

09.4-46 MONOMERIC AQUO AND HYDROXO COMPLEXES OF PLATINUM(II). By J.F. Britten, P. Pilon, B. Lippert, and C.J.L. Lock, Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada. L8S 4M1.

Previous attempts to prepare monomeric aquo and hydroxo complexes of platinum(II) have been unsuccessful, (Faggiani, R., Lippert, B., Lock, C.J.L., J. Amer. Chem. Soc. (1977) 99, 777; Inorg. Chem. (1977) 16, 1192; (1978) 17, 1941; Lippert, B., Lock, C.J.L., Rosenberg, B., Zvagulis, M., Inorg. Chem. (1978) 17, 2971). Crystallization at low pH was no more successful, the product containing coordinated nitrate ion (Lippert, B., Lock, C.J.L., Rosenberg, B., Zvagulis, M., Inorg. Chem. (1977) 16, 1525) and this work, $[\text{Pt}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2)(\text{NO}_3)]\text{NO}_3$.

It was possible to explain the results and postulate the conditions under which monomeric Pt(II) hydroxo and aquo complexes might be obtained (Lock, C.J.L., ACS Symposium Series, Inorganic Chemistry in Biology and Medicine (1980) 140, 209) using Brown's model (Brown, I.D., J. Chem. Soc., Dalton, in press). We have now obtained such complexes $[\text{Pt}(\text{NH}_3)_2(\text{OH})\text{C}_5\text{H}_7\text{N}_5\text{O}]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ and $[\text{Pt}(\text{NH}_3)_2(\text{OH}_2)(\text{C}_5\text{H}_7\text{N}_5\text{O})]\text{NO}_3 \cdot \text{H}_2\text{O}$ and have examined their structures. The predicted hydrogen bonding requirements are observed.

09.4-47 STUDIES OF THE INTERACTION OF PLATINUM(II) WITH 9-ETHYLGUANINE AND THE N1 DEPROTONATED 9-ETHYLGUANINATE ANION. By R. Faggiani, B. Lippert, C.J.L. Lock and R.A. Speranzini, Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada. L8S 4M1.

Structural studies have been undertaken of the complexes $[\text{Pt}(\text{NH}_3)_2(\text{C})(\text{G})](\text{ClO}_4)_2^{\text{A}}$, $[\text{Pt}(\text{NH}_3)_2(\text{C})(\text{G-H})][\text{Pt}(\text{NH}_3)_2(\text{C})(\text{G})](\text{ClO}_4)_3^{\text{B}}$, $[\text{Pt}(\text{NH}_3)_2(\text{C})(\text{G-H})](\text{ClO}_4)_2^{\text{C}}$, $[\text{Pt}(\text{NH}_3)_2(\text{G-H})_2]^{\text{D}}$, and $[\text{Pt}(\text{NH}_3)_2(\text{G-H})_2](\text{G}) \cdot 7\text{H}_2\text{O}^{\text{E}}$ (where C is 1-methylcytosine, G is 9-ethylguanine and G-H is the N1 deprotonated G anion). Platinum is bound at N3 of C and at N7 of G and G-H. The binding of G at N7 shifts the pK of N of G by about two pK units causing significant amounts of both complexed G and G-H at pH 7. An unusual type of (G-H)(G) base pairing then occurs which was first noted in B (Faggiani, R., Lippert, B., and Lock, C.J.L., J. Amer. Chem. Soc. (1981) 102, 5418) has now been observed in E, and may be the normal interaction between G and G-H. The structures of A-E will be discussed and the relevance of the Pt-induced "mispairing" will be discussed with respect to the biochemistry of platinum anti-cancer drugs.

09.4-48 STRUCTURES OF TECHNETIUM COMPOUNDS OF RADIOPHARMACEUTICAL INTEREST. By A. Davison, K.J. Franklin, and C.J.L. Lock, Institute of Materials Research, McMaster University, Hamilton, Ontario, Canada. L8S 4M1.

Complexes of technetium - 99m are widely used as scanning agents in nuclear medicine. However, relatively little is known about the chemistry and structures of these complexes. We report the x-ray structure determinations of 1-oxo-2,3,6(D-penicillaminato-S,N,O)-4,5-(D-penicillaminato-N,S)technetium(V), tetrabutylammonium oxobis-(catecholdiide)technetate(V) and triphenylmethylarsonium oxo(N,N¹-bis(mercaptoacetamide)ethylenediamine)technetate(V). The importance of these structures to the development of new radiopharmaceuticals will be discussed.

