

09.4-6 LEWIS BASE ADDUCTS OF LEAD(II) IODIDE. NOVEL CHAIN STRUCTURES OF LEAD(II) IODIDE WITH 2-PYRROLIDONE AND ETHYLENEUREA.

By H. Miyamae, M. Horiuchi, G. Hihara and M. Nagata, Department of Chemistry, Faculty of Science, Josai University, Saitama, Japan.

Crystals of  $PbI_2(pyd)_2$  and  $PbI_2(enu)_2$  (pyd=2-pyrrolidone; enu=ethyleneurea) were obtained by cooling their saturated N-methylformamide solution. The compounds crystallize in space group  $Pc2_1n$  with  $a=13.423(1)$ ,  $b=15.662(1)$ ,  $c=6.6898(6)$  Å and  $Z=4$ , and with  $a=13.287(1)$ ,  $b=15.458(2)$ ,  $c=6.5131(6)$  Å and  $Z=4$ , for the pyd and enu compounds, respectively. They are isostructural. The structure of the pyd compound is shown in Fig. 1.

The Pb atom is surrounded by four I and two O atoms in a distorted octahedron. The pyd and enu molecules coordinate through their O atom in trans positions. The two Pb-I bond distances, 2.92-3.08 Å, are shorter than that observed in  $PbI_2$  (3.22 Å). The other two, 3.54-3.80 Å, are too long to regard as ordinary single bonds. One of the I atoms only makes the shortest Pb-I bond. However, the other forms a shorter and two longer Pb-I bonds in a plane. Consequently, the structures are depicted as the  $Pb_2I_2$  plane sharing their opposite sides to be catenated chain along the c.

The angles between the shorter Pb-I bonds are  $97.5(1)$  and  $98.7(1)^\circ$ , and these between the longer ones are  $74.4(1)$  and  $75.8(1)^\circ$  for the pyd and enu compounds, respectively. The O-Pb-O bond angles,  $162(1)$  and  $163(1)^\circ$ , bending over the two shorter Pb-I bond regions, seem to indicate that the  $6s^2$  electron pair accumulate towards the longer Pb-I bonds.

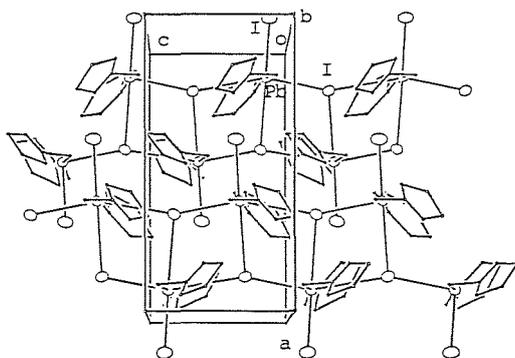


Fig. 1. Perspective view of  $PbI_2(pyd)_2$ .

09.4-7 CRYSTALLOGRAPHY OF COMPLEXES OF THIOUREA AND LEAD(II) SALTS. CRYSTAL STRUCTURES OF  $PbBr_2 \cdot tu(I)$  AND  $PbBr_2 \cdot 2tu(II)$ . By Frank-H. Herbstein, Moshe Kapon and George M. Reisner, Department of Chemistry, Technion - Israel Institute of Technology, Haifa, Israel 32000.

