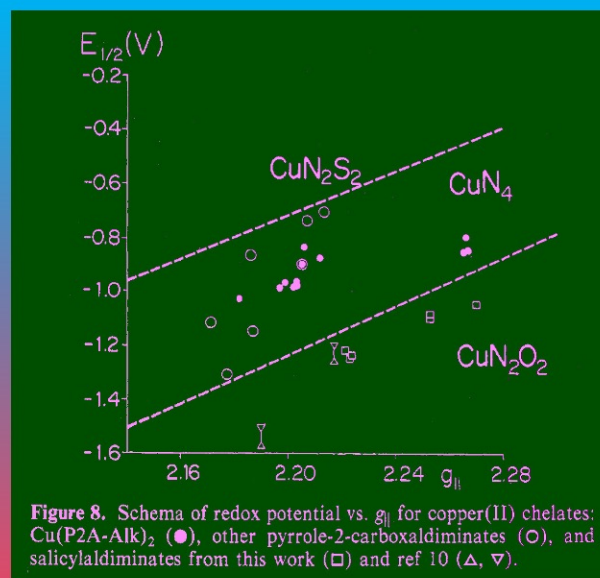


Figure 8. Schema of redox potential vs. $g_{||}$ for copper(II) chelates: $\text{Cu}(\text{P2A-Alk})_2$ (●), other pyrrole-2-carboxaldehydes (○), and salicylaldehydes from this work (□) and ref 10 (Δ, ▽).

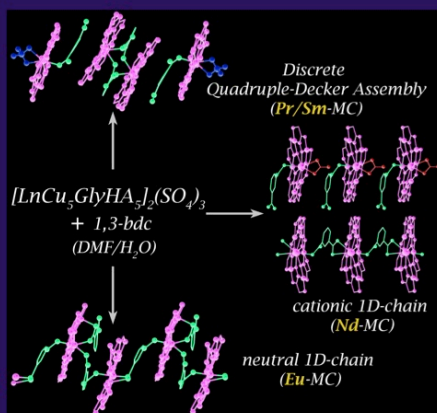
More published papers:

- A.V. Pavlishchuk*, S.V. Kolotilov, M. Zeller, S.E. Lofland, L.K. Thompson, A.W. Addison* & A.D. Hunter, "High Nuclearity Assemblies and 1D-coordination Polymers Based on Lanthanide-Copper 15-Metallacrown-5 complexes (LnIII = Pr, Nd, Sm, Eu)", *ACS Inorganic Chemistry* (2017) **56**(21), 13152–13165 [[doi: 10.1021/acs.inorgchem.7b01944](https://doi.org/10.1021/acs.inorgchem.7b01944)]

High-Nuclearity Assemblies and 1D-coordination Polymers Based on Lanthanide-Copper 15-Metallacrown-5 complexes (Ln= Pr, Nd, Sm, Eu)

Anna V. Pavlishchuk,* S.V. Kolotilov, M. Zeller, S.E. Lofland, L.K. Thompson, A.W. Addison* & A.D. Hunter

Glycine-hydroxamate pentacopper-metallacrowns combine with paramagnetic lanthanide trications to form deep blue ternary di-crown sulfates. Sulfate replacement by *m*-phthalate anions yields deep blue complex ternary products containing cationic 1-D polymer chains or unprecedented quadruple-decker neutral metallacrown assemblies. The magnetic exchange coupling constants within these assemblies have been analysed for the first time for such 15-Cu-5 crowns, using an additive/molecular field model.

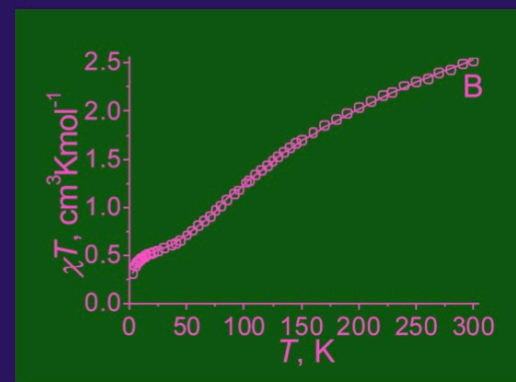
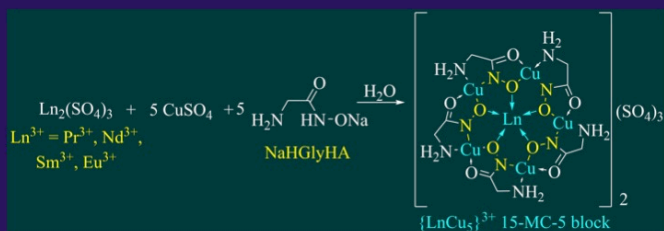


Central fragment of an SmCu₅ quadruple-decker system; phthalate lower right.

ACS Inorganic Chemistry (2017)

[doi: 10.1021/acs.inorgchem.7b01944](https://doi.org/10.1021/acs.inorgchem.7b01944)

Chemistry for assembly of the lanthanide copper metallacrowns.



