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SYNTHESIS AND MOLECULAR STRUCTURE OF TETRAAQUA [2,9 -DIFORMYL-1,10-PHENANTHROLINE BIS (SEMICARBAZONE)] CERIUM(III) PERCHLORATE, $[Ce(PHENSC)(H_2O)_4](CL0_4)_3$

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Abstract

The complex of Ce(III), $[Ce(PHENSC)(H_2O)_4](C10_4)_3$, was synthesized using the PHENSC, a hexadentate ligand,2,9-diformyl-1,10- phenanthroline *bis* (semicarbazone), and characterized by X-ray diffraction. The cerium atom has an unusual coordination number of ten involving six donor atoms of the planar ligand in the equatorial plane and four oxygen atoms from four axial water molecules. The complex crystallizes in the monoclinic space group $P2_1/c$ with four molecules per unit cell. The unit cell dimensions are a = 16.085(3), b = 12.229 (4), and c=15.436(4) Åwith β= 95.20 (2)°. The position of the cerium atom was determined by the heavy atom method and refined by least-squares techniques to a final R value ($R = |\Delta F| / \Sigma |F_{obs}|$ of 0.071 for the 3166 reflections used in the analysis. The coordination polyhedron is probably best described in terms of 1-6-3 polyhedron.

Introduction

The Ce(III) is a good example for consideration of high coordination number complexes [1]. In $Ce(NO_3)_5^{2-}$ anion, the Ce(III) has a coordination number of ten involving five bidentate nitrate groups. We have recently synthesized a few complexes, using the PHENSC, a hexadentate ligand, and characterized by X-ray diffraction [2-6]. In this work, we have recently prepared and characterized tetraaqua [2,9-diformyl-1,10-phenanthroline *bis* (semicarbazone)] cerium(III) perchlorate, $[Ce(PHENSC)(H_2O)_4](C10_4)_3$.

Keywords: Synthesis; Molecular, Structure Tetraaqua [2,9-Diformyl-1,10-Phenanthroline Bis (Semicarbazone)] Cerium (III) Perchlorate

Experimental Section

Preparation of Complex:

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 [7].

Data Collection and Reduction:

Preliminary photographs indicate that the space group was $P2_1/c$. The unit cell dimensions are reported in Table 1, and 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-$K\alpha$ radiation. The crystal size was 0.11×0.09× 0.07 mm.

Table 1. Crystal Data for $[Ce(PHENSC)(H_2O)_4](C10_4)_3$

Formula	$C_{16}H_{22}O_{18}N_8C1_3Ce$
Molecular weight	860.88
Space Group	$p2_1/c$
a,Å	16.085(3)
b,Å	12.229(4)
c,Å	15.436(4)
α,deg	90*
β,deg	95.20(2)
γ,deg	90*
Volume,Å^3	3024(1)
Z	4
D_m,g cm^{-3}	1.884
D_c,g cm^{-3}	1.891
Crystal Size,mm	0.11×0.09×0.07
μ, cm^{-1}	16.1
Radiation Used	Mo $K\alpha$-graphite monochromator
2θRange	0-45°
No. of Measured Reflections	3989
No. of Reliable Reflections	3166
K[in I≤$K\sigma$(I)]	2.0
Goodness of Fit	0.579
R	0.071

* Required by symmetry of space group.

Structure Determination and Refinement:

The position of the cerium atom was determined by the heavy atom method and the remaining non-hydrogen atoms were located in successive Fourier syntheses. The structure was refined by least squares to a final R value ($R=\sum\|F_{obs}\|-|F_{calc}\|/\sum|F_{obs}|$) of 0.071 for the 3166 reflections used in the analysis.

The scattering factors were taken from the usual sources [8]. The final positional parameters and thermal parameters for the non-hydrogen atoms are available as supplementary materials. The bond distances and angles are given in Tables 2 and 3, repectively.

Table2. Some Bond Distances (in Å) in $[Ce(PHENSC)(H_2O)_4](C10_4)_3$ with Estimated Standard Deviations in the Cation

Ce-O(1)	2.503(9)	Ce-O(2)	2.558(9)
Ce-O(3)	2.528(10)	Ce-O(4)	2.574(10)
Ce-O(5)	2.611(9)	Ce-O(6)	2.514(10)
Ce-N(1)	2.743(11)	Ce-N(10)	2.761(10)
Ce-N(2)	2.721(11)	Ce-N(5)	2.698(11)

Table3. Some Bond Angles (in deg) in $[Ce(PHENSC)(H_2O)_4](C10_4)_3$ with Estimated Standard Deviations in the Cation

O(1)-Ce-O(2)	63.0(3)	N(1)-Ce-N(10)	59.2(3)
O(1)-Ce-N(2)	59.0(3)	O(2)-Ce-N(5)	58.6(3)
N(2)-Ce-N(1)	58.4(3)	N(5)-Ce-N(10)	58.2(3)
O(3)-Ce-O(4)	65.2(3)	O(3)-Ce-O(5)	78.3(3)
O(3)-Ce-O(6)	132.1(3)	O(4)-Ce-O(5)	63.4(3)
O(4)-Ce-O(6)	146.9(3)	O(5)-Ce-O(6)	139.0(3)
Ce-N(1)-C(2)	120.6(9)	Ce-N(10)-C(9)	119.1(9)
Ce-N(1)-C(13)	118.8(8)	Ce-N(10)-C(11)	119.1(8)
Ce-N(2)-C(15)	124.0(9)	Ce-N(5)-C(7)	123.5(9)
Ce-N(2)-N(3)	116.0(8)	Ce-N(5)-N(6)	117.0(8)
Ce-O(1)-C(16)	126.4(9)	Ce-O(2)-C(18)	125.0(9)

Results and Discussion

The crystal consists of $[Ce(PHENSC)(H_2O_4)]^{3+}$ cation, illustrated in Figures 1 and 2. The cerium atom has an unusual coordination number of ten involving six donor atoms of the planar ligand in the equatorial plane and four oxygen atoms from four axial water molecules.

