

TWO DINUCLEAR NICKEL(II) COMPLEXES WITH DIFFERENT N₃ LIGAND BINDING TYPE

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We obtained two dinuclear Nickel(II) complexes having different N₃ ligand binding type; [Ni₂(L-Et)(N₃)(H₂O)](NO₃).2H₂O (1) (where: HL-Et=N,N,N',N'-trakis[(1-ethyl-2benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane) and [Ni₂(L-Et)(N₃)(H₂O)](NO₃).2C₂H₅OH (2), respectively. Complex 1 is synthesized from HL-Et, Ni(NO₃).6H₂O, NaOH and NaN₃ in MeOH, indicating weak antiferromagnetic interaction. 2 is synthesized from the quite same reagent as 1 with equivalent amount but in different solvent; EtOH, indicating strong antiferromagnetic interaction. We undertook the X-ray structural analyses of 1 and 2 to elucidate the crystal structures causing the different magnetic susceptibility.

Crystal Data: C₄₃H₅₉O₁₂N₁₅Ni₂, (1), F.W. = 1095.4, monoclinic, *P*2₁/*c*, *a* = 13.751(1) Å, *b* = 24.356(1) Å, *c* = 17.006(1) Å, β = 100.19(1)°, *V* = 5606(1) Å³, *Z* = 4, *D*_c = 1.298 g cm⁻³, λ(MoKα) = 7.39 cm⁻¹, *F*(000) = 2296, *R* (*R*_w) = 0.089(0.119). C₄₇H₆₅O₁₁N₁₅Ni₂, (2) F.W. = 1133.5, triclinic, *P*-1, *a* = 17.112(1) Å, *b* = 17.222(1) Å, *c* = 10.296(1) Å, α = 102.957(2)°, β = 103.413(2)°, γ = 64.233(1)°, *V* = 2632(1) Å³, *Z* = 2, *D*_c = 1.430 g cm⁻³, λ(MoKα) = 7.88 cm⁻¹, *F*(000) = 1192, *R* (*R*_w) = 0.072(0.060).

It is observed that 1 has the conformation with N₃ ligand being monodentated to one Ni atom, on the other hand, 2 has the conformation with N₃ ligand being end-to-end bridging to two Ni atoms.

Keywords: DINUCLEAR NICKEL COMPLEX, N₃ LIGAND, NICKEL**SINGLE-CRYSTAL NEUTRON DIFFRACTION STUDY OF BIS(ZINC(II) BIS(N,N'-DIETHYLDITHIOCARBAMATE))**W. T. Klooster¹ R. Piltz¹ E. R. T. Tiekink²¹Australian Nuclear Science And Technology Organisation Physics Division, Building 58 Pmb 1 MENAI NEW SOUTH WALES NSW 2234 AUSTRALIA²National University of Singapore

Zinc, cadmium and mercury 1,1-dithiolate complexes form a most important class of materials with wide ranging applications, e.g. as wear inhibitors for lubricating oils, accelerators in the vulcanization of rubber, precursors for nanotubes, etc. Underlying the understanding of their mode of action is the knowledge of their chemical structure. Crystallographic studies [1] have shown that these compounds adopt a remarkable variety of molecular architectures. Structural types discovered thus far range from monomeric to dimeric, tetrameric, 2D-sheets and 3D-networks. Over and above this, the adoption of a particular motif over another is unpredictable making the study of these systems tantalizing.

This contribution describes the crystal and molecular structure of one such example, i.e. bis{zinc(II) bis(N,N'-diethyldithiocarbamate)}, {Zn(S₂CNEt₂)₂}. To a first approximation, this centrosymmetric and dimeric complex features tetrahedral zinc centres arising from the presence of two bidentate bridging dithiocarbamate ligands and two chelating ligands. of particular interest in this structure is the nature of the trans-annular interaction. If significant, the coordination geometry about zinc could be regarded as being distorted towards a trigonal bipyramidal geometry.

Keywords: NEUTRON DIFFRACTION MOLECULAR ARCHITECTURE ZINC COMPLEX**GEOMETRICAL PRINCIPLES IN THE CONSTRUCTION OF MOLECULAR STRUCTURES OF HETEROMETALLIC ALKOXIDE COMPLEXES**

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The structures of both homo- and heterometallic alkoxide complexes can be described in the terms of polyhedral models, including such building blocks as tetrahedra, square pyramids and octahedra. Exchange for some fragments of the structures with the geometrically but not chemically identical or geometrically equivalent fragments permits to predict the molecular structures and compositions of the new compounds. This approach permitted to envisage the existence of such new complexes as Mo₂Ta₄O₈(OMe)₁₆, Mo₄M(v)₂O₈(OiPr)₁₄, Re_{4-x}M(vi)_xO₈(OMe)₁₂, M(v)₄O₂(OMe)₁₄(ReO₄)₂, M(v)₂(OMe)(ReO₄)₂, M(ii)₂M(v)₂(acac)₂(OMe)₁₂, M(ii)₂M(vi)₂O₂(OMe)₁₀, M(ii)Al₂(acac)₄(OiPr)₄, M(ii)₂Ti₂(acac)₂(OiPr)₁₀, M(ii)₂M(v)₂(OiPr)₁₄, M(ii)M(v)₂(OiPr)₁₂, where M(ii) = Co, Ni; M(v) = Nb, Ta; M(vi) = Mo, W.

Keywords: METAL ALKOXIDES MOLECULAR STRUCTURE DESIGN POLYHEDRAL MODELS**SOLID POLYMORPHS OF HEXA-AQUA Mg(II), Co(II), AND Ni(II) HYPHOSPHITE**N. V. Kuratieva¹ D. Yu. Naumov² N. V. Podbereskaya²¹Institute of Inorganic Chemistry SB RAS Crystal Chemistry Prosp. Lavrentiev, 3 NOVOSIBRSK 630090 RUSSIA ²Novosibirsk State University

We are researching in the chemistry of hypophosphorous acid salts with hexa-aqua-cations of magnesium, cobalt and nickel. Crystals was grown by slow evaporation of aqueous solutions of its salts at the room temperature (T = 293K). The forms of crystals are octahedrons and hexagonal plates. Our studies have shown hexa-aqua-metals hypophosphite to exist in the form of three polymorphs, which we have termed α, β, and γ polymorphs. The structures of α- and β -[Mg(H₂O)₆](H₂PO₂)₂ (octahedrons), α-[Co(H₂O)₆](H₂PO₂)₂ (both octahedrons and hexagonal plates) and γ -[Ni(H₂O)₆](H₂PO₂)₂ (thin hexagonal plates) polymorphs have been determined by X-Ray single crystal analysis. The geometry of aqua-complexes and hypophosphite anion and the differences between the structures of polymorphs were analyzed. Packing of the metal and phosphorous atoms is the same to the structure of CaF₂. Metal atoms have the pseudo face-centered cubic cell with the parameter about 1.03 nm and the phosphorous atoms occupied the tetrahedral cavities. In all polymorphs we might find the layers formed by the H-bonding of water molecules coordinated to metal and the O-atoms of hypophosphite anion. The structures of the layers in all polymorphs are different in the way of orientation of coordinated water molecules.

Keywords: POLYMORPHISM, HEXA-AQUA-COMPLEXES, HYPHOSPHITES