A Ten-coordinate Lead Complex with an Unusual 2-6-2 Coordination Polyhedron

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Effective therapeutic agents for the treatment of lead poisoning are not available [1] in spite of the awareness of lead as a serious health hazard. Furthermore, there are suprisingly few structural studies of complexes of lead(II). The coordination chemistry of Pb(II) is particularly interesting since the relatively large radius (1.33 Å for a CN of 6) [2] should yield complexes with high coordination numbers. However, only two nine- [3, 4] and one ten-coordinate [5] complexes has been established by X-ray crystal structure studies. Finally, the question of the stereochemical activity of the lone pair of electrons in the Pb(II) ion is not understood. For these reasons, we have started to investigate the stereochemistry of Pb(II). We now wish to report an unusual example of a ten-coordinate Pb(II) complex with a 2-6-2 polyhedron.

Synthesis of the planar hexadentate ligand PHENSC, 2,9-diformyl-1,10-phenanthrolinedisemicarbazone, has been described [6]. The complex was prepared by heating equimolar amounts of lead nitrate and PHENSC for six hours in a 2:1 mixture of methanol–water. The slurry was filtered, and clear yellow crystals suitable for X-ray diffraction studies were obtained from the filtrate by slow evaporation of the solvent.

Crystal Data: $Pb(PHENSC)(NO_3)_2$, $C_{16}H_{14}N_{10}O_8Pb$, M_r = 681.54, monoclinic, $C2/c$, a = 14.831(4), b = 16.722(4), c = 8.399(2) Å, β = 95.27(2)°, D_m = 2.175 g cm^{-3}, Z = 4, D_c = 2.182 g cm^{-3}. A $P\bar{1}$ diffractometer, a variable scan technique (1° to 24°/min), and graphite monochromatized Mo Kα radiation were used to measure the intensity data from a 0.12 × 0.07 × 0.07 mm crystal. The intensity distribution was centric and Fourier syntheses supported the space group $C2/c$. The structure was solved by the heavy atom method and refined by least-squares methods to a final R ($R = \Sigma|\Delta F|/\Sigma F_o$) of 0.039 for the 1241 reflections ($I \leqslant 2\sigma(I)$) used in the analysis.

The complex is illustrated in Fig. 1 and contains a 2-fold axis of symmetry passing through the Pb(II) ion and the PHENSC ligand. There are several noteworthy features in this complex. The overall geometry is best described as a 2-6-2 polyhedron with the two capping nitrates rotated 60° relative to each other. The 2-6-2 polyhedron was not considered in a recent review of nine, ten and twelve coordination [7].

A second interesting feature is the equality of the Pb–hexadentate ligand distances which range from 2.727 to 2.739 Å. There may be a slightly shorter Pb–N bond compared to the Pb–O distance but the difference is not significant. The two Pb–O nitrate distances are significantly different but still close to the values in the equatorial plane. In essence there is no evidence that the lone pair on the Pb(II) ion is stereochemically active. The stereochemical inactivity of the lone pair in many Pb(II) complexes is puzzling and further structural studies are in progress.

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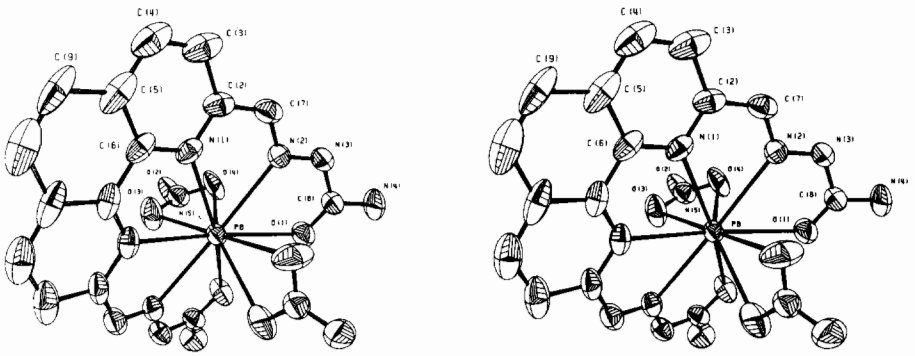

Fig. 1. A stereoview of the dinitrato(2,9-diformyl-1,10-phenanthrolinedisemicarbazone)lead(II) complex. There is a 2-fold axis through the Pb(II) and the PHENSC ligand. Pertinent distances are (in A ±0.009): Pb–O(1) 2.739, Pb–O(3) 2.823, Pb–O(4), 2.735 Pb–N(1) 2.731 and Pb–N(2), 2.727.

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