

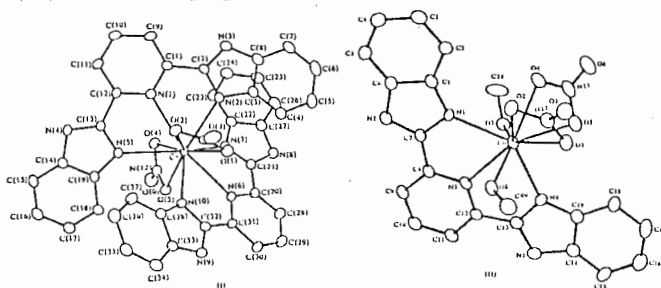
## 07-Crystallography of Organometallic and Coordination Compounds

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**PS-07.04.12** SYNTHESIS AND STRUCTURES OF Ce (III) AND Lu (III) COMPLEXES WITH 2,6-BIS(BENZIMIDAZOL-2'-YL) PYRIDINE. BY Zhu Ying\*, Instrumental Analysis and Research Center, Lanzhou University, Lanzhou 730000, China, Wang Shuangxi, Wang Jianqi, Department of Chemistry, Lanzhou University, Lanzhou 730000, China.

2,6-bis(benzimidazol-2'-yl) pyridine (BBP) complexes with transition metals have been studied due to their novel structure and significance in bioinorganic chemistry (Wang, S.X., Zhu, Y., Zhang, F.J., Wang, O.Y., Wang, L.F., Polyhedron, 1992, 11, 1909). Here we report on the syntheses and crystal structures of  $[\text{Ce}(\text{BBP})_2(\text{NO}_3)_2] \cdot (\text{NO}_3)_2 \cdot 3\text{MeOH}$  (I) and  $[\text{Lu}(\text{BBP}-\text{H})(\text{MeOH})_2(\text{NO}_3)_2] \cdot 2\text{MeOH}$  (II). The two complexes were obtained by slow evaporation of a methanol solution of  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  ( $\text{Ln} = \text{Ce}, \text{Lu}$ ) and BBP. The Ce and Lu crystal structures were solved by the Patterson method and refined by full-matrix least-squares procedure to final R values of 0.051 and 0.066 respectively. Crystal Data are: (I)  $P\bar{1}$ ,  $a = 10.907(1)$ ,  $b = 14.498(1)$ ,  $c = 16.187(2) \text{ \AA}$ ,  $\alpha = 63.02(1)$ ,  $\beta = 75.54(1)$ ,  $\gamma = 74.54(1)^\circ$ ,  $V = 2173.7 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 1.596 \text{ g cm}^{-3}$ ,  $\mu(\text{Cu}-\text{K}\alpha) = 89.50 \text{ cm}^{-1}$ ; (II)  $P1$ ,  $a = 12.810(1)$ ,  $b = 17.438(1)$ ,  $c = 10.504(1) \text{ \AA}$ ,  $\alpha = 103.09(1)$ ,  $\beta = 105.88(1)$ ,  $\gamma = 79.67(1)^\circ$ ,  $V = 2180.8 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_x = 1.599 \text{ g cm}^{-3}$ ,  $\mu(\text{Cu}-\text{K}\alpha) = 48.29 \text{ cm}^{-1}$ . It is interesting to compare the structures of the two complexes. The complex (I) has ten-coordinated Ce, the metal ion being co-ordinated to the four oxygen atoms from two bidentate nitrates and the six nitrogen atoms from two tridentate ligands forming a tetradecahedron. Due to the lanthanide contraction, the Lu atom shows nine-coordination, bonded to the four oxygen atoms from two bidentate nitrates and to the two oxygen atoms from two methanol molecules and to the three nitrogen atoms from one BBP-H anion, forming a distorted tricapped trigonal prism. In the complex (I), the shortest distance among Ce to ligands is Ce-O (nitrate) (2.552(2) \text{ \AA}) and the longest distance Ce-N (BBP) = 2.699(3) \text{ \AA}. While the shortest distance for Lu to ligands in the complex (II) is Lu-O (nitrate) = 2.347(4) \text{ \AA}, the second-shortest Lu-N (BBP) = 2.373(6) \text{ \AA}, and the longest Lu-N (nitrate) = 2.519(5) \text{ \AA}. It is shown that the interaction

