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A Pentagonal Pyramidal Lead(II) Complex with a Short Pb–Cl Distance

ANNA E. KOZIOL, RUTH C. PALENIK and GUS J. PALENIK

Center for Molecular Structure, Department of Chemistry, Gainesville, Fla. 32611, U.S.A.

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The environmental hazards of lead are well documented [1, 2]. However, the common therapeutic agents for lead poisoning have serious drawbacks and their mode of action is not well understood [3, 4]. In spite of the obvious importance, systematic studies of the coordination chemistry of Pb(II) and the effect of the lone pair on the stereochemistry are notable for their absence. As part of our program on Pb(II) chemistry, we wish to report the synthesis and structure of an unusual complex, chloro(2,6-diacetylpyridinedisemicarbazone)lead(II) nitrate.

The reaction of 2,6-diacetylpyridine with semicarbazide hydrochloride yields a planar pentadentate ligand 2,6-diacetylpyridinedisemicarbazone (DAPSC) which reacts with $Pb(NO_3)_2$ in ethanol–water to yield the complex $PbCl(DAPSC)^+NO_3^-$. Crystals suitable for diffraction studies were grown by slow evaporation of the solvent.

Crystal Data

$C_{11}H_{15}N_8O_5ClPb$, $Pb(DAPSC)(Cl)^+NO_3^-$, $M = 581.84$, triclinic, $P1$, $a = 8.009(2)$, $b = 8.563(1)$, $c = 14.408(3)$ Å, $\alpha = 76.51(1)$, $\beta = 78.03(2)$, $\gamma = 65.35(1)^\circ$, $U = 866.5(3)$ Å^3, $D_c = 2.230$ g cm^{-3}, $Z = 2$. The intensity data were measured using a Nicolet P3F diffractometer, with a variable speed (2° to 29.3°) $\theta - 2\theta$ scan technique and graphite monochromatized Mo Kα radiation. The crystal size was 0.12 × 0.22 × 0.30 mm. The structure was solved and refined using the NICOLET-SHELXTL system on the Eclipse-Model 30 [5]. The final values for R and R_w were 0.035 and 0.040 for the 2360 reflections used in the analysis.

The complex, illustrated in Fig. 1, is the first example of a mixed anion complex of Pb(II) that has been characterized. Furthermore, this is only the second chlorolead(II) complex with a chelating ligand whose structure has been determined. Since chloride ion is common in body fluids, chlorolead(II) complexes may play an important role in lead therapy.

The Pb–Cl distance of 2.707(4) Å is shorter than the Pb–Cl distance of 2.748(10) Å found in the $PbCl_2(thiourea)_2$ complex [6]. A slightly shorter distance of 2.682(3) Å was observed in the $Pb_2Cl_6^{2-}$ ion [7]. The Cl nonbonded contacts to the ligand vary from 3.285 to 4.043 Å. The shortest contact, 3.285 Å, is to N(2) and is surprisingly close to the values of 3.186 to 3.312 Å observed in the $M(DAPSC)(Cl)(H_2O)^+$ complexes [8]. This suggests that the Pb–Cl distance may be determined in part by the steric constraints of the ligand.

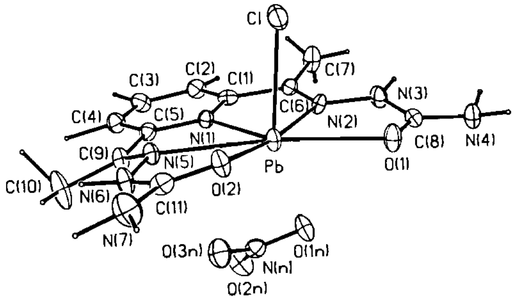

Fig. 1. A drawing of chloro(2,6-diacetylpyridinedisemicarbazone)lead(II) nitrate showing the thermal ellipsoids and atomic numbering.

A second unusual feature is the long Pb–O distances of 2.973 and 3.095 Å to the NO_3^- ion which may be due to the lone pair of electrons in the Pb(II) ion. The Pb(II) ion is almost equidistant from N(1) and N(2), 2.523(8) and 2.556(8) Å, and N(5) and O(1), 2.668(7) and 2.607(6) Å. However, the Pb–O(2) distance of 2.872(7) Å is longer than the other in-plane distances. The even longer distances to the NO_3^- opposite the Cl ion gives the complex a pentagonal bipyramidal geometry. Further studies of other chlorolead(II) complexes are required to understand fully the observed geometry and distances.

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