

**PS07.00.21 STRUCTURE INVESTIGATIONS OF RUTHENIUM-MANGANESE POLYPYRIDYL COMPLEXES.**

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Syntheses and structure determinations by single crystal X-ray diffraction techniques have been / is presently performed for: **1** [Ru-bis(dipyridyl)-6-carboxylate], **2** [Ru-bis(dipyridyl)(dipyridyl-6-yl-acetic acid)PF<sub>6</sub>], **3** [Ru(terpyridyl)(dipyridyl-6-carboxylate)Cl<sub>2</sub>](x=1-2) **4** [Ru-bis(dipyridyl)(picolinic acid)]PF<sub>6</sub>, **5** [Ru-Mn complex] 4PF<sub>6</sub>, **6** [Ru-Mn complex] 4PF<sub>6</sub>.

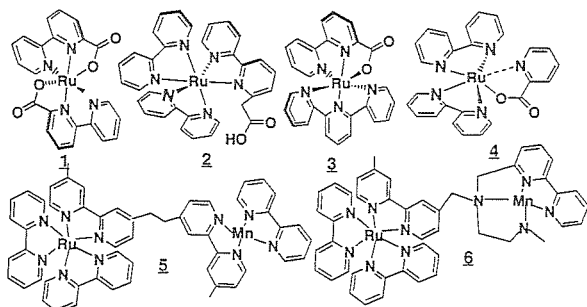
These investigations are part of a project focused on studies of artificial photosynthesis reactions [1,2]. Experiments performed comprehend the syntheses, structural characterisations by single crystal X-ray diffraction and NMR, UV-vis. techniques [3].

The more recent studies include *i.a.* investigation of new types of Ru-Mn-polypyridine complexes with possible applications in artificial photonelectron transfer reactions.

[1] Balzani, V. *et al.*, Ru(II)polypyridine complexes, *Coord. Chem. Rev.* 84 (1988) 85-277

[2] Meyer, T.J., *Chem. Appr. to Artificial Photosynthesis*, *Acc. Chem. Res.*, 22 (1989)163

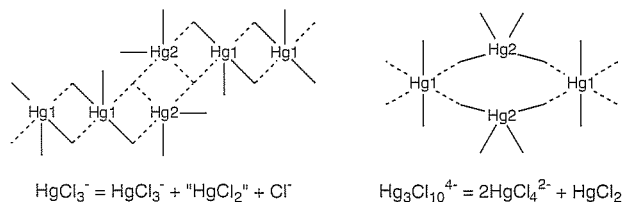
[3] L. Hammarström *et al.* To be published in *Journal of Organometallics*.


**PS07.00.22 STRUCTURAL DIVERSITY IN CHLOROMERCURY(II) SALTS.**

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Chloromercurate complexes are well known for the ability of their anions to exhibit a wide range of geometry, stoichiometry and connectivity. The anions of the salts formed by the addition of 2-, 3- and 4-chloropyridine to HgCl<sub>2</sub> in conc. HCl have remarkably different structures. The 2-chloropyridinium salt has the HgCl<sub>3</sub><sup>-</sup> stoichiometry, but the anions consist of infinite chains made up from HgCl<sub>3</sub><sup>-</sup> distorted HgCl<sub>2</sub> and Cl<sup>-</sup> moieties linked by longer Hg...Cl contacts which range from 2.80 to 3.30 Å. The Cl<sup>-</sup> ion bridges three Hg centres and is also hydrogen bonded to both of the independent cations. The Hg centres exhibit distorted trigonal bipyramidal and square pyramidal coordination. The 3- and 4-chloropyridinium salts have included an additional Cl<sup>-</sup> ion to give the Hg<sub>3</sub>Cl<sub>10</sub><sup>4-</sup> stoichiometry. The anions consist of infinite chains made up from HgCl<sub>2</sub> and HgCl<sub>4</sub><sup>2-</sup> entities interconnected by longer Hg...Cl contacts, so that Hg1 has octahedral coordination, while Hg2 is tetrahedrally coordinated. Although the 3- and 4-chloropyridinium salts have anions constructed in the same fashion, there is still considerable variation between the two structures in terms of the bond lengths and angles within the anionic chains and distortions of the coordination geometry at each Hg centre. Across the two structures, the long Hg...Cl contacts vary from 2.93

to 3.25 Å. A second preparation of the 3-chloropyridinium salt under similar conditions yielded crystals with distorted Hg<sub>2</sub>Cl<sub>6</sub><sup>2-</sup> dimers linked into chains by a single long Hg...Cl contact.