Antiferromagnetism of the di-crown Sm(III) sulfate

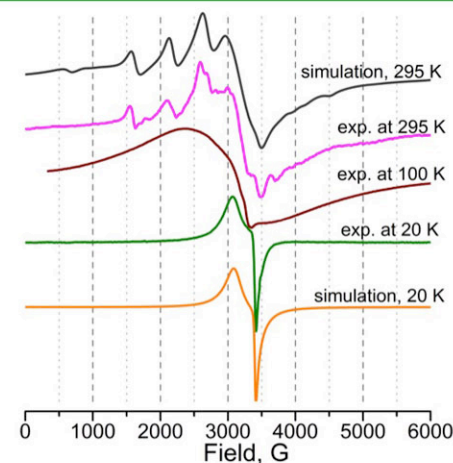
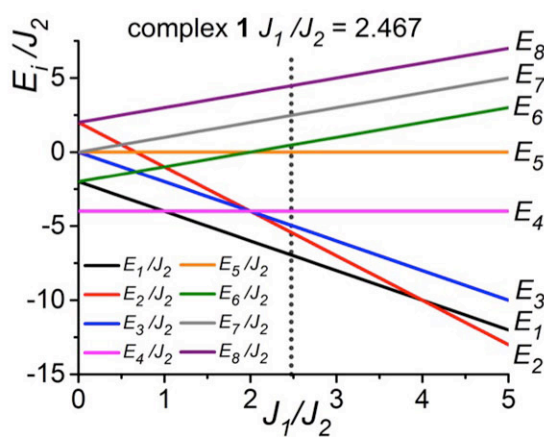
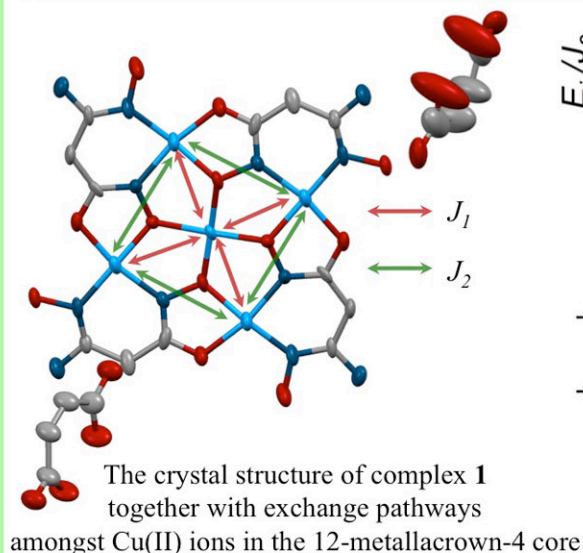
- A.V. Pavlishchuk, S.V. Kolotilov, M. Zeller, S.E. Lofland, M.A. Kiskin, N.N. Efimov, E.A. Ugolkova, V.V. Minin, V.M. Novotortsev & A.W. Addison*, "Supramolecular Maleate Adducts of Copper(II) 12-Metallacrown-4: Magnetism, EPR and Alcohol Sorption Properties" *The European Journal of Inorganic Chemistry* (2017) 4866-4878 [[doi: 10.1002/ejic.201700976](https://doi.org/10.1002/ejic.201700976)]

Supramolecular Maleate Adducts of Copper(II) 12-Metallacrown-4: Magnetism, EPR and Alcohol Sorption Properties

A.V. Pavlishchuk*, S.V. Kolotilov, M. Zeller, S.E. Lofland, M.A. Kiskin,
N.N. Efimov, E.A. Ugolkova, V.V. Minin, V.M. Novotortsev & A.W. Addison*

The European Journal of Inorganic Chemistry, 2017, DOI: 10.1002/ejic.201700976

X-Ray structures of two 12-metallacrowns-4 $[\text{Cu}_5(\text{alpha})_4(\text{DMF})_2](\text{MalH})_2 \cdot 2\text{DMF}$ (**1**) and $[\text{Cu}_5(\text{alpha})_4(\text{MalH})_2]$ (**2**) were reported. The ambient temperature X-band EPR of a polycrystalline 12-metallacrown-4 complex was detected for the first time. The room-temperature EPR spectrum of polycrystalline **1** was simulated as the sum of EPR spectra of different Cu(II)-derived spin states, with contributions proportional to the populations of these spin states.



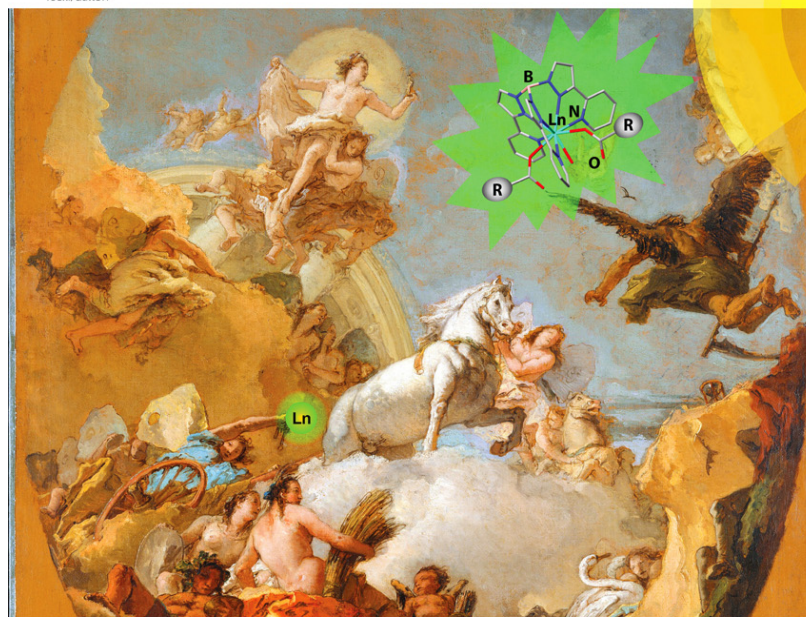
Experimental and simulated X-band EPR spectra of a polycrystalline sample of **1** at 20 and 295 K together with experimental spectrum at 100 K

- E.A. Mikhalyova, A.V. Yakovenko, M. Zeller, K.S. Gavrilenko, M.A. Kiskin, S.S. Smola, V.P. Dotsenko, I.L. Eremenko, A.W. Addison* & V.V. Pavlishchuk*, "Crystal structures and intense luminescence of tris(3-(2'-pyridyl)pyrazolyl)borate Tb³⁺ and Eu³⁺ complexes with carboxylate co-ligands", *Dalton Transactions* (2017) 46(11), 3457-3469 [DOI: 10.1039/c6dt04757b] [Cover]