Mon(thiourea) lead dibromide (form I) crystallizes in space group  $P2_1$ ,  $Z = 2$ ,  $a = 6.026(4)$ ,  $b = 15.369(6)$ ,  $c = 4.259(3)$  Å,  $\beta = 110.71(1)^\circ$ . Bis(thiourea) lead dibromide (form II) crystallizes in space group  $P2_1$ ,  $Z = 2$ ,  $a = 10.583(5)$ ,  $b = 12.457(5)$ ,  $c = 4.088(3)$  Å,  $\beta = 95.61(1)^\circ$ . Intensities were measured for both crystals on a Philips PW1100 four-circle diffractometer using  $Mo\ K\alpha$ ; absorption corrections were applied. The two structures were solved by Patterson methods and refined to  $R_F = 6.80$  and  $3.80\%$  respectively. The monothiourea complex has an octahedral arrangement of four Br and two tu ligands about the Pb atom, with two Br atoms and two S atoms of tu molecules shared between contiguous edge-sharing octahedra in the c direction and Br atoms at the apices of the octahedra shared in the a direction. Thus there are sheets of octahedra in (010). The crystal studied had a domain structure with a 65:35 ratio of the two enantiomorphic forms. The bis(thiourea) complex has a chain structure extended along c in which one Br and two tu ligands bridge between successive Pb atoms; the second Br is linked only to Pb, which is thus seven-coordinated. The structure has some points of resemblance to the other polymorph of this composition (form I, see Herbstein and Reisner, Z. Kristallogr., 169, 83-93 (1984)) but there are considerable differences. Work is underway to determine the absolute structure of this complex.

09.4-8 THE STRUCTURES OF COMPLEXES OF MERCURY(II) HALIDES WITH TETRAHYDROSELENOPHENE. By C. Stålhandske, Inorganic Chemistry 2, Chemical Center, University of Lund, P.O. Box 124, S-221 00 LUND, Sweden.

The crystal structures of three complexes of mercury(II) halides with tetrahydroselephenone (THSe) have been solved, viz.  $HgCl_2 \cdot THSe$ ,  $HgBr_2 \cdot 2THSe$  and  $HgI_2 \cdot 2THSe$ . The  $HgCl_2 \cdot THSe$  structure (C. Stålhandske and F. Zintl, Acta Cryst., 1986, C41, 1449-1450) is isomorphous with the corresponding tetrahydrothiophene (THT) compound (C.-I. Brändén, Ark. Kemi, 1964, 22, 495-500). The structures can be described either as comprised of  $[Cl-Hg-THSe, THT]^+$  cations and  $Cl^-$  anions or as built up of polymeric halogen-bridged double chains. The same arrangement is also found in  $HgCl_2 \cdot (PMe_3)$  (N.A. Bell, M. Goldstein, T. Jones and I.W. Nowell, Inorg. Chim. Acta, 1981, 48, 185-189). The Hg-atoms have distorted trigonal bipyramidal environments in these compounds.

$HgBr_2 \cdot 2THSe$  is monoclinic, space group  $Cc$  with  $a = 23.551(3)$ ,  $b = 5.1288(5)$ ,  $c = 14.596(2)$  Å,  $\beta = 128.14(1)^\circ$ ,  $Z = 4$ ;  $HgI_2 \cdot 2THSe$  crystallizes in  $P\bar{1}$  with  $a = 5.1653(8)$ ,  $b = 9.001(1)$ ,  $c = 16.884(4)$  Å,  $\alpha = 92.21(2)$ ,  $\beta = 91.29(2)$ ,  $\gamma = 101.75(2)^\circ$  and  $Z = 2$ .

The two compounds are built up of isolated monomeric pseudotetrahedral molecules  $Hg(THSe)_2X_2$  ( $X = Br, I$ ) of approximately  $C_{2v}$  point symmetry. The Br-Hg-Br and Se-Hg-Se angles are  $110.1$  and  $114.8^\circ$  in  $HgBr_2 \cdot 2THSe$ , corresponding angles in  $HgI_2 \cdot 2THSe$  are  $120.8$  and  $109.6^\circ$ . Similar discrete tetrahedral complexes are found in the compounds  $HgCl_2 \cdot 2THT$  and  $HgBr_2 \cdot 2THT$  (M. Sandström and I. Persson, in preparation) and also in  $HgBr_2(py)_2$  and  $HgI_2(py)_2$  (A.J. Canty, C.L. Raston, B.W. Skeleton and A.H. White, J. Chem. Soc., Dalton Trans., 1982, 15-18).