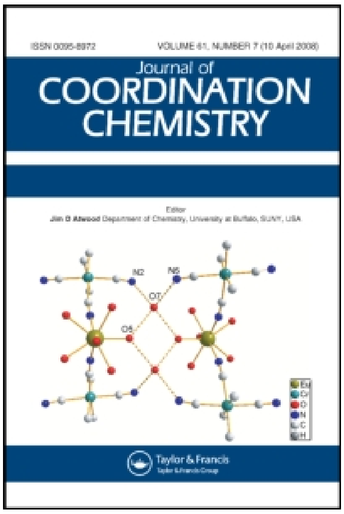

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Note: The crystal structure of Tris(nitrato-*O*,*O'*)bis(1,10-phenanthroline-*N*,*N'*)terbium(III)

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Note

THE CRYSTAL STRUCTURE OF TRIS(NITRATO-*O,O′*)BIS(1,10-PHENANTHROLINE-*N,N′*)TERBIUM(III)

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Our recent research interest has focussed on rare earth phenanthroline complexes, which are obviously of significant value for modern coordination chemistry. As a continuing part of a systematic investigation of ternary rare earth phenanthroline nitrato complexes [Y.Q. Zheng, L.-X. Zhou, J.L. Lin and S.-W. Zhang (2000). *Z. Anorg. Allg. Chem.*, **626**, 1715 [1]; Y.Q. Zheng, L.-X. Zhou, J.L. Lin and S.-W. Zhang (2001). *Z. Anorg. Allg. Chem.*, **627**, 1643 [2]; Y.Q. Zheng, L.-X. Zhou, J.L. Lin and S.-W. Zhang (2001). *Z. Kristallogr. NCS*, **216**, 357 [3]; Y.Q. Zheng, L.-X. Zhou, J.L. Lin and S.-W. Zhang (2001). *Z. Anorg. Allg. Chem.*, **627**, 2425 [4]], we report the synthesis and crystal structure of tris(nitrato-*O,O′*)bis(1,10-phenanthroline-*N,N′*)terbium(III), $Tb(phen)_2(NO_3)_3$.

Keywords: Terbium; Phenanthroline; Nitrate; ; X-ray structure

EXPERIMENTAL

Synthesis

All chemicals of p.a. grade were purchased from the Shanghai Chemicals Company and used without further purification.

A solution obtained by dissolving 0.200 g (0.268 mmol) of Tb_4O_7 in 4 cm^3 of (1 : 1) HNO_3 was evaporated to dryness. To the solid was added 25 cm^3 of CH_3OH/H_2O (1 : 1 v/v) and to the resulting solution was added 0.054 g (0.270 mmol) of phenanthroline monohydrate with stirring. This gave a clear solution, which turned orange. After several days, faintly reddish crystals were grown by slow evaporation at room temperature. Yield: *ca.* 25% on the basis of initial Tb_4O_7. *Anal.* Calc. for $C_{24}H_{16}N_7O_9Tb$ (%): C, 40.84; H, 2.28; N, 13.89. Found: C, 40.20; H, 2.75; N, 13.49. Thermogravimetric analysis indicated that the complex is stable below 415°C. The paramagnetic complex obeys the Curie–Weiss law $\chi_m(T - 0.05) = 12.180$ ($cm^3\ mol^{-1}\ K$) between 4.7 and 300 K.

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Crystal Structure Determination

