Fig. 1   COORDINATION AROUND Hg IN

$Hg(BrO_3)_2 \cdot 2H_2O$ $K_2Hg(BrO_3)_2(NO_3)_2$
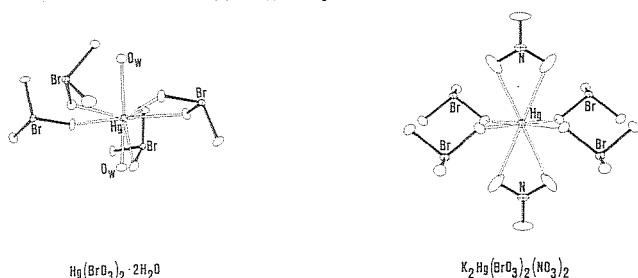
There also exist analogous Cd compounds with the compositions $Cd(BrO_3)_2 \cdot 2H_2O$ (Murty & Murty, Z. Kristallogr. (1978) 148, 10) and $K_2Cd(BrO_3)_2(NO_3)_2$. We have found that $Cd(BrO_3)_2 \cdot 2H_2O$ is isomorphous with $Hg(BrO_3)_2 \cdot 2H_2O$ and that $K_2Cd(BrO_3)_2(NO_3)_2$ has most probably a structure very similar to that of the Hg-compound. The cell dimensions are close to those of $K_2Hg(BrO_3)_2(NO_3)_2$ but the space group has changed from Pnnm to $P2_1/n$.

08.2-27   TRIPOTASSIUM cis-DIBROMO(HYDROGENDI-SULFITO)PLATINATE(II) MONOHYDRATE $K_3[Pt\{(SO_3)_2H\}Br_2] \cdot H_2O$ (I) AND ITS STRUCTURAL RELATIONSHIP TO $K_3[Pt\{(SO_3)_2H\}Cl_2]$ (II). D.K.Breitinger, G.Petrikowski and G.Bauer, Institut für Anorganische Chemie, Universität Erlangen-Nürnberg, Egerlandstr.1, D-8520 Erlangen, F.R.G.

(I) crystallizes in $P2_1/c$ with $\underline{a} = 8.764(4)$, $\underline{b} = 6.934(2)$, $\underline{c} = 21.544(9)$ Å, $\beta = 99.32(4)°$, $Z = 4$. The structure was solved by Patterson and Fourier methods using 1801 unique diffractometer data and refined to $R_w = 0.0288$. In the distorted square-planar anion Pt is surrounded by two S and two Br atoms in cis position. Short Pt-S and long Pt-Br bonds (averages 2.244 and 2.488 Å, respectively) suggest a strong trans influence of the sulfite ligand. An extremely short intramolecular hydrogen bond [O··H··O distance 2.380(8) Å] links the sulfite ligands to form a six-membered ring. The anions are arranged in layers, held together mainly by one kind of K^+ ions and H_2O molecules. Linkage of the layers is performed by two further sets of K^+ ions. In the anions of (II), $Cmc2_1$, $Z = 4$ (Kehr,W.G., Breitinger,D.K. and Bauer,G. (1980). Acta Cryst. B 36, 2545 – 2550) and of (I) the Pt-S and hydrogen bonds are very similar. For comparison of the structural arrangements (I) is transformed by 1,0,0;2,0,0;0,-1,0 (setting $P2_1/b$) and (II) by 1/2,1/2,0;0,1,0;0,0,1. Then $\underline{a}'$, $\underline{c}'$ and γ' are almost the same in both structures, with $\underline{b}'$(I) about 2.4 times that of (II). Building blocks common to both structures are pairs of anions correlated by 2_1 axes (|| $\underline{c}'$); in (II) these pairs are the translational unit, whereas in (I) pairs of such pairs correlated by inversion centres constitute the translational unit in the layers.

08.2-28   STRUCTURE DETERMINATION OF $Li_xPt_3O_4$ AND $Co_xNa_yPt_3O_4$ BY NEUTRON POWDER DIFFRACION. By K.B. Schwartz, J.B. Parise, Department of Earth and Space Sciences, SUNY, Stony Brook, New York, USA and R.D. Shannon, Central Research and Development, E.I. du Pont de Nemours and Company, Wilmington, Delaware, USA.

