arrangements steric effects, including the phenyl groups, also become important (Brown & Canning, 1984). Thus distorted trigonal-bipyramidal structures are typically involved if large groups are present (Rappoli, Churchill, Janik, Rees & Atwood, 1987). All intermolecular distances of the crystal structure of (1) are larger than the corresponding van der Waals radii and no packing effects are observed.

As has been stated earlier (Brüggeller & Hübner, 1990) the square-planar arrangement of (4) is destabilized by the angular requirements of chiral P_4. A similar steric destabilization of square-planar platinum(II) complexes by repulsive ligand interactions leads to the favoured addition of fifth ligands and the formation of trigonal-bipyramidal species in the case of several platinum(II) complexes containing N—N bidentate ligands (De Felice, Ganis, Vitagliano & Valle, 1988; Albano, Braga, De Felice, Panunzi & Vitagliano, 1987). It has been shown that the electronic properties of the fifth ligands also play an important role in the stabilization of these five-coordinate platinum(II) complexes. In (1) the high electron-releasing ability of the hydride acting as a fifth ligand together with the destabilized coordination in (4) leads to a fluxional solution behavior with non-planar coordinated P_4 and a distorted trigonal-bipyramidal structure in the solid state. A similar complete destabilization of planar P_4 arrangements in five-coordinate platinum(II) species occurs upon addition of other fifth ligands with strong σ-donor abilities (Brüggeller, unpublished results).

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Structure of Triaqua(*N*,*N*-dimethylformamide)trinitratoneodymium(III) Monohydrate

By C. N. Dao, R. Rudert and P. Luger

Institute for Crystallography, Free University of Berlin, Takustrasse 6, *D*-1000 *Berlin* 33, *Germany*

and J. Legendziewicz and G. Oczko

Institute of Chemistry, University of Wroclaw, 14 *Joliot-Curie Street*, 50–383 *Wroclaw*, *Poland*

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Abstract. $[Nd(C_3H_7NO)(NO_3)_3(H_2O)_3].H_2O$, $M_r = 475.5$, triclinic, $P\bar{1}$, $a = 7.255\,(3)$, $b = 9.100\,(5)$, $c = 12.456\,(4)$ Å, $\alpha = 74.32\,(3)$, $\beta = 73.65\,(3)$, $\gamma = 84.81\,(3)°$, $V = 759.6$ Å^3, $Z = 2$, $D_m = 2.10$, $D_x = 2.08$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 3.574$ mm^{-1}, $F(000) = 466$, $T = 291$ K, final $R =$

0.025 for 3313 independent observed reflections. The Nd^{3+} ion is tenfold coordinated with O atoms. The nitrate molecules coordinate to Nd as bidentate ligands. The coordination polyhedron is in the form of a distorted bicapped square antiprism (BCSAP).

Introduction. Recently we have studied the crystal structures of a series of lanthanide complexes with carboxylic acids and amino acids. Up to now, the complexes were obtained from either aqueous solution (Dao, Glowiak, Huskowska & Legendziewicz, 1988, and references therein) or non-aqueous solution (Legendziewicz, Glowiak, Oczko & Dao, 1986). Now, the crystals of the title compound have been obtained from hydrated trinitratoneodymium salt and dimethylformamide solution. It is interesting to solve their structure, in order, as a continuation of our programme, to investigate the coordination sphere of lanthanide ions in the presence of both kinds of solvent molecules: water and dimethylformamide.