between the Lu atom and the BBP-H ligand is stronger than between the Ce atom and the BBP ligands. In compound (II), the coordinated BBP loses a proton from the NH groups of one benzimidazole. There is a striking difference between the two benzimidazoles. The unprotonated one has an average N-C bond length of 1.358 \text{ \AA} and extended conjugation. The geometry of the other benzimidazole (N-C average = 1.372 \text{ \AA}) more closely resembles that of uncoordinated BBP (N-C average 1.376 \text{ \AA}). The uncoordinated BBP ligand in the complex (II) is linked by hydrogen bonds.



**PS-07.04.13** EFFECTS ON GEOMETRY OF THE NUMBER OF SUBSTITUTED METHYL GROUP ON ETHYLENE-DIAMINE IN LEAD (II) HALIDES - ETHYLENEDIAMINE-(1/1) ADDUCTS. By H. Miyamae\*, Y. Iijima, Y. Hatanaka, G. Hihara and M. Nagata, Department of Chemistry, Josai University, Japan.

Methyl groups (Me) substituted on N atoms weaken the coordination bond through steric hindrance within a molecule (Huheey, J.E., "Inorganic Chemistry-Principles of Structure and Reactivity", 3rd Ed., 1983, 298-299).

There are five different N-methylated ethylenediamines (en): N-Me-en, N,N-Me<sub>2</sub>en, N,N'-Me<sub>2</sub>en, Me<sub>3</sub>en, and Me<sub>4</sub>en. When combined with lead (II) halides (PbX<sub>2</sub>; X=Cl, Br or I), a total of 15 1:1 adducts were crystallized. Analysis of these structures led to the following conclusions:

(i) Coordination numbers are six (N<sub>2</sub>X<sub>4</sub>) or seven (N<sub>2</sub>X<sub>5</sub>). In coordination number seven, at least one of the Pb-X bond distances is very long.

(ii) N<sub>2</sub>X<sub>5</sub> coordination is pentagonal bipyramid. Most N<sub>2</sub>X<sub>4</sub> coordination is distorted octahedral in which the X-Pb-X angle *trans* to two Pb-N bonds is expanded more than 110°, indicating stereochemical activity of 6s<sup>2</sup> electrons on Pb; a trigonal prism form is observed for PbCl<sub>2</sub>-Me<sub>4</sub>en.

(iii) Substituted Me groups exhibit steric hindrance between ligated halogens making the Pb-N bond longer than those for non-substituted N atoms. This feature makes the stereochemical activity of 6s<sup>2</sup> electrons decrease in the complex.

Some of the structures are depicted in Fig. 1, showing the gradual change caused by the substitution.

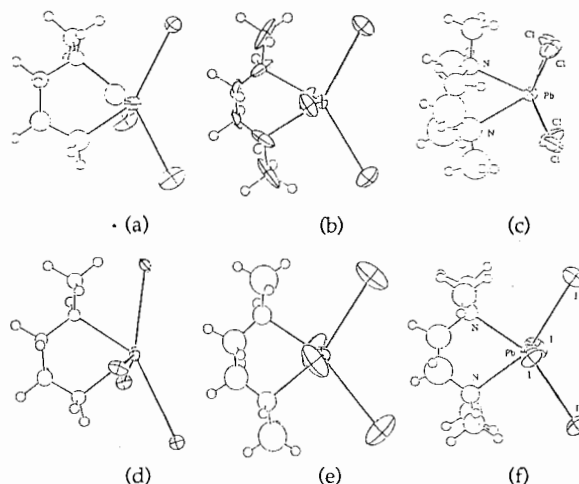


Fig. 1. Coordination geometry around Pb atoms in PbX<sub>2</sub>-Me<sub>n</sub>en(1/1) adducts. (a) PbCl<sub>2</sub>-N-Me-en, (b) PbCl<sub>2</sub>-N,N'-Me<sub>2</sub>en, (c) PbCl<sub>2</sub>-Me<sub>4</sub>en, (d) PbI<sub>2</sub>-N-Me-en, (e) PbI<sub>2</sub>-N,N'-Me<sub>2</sub>en, (f) PbI<sub>2</sub>-Me<sub>4</sub>en.