The PHENSC hexadentate ligand in the $[Ce(PHENSC)(H_2O)_4]$-$(ClO_4)_3$ complex are involving four nitrogen atoms and two oxygen atoms. The least-squares planes data are also available. The deviations of the six donor atoms are from -0.452 to 0.388 Å, which are significantly larger than the deviations of the five donor atoms in $[Co(PHENSC)(H_2O)_2](NO_3)_2$ [6].

Dihedral angles for the $[Ce(PHENSC)(H_2O)_4](ClO_4)_3$ are given in Table 4. The two side arms are twisted (side (1), 10.0° and side (2), 16.8°) relative to the 1,10- phenanthroline ring. Therefore, the two sides are twisted in the opposite direction (see Table 4). The coordination polyhedron is probably best described in terms of 1-6-3 polyhedron.

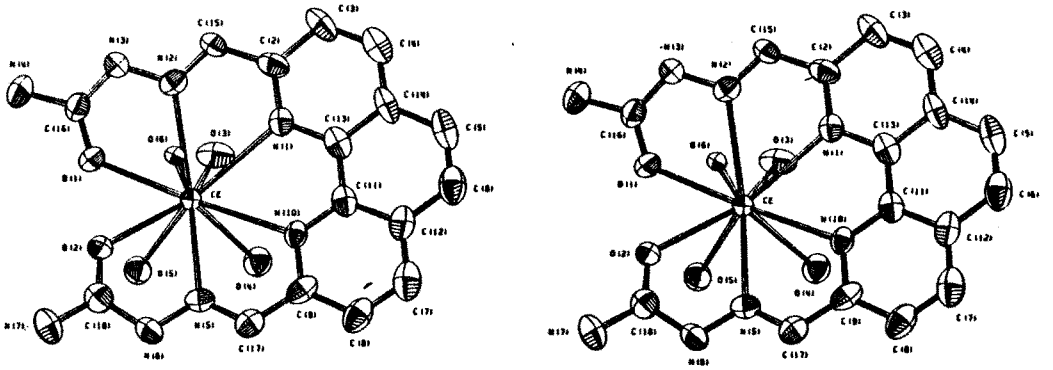

Figure 1. Stereoview of $[Ce(PHENSC)(H_2O)_4](ClO_4)_3$

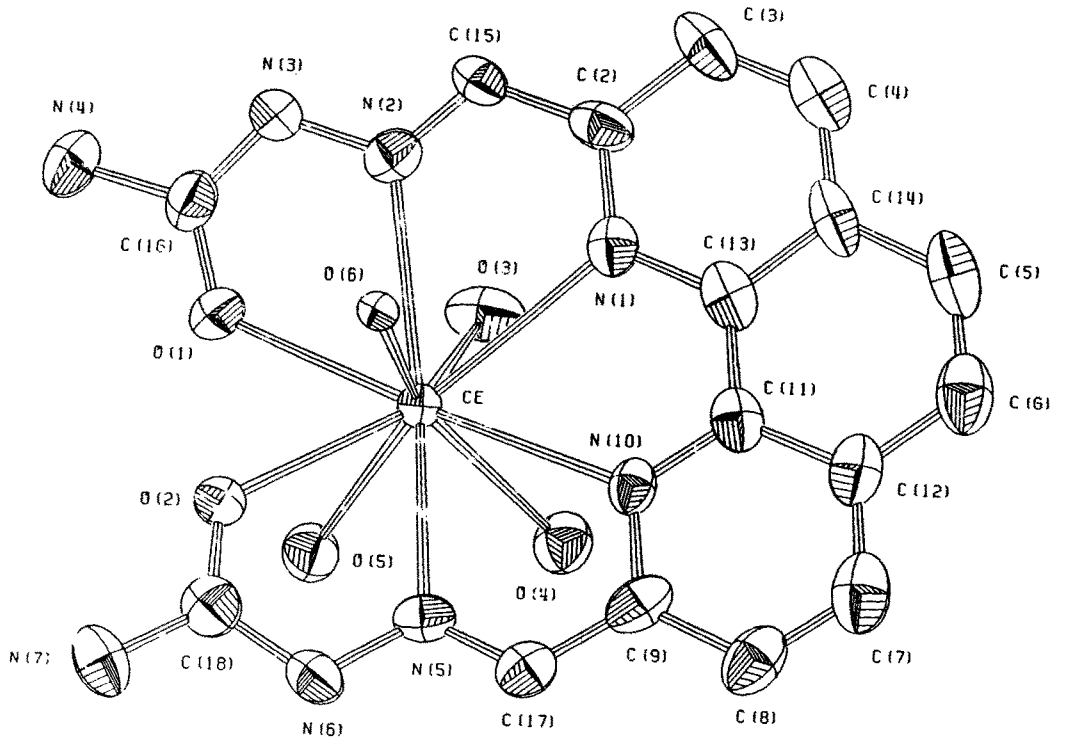

Figure 2. An ORTEP View of $[Ce(PHENSC)(H_2O)_4](ClO_4)_3$ showing the atomic numbering and the thermal

Table 4- Dihedral Angles for Various Planes in $[Ce(PHENSC)(H_2O)_4](C10_4)_3$

Plane(1)	Plane(2)	Angles(deg)
Phen	Side(1)	10.0
Phen	Side(2)	16.8
Side(1)	Side (2)	26.7

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