09.4-49 ADDUCTS OF ANTIMONY TRIHALIDES WITH N- AND π -DONORS: THE STRUCTURES OF $2\text{SbCl}_3 \cdot 3(4\text{-PHENYLPYRIDINE})$ AND $2\text{SbBr}_3 \cdot \text{BIPHENYL}$. STEREO-CHEMISTRY OF TRIVALENT ANTIMONY. By A. Lipka, Institut für Anorganische Chemie und Strukturchemie, Universität Düsseldorf, D-4000 Düsseldorf, Germany

The investigation of the title compounds forms part of a study of the stereochemistry of trivalent antimony in donor-acceptor compounds. Antimony trihalides as Lewis acids are acceptors towards various neutral donors. Adducts of SbCl_3 with aromatic amines and N-heterocycles are stabilized either by Sb-N or by Sb- π interactions. Interestingly with regard to

compound	D	d(Sb-D) Å	ref.
$\text{SbCl}_3 \cdot \text{Aniline}$	N	2.53	1
$\text{SbCl}_3 \cdot 2\text{Aniline}$	N	2.64	2
$\text{SbCl}_3 \cdot \text{Diphenylamine}$	π	3.13	3a
$2\text{SbCl}_3 \cdot \text{Diphenylamine}$	π	3.08, 3.09	3b
$2\text{SbCl}_3 \cdot \text{Triphenylamine}$	π	3.13	4
$\text{SbCl}_3 \cdot 2,2'\text{-Bipyridine}$	N	2.25, 2.32	5
$2\text{SbCl}_3 \cdot 3(4\text{-Phenylpyridine})$	N	2.39, 2.39	this work
		2.47	

(1. Hulme & Scruton, J. Chem. Soc. A (1968), 2448; 2. Hulme, Mullen & Scruton, Acta Cryst. (1969) A25, S171; 3a; b: Lipka, Z. anorg. allg. Chem. (1980) 466, 195; (1978) 440, 224; 4. Korte, Lipka & Mootz, ECM-5 (1980); 5. Lipka & Wunderlich, Z. Naturforsch. (1980) 35b, 1548)

Sb-Cl bonds, donor-acceptor interactions and short intermolecular Sb...Cl contacts the

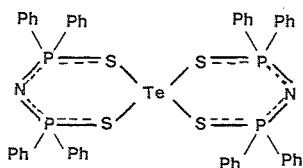
coordination of the Sb atoms is distorted octahedral or ψ -octahedral.

$2\text{SbCl}_3 \cdot 3(4\text{-phenylpyridine})$: $a = 9.622(1)$, $b = 13.363(3)$, $c = 14.445(3)$ Å, $\alpha = 72.48(2)$, $\beta = 83.28(2)$, $\gamma = 87.70(1)^\circ$, $P\bar{1}$, $Z = 2$. The most characteristic feature of the structure is the T-shaped geometry of one of the SbCl_3 molecules, whereas the other is pyramidally shaped as the molecules in SbCl_3 itself (Lipka, Acta Cryst. (1979) B35, 2020) and in adducts with amines. Another T-shaped SbCl_3 -fragment has only been found in the complex with 2,2'-bipyridine. Sb-Cl bond lengths vary from 2.36 to 2.74 Å, depending on the strength of bonds in trans position.

$2\text{SbBr}_3 \cdot \text{biphenyl}$: $a = 11.301(15)$, $b = 11.638(16)$, $c = 8.194(5)$ Å. $\beta = 107.54(8)^\circ$, $P2_1/c$, $Z = 2$. SbBr_3 molecules and biphenyl molecules form a centrosymmetric complex with coplanar arrangement of the phenyl rings. In agreement with NQR (Grechiskin & Kyuntsel, Opt. Spectry. (1964) 16, 87) and Raman (Perkampus & Schönberger, Chem. Phys. Lett. (1976) 44 (2), 348) results this complex differs significantly from $2\text{SbCl}_3 \cdot \text{biphenyl}$ (Lipka & Mootz, Z. anorg. allg. Chem. (1978) 440, 217), where the independent SbCl_3 molecules are differently arranged to the phenyl rings, which are not coplanar but display a dihedral angle of 40.5° .

