

PS07.02.06 STABILISATION OF MOLYBDENUM THIOLATE COMPLEXES BY BRIDGING NITROGEN LIGANDS. Ljubica Manojlovic-Muir^a, Kenneth W. Muir^a, Philippe Schollhammer^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 $[\{Cp^*Mo(CO)_2(m-SMe)_2(m-SH)\}][BF_4]$ and $[CpMo(CO)(m-SMe)_3Mo(CO)_2(m-SMe)Mo(CO)_2Cp]$ (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.

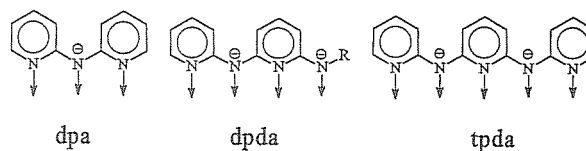
PS07.02.07 CRYSTAL STRUCTURES AND DISORDER IN TWO HETEROBIMETALLIC POLYSULFIDO COMPLEXES. Alok Kumar Mukherjee, Department of Physics, Jadavpur University, Calcutta-700032, India, Monika Mukherjee, Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700032,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

Crystal structures and disorder of two heterobimetallic polysulfido complexes $(PPh_4)_2[S_2WS_2MR_2]$, (1) $M = Hg$ and $R = CHCH_2$ (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 [$S, CHCH_2$ in 1 and S, I in 2] the centrosymmetric space group $P\bar{1}$ is accommodated by a two fold anionic disorder. Due to crystallographically imposed inversion centers in the anions, only half of the dimer and one $(PPh_4)^+$ cation comprise the asymmetric unit in each case. The molecular geometries of the anions in the complexes containing (WS_2M) cores coordinated by terminal $S^2-, CHCH_2-$ and $I-$ 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 $Hg-C-C$ angles in 1 [$177.9(6)^\circ/165.8(4)^\circ$] 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) $a=9.923(6)$, $b=10.089(3)$, $c=13.171(4)Å$, $\alpha=108.62(4)$, $\beta=94.65(2)$, $\gamma=100.24(3)^\circ$; 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, $[Ru_3(dpa)_4Cl_2]$, 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 metal complexes $[M^{II}_3(\mu_3dpa)_4X_2]^0$ ($M = Ru^{II}, Rh^{II}, Co^{II}, Ni^{II}$; $X = Cl^-, NCS^-$ etc) are discussed. The work of further extension to tpda and dpda 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, C^1 and C^2 are synthesized ($C^1 = [Co(en)L^1]^{2+}$, $C^2 = [Co(dien)L^2]^{2+}$, L^1 and L^2 N,N-bis(2-aminoethyl) amino-3-propionate or S-ornithinate ions respectively). L^1 anions were prepared by the Hofmann destruction of corresponding amide, N,N-bis(2-carbamoyl ethyl)amino-3-propionate, prepared, in its turn, from β -alanine and acrylamide.

The crystal and molecular structures of the C^2 perchlorate, $[C^2](ClO_4)_2 \cdot 1/2H_2O$, and chloromercurates of both cations characterized by general formulae $[C]HgCl_4$ and $[C]Hg_2Cl_6$ 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 C^1 cations, three N atoms of the L^1 ligand are arranged facially, whereas in the C^2 cations middle N atom of the dien ligand lies in *trans* position to N atom of the ornithinate side chain.

The crystals of $[C]HgCl_4$ compounds contain discrete tetrahedral tetrachloromercurate(II) anions. Anionic parts of $[C]Hg_2Cl_6$ 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 $[C^1]Hg_2Cl_6$ crystals: a) $HgCl_3$ anions coupled to O atom (tetrahedral $HgCl_3O$ species); b) $Cl_3Hg(\mu-Cl)HgCl_2$ dimers; c) centrosymmetric $Cl_2Hg(\mu-Cl)_2HgCl_2$ dimers. The $[C^2]Hg_2Cl_6$ crystals contain two crystallographically nonequivalent $HgCl_3$ and $HgCl_3O$ ions as well as $Cl_3Hg(\mu-Cl)HgCl_2O$ dimers.