**PS07.00.23 STRUCTURAL CHEMISTRY OF MULTIPLY BUTYLATED CYCLOPENTADIENE TRANSITION-METAL COMPLEXES.**

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Representative structures of polybutylcyclopentadiene dicarbonyl triphenyl phosphineiron have been determined with single crystal X-ray diffraction to see to what extent the structure deformations are as caused by the presence of bulky butyl groups on the ring. Revealed in these structures is the common feature of complexes - a square-pyramidal Fe(0) center with one of the CO groups in the apical position and one olefin of diene moiety *trans* to the second CO, and the other olefin of diene *trans* to PPh<sub>3</sub> in the basal plane. The IR data indicates that the increase of butyl substitution on the ring red-shifts the ν<sub>CO</sub> stretching frequencies by 4-5 cm<sup>-1</sup> per butyl group. With increasing number of butyl substitutions on the ring, the Fe-P bond length increases from 2.211(1) Å in **1Bu**, 2.216(1) Å in **1,2,5-3Bu**, 2.229(1) Å in **1,2,3,5-4Bu**, to 2.236(1) Å in **5Bu** where **1Bu** = (η<sup>4</sup>-*exo*-BuC<sub>5</sub>H<sub>5</sub>)-Fe(CO)<sub>2</sub>PPh<sub>3</sub>, **1,2,5-3Bu** = (η<sup>4</sup>-*exo*-1,2,5-Bu<sub>3</sub>C<sub>5</sub>H<sub>3</sub>)Fe(CO)<sub>2</sub>PPh<sub>3</sub>, **1,2,3,5-4Bu** = (η<sup>4</sup>-*exo*-1,2,3,5-Bu<sub>4</sub>C<sub>5</sub>H<sub>2</sub>)Fe(CO)<sub>2</sub>PPh<sub>3</sub> and **5Bu** = (η<sup>4</sup>-*exo*-Bu<sub>5</sub>C<sub>5</sub>H)Fe(CO)<sub>2</sub>PPh<sub>3</sub>.

**PS07.00.24 CRYSTAL STRUCTURES OF TWO Cu(II) COMPLEXES WITH TETRADENTATE SCHIFF BASE LIGANDS.**

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Transition-metal complexes containing tetradentate Schiff base ligand have been extensively studied. The magnetic, electronic and electrochemical properties of these complexes depend markedly on different derivatives of Schiff base ligands. Among bridged Schiff base complexes, the imino nitrogen atoms are bound together with polymethylene chains which, through variation of their length, allow tuning of geometry around the metal centre. (Garnovskii, Nivorozhkin & Minkin, *Coord. Chem. Rev.*, 1993, 126, 1-69) In order to study the effect of polymethylene chains on the structures of Cu(II) complexes, we have prepared and studied the structures of the two Cu(II) complexes which were determined by x-ray diffraction. (A). Cu(II) complex of N,N'-bis-(2-hydroxybenzyl)1,3-diiminopropane, [Cu(C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>)], Orthorhombic, Pna2<sub>1</sub>, a=12.021(1), b=17.918(3), c=6.8740(7) Å, R=0.044, wR=0.072 for 2317 observed reflections; (B). Cu(II) complex of N,N'-bis-(2 hydroxybenzyl)1,3-diimino-2,2-dimethylpropane, [Cu(C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>)], Monoclinic, P2<sub>1</sub>/n, a=9.7329(9), b=17.186(2), c=11.338(1) Å, β=112.99(1), R=0.064, wR=0.077 for 3998 observed reflections. Both of the two complexes are four coordinated with Cu(II) in distorted tetrahedral geometry with two imines N atoms and two phenol O atoms. The related ethylene diamine analogue, N,N'-bis-(2hydroxybenzyl)1,2 diiminoethane copper, exhibits a square-planar coordination. (Hall & Waters, *J. Chem. Soc.*, 1960, 2644)