09. X–1   MIXED-VALENCE PLATINUM COORDINATION COMPOUNDS

WITH SPECIAL ATTENTION FOR CHAIN-TYPE SPECIES. C.J.L. Lock, Laboratories for Inorganic Medicine, Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada L8S 4M1.

The structural features of platinum dimeric and tetrameric complexes with pyrimidines with platinum in oxidation states 2.25, 2.5, 2.75, 3.0 will be contrasted with platinum infinite chain polymers. These in turn will be contrasted with compounds containing the $\cdot-X-Pt^{II}-X-Pt^{IV}-X\cdots$ chains.

09. X–2   PLATINUM BLUE STRUCTURES.

By B. Lippert, Anorganisch-Chemisches Institut der Technischen Universität München, 8046 Garching, F.R.G.

The paper reviews our present understanding of the nature and structure of "platinum pyrimidine blues", a class of potent antitumor agents, which are formed on reaction of cis-$(NH_3)_2Pt(H_2O)_2^{2+}$ with cyclic amides such as uracil, thymine, α-pyridone, α-pyrrolidone, 1-methylhydantoin etc. The blues are a heterogeneous mixture of compounds containing both diamagnetic and paramagnetic, mixed-valence state Pt species.

Selected examples of crystallographically characterized compounds containing one, two, and four Pt atoms in the oxidation states +2, +2.25, +2.5, +3, and +4 will be discussed. Other feasible structures of platinum blue components, derived from crystallographic studies on heteronuclear Pt_x, M_y compounds with 1-methyluracil and 1-methylthymine ligands, are proposed.

09. X–3   COPPER(I) AND COPPER(II) COMPLEXES OF

BINUCLEATING MACROCYCLIC LIGANDS. By S.M. Nelson, Queen's University, Belfast, N. Ireland, and M.G.B. Drew, The University, Reading, U.K.

The recognition of the occurrence of pairs of copper atoms in close proximity in the so-called Type 3 copper proteins such as hemocyanin, tyrosinase, laccase, etc., has stimulated efforts by inorganic chemists to synthesise low molecular weight di-copper complexes as potential models for the active sites in the natural systems. This paper outlines the development of recent work in several laboratories but with an emphasis on di-copper complexes of binucleating macrocyclic ligands. The structures of a wide range of di-Cu(I) and di-Cu(II) complexes differing in metal-metal separation, nature of donor atoms, and coordination geometry will be described. Many of the complexes are capable of binding small molecules and ions as bridging ligands between the metal centres leading, in the di-Cu(II) systems, to magnetic coupling. The magnitude of the coupling, as determined by ESR spectra and magnetic susceptibility measurements, is governed largely by the metal ion geometry and the nature of the bridging ligands which include OH^-, OR^-, SR^-, pyrazolate, pyridazine, imidazolate. Since the biological function of Type 3 copper proteins is associated with reactions involving dioxygen (as carriers, oxygenases and oxidases), the reactivity of the synthetic di-Cu(I) complexes with dioxygen will be briefly discussed.

09. 1–1   STRUCTURE OF HYDROGEN BONDED COMPLEXES. RELATION BETWEEN O$\cdots$O

DISTANCES AND DISSOCIATION CONSTANTS OF ACIDS AND BASES.

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The structures of the 1:1 complexes formed by 4-nitropyridine N-oxide (NPNO) with 4-aminobenzoic acid (ABA) and 8-chlorophenol (CP) have been determined. The variation of the O ... O distances (R_{O-O}) observed by X-ray diffraction with respect to the acid-base properties of the moieties responsible for the hydrogen bond has been analyzed. The H-bonded complexes of the type A–H...B were characterized by ΔpKa equal to the difference between pKa of AH and pKa of the acid conjugated to B($\overset{+}{B}H$). The complexes studied were hydroquinone(HQ)1,4-naphthoquinone (ΔpKa = 17.95, R_{O-O} = 2.73), HQ acetone (17.55, 2.74), 3-aminophenol. NPNO (11.98, 2.695), HQ.NPNO (12.05, 2.690), CP.NPNO (10.55, 2.668), ABA.NPNO (6.62, 2.618), oxalic acid . furamide (3.84, 2.53), trichloracetic acid. triphenylphosphine oxide (2.80, 2.496), hydrogenobistribenzylphosphine oxide (0, 2.378). The following expression :

$$R_{OO}(\text{Å}) = 2.374 + 0.1754 \ln (0.405 \Delta pKa + 1)$$

where the parameters have been adjusted by least-squares by minimizing the function $\Sigma[(R_{OO \ obs})-(R_{OO \ calc.})]^2$ was found which reproduces the observed distances with an error less than 0.02 Å.