

PS07.02.10 BI-AND TRINUCLEAR CARBOXYL RUTHENIUM CLUSTERS: A CRYSTALLOGRAPHIC AND ELECTRONIC COMPARATIVE STUDY. J. F. Van der Maelen Uría, D. Ardura, S. García-Granda (Dpto. Química Física y Analítica), J. A. Cabeza (Dpto. Química Orgánica e Inorgánica), Facultad de Química, Universidad de Oviedo, E-33006 Oviedo Spain

Results on the structure determination and molecular aspects of a series of Ru₃ cluster complexes are presented. Details on their potential significance as homogeneous catalysts, as well as their electronic structure in some cases, are also given. The study includes, among others, the following trinuclear compounds: [Ru₃(μ-H)(μ,η²-o-SC₆H₄NH₂)(CO)₉] (o-HSC₆H₄NH₂=2-aminothiophenol) [1], [PPN][Ru₃(μ-dmpz)(μ₃-Ph₂C₂)(μ-CO)₂(CO)₆] (Hdmpz = 3,5-dimethylpyrazole) [2], [Ru₃(μ₃-ampy)(CO)₉(PPh₃)] [BF₄]-C₃H₁₂ (Hampy = 2-amino-6-methylpyridine) [3], [Ru₃(μ-H)(μ₃-ampy)(μ-η¹:η²PhC=CHPh)(CO)₈][BF₄]-CH₂Cl₂ [4], and [Ru₃(μ-Ph)(μ₃-ampy)(μ-PPh₂)₂(CO)₆] [5]. Refinement procedures for the treatment of solvent and other disordered areas, as published elsewhere [6], will also be given. Finally, semiempirical electronic structure calculations for new binuclear compounds will be shown as well.

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PR07.02.11 NEW COPPER (II) LEAD (II) HETEROTETRANUCLEAR COMPLEX: DIRECT SYNTHESIS AND STRUCTURE. Olga Yu. Vassilyeva, Larisa A. Kovbasyuk, Dept of Chemistry, Kiev Shevchenko University, Volodimirska, 64, Kiev 252033, Ukraine

Method of direct synthesis was successfully applied for the preparation of a number of the heteronuclear Cu^{II}Pb^{II} complexes containing aminoalcohols. The structure of the heterotetranuclear Cu^{II}Pb^{II} complex containing 2-dimethylaminoethanol (HL) was solved by direct methods and refined by full-matrix least-squares computations to R=0.0438 for the 2359 reflections with $I > 2\sigma(I)$. The crystal of the compound comprises dimeric centrosymmetric molecules {Cu₂Pb₂[(CH₃)₂NCH₂CH₂O]₄(DMSO)₂} bridged by oxygen atoms of chelated L-groups, and DMSO molecules of crystallization in the lattice cavities. The copper co-ordination environment formed by oxygen and nitrogen atoms of the two co-ordinated L-groups (appropriate bond distances are 1.914(8) - 2.07(1) Å) has somewhat distorted square planar geometry. The close lead atom co-ordination environment is formed by three oxygen atoms of L-groups and oxygen atom of co-ordinated DMSO molecule; appropriate bond distances are 2.343(7) - 2.601(7) Å. The remote iodine atoms, located at a distance from the lead atom of 3.285(1) - 3.390(1) Å, complete co-ordination of lead to give a highly distorted octahedral configuration. The Pb—I(2) distance is elongated compared with Pb—I(1) one probably because of the bridging of the I(2) to the copper atom. Pb—Cu separations (3.394(2) and 3.634(2) Å) are similar to those of known Cu^{II}Pb^{II} complexes of macrocycles (3.344(3) - 3.577(2) Å). Oxygen atoms of L-groups bridging both metal centres arrange a strictly planar central Pb₂O₂ rhombus in the structure of the complex.

{Cu₂Pb₂[(CH₃)₂NCH₂CH₂O]₄(DMSO)₂}-2DMSO crystallizes in the triclinic space group P-1 with a=8.305(3), b=12.132(3), c=12.755(3) Å, α=84.86(2), β=80.79(3) and γ=73.26(3)°, with two formula units per primitive unit-cell.

PS07.02.12 POLYMORPHS OF [Au(dppm)Cl]₂. Ju-Chun Wang, Lin-Shu Liou and Shin-Jine Chen, Department of Chemistry, Soochow University, Taipei, Taiwan 11102, Rep. Of China

Three different polymorphs of [Au(dppm)Cl]₂ have been successfully grown from dichloromethane (DCM). The only different grown condition is that the DCM solution of the title compound contains different amount of water. Polymorphs I and II were obtained from dried DCM solution. Two other polymorphs, which were co-crystallized with either acetone or acetonitrile were reported. The molecular structures of these four polymorphs were similar except that they have different co-crystallized solvents. Short Au-Au contact and terminal type of Au-Cl bond have been observed in these polymorphs. They are 2.975(3) Å for polymorph I and 3.007(1) Å for polymorph II, which are comparable to those found in the other two polymorphs. Though all of these polymorphs show similar terminal Au-Cl bond, polymorph II has exceptional short Au-Cl distance of 2.760(3) Å. Polymorph III was crystallized from DCM solution saturated with water. The molecular structure in this polymorph is totally different from the others. One of Cl-bridging between two Au(I) centers and the other is served as a counter ion. Two Au-Cl distances are 2.977(9) and 2.955(9) Å. This is the first and the only polymorph of [Au(dppm)Cl]₂ with bridging Cl-. The Au-Au separation, 2.938(2) Å, is significant short than those found in the terminal type of polymorphs. Due to the structural difference, the luminescent maximum for polymorph III is different from the others.

Crystal Data: polymorph I, a=13.047(1), b=19.425(2), c=11.531(1) Å, β=116.120(1)°, V=2623.8(6) Å³, monoclinic, P2₁/c, R=0.0475; polymorph II, a=10.962(1), b=11.276(1), c=12.147(1) Å, α=109.091(1), β=107.667(2), γ=97.707(2)°, V=1305.7(4) Å³, triclinic, P-1; R=0.0495; polymorph III, a=23.712(2), c=19.931(2) Å, V=11206(2) Å³, tetragonal, I4, R=0.0549.

PS07.02.13 LOW TEMPERATURE STUDIES OF MIXED VALENCE DINUCLEAR Mn COMPOUNDS. Claire Wilson, F. Krebs Larsen, Department of Inorganic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark, and Brian N. Figgis, Department of Chemistry, University of Western Australia, Nedlands, WA 6009, Australia.

Mixed valence Mn compounds provide important, small molecule models for the metalloenzyme OEC (Oxygen Evolving Complex) of photosystem II involved in photosynthesis in green plants.

The first charge density study of a bis(μ-oxo)Mn(III)Mn(IV) dimer, bis(μ-oxo) tetrakis (2,2'-bipyridine) dimanganese(III,IV),¹ revealed a substantial accumulation of electron density at the μ-oxygen atoms in the MnO₂ ring. In an attempt to follow up this study with a combined X-ray and neutron diffraction study of the perchlorate salt of this compound different media for crystal growth were tested, particularly with the growth of large crystals for the neutron study in mind.

Very nice crystals were indeed formed with the surprising incorporation of nitrobenzene molecules in the crystal. X-ray data for these crystals have been collected at room temperature, 200 K and 9 K. However, some effect causing reversible splitting of diffraction intensities is at work below 200 K resulting in the 200 K structure being the best determined at this point.

Crystal data: Space group P2₁/n (No. 14), a= 16.374(6), b= 15.515(7), c= 21.969(8) Å, β= 93.17(2)° at 200 K.

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