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A Ten-Coordinate Oxo-Bridged Thorium Complex with an Unusual Coordination Polyhedron

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We have recently synthesized and characterized μ-oxo-bis[aquanitrato(2,9-diformyl-1,10-phenanthrolinedisemicarbazone)thorium(IV)] nitrate hydrate, the first example of an oxo-bridged thorium complex. The thorium atom is ten-coordinate, being in the center of an unusual 1-6-3 polyhedron which is a consequence of the planar hexadentate ligand.

The planar hexadentate ligand PHENSC, 2,9-diformyl-1, 10-phenanthroline disemicarbazone, was prepared by the treatment of 2,9-diformyl-1,10-phenanthroline with semicarbazide hydrochloride*. The synthesis of the complex followed procedures we had developed for the preparation of complexes with planar pentadentate ligands [1]. Thorium nitrate (1.0 mmol) was added to a slurry of the ligand PHENSC (1.0 mmol) in 100 ml of 95% ethanol. After heating for about 30 minutes, water was added until the solution cleared. The solution was filtered and cooled. Suitable single crystals were formed by slow evaporation of the solvent. The C=O absorption in the free ligand is a broad peak covering the region from 1675 to 1720 cm^{-1}. However, in the complex there are two sharp, well-defined absorptions at 1685 and 1708 cm^{-1}, suggesting an interaction between the CO group and the thorium ion.

Crystal Data: $C_{32}H_{34}O_{26}N_{22}Th_2$, $[[(Th(PHENSC)(NO_3)(H_2O)]_2O](NO_3)_4 \cdot H_2O$, M = 1606.83u, monoclinic, $P2_1/c$, a = 14.423(3), b = 25.833(10), c = 13.140(3) Å, β = 93.52(2)°, D_m = 2.190 g cm^{-3}, Z = 4, D_c = 2.146 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 Mo-K_α radiation. The crystal size was 0.20 X 0.16 X 0.06 mm. 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 0.086 for the 3489 reflections used in the analysis.

The complex cation is illustrated in Fig. 1. Each thorium atom is coordinated to the six donor atoms of the PHENSC ligand, three oxygen atoms to one side of the ligand plane and the oxo-bridge to the opposite side of the plane. The geometry around each thorium atom is best described in terms of a 1-6-3 polyhedron, a geometry which is not usually found in ten-coordinate species**. The phenanthroline

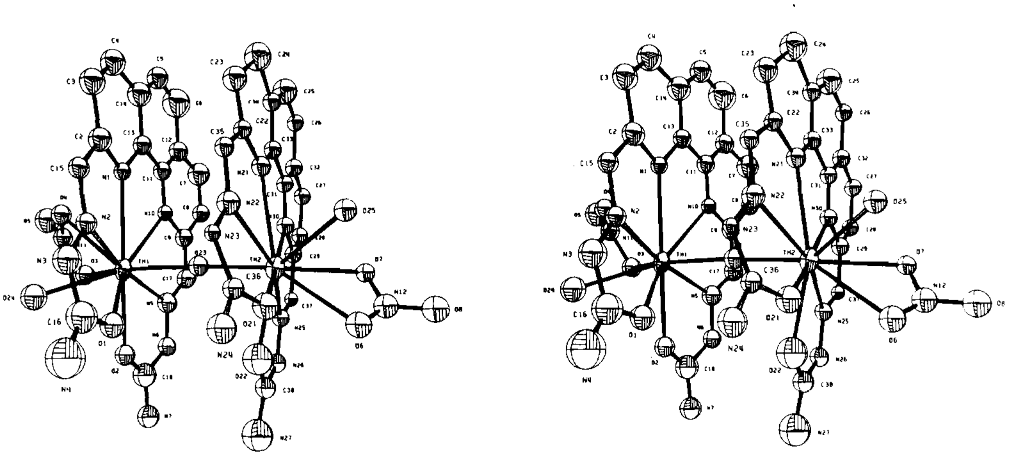

Fig. 1. A stereoview of the μ-oxo-bis[aquanitrato-(2,9-diformyl-1,10-phenanthroline-disemicarbazone)thorium(IV)] cation. Pertinent distances (in Å ± 0.02) involving Th(1): O(1) 2.50, O(2) 2.45, O(3) 2.66, O(4) 2.63, O(23) 2.15, O(24) 2.52, N(1) 2.69, N(2) 2.77, N(5) 2.71, N(10) 2.78 and involving Th(2): O(21) 2.42, O(22) 2.46, O(6) 2.62, O(7) 2.69, O(23) 2.10, O(25) 2.54, N(21) 2.75, N(22) 2.73, N(25) 2.74 and N(30) 2.79.

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*We had prepared the dialdehyde by oxidation of the 2,9-dimethyl derivative in a manner similar to that reported recently by E. König, G. Ritter and K. Madeja, *J. Inorg. Nucl. Chem.*, *43*, 2273 (1981).

**The tricapped trigonal prism and the bicapped square antiprism are the two favored polyhedra for a ten-coordinate species. An extensive discussion of the possible polyhedra has been given by M. C. Favas and D. L. Kepert, *Prog. Inorg. Chem.*, *28*, 309 (1981). However, the 1-6-3 polyhedron was not considered by Favas and Kepert in their discussion.

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backbone is rigid so that the ligand cannot distort to any great extent; consequently the favored polyhedron for ten-coordination cannot be formed. The semicarbazone side chains are twisted slightly relative to the phenanthroline plane (6.7 and 7.3° around Th(1) and 7.1 and 17.6° around Th(2). The twist is such that the cavity becomes slightly larger than for a completely planar arrangement.

The oxo-bridge between the two thorium atoms is one of the most unusual features in the cation. The Th–O (bridge) distance, avg 2.13(2) Å, is quite short relative to the other Th–O distances; Th–O(ligand) avg 2.46(3) Å; Th–O (water), avg 2.53(2) Å; and Th–O (nitrate), avg 2.65(3) Å. The short Th–O distances together with the Th–O–Th angle of 174(1)° imply a strong Th–O interaction. The correlation of the M–O–M angle with the nature of the M–O bond is of current interest [2, 3]. However, the majority of the examples have been with transition metals while the present study is the first example of an actinide oxo-bridged species. The question of whether the short Th–O distance is due to an electrostatic interaction between the Th^{4+} and O^{2-} ions or whether there is some double bond character in the Th–O bonds cannot be answered at present. Nevertheless, our results provide the first structural evidence that thorium-oxo species should be considered in the solution chemistry of Th(IV).

Acknowledgement

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References

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