A crystal of the title complex with approximate dimensions 0.33 × 0.13 × 0.13 mm was selected under a polarizing microscope and fixed with epoxy cement on a fine glass fibre which was then mounted on a Bruker P4 diffractometer for cell determination and data collection. The lattice parameters were refined from the 2ϑ values $(10-25^\circ)$ of 25 carefully centred reflections. X-ray diffraction intensity data were collected up to a 2ϑ value of 55° with graphite-monochromatized Mo*Kα* radiation ($\lambda = 0.71073$ Å) by the $\vartheta - 2\vartheta$ scan technique at 293 K. A total of 2948 independent reflections was collected, of which 2725 reflections with $I \geq 2\sigma(I)$ were considered as being observed and which were used for the structure determination. Usual *L*p and empirical adsorption corrections were applied. The structure was solved using direct methods [5]. Subsequent difference Fourier syntheses enabled all heavier atoms to be located. After several cycles of refinement, all hydrogen atoms of the 1,10-phenanthroline were derived from successive difference Fourier syntheses. Hydrogen and nonhydrogen atoms were refined with isotropic and anisotropic displacement parameters, respectively. Final refinement based on full-matrix least-squares technique [6] converged smoothly to $R1 = 0.0244$ and $wR2 = 0.0586$. Atomic scattering factors were supplied by the SHELX programs [5,6]. Final atomic coordinates and thermal parameters are summarized in Table I.

Crystal Data: $C_{24}H_{16}N_7O_9Tb$, $Mr = 705.36$, monoclinic, space group $C2/c$, $a = 11.155(1)$, $b = 17.914(2)$, $c = 13.026(1)$ Å, $\beta = 100.55(1)^\circ$, $V = 2559.0(4)$ Å^3, $Z = 4$, $F(000) = 1384$, $D_c = 1.831\,\mathrm{g\,cm^{-3}}$, $\mu(\mathrm{Mo}K\alpha) = 2.832\,\mathrm{mm^{-1}}$. Crystallographic data (excluding structure factors) for the structure in this article have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 169824 ($\mathrm{Tb(phen)_2(NO_3)_3}$). Copies of the data can be obtained, free

TABLE I Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for nonhydrogen atoms. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Tb	1/2	0.32497(1)	1/4	0.02784(9)
O(1)	0.4860(3)	0.4494(2)	0.1633(3)	0.0572(8)
O(2)	1/2	0.5539(3)	1/4	0.105(3)
O(3)	0.2900(3)	0.3688(2)	0.2531(2)	0.0441(6)
O(4)	0.3202(3)	0.3352(2)	0.1010(2)	0.0446(6)
O(5)	0.1424(3)	0.3758(3)	0.1194(3)	0.077(1)
N(1)	1/2	0.4863(3)	1/4	0.058(1)
N(2)	0.2475(3)	0.3601(2)	0.1562(3)	0.0407(7)
N(3)	0.3710(3)	0.2056(2)	0.2359(2)	0.0343(6)
N(4)	0.5568(3)	0.2806(2)	0.0821(2)	0.0346(6)
C(1)	0.3345(4)	0.1683(2)	0.1471(3)	0.0419(8)
C(2)	0.2884(5)	0.0957(2)	0.1432(3)	0.053(1)
C(3)	0.2791(5)	0.0606(3)	0.2336(4)	0.055(1)
C(4)	0.3115(4)	0.0987(2)	0.3289(3)	0.0430(8)
C(5)	0.3582(3)	0.1709(2)	0.3262(3)	0.0336(7)
C(6)	0.2980(6)	0.0668(2)	0.4271(4)	0.062(1)
C(7)	0.6727(5)	0.1055(3)	−0.0161(3)	0.056(1)
C(8)	0.6252(4)	0.1793(2)	−0.0169(3)	0.0387(8)
C(9)	0.6066(3)	0.2120(2)	0.0777(2)	0.0308(6)
C(10)	0.5960(4)	0.2230(3)	−0.1075(3)	0.0467(9)
C(11)	0.5511(4)	0.2925(3)	−0.1020(3)	0.0503(9)
C(12)	0.5309(4)	0.3195(2)	−0.0057(3)	0.0446(9)

of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, (Fax: +44 1223 336033 or E-mail: deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The title complex compound is isostructural with $La(phen)_2(NO_3)_3$ [7] and the crystal structure consist of $[Tb(phen)_2(NO_3)_3]$ molecules. As illustrated in Fig. 1, the terbium atoms are each surrounded by four N atoms from two chelating phen ligands and six O atoms from three chelating nitrate groups to form a distorted dicapped dodecahedron. The Tb–O bond distances vary from 2.474 to 2.529 Å and the Tb–N bond lengths are equal to 2.515 (2 ×) and 2.566 Å (2 ×). The coordination spheres about the terbium atoms closely resemble those around the lanthanum atoms in

