

07-Crystallography of Organometallic and Coordination Compounds

205

respect to one another. The distance between Pc planes equals 2.57 Å. The tin atom is coordinated by eight isoindole nitrogen atoms forming a square antiprism. The Sn-N distances ranging from 2.312(3) to 2.330(3) Å.

(111) In_2Pc_3 . Crystal Data: $(\text{C}_{32}\text{H}_{16}\text{N}_8)_3\text{In}_2$, $M_r = 589.1$, triclinic, $P1$, $a = 14.492(3)$, $b = 13.179(3)$, $c = 11.493(2)$ Å, $\alpha = 113.96(2)$, $\beta = 97.15(2)$, $\gamma = 66.13(2)^\circ$, $V = 1832.2 \text{ \AA}^3$, $Z = 1$, $D_o = 1.60 \text{ g cm}^{-3}$, $D_c = 1.602 \text{ g cm}^{-3}$, $\lambda(\text{CuK}\alpha)$, $\mu = 56.97 \text{ cm}^{-1}$, $T = 300 \text{ K}$, $F(000) = 890$, $R = 0.028$, $wR = 0.037$ and $S = 1.22$ for 7019 observed ($I > 4\sigma$) reflections. The centrosymmetrical molecule of In_2Pc_3 consists of three Pc ligand plane and two indium anions and forms double sandwich-type complex. The In atoms are located between Pc ligands plane and have six-coordinate geometry. The intramolecular mean distance between Pc planes is about 2.84 Å. The two opposite Pc ligand planes are parallel to each other and the third central Pc plane is rotated about 39.3° in relation to the peripheral Pc. The intramolecular In-In distance is equal 4.036 Å. The shortest intermolecular distance between neighbouring successive Pc planes is 3.477 Å. References

J. Janczak, R. Kubiak, *J. Alloys Comp.*, **190** (1992) 121-124.
R. Kubiak, J. Janczak, *J. Alloys Comp.*, **190** (1992) 117-120.

PS-07.01.20 SIMULTANEOUS BINDING OF BETAININE AND PSEUDOHALIDE TO CADMIUM: CRYSTAL STRUCTURES OF FOUR POLYMERIC MIXED-LIGAND CADMIUM(II) COMPLEXES. By Mok-Yin Chow, Xiao-Ming Chen and Thomas C.W. Mak,* Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong.

Four polymeric cadmium complexes containing betaine and pseudohalide ligands have been synthesized and characterized by single-crystal X-ray analysis. The betaine-azide complex $\text{Cd}_2(\text{Me}_3\text{NCH}_2\text{CO}_2)_2(\text{N}_3)_4(1)$ and betaine-isocyanate complex $\text{Cd}_2(\text{Me}_3\text{NCH}_2\text{CO}_2)_2(\text{NCO})_4(2)$ are isomorphous, crystallizing in the monoclinic space group $C2/c$ with $Z = 4$. The two betaine-thiocyanate complexes $\text{Cd}_3(\text{Me}_3\text{NCH}_2\text{CO}_2)_4(\text{SCN})_6(\text{H}_2\text{O})_2(3)$ and $\text{Cd}(\text{Me}_3\text{NCH}_2\text{CH}_2\text{CO}_2)(\text{SCN})_2(4)$ are both triclinic, space group $P\bar{1}$, with $Z = 1$ and 2, respectively. In this series of complexes the carboxy groups of the betaine ligands act in three coordination modes and the pseudohalide ligands in two typical bridging modes. The structure of 1 or 2 consists of a virtually linear chain in which each pair of adjacent cadmium(II) ions are triply bridged by two $\mu-1,1$ -azido (or -isocyanato) and one μ -carboxy- O,O' ligands. The framework of structure 3 is a one-dimensional chain built of corner-sharing centrosymmetric sixteen-membered $(-\text{N}-\text{C}-\text{S}-\text{Cd})_4$ puckered rings that contain $\mu-1,3$ -bridging thiocyanate groups in both *anti* and *skew* modes; both unidentate and bidentate chelate modes of the betaine ligands coexist in this complex. The structure of 4 is constructed from an alternate arrangement of two kinds of rings that share corners to form a linear chain: one is an eight-membered chair-like $(-\text{N}-\text{C}-\text{S}-\text{Cd})_2$ ring bridged by a pair of $\mu-1,3$ thiocyanate ligands and the other a four-membered $(-\text{O}-\text{Cd})_2$ ring bridged by two $\eta^2-\mu-O$ carboxylate ligands. The significance of these structural features and the coordination geometries at the cadmium centres are discussed.

PS-07.01.21

Crystal Structures of Alkalides with Mixed Sandwich Crown Ether Cations, a New Type of Complexation Compound

Rui H. Huang and James L. Dye

Department of Chemistry
Michigan State University
East Lansing, MI 48824
U. S. A.

