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,
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The structural features of platinum dimeric and tetra­
meric complexes with pyrimidines with platinum in oxid­
ation 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 --X--
PtII-X-PtIV-X---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 pyrimi­
dine blues", a class of potent antitumor
agents, which are formed on reaction of cis-
(NH₃)₂Pt(H₂O)₂²⁺ with cyclic amidines such as
uracil, thymine, α-pyrrole, α-pyrrolidine,
1-methylhydantoin etc. The blues are a hetero­
geneous mixture of compounds containing both
diamagnetic and paramagnetic, mixed-valence
state Pt species.

Selected examples of crystallographically
characterised 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 Pt₂X₆ 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 synthe­
sise 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
diffusing 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⁻, O₂⁻,
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 COM­
PLEXES. RELATION BETWEEN D...O
DISTANCES AND DISSOCIATION CONSTANTS OF ACIDS
AND BASES.
J. LECHAT - Instituto de Fisica e Quimica de SÃO CARLOS,
Universidade de SÃO PAULO, SÃO CARLOS, BRASIL

The structures of the 1:1 complexes formed by 4-aminopyr­
ridine N-oxide (NPNO) with 4-aminobenzoic acid (ABA) and
3-chlorophenol (CP) have been determined. The variation of
the O ... O distances (R₀₀), observed by X-ray
diffraction with respect to the structural basis 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(OH). The complexes studied were hydroquinone(NO1),4-
naphthoquinone (ΔpKa = 17.85, pKₐ = 2.79), HO acetone
(17.85, 2.74), 3-aminopyridine, HNO (12.98, 2.695),
H₃NPNO (12.05, 2.690), CP.NPNO (10.55, 2.688), ABA.NPNO
(6.62, 2.618), oxalic acid formic acid (5.54, 2.53),
trichloracetic acid triphenylphosphine oxide (2.80,
2.496), hydrogenobistrizylphosphine oxide (0, 2.378).
The following expression:

\[ R₀₀(Å) = 2.374 + 0.1754 \ln (0.405 \Delta \text{pKa} + 1) \]

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

This work has been supported by CNPq.