

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

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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)°, and these between the longer ones are 74.4(1) and 75.8(1)° for the pyd and enu compounds, respectively. The O-Pb-O bond angles, 162(1) and 163(1)°, 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.

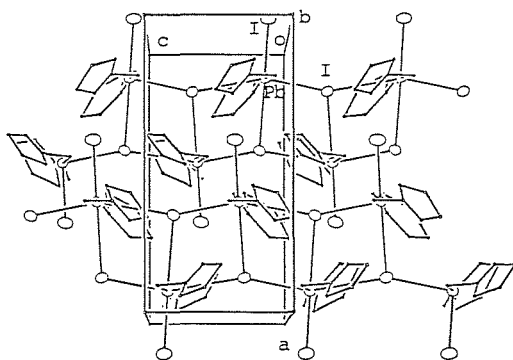


Fig. 1. Perspective view of $PbI_2(pyd)_2$.

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° in $HgBr_2 \cdot 2THSe$, corresponding angles in $HgI_2 \cdot 2THSe$ are 120.8 and 109.6°. 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).