Inorganica Chimica Acta, 44 (1980) L303–L304
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

A Novel Decacoordinate Cerium Complex: the Synthesis and Characterization of Bis[2,6-diacetylpyridine bis(semicarbazone)] cerium(III) Perchlorate Trihydrate

JOHN E. THOMAS and GUS J. PALENIK*

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

Received January 18, 1980

We have recently synthesized and characterized a novel 10-coordinate complex cation, bis[2,6-diacetylpyridine bis(semicarbazone)] cerium(III), as the perchlorate salt. There are relatively few ten coordinate complexes [1–3], and the majority of those reported have either monodentate ligands or bidentate ligands with a small bite. Multidentate ligands usually do not have the flexibility nor the small bite required to form metal complexes with high coordination numbers. However, we have found that the planar pentadentate ligand DAPSC, 2,6-diacetylpyridine bis(semicarbazone), forms an unusual bis(DAPSC)cerium(III) cation which is ten-coordinate while the lighter lanthanides form a nine-coordinate $M(DAPSC)(H_2O)_4^{3+}$ cation.

The synthesis of the ligand and various metal complexes of DAPSC has been reported [4]. The cerium(III) perchlorate (1.25 mmol) was added to a slurry of the ligand DAPSC (1.25 mmol) in 50 ml of ethanol. After heating for about 30 min, water was added until the solution cleared. The solution was filtered, cooled, and suitable crystals were obtained by slow evaporation of the solvent. The C=O absorption at 1690 cm^{-1} in the free ligand had shifted to 1650 cm^{-1}, indicating that the ligand was coordinated. The final stoichiometry was two ligands per cerium, even though the starting ratios were 1:1.

Crystal Data: $C_{22}H_{36}N_{14}O_{19}Cl_3Ce$, $Ce(DAPSC)_2^{3+}\,3ClO_4^{-}\cdot 3H_2O$, M = 1047.09 u, monoclinic, $P2_1/c$, a = 13.220(2), b = 23.744(6), c = 12.559(3) Å, β = 97.30 (2)°, D_m = 1.80 g cm^{-3}, Z = 4, D_c = 1.779 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 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 0.045 for the 4185 reflections used in the analysis.

The complex cation is illustrated in Fig. 1. The cerium atom is coordinated to all ten donor atoms of the two pentadentate ligands. The polyhedron was analyzed in terms of the δ values for the reduced polyhedron [5] and in terms of the rms deviations of the coordinates from the idealized polyhedron [6]. Both calculations indicated that the complex is best described as a bicapped square antiprism, BCSAP. The atoms O(1)–O(2)–N(12)–N(9) and O(3)–O(4)–N(2)–N(9) form the two square faces, with N(1) and N(8) as the capping atom. The N(1)–Ce–N(8) angle of 171.1(2)° is very close to the ideal value of 180.0° expected for a BCSAP. The ligand must distort to achieve the BCSAP configuration since two planar pentadentate ligands at 90° to each other would have a bicapped cube arrangement of donor atoms. However, the cube is rarely found as a coordination polyhedra so that the absence of the bicapped cube even at the expense of ligand distortion is not surprising. Furthermore, there are indications that the BCSAP may be the favored ten-coordinate polyhedron, although the number of examples is still so small that a definitive choice is speculative.

The cerium-donor atom distances (all ± 0.006 Å) fall into three groups. The Ce–N of the pyridine rings are the longest at 2.724 and 2.717 Å. The Ce–N of

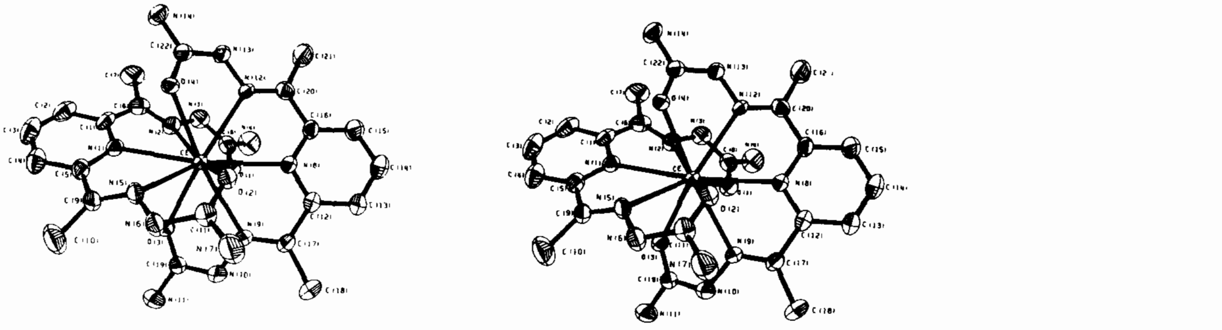

Fig. 1. A stereoview of the bis[2,6-diacetylpyridinebis(semicarbazone)]cerium(III) cation. Pertinent distances (in Å ± 0.006) involving the cerium atom are: N(1) 2.724, N(2) 2.664, N(5) 2.674, N(8) 2.717, N(9) 2.671, N(12) 2.642, O(1) 2.484, O(2) 2.526, O(3) 2.483 and O(4) 2.597. The polyhedron is a bicapped square antiprism with N(1) and N(8) as the two capping atoms.

---

*Author to whom correspondence should be addressed.

the ligand side arms are 2.664, 2.674, 2.671 and 2.642 Å, while the Ce–O distances are 2.484, 2.526, 2.483 and 2.597 Å. The fact that the capping Ce–N distances are the longest is in agreement with theoretical predictions of the expected geometry of a BCSAP [7].

Acknowledgement

We thank the Center for Instructional Research Computing Activities, University of Florida, for grant time.

References

1 S. P. Sinha, *Structure and Bonding, 25,* 69 (1976).
2 M.G. B. Drew, *Coord. Chem. Revs., 24,* 179 (1977).
3 In addition we searched the Cambridge Crystallographic Data file for ten-coordinate species.
4 G. J. Palenik, D. W. Wester, U. Rychlewska and R. C. Palenik, *Inorg. Chem., 15,* 1814 (1976), and references therein.
5 B. E. Robertson, *Inorg. Chem., 16,* 2735 (1977).
6 The program POLYFIT written by W. A. Dollase and described in *Acta Cryst., A30,* 513 (1974).
7 A. R. Al-Karaghouli and J. S. Wood, *Inorg. Chem., 11,* 2293 (1972), and also discussed in reference 2.