Volume 46 | Number 11 | 21 March 2017 | Pages 3413–3772

Dalton Transactions

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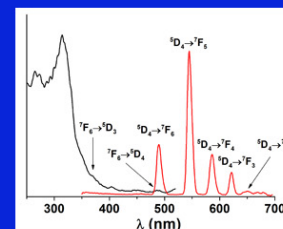
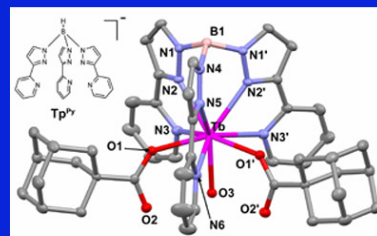


PAPER
Anthony W. Addison, Vitaly V. Pavlishchuk et al.
Crystal structures and intense luminescence of tris(3-(2'-pyridyl)-pyrazolyl)-borate Tb³⁺ and Eu³⁺ complexes with carboxylate co-ligands

Crystal structures and intense luminescence of tris(3-(2'-pyridyl)pyrazolyl)borate Tb³⁺ & Eu³⁺ complexes with carboxylate co-ligands

E.A. Mikhalyova, A.V. Yakovenko, M. Zeller, K.S. Gavrilenko, M.A. Kiskin, S.S. Smola, V.P. Dotsenko, I.L. Eremenko, A.W. Addison* & V.V. Pavlishchuk*

RSC Dalton Transactions 2017 Cover Article
After Giovanni Tiepolo's "The Chariot of Aurora" 1763
DOI: 10.1039/c6dt04757b



Tb absorption (black line) & emission (red line): intensity vs. wavelength

These brightly luminescent mono- & dinuclear, nonacoordinate Eu(III) & Tb(III) carboxylate derivatives exhibit unusually high quantum efficiencies, from 30 to 50% at room temperature. The green-emitting Tb-complex is also electroluminescent, while both the Tb & Eu complexes are triboluminescent.

Yakovenko
& Mikhalyova



Addison
& Eremenko



- M. Nozari, J.P. Jasinski, M. Kaur, A.W. Addison, A.A. Shamsabadi & M. Soroush, "Crystal structure of 5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene-6,13-dione". *Acta Crystallographica Section E: Crystallographic Communications* (Dec. 2016) **72E**(12) 1734-1738 [DOI: 10.1107/S2056989016017461] *An Acta Cryst. E 'most-read' article in 2017.*
- V. I. Smith, M. Nozari*, M. Zeller & A. W. Addison, "Crystal structure of (2,2'-bipyridyl)[2,6-bis-(1-butyl-1H-benzimidazol-2-yl)pyridine]chloridoiridium(III) trifluoromethanesulfonate", *Acta Crystallographica* (2017) **E73**, 127-132 [[doi: 10.1107/S205698901700010X](https://doi.org/10.1107/S205698901700010X)]

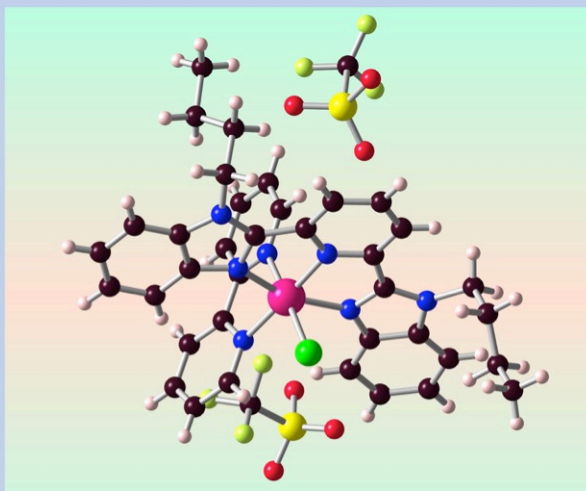
“Crystal structure of (2,2'-bipyridyl)[2,6-bis(1-butyl-1H-benzimidazol-2-yl)pyridine]chloridoiridium(III) trifluoromethanesulfonate”

Authors: **Victoria I. Smith**[‡], Mohammad Nozari,
Matthias Zeller, and Anthony W. Addison

Article Information: *Acta Cryst.* (2017). **E73**, 127-132

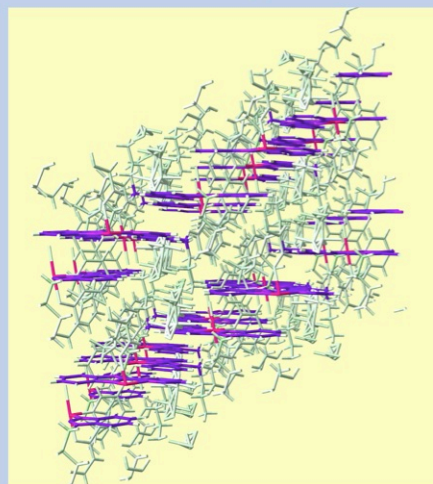
DOI: 10.1107/S205698901700010X

The title complex was synthesized within a project exploring the nature of iridium(III)/periodate (IO_4^-) systems in water, as some iridium complexes have been shown to catalyze the oxidation of water in the presence of periodate.

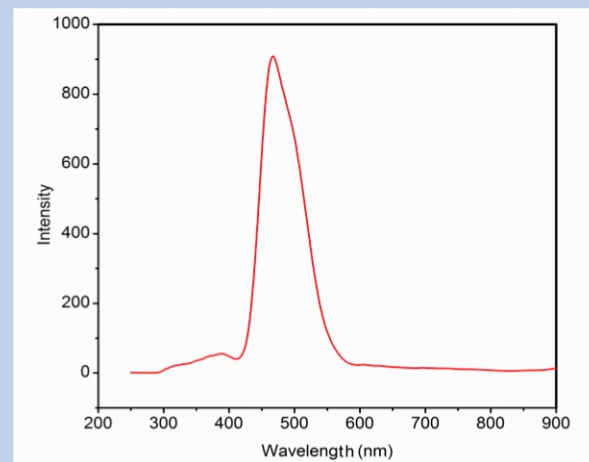


Crystal structure of the title complex

[‡] 2015 Maryanoff Research Fellow



A perspective view (from 150 Å) along the *c*-axis direction, showing the ‘staircase’ stacking.