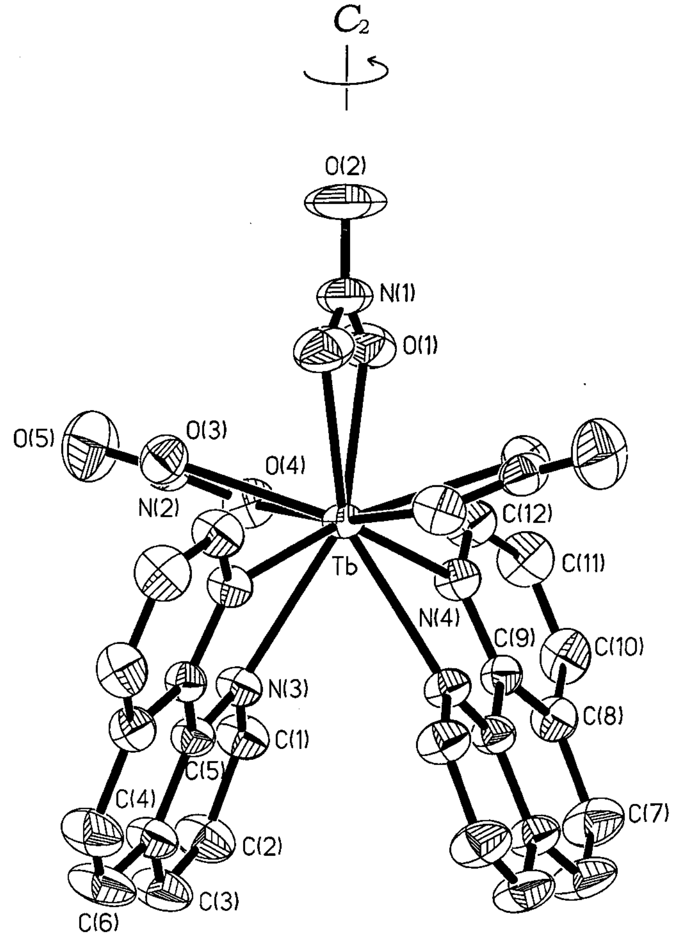

FIGURE 1 Ortep view of the $[Tb(phen)_2(NO_3)_3]$ complex molecule with displacement ellipsoids (45% probability) and atom labeling. Selected bond distances: Tb–O1$^{\#1}$ 2.474(3), Tb–O3$^{\#1}$ 2.478(3), Tb–O4$^{\#1}$ 2.529(3), Tb–N3$^{\#1}$ 2.566(3), Tb–N4$^{\#1}$ 2.515(3) (#1: $1-x$, y, $1/2-z$).

$[La(phen)_2(H_2O)_2(NO_3)_2](NO_3)(phen)_2(H_2O)$ [1]. The $[Tb(phen)_2(NO_3)_3]$ complex molecules possesses C_2 symmetry whose two-fold axis passes through O2, N1 and Tb atoms. Owing to coordination and site effects, the bidentate nitrate groups chelating the central terbium atom exhibit substantial deviation from D_{3h} symmetry N–O bond distances to coordinating O atoms are considerably longer than others (mean value: 1.213 Å). The bidentate chelating phen ligands display nearly perfect coplanarity. The dihedral angle between both phen ligands chelating the common Tb atom is 44.64(4)°. In the crystallographic $[0\bar{1}1]$ direction, the complex molecules are aligned in such a way that neighboring phen planes face in anti-parallel fashion with an interplanar distance of 3.51 Å, suggesting significant π–π stacking interactions [7–11]. One pyridyl component of the phen ligand is engaged in the π–π stacking interactions responsible for supramolecular assemblies of complex molecules into 1D columnar chains parallel to $[0\bar{1}1]$. The resulting chains are in turn arranged on the basis of *pseudo* 1D close-packing patterns.

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