$Li_xPt_3O_4$, a member of the $Na_xPt_3O_4$ structural family (Bergner and Kohlhaas, Z. Anorg. Allg. Chem. (1973) 401, 15), has been synthesized by solid state reaction of LiF, $LiNO_3$ and α PtO_2. Refinement of neutron powder diffraction data by profile analysis (Rietveld, J. Appl. Cryst. (1969) 2, 65) has determined that $Li_{.65}Pt_3O_4$ is not isostructural with $Na_xPt_3O_4$ (space group Pm3n), but belongs to the acentric subgroup P$\bar{4}$3n. $Li_{.65}Pt_3O_4$, with unit cell dimension a=5.6242 A, contains Li in position 2a (0,0,0), Pt in position 6d (1/4,0,1/2) and O in position 8e (x,x,x) with x=0.2720(3). Equivalent isotropic temperature factors for Li, Pt and O are 2.8(4), 0.11(4) and 0.95(4), respectively. The structure is distinguished by distortion of the cubic coordination polyhedron about Li to two interpenetrating tetrahedra with Li-O distances of 2.22 A and 2.65 A. Pt coordination remains square-planar with a slight tetrahedral distortion and a Pt-O distance of 2.00 A. Refinement of scattering power on the Li site yields a Li occupancy of 0.67(5) atoms per formula unit, in close agreement with chemical analysis (0.64(11) by atomic absorption). Final discrepancy factors for this refinement are R_1=3.60, R_2=11.70 and R_3=15.94%. $Co_xNa_yPt_3O_4$, with x~0.4 and y~0.1 as determined by atomic absorption, was synthesized by solid state reaction of CoF_2, NaF, $Co(NO_3)_2 \cdot 6H_2O$ and α PtO_2. Neutron powder diffraction experiments have indicated the presence of reflections of the type hhl: l$\neq$2n, in violation of both space groups Pm3n and P$\bar{4}$3n. This reduction in symmetry is a result of ordering of Co and Na on distinguishable eight-coordinated sites. $Co_xNa_yPt_3O_4$ belongs to a subgroup of Pm3n, either the centric Pm3 or the acentric P23. Both these space groups are characterized by positions at 0,0,0 and 1/2,1/2,1/2 unrelated by symmetry, which is compatible with ordering of Co and Na.

08.2-29   PREPARATION,X-RAY STRUCTURE OF THE LINEAR CHAIN MIXED-VALENCE TETRAKIS(DITHIOACETATO)DIPLATINUM IODIDE:$Pt_2(CH_3CS_2)_4I$. By C.Bellitto,A.Flamini,L.Gastaldi and L.Scaramuzza,C.N.R.,Istituto Teoria,Struttura Elettronica Composti di Coordinazione,Area della Ricerca,P.B. 10,Monterotondo Staz.(Roma)Italy.

In the past decade there has been a considerable interest in the chemical and physical properties of highly conducting 1-D systems.(See for ex. "Synthesis and properties of low-dimensional materials",Ann.N.York,Acad.Scie.313 (1978)). In an attempt to synthesize new partially oxidized compounds,we studied the reaction of tetrakis(dithiocarboxylato)diplatinum(II)complexes with halogens (C.Bellitto , A.Flamini,unpublished results).Here we report the reaction of the tetrakis(dithioacetato)diplatinum(II) with iodine,and the crystal and molecular structure of $Pt_2(CH_3CS_2)_4I$ .Direct reaction of equimolecular tetrakis(dithioacetato)diplatinum(II) with iodine,in toluene,gives a dark violet powder of $Pt_2(CH_3CS_2)_4I_2$, while the same reaction carried out through a glass frit/polystyrol membrane,gives dark microcrystals of $Pt_2(CH_3CS_2)_4I$.The latter compound crystallises in the monoclinic C2/c space group with cell dimension : $\underline{a}$=16.838(4),$\underline{b}$=8.633(2),$\underline{c}$=13.634(4) Å, β=109.39(5)°,$\underline{Z}$=8. The structure was refined to R=0.06 for 1206 significant reflections. The structu-

re consists of chains of   --$Pt_2(CH_3CS_2)_4$--I--
$Pt_2(CH_3CS_2)_4$--I--,with an intradimeric Pt-Pt
distance of 2.677(2) Å and the Pt-I distances
of 2.975(2) and 2.981(3) Å.The Pt and I atoms
lie along the twofold axes of the unit cell.
Each platinum is surronded by four sulphur a-
toms in a square planar arrangement with   an
average Pt-S distance of 2.324 Å. The two [Pt-
S_4] units are rotated by 21° from the eclipsed
structure.The full structure with some   rele-
vant physical properties will be discussed.

08.2-31   CRYSTAL DATA OF $NH_3(MoO_3)_3$. By <u>J. Garin</u>
and Johnny Blanc. Departamento de Metalurgia, Universi-
dad Técnica del Estado. Santiago, Chile.

