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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1416). Services for accessing these data are described at the back of the journal.

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Triaquabis(nitrato-*O*,*O*′)(2,2′:6′,2″-terpyridine-κ^3*N*)gadolinium(III) nitrate

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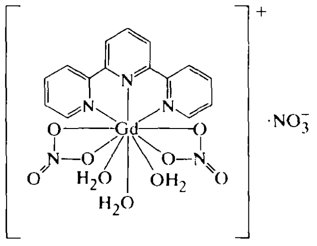
Abstract

Gadolinium nitrate forms a complex with terpyridine at the interface between an aqueous solution of the metal cation and a chloroform solution of the organic ligand. The title complex, $[Gd(terpy)(NO_3)_2(H_2O)_3]NO_3$ (terpy = terpyridine, $C_{15}H_{11}N_3$), is ten-coordinate and its coordination polyhedron can be described as a distorted bicapped square antiprism. The coordinated nitrates are bidentate. The three water ligands form hydrogen bonds in the lattice.

Comment

Lanthanide cations are present, along with the actinides, in radioactive waste solutions produced by the nuclear industry. Their separation in aqueous nitric acid solutions using selective extractants is an important goal for the management and recycling of nuclear fuels. In this respect, the comparative study of the coordination of various classes of complexing agents, in particular the terpyridine family, with lanthanide nitrates has been undertaken. Characterization of the complexes thus obtained is of particular importance for the understanding of extraction processes. Crystal structures of lanthanide salts coordinated with terpyridine derivatives were reported as early as 1969 (Frost *et al.*, 1969; Radonovitch & Glick, 1971; Holtz & Thompson, 1988; Mallet *et al.*, 1993; Kepert *et al.*, 1994), but to our knowledge only two structures of nitrate compounds have been published, namely, $[Eu(spy)(NO_3)_2]NO_3$ (spy = hexapyridine; Constable *et al.*, 1992) and $[La(terpy)_2(NO_3)_2][La(terpy)(NO_3)_4]$ (terpy = terpyridine; Fréchette & Bensimon, 1995). Both were synthesized in organic media. We present herein the crystal structure of the title compound, $[Gd(terpy)(NO_3)_2(H_2O)_3]NO_3$, (I).



(I)

In (I) (Fig. 1), the Gd cation is ten-coordinate, with three N donors from the terpyridine ligand, and seven O atoms from the three molecules of water and the two bidentate NO_3^- ligands. The coordination polyhedron can best be described as a distorted bicapped square antiprism, with O1*A* and O2*B* occupying the capping sites and N5/N6/O6/O2*A* and O4/O5/O1*B*/N4 defining the faces. Averaged Gd—N, Gd—O_{NO_3} and Gd—O_{H_2O} distances are 2.553 (3), 2.582 (3) and 2.433 (3) Å, respectively. These are slightly longer than those reported previously for the related complexes $[Gd(terpy)Cl_3(H_2O)_{7.1}]$ [Gd—N 2.537 (5) and Gd—O_{H_2O} 2.45 (4) Å; Kepert *et al.*, 1994], $[Gd(H_2O)_9]^{3+}$ [Gd—O_{H_2O} 2.474 (2) Å; Harrowfield *et al.*, 1983] or [Gd-

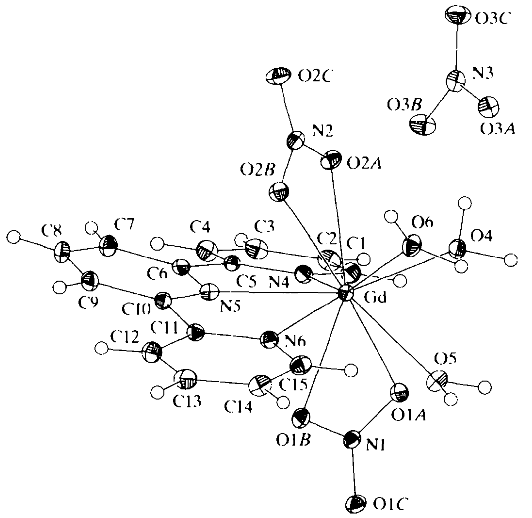


Fig. 1. The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level, except for H atoms, which are represented as spheres of arbitrary radii.