09.4-50 THE PREPARATION AND CRYSTAL STRUCTURE OF BIS(IMIDOTETRAPHENYLDITHIODIPHOSPHINO-S,S')-TELLURIUM(II). By S. Bjørnevåg, S. Husebye and K. Maartmann-Moe, Department of Chemistry, University of Bergen, N-5014 Bergen-Univ., Norway.

The title compound, $[\text{Te}\{\text{N}(\text{Ph}_2\text{PS})_2\}_2]$, has been prepared from a mixture of $[\text{Te}(\text{tu})_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (tu=thiourea) and $\text{NH}_4\{\text{N}(\text{Ph}_2\text{PS})_2\}$ dissolved in methanol. Its structure has been determined by means of X-ray crystallographic methods. The yellow crystals are triclinic, space group $P\bar{1}$, with $a = 10.187(1)$ Å, $b = 12.929(5)$ Å, $c = 18.282(3)$ Å, $\alpha = 89.04(2)^\circ$, $\beta = 82.98(1)^\circ$, $\gamma = 77.40(2)^\circ$ and $Z = 2$. The crystals are built up of centrosymmetric, square planar $\text{Te}(\text{II})$ complexes. This is the first such complex where tellurium is bonded to two bidentate ligands. There are two crystallographically independent half molecules in the unit cell with an average Te-S bond length of 2.685(13) Å. Average intraligand S-Te-S angle is $86.8(1.1)^\circ$. Ignoring the phenyl groups the complex molecules have an approximate chair configuration.



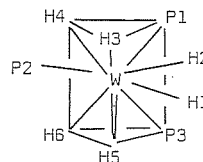
09.4-51 THE LOW TEMPERATURE NEUTRON DIFFRACTION STUDY OF $[\text{WH}_6(\text{PPhPr}_2)_3]$. By David Gregson, Judith A. K. Howard, John L. Spencer, David Turner, Department of Inorganic Chemistry, The University, Bristol BS8 1TS, England, and Sax Mason, Institut Laue Langevin, Grenoble, France.

Hydrogenolysis of hexamethyl tungsten in the presence of $(\text{PPhPr}_2)_3$ gives the title compound. The structure of these nine co-ordinate species had been a matter of conjecture, until this definitive study was carried out. The molecular symmetry is approximately C_{2v} rather than D_{3h} , with two of the phosphine ligands occupying prism vertices rather than the equatorial capping positions of the trigonal prism.

The results of the low temperature neutron experiment are summarised in the Figure (schematic representation).

Full details will be presented, and compared with the low temperature X-ray diffraction study.

Data were collected at the Institut Laue Langevin, Grenoble, the facilities of which are gratefully acknowledged.



W - P(1),P(3)	2.521(2)	P(1) - W - P(3)	107.8(1)°
W - P(2)	2.422(2)	P(2) - W - P(1,3)	126.0(1)
W - H(mean)	1.732(3)	H(1) - W - H(2)	123.8(2)

09.4-52 THE STRUCTURE OF THE ADDITION COMPOUND OF TRIS-(N,N-DIMETHYLACETAMIDE) HEXAAQUO PRASEODYMIUM TRIFLUOROMETHANE SULPHONATE.

By R.W. Becker, E.E. Castellano, G. Vicentini and T. Tamura, Instituto de Fisica e Quimica de São Carlos, 13560 São Carlos, S.P., Brazil.

The crystal structure of the title compound $[\text{Pr}(\text{DMA})_3(\text{H}_2\text{O})_6](\text{F}_3\text{CSO}_3)_3$ has been determined by ^3X -ray diffractometer data and refined anisotropically to an R-factor of 9%. This is part of a series of studies on the coordination of lanthanide adducts and their optical properties (Castellano and Becker, Acta Cryst. (1981), in press). 2299 independent reflections with intensities above background were measured. Space group is $P2_1$ and unit cell parameters are $a = 8.63(1)$, $b = 19.89(1)$, $c = 11.44(1)$ Å, $\beta = 103.6(1)^\circ$, with $Z = 2$. The cation is coordinated to nine oxygen atoms located at the vertices of a tricapped trigonal prism with approximate symmetry D_{3h} . Six oxygen atoms from equal number of water molecules are located at the vertices of the trigonal prism and three oxygen atoms from DMA groups are at the capping positions. The trifluoromethane sulphonate anions are not coordinated to the cation and are somewhat disordered. The fluorescence spectrum data obtained from the compound doped with Eu^{3+} , shows selection rules approximately consistent with the ones expected for point group D_{3h} on pure symmetry grounds.

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