Emission spectrum of the title complex (0.8 μM) in non-purged acetonitrile, excited at 295 nm

- E.A. Mikhalyova, M. Zeller, S. Trofimenko, A. W. Addison* & V. V. Pavlishchuk, “New homodinuclear tris(3-alkylpyrazolyl)borate complexes of Co(II) and Ni(II) with tetraacetylene dianion as a bridging ligand” (invited paper for special issue celebrating the golden anniversary of the discovery of scorpionates by Swiatoslaw “Jerry” Trofimenko), *Acta Crystallographica* (2016) **C72**(11), 777-785. [DOI: [10.1107/S205322961601398X](https://doi.org/10.1107/S205322961601398X)]

“New homodinuclear tris(3-alkylpyrazolyl)borate complexes of Co(II) and Ni(II) with tetraacetylene dianion as a bridging ligand”

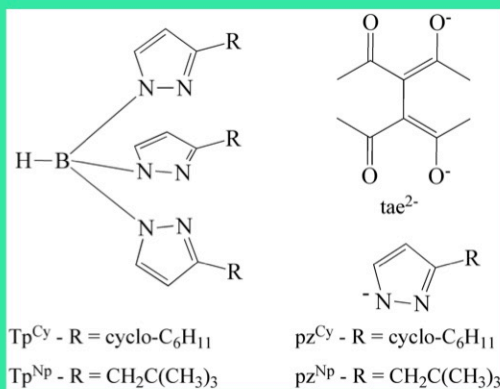
Elena A. Mikhalyova, M. Zeller, S. Trofimenko, A.W. Addison* & V.V. Pavlishchuk*

Acta Crystallographica (2016) **C72**, 777-785

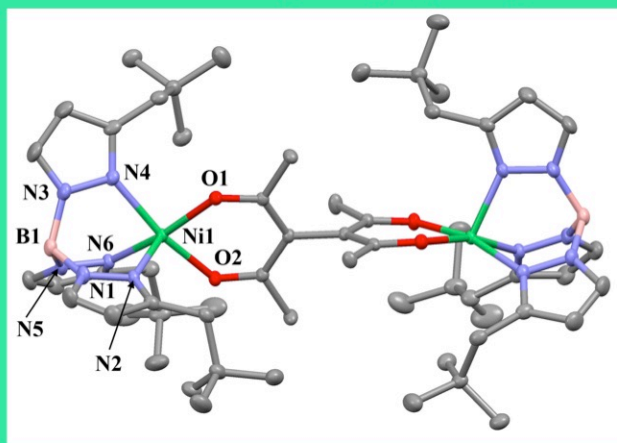
doi.org/10.1107/S205322961601398X

Invited paper for the Golden Anniversary of Swiatoslaw “Jerry” Trofimenko’s discovery of scorpionates.

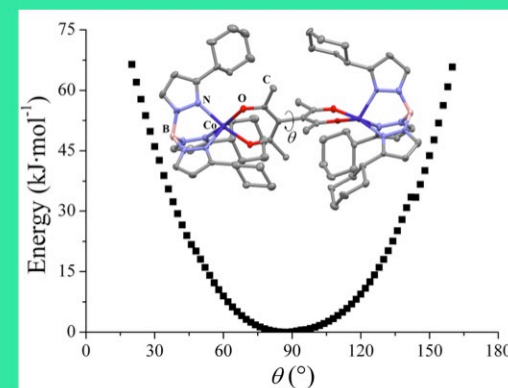
Tris(3-alkylpyrazolyl)borate complexes (alkyl= neopentyl, cyclohexyl) were dinucleated using tetraacetylene as a bridging dianion. The cobalt(II) and nickel(II) ions are tetragonally pentacoordinate. Steric effects push the two halves of the bridge slightly away from the usual 90° interplanar angle.



The ligands used



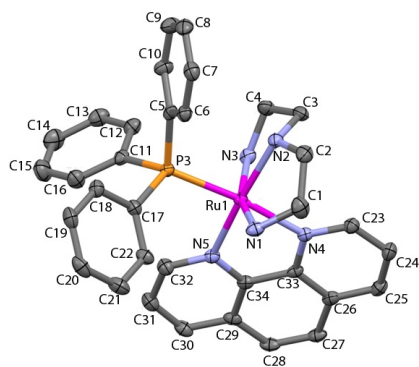
A view of the neopentyl-version of the nickel(II) complex.



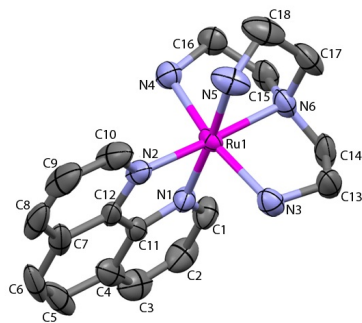
Energy profile for the cobalt(II) complex as a function of intramolecular twist angle.

- G.T. Reeves*, A.W. Addison & M. Zeller, "Ruthenium(II) complexes of some simple classic amine ligands", *Inorganica Chimica Acta*, **432** (June 2015) 185-191 [[doi:10.1016/j.ica.2015.04.007](https://doi.org/10.1016/j.ica.2015.04.007)]

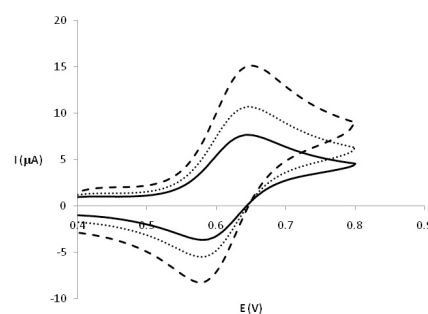
Several new Ru(II) complexes of tris(2-aminoethyl)amine (Tren) and diethylenetriamine (Dien) have been prepared using Ru(PPh₃)₃Cl₂ and (Me₄N)₂[Ru(Phen)Cl₄] as starting materials. The reaction of Tren or Dien with Ru(PPh₃)₃Cl₂ leads to the formation of either the [Ru(Tren)(PPh₃)Cl]Cl or the [Ru(Dien)(PPh₃)Cl₂] complex, of which the latter then reacts further with a heterocyclic diimine (N–N) ligand to yield [Ru(Dien)(PPh₃)(N–N)]Cl₂. Addition of Tren or Dien to solutions of the (Me₄N)₂[Ru(Phen)Cl₄] complex replaces the coordinated chlorides with the N-donor ligand, forming [Ru(Tren)Phen](ClO₄)₂ and [Ru(Dien)(Phen)Cl]Cl respectively. The complexes show strong luminescence in the UV range and redox chemistry shows single-electron Ru(II)→Ru(III) oxidations over a wide range of potentials.