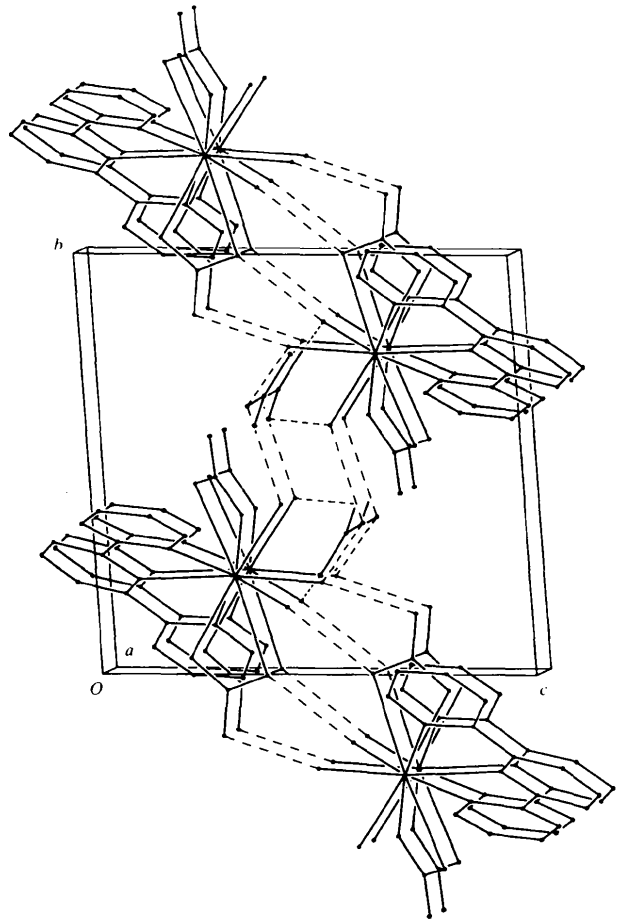


Fig. 2. View of the hydrogen bonding in (I). Hydrogen bonds are indicated by dashed lines. The corrugated sheets extend infinitely in the view direction (parallel to the *x* axis). H atoms have been omitted for clarity.

$(NO_3)_3(H_2O)_3]\cdot$(18-crown-6) [mean Gd—O_{NO_3} 2.45 (2) and mean Gd—O_{H_2O} 2.39 (1) Å; Backer-Dirks *et al.*, 1980].

Replacement of a nitrate by the organic ligand has taken place in the reaction and this anion is left uncoordinated, each of its O atoms forming hydrogen bonds with coordinated water molecules. All water H atoms act as hydrogen-bond donors and the pattern they form is displayed in Fig. 2; the extended structure consists of residues linked into sheets parallel to the [110] plane. In contrast to the complexes reported previously, *i.e.* [Eu(spy)$(NO_3)_2$]NO_3 (Constable *et al.*, 1992) and [La(terpy)$_2(NO_3)_2$][La(terpy)$(NO_3)_4$] (Fréchette & Bensimon, 1995), the title complex does not show expulsion of water from the metal coordination sphere.

Experimental

The title complex was synthesized by shaking a solution of gadolinium nitrate [$Gd(NO_3)_3\cdot 5H_2O$; 0.2 g, 0.46 mmol] in water (10 ml) with a solution of one equivalent of terpyridine ($C_{15}H_{11}N_3$, 0.108 g, 0.46 mmol) in chloroform (10 ml) for 12 h. The reaction mixture was then evaporated slowly until single crystals suitable for structure determination were obtained at the interface between the two immiscible solutions.