Many compounds are formed in the system
MoO_3-NH_3-H_2O. Several new ones have been prepared by
direct synthesis from the component chemicals, and pow-
der and single crystal data have been collected.
The crystal data for $NH_3(MoO_3)_3$ has been
determined by recording three dimensional data on Weis-
senberg and precession photographs, using Ni-filtered
Cu K_α radiaton. The compound crystallizes in the hexa-
gonal system with space group $P6_3/m$. The unit cell di-
mensions are:

$$a = 10.568 \pm 0.003 \text{ Å}, \quad c = 3.726 \pm 0.001 \text{ Å}$$

The density calculated assuming two formula
units in the unit cell is 4.137 g cm^{-3}; the measured
value is 4.100 g cm^{-3}. The chemical composition of the
crystal, calculated from data given by usual analysis
techniques, was found to be very close to stoichiometry.
Studies to determine the precise crystal
structure are being continued.

08.2-30   THE DISORDER STRUCTURE OF BENZYLURANOCENE,
$(C_4H_4C_8H_6)_2U$. <u>Allan Zalkin</u>, Robert Kluttz and David H.
Templeton, Materials and Molecular Research Division,
Lawrence Berkeley Laboratory and Department of Chemistry,
University of California, Berkeley, California 94720
U.S.A.

Benzyl uranocene crystallizes in the monoclinic system,
space group $P2_1/c$ with cell dimensions, a = 9.524(4) Å,
b = 8.558(4) Å, c = 11.758(6) Å, β = 113.52(4)°. For
Z=2 d_x = 2.065 g/cm^3. The uranium-phased Fourier showed
severe disorder and did not reveal the molecular
structure. The structure was solved by recognizing
the nature of the disorder and then refining the struc-
ture by least-squares using distance restraints on the
geometry of the ligands. The conventional R factor was
0.056. In each molecule the two octagonal rings are
intermediate between eclipsed and staggered configura-
tions, with the hexagonal rings about 20° from being
eclipsed. Thus the external shape is somewhat symmetri-
cal, but the uranium atom, which is sandwiched by the
octagonal rings, is not in the center of the molecule.
The disorder consists of a mixture of this structure
and its inverse, located at the centers of symmetry
of the space group in such a way that the carbon atoms
of the two kinds of rings are intermingled.

08.2-32   THE CRYSTAL STRUCTURE OF A SODIUM DODECA-
MOLYBDOMONOPHOSPHATE. By <u>B. Hedman</u>, Department of
Inorganic Chemistry, University of Umeå, S-901 87 Umeå
Sweden.

Aqueous equilibrium studies of the H^+-MoO_4^{2-}-HPO_4^{2-}
system have shown that complexes $(H^+)_p(MoO_4^{2-})_q(HPO_4^{2-})_r$
are formed (Pettersson, L., Chem. Scr. (1975) 7, 145).
In solutions with Mo/P ratios $\sim$2.5 complexes (p,5,2)
with p=8, 9 and 10 dominate, while for Mo/P ratios 9
complexes (p,9,1) with p=14,15,16 and 17 are formed.
In the most acidic range weak indications of an addi-
tional complex was found and it was assumed to be a
(23,12,1) complex. Numerous solid phases with an Mo/P
ratio of 12 have been reported (Gmelin, 8. Aufl., 53,
(1935), 347), and the pure acid $H_3Mo_{12}PO_{40}\cdot29$-$30H_2O$
has been structurally investigated (Strandberg, R.,
Acta Chem. Scand. (1975) A29, 359). However, apart
from the present phase, no single crystal investigation
of a sodium salt has been reported.
  By slow evaporation of extremely acidic solutions
(pH<0) with a slight excess of P (Mo/P=12/1.33) bright
yellow crystals were obtained. They are triclinic, P1,
a=14.100(2), b=15.514(2), c=20.385(3) Å, α=85.39(1),
β=83.68(1), γ=81.23 °, V=4370.9 Å^3, D_m=3.20 Mg m^{-3}.
A total of 22601 unique reflexions within 2θ<58 ° were
measured (4-circle diffractometer, MoKα-radiation,
θ-2θ scan). The unit cell contains four $Mo_{12}PO_{40}^{3-}$
anions with the Keggin structure (Keggin, J.F., Proc.
Roy. Soc. London (1934) A144, 75). Sodium ions and
water molecules connect the anions in a three-dimen-
sional framework. Raman spectra (Lyhamn, L. and Petter-
son, L.) and ^{31}P NMR spectra of solutions prepared
from the solid phase as well as of the corresponding
equilibrium solutions will be discussed. In addition,
structural relationships between this anion and other
molybdophosphate anions will be described.