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A Decahexahedral Lanthanum Complex: Synthesis and Characterization of the Eleven Coordinate tris-Nitrato[2,6-diacetylpyridinebis(benzoic acid hydrazone)]lanthanum(III)

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We wish to report the synthesis and characterization of the first eleven coordinate complex, trisnitrato[2,6-diacetylpyridinebis(benzoic acid hydrazone)]lanthanum(III), an example of decahexahedral geometry [1]. Eleven coordinate complexes are noticeably absent in recent reviews of lanthanides [2, 3] and of high coordination complexes [4]. In fact, to our knowledge no other eleven coordinate metal complexes with an organic-type ligand have been reported. The absence of eleven coordinate complexes has been rationalized on the basis of a relatively easy expansion to a twelve coordinate geometry, with little penalty in increased ligand repulsions. However, our results suggest that the final geometry of lanthanide complexes depends on a variety of subtle effects which may not be predicted a priori. Consequently, using lanthanides as probe or reporter ions in biological systems may yield perturbed structural information regarding the receptor site.

The synthesis of 2,6-diacetylpyridinebis(benzoic acid hydrazone), DAPBAH, and the cobalt(II) and nickel(II) complexes with DAPBAH have been reported [5]. Lanthanum nitrate, prepared from the oxide (1.25 mmol) and nitric acid, was added to 2.50 mol of DAPBAH in 75 ml of ethanol. The mixture was heated (55 °C) and stirred for about one hour; then 25 ml of water was added, and stirring continued for another 1½ hours. There was very little solid remaining in the yellow solution which was then filtered. After filtering and collecting several crops of product, clear yellow crystals suitable for X-ray diffraction studies were obtained. The C=O absorption at 1665 cm^{-1} in DAPBAH is shifted to 1645 cm^{-1} with a weak band at 1620 cm^{-1}, indicating that the ligand is coordinated. In addition, the band at 1035 cm^{-1} indicated coordinated nitrate groups.

Crystal Data

$C_{23}H_{21}N_8O_{11}La$, La(DAPBAH)$(NO_3)_3$, $M = 724.38$, monoclinic, $P2_1/c$, $a = 16.113(5)$, $b = 9.782(2)$, $c = 17.901(5)$ Å, $\beta = 95.92(3)°$, $D_m = 1.71$ g cm^{-3}, $Z = 4$, $D_c = 1.714$ g cm^{-3}. The intensity data were measured using a Syntex P$\bar{1}$ diffractometer with a variable speed (1 to 24°/min) scan technique and graphite monochromatized MoKα radiation. The structure was solved by the heavy atom method and refined by least-squares techniques to a final R value ($R = \Sigma|\Delta F|/\Sigma F_{obs}$) of 0.030 for the 4080 reflections used in the analysis.

The complex ion is illustrated in Fig. 1. The central La atom is coordinated to the planar pentadentate ligand DAPBAH and three tridentate nitrate ions. The polyhedron was analyzed in terms of the δ values for the reduced polyhedron [6] and in terms of the rms deviations of the coordinates from the idealized polyhedron [7]. Both calculations indicated that the complex is best described as a decahexahedron. The absence of eleven coordinate complexes precludes any discussion of polyhedral preferences.

The La donor distances vary with the type of donor atoms; La–O (NO_3 groups) range from 2.563 (3) to 2.648(3) Å, La–O (ligand) are 2.560(3) and 2.507(3) Å, and La–N (ligand) are 2.772(3), 2.769(4), 2.790(3) Å. The La-donor distances are slightly longer than in the few reported ten-coordinate complexes but, as expected, are slightly shorter than in twelve coordinate complexes [2].

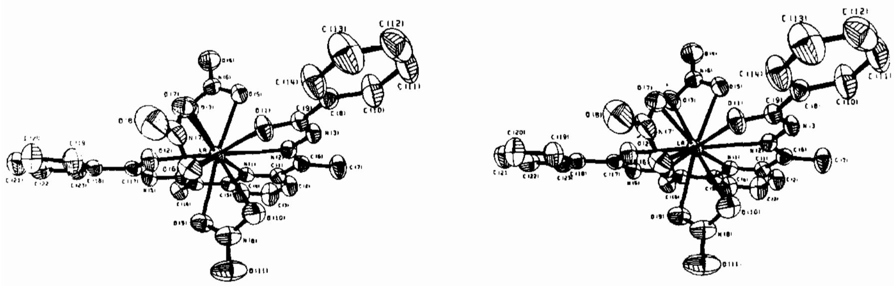

Fig. 1. A stereoview of the trisnitrato[2,6-diacetylpyridinebis(benzoic acid hydrazone)]lanthanum(III) complex. Pertinent distances (in Å) involving the La atom are: N(1) 2.790(3), N(2) 2.769(4), N(4) 2.772(3), O(1) 2.560(3), O(2) 2.507(3), O(3) 2.627(4), O(5) 2.634(3), O(6) 2.563(3), O(7) 2.619(3), O(9) 2.612(3), and O(10) 2.648(4).

The apparent flexibility and resulting planarity of the DAPBAH ligand were surprising, especially in comparison with the pentagonal bipyramidal cobalt and nickel complexes [5]. Apparently, the large La atom expands the ligand cavity and produces a nearly planar arrangement of the La and five ligand donor atoms. The ability of the La atom to form not only an unusual eleven coordinate complex, but also to alter the ligand geometry in the process, suggests that the use of lanthanide ions as probes in biological systems can cause substantial changes in the ligand.

A final point is the absence of either coordinated or lattice water molecules in spite of the fact that the synthesis was completed in an aqueous media. Since lanthanides are considered to be 'hard' acids and highly hydrated, the absence of water molecules was unexpected. However, the large phenyl groups of the ligand may dictate the crystal packing, and their hydrophobic character may exclude water molecules.

Acknowledgements

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