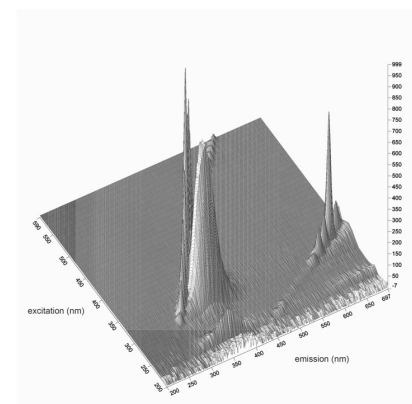
[Ru(PPh₃)(Phen)(Dien)]²⁺ cation



[Ru(Phen)(Tren)]²⁺ cation



Anodic CV of [(CH₃)₄N][Ru(Phen)Cl₄] in MeCN/NBu₄PF₆ showing an E_{1/2} of +614 mV vs. APE.



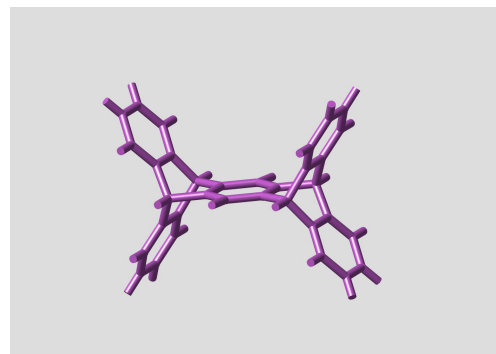
Excitation/emission map for luminescence of [Ru(Phen)(Tren)](ClO₄)₂ in MeCN

- Y.A. Satska, E.A. Mikhalyova, Z.V. Chernenko, S.V. Kolotilov,* M. Zeller, I.V. Komarov, A.V. Tymsunik, A. Tolmachev, K.S. Gavrilenko & A.W. Addison*, "Sorption discrimination between secondary alcohol enantiomers by chiral alkyl-dicarboxylate MOFs"; *RSC Advances* (Sept. 2016), [[doi: 10.1039/C6RA09353A](https://doi.org/10.1039/C6RA09353A)]

The 3D coordination polymer [Co₂(H₂O)(cpda)₂(py)₄·py]_n (cpdaH₂ is *trans*-(*S,S*)-1,2-cyclopropane dicarboxylic acid, py = pyridine) crystallizes from pyridine as 1·5py (one py is not coordinated) and was characterized by X-ray single crystal diffraction. Desolvation of 1·5py was accomplished with decoordination of pyridine and transformation of the Co^{II} octahedral coordination into tetrahedral, as confirmed by electronic spectroscopy. Sorption of individual optical isomers – (*S*)-2-butanol and (*R*)-2-butanol – from the gas phase at 303 K by desolvated **1** was studied, and for comparison sorption of these substrates by the chiral MOFs [Zn₂(camph)₂(bipy)]_n (**2**) and [Zn₂(camph)₂(dpe)]_n (**3**) was examined (camphH₂ is (1*R*,3*S*)-camphoric acid, bipy is 4,4'-bipyridine, dpe is *trans*-1,2-di(4-pyridyl)ethylene). Chiral sites in **1** – **3** contain only

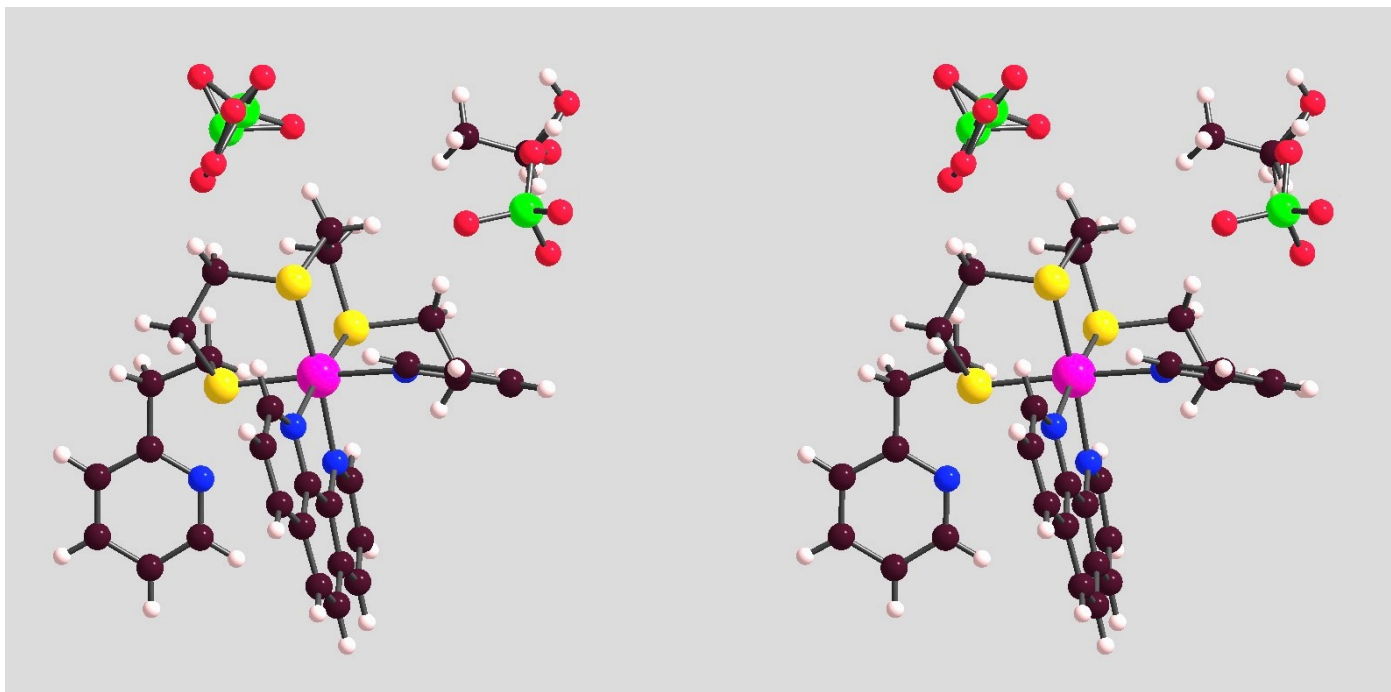
one polar group (carboxylate) in close proximity to the asymmetric C atom, while the other groups contain only C–H or C–C bonds. In the cases of **1** or **2** the absorption isotherms grew abruptly at certain pressure values P , and these values were different for the (*R*) or (*S*) isomers' sorptions. Such differential growth can be accounted for through the polymeric framework's rearrangement induced by interaction with 2-butanol, the difference in P values for (*R*) and (*S*) isomers being an indication of different interaction energies for these isomers with the MOF. There was no significant difference between the values of total sorption capacity of **1** for the two enantiomers of 2-butanol at pressures close to the saturation vapor pressure. In contrast, the sorption capacity of **3** was higher for (*R*)-2-butanol than for (*S*)-2-butanol in the whole pressure range.