Experimental. Rose-coloured crystals obtained from dimethylformamide solution of $Nd(NO_3)_3.5H_2O$ salt. Crystal of approximate size 0.30 × 0.30 × 0.40 mm. D_m measured by flotation in chloroform/ethylene bromide. Automatic Siemens four-circle diffractometer used for the X-ray measurements. Cell parameters from 19 reflections in the range $18 < 2\theta < 35°$. Intensity measurement: $\omega/2\theta$ step scan, minimum and maximum time per step 0.3 and 1.8; $\sin\theta/\lambda < 0.639$ Å^{-1}, $-8 < h < 9$, $-3 < k < 11$, $-15 < l < 15$; four standard reflections, intensity variation 2.2%. 3489 reflections measured, value of $R_{\rm int}$ from merging equivalent reflections 0.012, 3313 independent observed, 88 independent unobserved with $F_o < 2\sigma(F_o)$. Calculations performed with the *XTAL* program system (Stewart & Hall, 1986). Absorption correction: program *ABSORB* of *XTAL* (Gaussian integration), minimum and maximum transmission factors 2.33 and 3.34. Structure solved by Patterson and difference Fourier techniques; H atoms from difference Fourier synthesis. Refinement: full-matrix least squares (on F), minimizing $\sum[w(|F_o| - |F_c|)]^2$, $w = 1/\sigma(F_o)$; 3313 reflections; 199 variables including anisotropic temperature factors for non-H atoms; coordinates and isotropic temperature factors of H atoms fixed; anomalous-dispersion correction for non-H atoms; atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final parameters: $R = 0.025$, $wR = 0.028$, $S = 4.01$. $(\Delta/\sigma)_{\max} = 0.009$, $(\Delta\rho)_{\min} = -0.5$, $(\Delta\rho)_{\max} = 1.3$ e Å^{-3} (highest peaks around Nd atom).

Discussion. The final atomic coordinates and equivalent isotropic displacement factors are given in Table 1.* Fig. 1 is a *SCHAKAL*88 plot (Keller, 1988) of the complex. The dimethylformamide (DMF) molecule coordinates to the Nd ion *via* its O atom. Each nitrate group has two O atoms in the coordination sphere. The other coordination bonds are from the water molecules. In Table 2 the geometries of the coordination sphere and ligands are given. It is obvious that the bidentate nitrate groups cause a large repulsion in the coordination sphere. Therefore, the bond distances involving Nd and nitrate O atoms are significantly larger than those of other Nd—O bonds. These Nd—$O_{\rm nitrate}$ bond distances [average 2.602 (4) Å] are similar to those found in the complexes $[Ln(NO_3)_3(H_2O)_4].2H_2O$, where Ln = Pr (Fuller & Jacobson, 1976) and Nd (Rogers, Taylor & Toogood, 1983). Nevertheless, it is noteworthy that the presence of the DMF molecule inside the coordination sphere disturbs the approximate molecular mirror symmetry observed in these tetraaquatrinitrato complexes. All three nitrate groups are coplanar, the average deviations of contributing atoms from least-squares planes are 0.003 (5), 0.002 (6) and 0.002 (4) Å. The Nd atom lies near planes of N(3), O(5), O(6), O(7) and N(4), O(8), O(9), O(10) [deviations 0.02 (1) and 0.06 (1) Å, respectively], but lies significantly out of the plane of N(2), O(2), O(3), O(4) [deviation 0.40 (1) Å]. For all nitrate groups the N—O terminal bond is shorter than the two N—O bonds involved in coordination to the metal. The O—N—O angles in the chelate ring for the three groups are 116.6 (4), 115.3 (5) and 116.4 (3)°. These bond distances and angles are well characterized when nitrate groups are bidentate ligands (Al-Karaghouli & Wood, 1972). The bond distances and angles in the dimethylformamide molecule of the title complex are comparable with those found in other complexes containing dimethylformamide (Brun & Brändén, 1966).

The coordination polyhedron can be described as a distorted BCSAP (Fig. 2*a*). One of the squares is formed by the atoms O(1), O(2*w*), O(9), O(4) [maximum deviation = 0.128 (5) Å], while the atoms O(1*w*), O(6), O(2), O(3*w*) define a second square [maximum deviation = 0.172 (5) Å]. The dihedral angle between these planes is 14.24 (9)°. The 'cap' atoms are then O(5) and O(8). An alternative description of a tenfold coordination can be made in terms of a 4A,6B-extended dodecahedron (46Dod) (Drew, 1977), which requires a trapezoidal plane and a square normal to it for its definition (Fig. 2*b*). The trapezoidal plane can be approximated by the atoms