Crystal data

[Gd($C_{15}H_{11}N_3$)$(NO_3)_2$-
($H_2O)_3$]NO_3
M_r = 630.60
Triclinic
$P\overline{1}$
a = 8.8005 (3) Å
b = 11.1000 (5) Å
c = 11.6280 (5) Å
α = 89.746 (2)°
β = 69.678 (3)°
γ = 75.414 (3)°
V = 1026.53 (7) Å^3
Z = 2
D_x = 2.036 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from all
reflections
θ = 2.88–29.63°
μ = 3.303 mm^{-1}
T = 123 (2) K
Block
0.26 × 0.2 × 0.16 mm
Colourless

Data collection

Nonius CCD diffractometer
Area-detector scans
Absorption correction:
empirical (*MULABS* in
PLATON; Spek, 1998)
T_{min} = 0.507, T_{max} = 0.590
8435 measured reflections
4326 independent reflections

3962 reflections with
$I > 2\sigma(I)$
R_{int} = 0.034
θ_{max} = 29.63°
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$
Intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.027
$wR(F^2)$ = 0.062
S = 0.972

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.826 e Å^{-3}
$\Delta\rho_{min}$ = −0.949 e Å^{-3}
Extinction correction: none

4312 reflections
307 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 3.2317P]$
where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

Gd—O4	2.414 (3)	Gd—O1*B*	2.531 (3)
Gd—O6	2.422 (3)	Gd—N5	2.546 (3)
Gd—O5	2.462 (3)	Gd—N4	2.583 (3)
Gd—O2*A*	2.497 (3)	Gd—O2*B*	2.606 (3)
Gd—N6	2.530 (3)	Gd—O1*A*	2.695 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6*B*···O3*A*	0.922	1.847	2.754 (4)	167
O4—H4*B*···O3*A*	0.894	1.843	2.733 (4)	174
O5—H5*B*···O3*B*	1.041	1.670	2.700 (4)	170
O6—H6*A*···O3*C*	1.069	2.054	3.052 (4)	154
O4—H4*A*···O1*C*	1.070	1.834	2.809 (4)	149
O5—H5*A*···O1*A*	1.009	1.832	2.816 (4)	164

After positioning the detector 26 mm from the crystal, the data collection was performed by recording 90 images, while applying a 180° scan on φ (2° steps). Data are 95% complete to 2θ (52.6°). The H atoms of the ligand were included as riding atoms at calculated positions (U = 1.2 times that of the corresponding C atom). The H atoms of the water molecules were introduced into the calculation from positions found on the final difference Fourier map and were not refined.

Data collection: *DENZO* (Otwinowski & Minor, 1997). Cell refinement: *DENZO*. Data reduction: *DENZO*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL* (Bruker, 1997). Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1321). Services for accessing these data are described at the back of the journal.

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Di-μ-oxo-bis[(2,2′-bipyridine)(difluoroacetato)oxomolybdenum(V)] dihydrate

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Abstract

The structure of the title complex, $[Mo_2O_4(C_2HF_2O_2)_2(C_{10}H_8N_2)_2]\cdot 2H_2O$, is reported. The structure consists of the Mo_2O_4 core, with each metal center bonded to terminal and bridging oxo ligands, a monodentate difluoroacetate ligand and a chelating 2,2′-bipyridine group. The water molecules are each hydrogen bonded to a terminal oxo ligand and a difluoroacetate carbonyl group. The product, a result of accidental air oxidation, is similar in structure to other Mo_2O_4 complexes with similar ligation.

Comment

For some years we have been interested in the nature of the quadruply bonded dimolybdenum(II) carboxylates in solution (Webb & Dong, 1982; Islam *et al.*, 1990; Snowden *et al.*, 1993; Webb *et al.*, 1995). These complexes are often quite labile to substitution, and their solution chemistry is often richer and more complex than might be expected from solid-state studies. The chemistry of these complexes is also affected by carboxylate basicity (Webb *et al.*, 1995).

We were interested in examining the chemistry of $Mo_2(O_2CCHF_2)_4$ with 2,2′-bipyridine in comparison with an earlier study involving trifluoroacetate (Matonic *et al.*, 1991). ^{19}F NMR studies indicate that 2,2′-bipyridine forms several complexes with $Mo_2(O_2CCHF_2)_4$ in DMSO or acetonitrile, and that the species in solution change with the bipyridine:Mo_2 ratio; NMR evidence also suggests that free difluoroacetate is not produced in the reaction. However, it has not proven possible to date to identify any of the species in solution. We therefore set out to crystallize one or more complexes for comparison with the earlier trifluoroacetate study. From reaction mixtures, we could isolate a mixture of three different solids (white, orange–red and dark).