- L. Serpas, B. Milorey, L.A. Pandiscia, A.W. Addison & R. Schweitzer-Stenner*, "Autoxidation of Reduced Horse Heart Cytochrome *c* Catalyzed by Cardiolipin-Containing Membranes", *The Journal of Physical Chemistry* (2016) **B120**, 12219–12231. [DOI: [10.1021/acs.jpcc.6b05620](https://doi.org/10.1021/acs.jpcc.6b05620)] We used visible circular dichroism, absorption and fluorescence spectroscopy to probe the binding of horse heart ferrocyanochrome *c* to anionic cardiolipin head-groups on the surface of TOCL/DOPC (20%:80%) liposomes in an aerobic environment. We found that upon binding, ferrocyanochrome *c* undergoes a conformational transition that leads to the complete oxidation of the protein at intermediate and high cardiolipin concentrations. At low lipid concentrations, the protein maintains a structure only slightly modified from its native one, while a partial conversion to a misligated, non-native state occurs at high lipid concentrations. The conformational mixture of proteins contains a substantial fraction of high spin species (penta- and hexacoordinated), which can be expected to exhibit significant peroxidase activity. The population of the non-native state is less pronounced than was found for cytochrome *c* – cardiolipin interactions initiated with oxidized cytochrome *c*. Under anaerobic conditions, the protein maintains its reduced state but still undergoes some conformational change upon binding to CL head groups on the liposome surface. Our data suggest that CL-containing liposomes function as a catalyst by reducing the activation barrier for a $\text{Fe}^{2+} \rightarrow \text{O}_2$ electron transfer. Adding NaCl to existing cytochrome-liposome mixtures under aerobic conditions inhibits protein auto-oxidation of ferrocyanochrome *c* and stabilizes the reduced state of the membrane-bound protein.
- M. Nozari, J.P. Jasinski, M. Kaur, A.W. Addison, A.A. Shamsabadi & M. Soroush, "Crystal structure of 5,7,12,14-tetrahydro-5,14:7,12-bis([1,2]benzeno)pentacene-6,13-dione". *Acta Crystallographica Section E: Crystallographic Communications* (Dec. 2016) **72E**(12) 1734-1738 [DOI: [10.1107/S2056989016017461](https://doi.org/10.1107/S2056989016017461)] *An Acta Cryst. E 'most-read' article in 2017.*



- G.T. Reeves*, A.W. Addison, M. Zeller & A.D. Hunter, "Ru(II) thioether complexes with dangling pyridine ligands", *Polyhedron*, **68** (2014) 70-75 [DOI [10.1016/j.poly.2013.10.001](https://doi.org/10.1016/j.poly.2013.10.001)]

Through two different methods, new Ru(II) polypyridyl complexes were prepared in an attempt to replicate previously reported heptacoordinate Ru(II) syntheses. The tetradentate thioethers, 1,8-bis(2'-pyridyl)-3,7-dithianonane (Pdto), 1,9-bis(2'-pyridyl)-3,7-dithianonane (Pdtn), and 1,10-bis(2'-pyridyl)-3,8-dithiadecane (Pddd), were used to form dinuclear ruthenium(II) complexes of the type $[\{\text{Ru}(\text{L}1)\}_2(\mu\text{-Cl})_2]^{2+}$ via reaction with $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$. Upon reaction of the dinuclear complexes with the triimine ligand 2,6-bis(N'-methylbenzimidazolyl)pyridine (Me_2Bzimpy), facile symmetrical bridge cleavage occurs, producing mononuclear complexes of the form $[\text{Ru}(\text{L}1)(\text{L}2)]^{2+}$, where L1 is one of the three tetradentate thioether ligands and L2 is the tridentate triimine. A second method of producing the mononuclear $[\text{Ru}(\text{L}1)(\text{L}2)]^{2+}$ complexes involves the reaction of $\text{Ru}(\text{L}2)\text{Cl}_3$ with L1 under ethanolic conditions. In such mononuclear complexes, one of the pyridine arms of the tetradentate thioether is forced to be uncoordinated, due to the firmly hexacoordinate nature of Ru(II). A similar experiment was conducted using the pentadentate thioether 1,11-Bis(2'-pyridyl)-3,6-9-dithianonane (Pttu) and the diimine Phen, forming the stable hexacoordinate $[\text{Ru}(\text{Pttu})(\text{Phen})]^{2+}$ complex. The mononuclear complexes exhibit single-electron Ru(II) \rightarrow Ru(III) oxidative response, in the range of +825 to +845 mV vs. APE, involving the removal from an electron from the t_{2g} orbital set. The "heptacoordinate" Ru(II) was shown to be hexacoordinate, with a dangling pyridyl unit.



