PS07.02.06 STABILISATION OF MOYDBDENUM THIOLATE COMPLEXES BY BRIDGING NITROGEN LIGANDS, Ljubica Manojlovic-Muir, Kenneth W. Muir, Philippe Schollhammer and Francois Y. Peillot. a) Chemistry Department, Glasgow University, Glasgow G12 8QQ, UK; b) URA CNRS 322, Faculte des Sciences, Universite de Bretagne Occidentale, B.P. 800, Brest-Cedex, France.

Our interest in the structures of dinuclear and polynuclear molybdenum complexes stabilised by thiolate bridges arises from their importance as models for metal-sulphur sites in biological and catalytic systems. Besides this, such compounds have found applications as syntheses for the production of heteronuclear clusters. Our previous studies of the products of reactions of mono- and binuclear molybdenum organometallics with dimethyl sulfoxide have involved characterisation of new dinuclear and trinuclear molybdenum species such as [(CpMo(CO)2(m-SMe)2(m-SH))][BF4] and [CpMo(CO)(m-SMe)3Mo(CO)2(m-SMe)Mo(CO)2(Cp)] (see Schollhammer et al., 1995). A complication in this work has been the frequent occurrence of disorder in the bridging group of complexes based on a CpMo(m-SMe)3MoCp core. Examples of this will be presented. In addition, the structures of a number of compounds currently under investigation in this laboratory in which bridging nitrogen atoms are thought to stabilise the CpMo(m-SMe)3MoCp units will be described.


PS07.02.07 CRYSTAL STRUCTURES AND DISORDER IN TWO HETEROMETALLIC POLYSULFIDE COMPLEXES, Alok Kumar Mukherjee, Department of Physics, Jadavpur University, Calcutta-700032, India, Monika Mukherjee, Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700032, India.

Crystal structures and disorder of two heterometallic polysulfide complexes (PPh3)2[S2W5S5MnR2]. (1) M = Hg and R = CH3CH2 (2) M = Cd and R = I, have been studied by x-ray diffraction. Both the complexes crystallize in triclinic system. With Z=1 (established by density measurements) and the anions containing dissimilar metals [WI: Hg in 1 and WCd in 2] and terminal ligands [S,CHCH2 in 1 and S, I in 2] the centrosymmetric space group P1 is accommodated by a two fold anionic disorder. Due to crystallographically imposed inversion centers in the anions, only half of the dimer and one (PPh3)+ cation comprise the asymmetric unit in each case. The molecular geometries of the anions in the complexes containing (WS5-M) cores coordinated by terminal S2-CH2-CH2-I ligands are best described as distorted edge-condensed bitetrahedrons. The bridging sulfur atoms are bonded symmetrically to the metal atoms with W-Hg and W-Cd distances 3.180(1)Å and 3.178(2)Å in complexes 1 and 2 respectively. The discrepancy between the two Hg-Cl-C angles in 1 [177.9(6)°/165.8(4)°] and the two Cd-1 distances in 2 [2.714(2)/2.581(2)Å] can be attributed to the unresolved anionic disorder at the terminal sites. The relevant crystalographic data are summarised below:

1. a=9.841(2), b=10.070(1), c=13.454(5), α=105.11(1), β=95.51(2), γ=103.75(1); R (on F)=0.0318.
2. a=9.923(6), b=10.089(3), c=13.171(4), α=108.62(4), β=94.65(2), γ=100.24(3); R (on F)=0.0511.

PS07.02.08 LINEAR OLIGONUCLEAR METAL-METAL MULTIPLE BONDS, Shie-Ming Peng, Shen-Jye Shieh, Cheng-Chen Lin, Jint-Tsaur Sheu, Chin-Cheng Chou, Gene-Hsiang Lee. Department of Chemistry National Taiwan University Taipei Taiwan, R.O.C.

The nature of metal-metal bonding in dinuclear metal complexes is well understood. The extension of dinuclear metal complexes to oligonuclear metal-chain complexes is rare.

The bis(2-pyridyl)amido ligand (dpa) in the syn-syn conformation allows each nitrogen atom to coordinate with a separate metal ions forming metal-metal multiple bonds: e.g. the triruthenium(II) complex, [Ru(dpa)2Cl2]+, exhibits a three-centred triple bond among the three ruthenium ions (Ru-Ru, 2.2537(5)Å). The structure and magnetic interaction of quadruply bridged trinuclear molydate complexes [MII(dpa)2X3]+ (M=Rh, Rb, Co, Ni; X=Cl-, NCS- etc) are discussed. The work of further extension to tpda and tpda ligands will be presented.


For the first time, compounds of two cobalt(III) complexes, C1 and C2 are synthesized [C1=[Co(en)L1]+, C2=Co(dien)L2]+, L1 and L2 N,N-bis(2-aminomethyl)amino-3-propionate or S-ornithinic ions respectively]. L1 anions were prepared by the Hofmann destruction of corresponding amide, N,N-bis(2-carbamoylmethyl)amino-3-propionate, prepared, in its turn, from β-alanine and acrylamide.

The crystal and molecular structures of the C2 perchlorate, [C2][ClO4]2/1/2H2O, and chloromercuroates of both cations characterized by general formulae [C1][HgCl4] and [C2][HgCl4] are determined by x-ray analysis. Chloromercuroates of both types are deposited simultaneously from solutions of the corresponding perchlorates or chloride after addition of mercuric chloride in excess.

Both cations are low-spin octahedral cobalt(III) complexes of the Co(N3)2(O) type of the C1 cations, three N atoms of the L1 ligand are arranged facially, whereas in the C2 cations middle N atom of the din ligand lies in trans position to N atom of the ornithine side chain.

The crystals of [C1][HgCl4] compounds contain discrete tetrahedral tetracloromercurocetrilid(II) anions. Anionic parts of [C1][HgCl4] crystals are built of a variety of species. In some of them, there is interaction of Hg atoms with carboxylate O atoms of the complex cations. Three Hg-containing species are found in [C1][HgCl4] crystals:

a) HgCl4 anions coupled to O atom (tetrahedral HgCl4O species);

b) Cl3Hg(μ-Cl)HgCl3 dimers; and
c) centro symmetric Cl3Hg(μ-Cl)2HgCl3 dimers. The [C2][HgCl4] crystals contain two crystallographically unique HgCl3 and HgCl4O ions as well as Cl3Hg(μ-Cl)HgCl4O dimers.