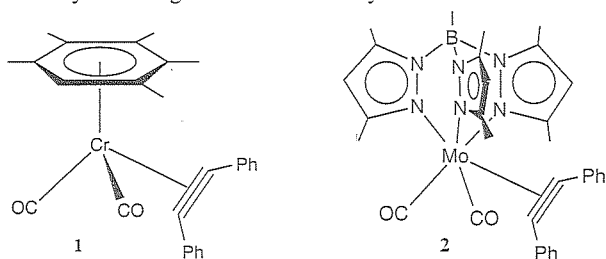


**PS07.01.12 BONDING IN METAL-ALKYNE COMPLEXES: CRYSTALLOGRAPHIC STUDIES OF REDOX PAIRS.**

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Structural changes occurring as a result of one electron oxidation may be used as a probe of electronic structure. In this study we report a study of metal-alkyne bonding based on redox pair structures determined by low-temperature X-ray crystallography. The complexes studied include  $[\text{Cr}(\text{CO})_2(\eta^2\text{-C}_2\text{Ph}_2)(\eta^6\text{-C}_6\text{Me}_5\text{H})]$  (1) and  $[\text{Mo}(\text{CO})_2(\eta^2\text{-C}_2\text{Ph}_2)\text{Tp}']$  (2) (see below).<sup>1</sup> In each case both the neutral and cationic complexes were studied. Formally these are sixteen (2+), seventeen (1+, 2), and eighteen (1) electron alkyne complexes. In practice the alkyne may act in the limit as either a two-electron or a four-electron donor. In the latter case there is a  $\pi$ -symmetry interaction between an empty d-orbital on the metal and a filled  $\pi_1$  orbital on the alkyne.<sup>2</sup> The structural changes observed are significant and together with Extended Hückel MO and ESR spectroscopic studies provide a detailed insight into the nature of the metal-alkyne bonding in these and related systems

**References.**

1. N.G. Connelly *et al* *J. Chem. Soc. Chem. Comm.*, 1992, 1293 and unpublished work
2. J.L. Templeton *et al* *J. Am. Chem. Soc.*, 1981, 103, 7713.

**PS07.01.13 THE STRUCTURE AND MOLECULAR STRUCTURE OF COPPER L-TARTRATE,  $\text{CuC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ .**

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The investigation of the crystal structure of copper L-tartrate was taken as a part of study of coordination of copper (II) complexes and for providing basic structural data to make clear the influence of structural characteristics of complexes on their biological activities. The first compound to be studied in this series was manganese L-tartrate tetrahydrate<sup>1</sup>.

The title compound crystallises in the monoclinic space group  $P2_1(P2_1/m)$  with  $a=8.374(4)\text{Å}$ ,  $b=12.849(7)\text{Å}$ ,  $c=8.758(6)\text{Å}$  and  $Z=4$ . The structure was solved by Patterson and Fourier method and refined by full matrix least squares technique to  $R=0.10$  for 580 independent reflections collected photographically.

Each Cu atom forms a total of five bonds with three tartrate molecules. A six bond is formed with water, resulting in a distorted octahedral coordination geometry. Each copper atom are chelated by two tartrate groups and each tartrate group chelates two copper atoms. The coordination around each copper atom is completed by a water molecule and a non-chelating carboxy-oxygen atom of another tartrate group. The dimensions of the tartrate groups are significantly different from those found manganese L-tartrate tetrahydrate.

**PS07.01.14 THE CRYSTAL AND MOLECULAR STRUCTURE OF GADOLINIUM 3,5-DINITROBENZOATE TRIHYDRATE.**

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In the crystal structure of the title molecule,  $\text{Gd}(\text{C}_7\text{H}_3\text{N}_2\text{O}_6)_3 \cdot 3\text{H}_2\text{O}$ , Gd ions are bridged by the carboxylate groups to form linear polymeric chains. The coordination around Gd is eight fold; six O atoms from six carboxylate groups and two from water molecules. The third water molecule in the formula unit is crystal water. The structural studies of rare earth carboxylates except Cerium 3,5-dinitrobenzoate dihydrate has shown that the carboxylate groups may be coordinated simultaneously in three modes: chelating, bridging and chelating-bridging. The structure of Gd-compound has only bridging type of bonding as observed in the Ce-compound. The bridges between the consecutive Gd-atoms involve four ligands on one side and two on the other; causing a nonequidistant and alternating Gd-Gd order within the polymeric chains. Alternating Gd-Gd distances are 4.255 and 5.061 Å respectively. The average GdO distances for carboxylate oxygens is 2.375 Å while for water oxygens the same distance has an average value of 2.500 Å. Crystals are triclinic, space group P1, with  $a=9.274$ ,  $b=11.483$ ,  $c=13.745\text{Å}$ ,  $\alpha=107.11^\circ$ ,  $\beta=90.50^\circ$ ,  $\gamma=93.82^\circ$  and  $Z=2$ . Data collection CAD4, structure solution MolEN software package.

**Two or More Metal Ions****PS07.02.01 MOLECULAR MODELLING OF DIMETAL SYSTEMS.**

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A significant feature of the dinuclear metal cluster complexes with multiple metal-metal bonds are their geometries; typically very short metal-metal bonds and eclipsing ligand atoms. These features have been modelled by Boeyens using Molecular Mechanics [1]. This study extends the techniques developed by Boeyens to dinuclear clusters where the bond order is uncertain and to clusters containing mixed metal atoms. This allows for the electronic effects in the metal-metal bond to be studied by quantifying and hence subtracting contributions made by steric effects to the overall metal-metal bond interaction. Thus the electronic nature of the dimetal bond can be studied in greater detail.

The force field for metal-metal bonds is not well established in the literature. Therefore suitable values of the force constant,  $k$  and the undistorted bond length,  $r_0$  of the metal-metal bond are chosen empirically. A likely value of  $r_0$  is assumed and  $k$  is adjusted until a combination ( $k$ ,  $r_0$ ) is found to reproduce the observed structure after refinement. The transferable force field parameters for the dimetal bond are determined by identifying a unique pair ( $k$ ,  $r_0$ ) for the metal-metal bond occurring in two different steric environments.

1. J. C. A. Boeyens, *Inorganic Chemistry*, 1985, 24, 4149.