Inverse stereoview of $[\text{Ru}(\text{Pttu})(\text{Phen})](\text{ClO}_4)_2 \cdot \text{EtOH}$, dangling pyridine at lower left.

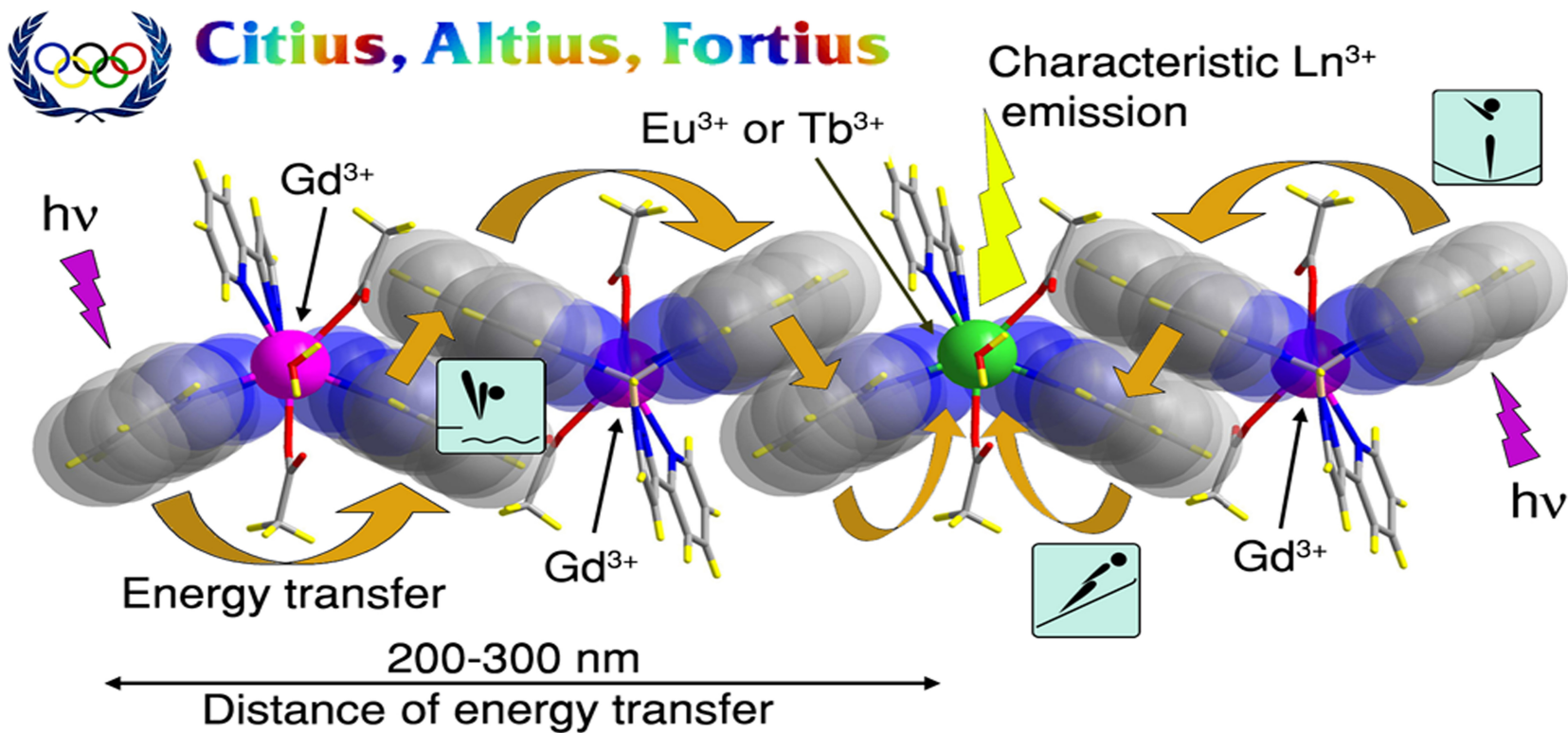
- E. A. Mikhalyova, A. V. Yakovenko, M. Zeller, M. A. Kiskin, Y. V. Kolomzarov, I.L. Eremenko, A. W. Addison* & V. V. Pavlishchuk*, "Manifestation of π - π Stacking Interactions in Luminescence Properties and Energy Transfer in Aromatically-Derived Tb, Eu and Gd Tris(pyrazolyl)borate Complexes". *Inorganic Chemistry*, **54**(7) (2015) 3125-3133. [DOI: [10.1021/ic502120g](https://doi.org/10.1021/ic502120g)] *Featured also in a specially-curated online edition of ACS Inorganic Chemistry.*

Manifestation of π - π Stacking Interactions in Luminescence Properties and Energy Transfer in Aromatically-Derived Tb, Eu and Gd Tris(pyrazolyl)borate Complexes

Elena A. Mikhalyova, Anastasiya V. Yakovenko, Matthias Zeller, Mikhail A. Kiskin, Yuriy V. Kolomzarov, Igor L. Eremenko, Anthony W. Addison* & Vitaly V. Pavlishchuk*