Crystal structures of several alkalides (ionic compounds with alkali metal anions and complexed alkali metal cations) with mixed sandwich crown ether cations, $\text{K}^+(18\text{C}6)(12\text{C}4)\text{Na}^-$, $\text{K}^+(18\text{C}6)(12\text{C}4)\text{K}^-$ and $\text{K}^+(18\text{C}6)(12\text{C}4)\text{K}^-(18\text{C}6)$, have been determined. These structures thus provided evidence of the stability of these mixed sandwich cations over their "parents" with single type of crown ethers. This research project was supported by U. S. National Science Foundation Grant No. DMR 90-17292. The X-ray diffractometer system was provided by NSF Grant No. CHE-84-03823 and CHE89-08088.

PS-07.01.22 STRUCTURES OF INCLUSION COMPOUNDS BETWEEN URANYL / CROWN ETHER AND URANYL / AZACROWN BY M. Nierlich*, L. Deshayes, N. Keller, M. Lance and J.D. Vigner, CEA, CE Saclay - SCM - Bât. 125 - 91191 Gif sur Yvette Cedex - FRANCE.

Complexation of the dioxouranium by macrocycles, particularly by crown-ether, has been widely studied; however the majority of structural studies concerns complexes in which the crown ligand is linked to the uranyl ion via hydrogen bonds (Rogers et al., *Inorg. Chem.*, **30**, 2671, 1991; Deshayes et al. *Acta Cryst.* **C49**, 1, 1993) and few structural studies show a direct uranyl crown coordination (Navaza et al., *Polyhedron*, **3**, 143, 1984; Dejean et al., *Polyhedron*, **6**, L189, 1987). The probability of inclosing UO_2 in the crown cavity is increased by a good choice of the pair solvent-anion which has to be poorly uranyl coordinating. We have chosen as poorly coordinating anion CF_3SO_3^- and the aim of these studies is to correlate the influence of the solvent on the direct uranyl crown coordination.

- In aqueous solution, we have crystallised: $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+} (\text{CF}_3\text{SO}_3)_2^- (18\text{-crown-6})_2$ in which the UO_2^{2+} is coordinated to five water molecules, the CF_3SO_3^- and the crown ether being linked to the uranyl via H bonds. (system triclinic, $P\bar{1}$, $a = 10.411(7)$, $b = 10.760(5)$, $c = 15.801(8)$ Å, $\alpha = 83.52(4)$, $\beta = 89.78(5)$, $\gamma = 61.4(5)^\circ$, $R = 0.045$ for 3459 unique observed reflections).

- In a mixture $\text{H}_2\text{O}-\text{CH}_3\text{CN}$, the complex $\text{UO}_2(\text{H}_2\text{O})_3(\text{CF}_3\text{SO}_3)_2^- (\text{benzo}15\text{-crown-5})_2$ crystallise. The linear uranyl is equatorially surrounded by five O atoms from 3 water molecules and 2 CF_3SO_3^- , the crown ether being H bonded to the 3 water molecules (system monoclinic, $P2_1/n$, $a = 15.749(3)$, $b = 14.283(6)$, $c = 19.010(8)$ Å, $\beta = 90.35(5)^\circ$, $R = 0.041$ for 2521 unique observed reflections).

- In organic solution CH_3CN , inclusion compounds crystallise. The uranyl ion is hexacoordinated to the six O atoms of the crown ether or the 6 N atoms of the azacrown.

07-Crystallography of Organometallic and Coordination Compounds

$[\text{UO}_2(18\text{-crown-6})]^{2+} (\text{CF}_3\text{SO}_3)_2^-$, (system triclinic, $\bar{P}1$, $a = 10.789(5)$, $b = 12.117(4)$, $c = 12.789(5)$ Å, $\alpha = 117.94(5)$, $\beta = 103.07(6)$, $\gamma = 105.36(5)^\circ$, $R = 0.079$ for 1120 unique observed reflections).

$(\text{UO}_2 \text{ dcc})^{2+} (\text{CF}_3\text{SO}_3)_2^-$ (system monoclinic, $P2_1/c$, $a = 13.367(5)$, $b = 18.454(6)$, $c = 13.455(4)$, $\beta = 99.63(4)^\circ$, $R = 0.074$ for 1089 unique reflections).

$[\text{UO}_2(\text{hexaaza}18\text{-crown-6})]^{2+} (\text{CF}_3\text{SO}_3)_2^-$ (system monoclinic, $P2_1/n$, $a = 13.236(6)$, $b = 11.551(9)$, $c = 17.416(9)$ Å, $\beta = 96.78(5)^\circ$, $R = 0.034$ for 2450 independent reflections).