PS07.02.06 STABILISATION OF MOLYBDENUM THIOLATE COMPLEXES BY BRIDGING NITROGEN LIGANDS. Ljubica Manojlovic-Muira, Kenneth W. Muira, Philippe Scholhammer^b and Francois Y. Petillon^{b.} aChemistry Department, Glasgow University, Glasgow G12 8QQ, UK; ^bURA CNRS 322, Faculte des Sciences, Universite de Bretagne Occidentale, B.P. 809, 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 synthons for the production of heteronuclear clusters.Our previous studies of the products of reactions of mono- and binuclear molybdenum organometallics with dimethyl disulphide have involved characterisation of new dinuclear and trinuclear molybdenum species, such as [{Cp*Mo(CO)}2(m-SMe)2(m-SH)][BF4] and $[CpMo(CO)(m-SMe)_3Mo(CO)_2(mSMe)Mo(CO)_2Cp]$ (see Schollhammer et al., 1995). A complication in this work has been the frequent occurrence of disorder in the bridging groups of complexes based on a CpMo(m-SMe)nMoCp 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 unit will be described.

Schollhammer, P., Pichon, R., Poder-Guillou, S., Talarmin, J., Muir, K.W., & Manojlovic-Muir, Lj. (1995). Organometallics, 14, 2277 - 2287 and refs therein.

PS07.02.07 CRYSTAL STRUCTURES AND DISORDER IN TWO HETEROBIMETALLIC POLYSULFIDO COMPLEX-ES. 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

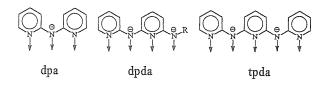
Crystal structures and disorder of two heterobimetallic polysulfido complexes $(PPh_4)_2[S_2WS_2MR_2]$, (1) M = Hg and R=CHCH₂ (2) M =Cd and R =I, have been studied by x-ray diffraction. Both the complexes crystallize in triclinic system. With Z = 1 (established by density measurements) and the anions containing dissimilar metals [W,Hg in 1 and W,Cd in 2] and terminal ligands [S,CHCH₂ in 1 and S, I in 2] the centrosymmetric space group $P\overline{1}$ is accommodated by a two fold anionic disorder. Due to crystallographically imposed inversion centers in the anions, only half of the dimer and one (PPh₄)+ cation comprise the asymmetric unit in each case. The molecular geometries of the anions in the complexes containing (WS2M) cores coordinated by terminal S2-,CHCH2- and I-ligands are best described as distorted edgecondensed 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-C-C angles in 1 [177.9(6)°/ 165.8(4)°] and the two Cd-I distances in 2 [2.714(2)/2.581(2)Å] can be attributed to the unresolved anionic disorder at the terminal sites. The relevant crystallographic data are summarised below: (1) a=9.841(2), b=10.070(1), c=13.045(3)Å, $\alpha=105.11(1)$, $\beta=95.51(2)$, $\gamma = 103.75(1)^\circ$; R (on F)= 0.0318.

(2) a=9.923(6), b=10.089(3), c=13.171(4)Å, 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, Jinn-Tsair 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, [Ru₃(dpa)₄Cl₂], exhibits a three-centred triple bond among the three ruthnium ions (Ru-Ru, 2.2537(5) Å). The structure and magnetic interaction of quadruply bridged trinuclear metal complexes [MII₃(μ_3 dpa)₄X₂]° (M = Ru^{II}, Rh^{II}, Co^{II}, Ni^{II}; X = Cl-, NCS- etc) are discussed. The work of further extension to tpda and tpda ligands will be presented.



PS07.02.09 CHLOROMERCURATES OF TWO AMINECARBOXYLATE COBALT(III) COMPLEXES. Kerry D. Robinson and Izya F. Burshtein, Siemens Energy and Automation, Inc., 6300 Enterprise Ln., Madison, WI 53719-1173, USA, Anatolii L. Poznyak, Institute of Molecular and Atomic Physics, 220072, Minsk, Belarus

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

The crystal and molecular structures of the C² perchlorate, [C²] (ClO₄)₂. 1/2H₂O, and chloromercurates of both cations characterized by general formulae [C]HgCl₄ and [C]Hg₂Cl₆ are determined by x-ray analysis. Chloromercurates 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 $Co(N)_5(O)$ 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 dien ligand lies in *trans* position to N atom of the ornithinate side chain.

The crystals of [C]HgCl₄ compounds contain discrete tetrahedral tetracloromercurate(II) anions. Anionic parts of [C]Hg₂Cl₆ 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]Hg₂Cl₆ crystals: a) HgCl₃ anions coupled to O atom (tetrahedral HgCl³O species); b) Cl₃Hg(μ -Cl)HgCl₂ dimers; c) centrosymmetric Cl₂Hg(μ -Cl)₂HgCl₂ dimers. The [C₂]Hg₂Cl₆ crystals contain two crystallographically unequivalent HgCl₃ and HgCl₃O ions as well as Cl₃Hg(μ -Cl)HgCl₂O dimers.