ACS Inorganic Chemistry (2015) **54**(7) 3125-3133; DOI: 10.1021/ic502120g

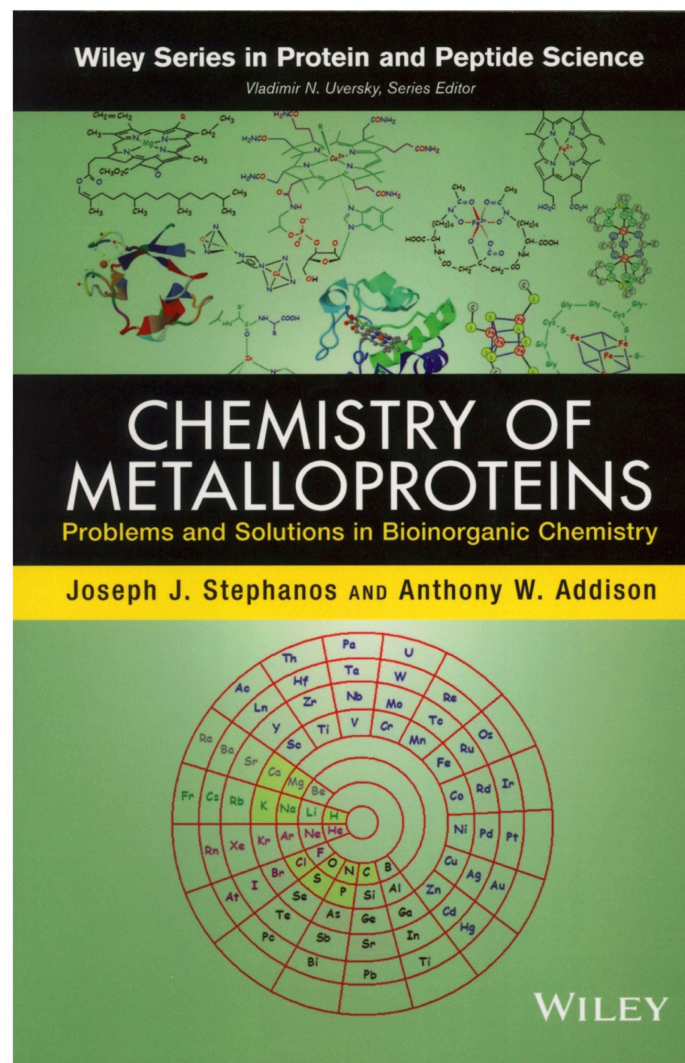
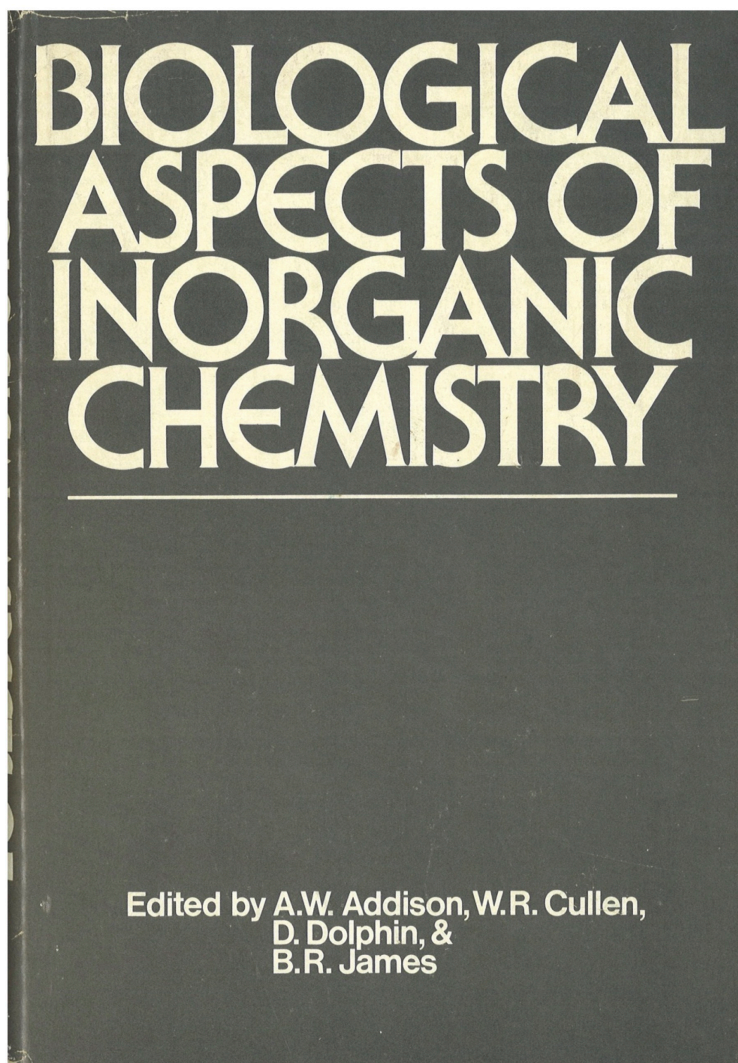
In the crystal lattices of the tris(pyrazolyl)borate-lanthanide complexes described, the molecules are π -stacked into infinite 1-D chains. The stack acts as a "superantenna" for capturing photon energy and conducting it to a luminescent light-emitting center.



Some nicely-cited papers.

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- K. K. Nanda, A. W. Addison* & E. Sinn, "The First Oxovanadium(V) Thiolate Complex, [VO(SCH₂CH₂)₃N]". *Inorganic Chemistry*, **35**, 1-2 (1996) (Communication to the Editor) [DOI: [10.1021/ic9512486](https://doi.org/10.1021/ic9512486)] [29 citations; Cited in Cotton & Wilkinson's textbook, 'Inorganic Chemistry'; e.g. 6th Edn., p.720]
- A.W. Addison, "One-Electron Redox Processes at Binuclear Copper Centres", *Inorganic & Nuclear Chemistry Letters*, **12**, 899-903 (1976) [DOI: [10.1016/0020-1650\(76\)80004-9](https://doi.org/10.1016/0020-1650(76)80004-9)] (128 citations)
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- A.W. Addison, "Spectroscopic and Redox Trends From Model Systems", in "Copper Coordination Chemistry: Biochemical and Inorganic Perspectives", Eds. K.D. Karlin & J.A. Zubieta, Adenine Press, Guilderland, NY, 1983, pp109-128. ISBN 0-940030-03-9 (178 citations)
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