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* Lists of structure factors, anisotropic thermal parameters, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54619 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and thermal parameters* (Å^2 × 10^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Nd	0.40429 (3)	0.26245 (2)	0.26345 (2)	2.565 (7)
O(1*w*)	0.6923 (4)	0.1548 (4)	0.3292 (3)	4.10 (10)
O(2*w*)	0.4570 (5)	0.4040 (4)	0.3954 (3)	5.50 (12)
O(3*w*)	0.6738 (4)	0.4132 (4)	0.1280 (3)	5.00 (12)
O(4*w*)	0.3232 (5)	0.6856 (4)	0.4430 (3)	5.51 (12)
O(1)	0.2688 (5)	0.5085 (4)	0.2174 (3)	5.77 (13)
O(2)	0.3287 (4)	0.3245 (4)	0.0582 (3)	4.66 (11)
O(3)	0.0468 (4)	0.3143 (4)	0.0337 (3)	5.45 (12)
O(4)	0.0979 (4)	0.2244 (4)	0.2035 (3)	4.40 (11)
O(5)	0.6062 (5)	0.1113 (4)	0.1221 (3)	5.86 (14)
O(6)	0.4015 (5)	−0.0202 (4)	0.2684 (4)	6.11 (14)
O(7)	0.5825 (6)	−0.1310 (5)	0.1400 (5)	10.0 (2)
O(8)	0.0829 (4)	0.2498 (4)	0.4245 (3)	4.47 (11)
O(9)	0.2992 (4)	0.0884 (4)	0.4719 (3)	4.37 (11)
O(10)	0.0202 (5)	0.0909 (4)	0.5939 (3)	5.81 (13)
N(1)	0.0746 (5)	0.7150 (4)	0.1938 (3)	3.80 (12)
N(2)	0.1547 (5)	0.2873 (4)	0.0971 (3)	3.67 (12)
N(3)	0.5326 (6)	−0.0166 (5)	0.1743 (4)	5.66 (17)
N(4)	0.1304 (5)	0.1419 (4)	0.4999 (3)	3.78 (12)
C(1)	0.2398 (6)	0.6445 (5)	0.1713 (4)	4.11 (15)
C(2)	−0.0936 (8)	0.6358 (7)	0.2765 (5)	7.0 (2)
C(3)	0.0532 (7)	0.8762 (5)	0.1369 (4)	5.19 (18)

Table 2. *Selected geometry* (Å,°)

Coordination polyhedron			
Nd—O(1*w*)	2.481 (3)	Nd—O(4)	2.614 (4)
Nd—O(2*w*)	2.469 (4)	Nd—O(5)	2.575 (4)
Nd—O(3w)	2.435 (3)	Nd—O(6)	2.557 (4)
Nd—O(1)	2.352 (3)	Nd—O(8)	2.601 (3)
Nd—O(2)	2.666 (4)	Nd—O(9)	2.591 (3)
Ligand molecules			
C(1)—O(1)	1.242 (5)	C(1)—N(1)	1.302 (6)
N(1)—C(2)	1.455 (6)	N(1)—C(3)	1.463 (6)
N(1)—C(1)—O(1)	124.2 (4)	C(2)—N(1)—C(3)	118.1 (4)
C(3)—N(1)—C(1)	120.8 (3)	C(1)—N(1)—C(2)	121.1 (4)
N(2)—O(2)	1.260 (4)	N(4)—O(9)	1.265 (4)
N(3)—O(5)	1.253 (6)	N(2)—O(3)	1.226 (6)
N(4)—O(8)	1.260 (5)	N(3)—O(7)	1.218 (7)
N(2)—O(4)	1.257 (4)	N(4)—O(10)	1.214 (4)
N(3)—O(6)	1.279 (6)		
O(2)—N(2)—O(4)	116.6 (4)	O(5)—N(3)—O(6)	115.3 (5)
O(2)—N(2)—O(3)	121.1 (3)	O(5)—N(3)—O(7)	123.2 (4)
O(3)—N(2)—O(4)	122.3 (3)	O(6)—N(3)—O(7)	121.6 (4)
O(8)—N(4)—O(9)	116.4 (3)	O(9)—N(4)—O(10)	121.6 (4)
O(8)—N(4)—O(10)	122.0 (3)		

O(5), O(6), O(8), O(3*w*) [average deviation 0.139 (5) Å]. A square almost perpendicular to this plane is then given by O(2*w*), O(1), O(42), O(91*w*) [with O(42) and O(91) midpoints of O(4)–O(2) and O(9)–O(1*w*), respectively], the dihedral angle being 95.10 (6)°. For both alternatives, polyhedra with ideal geometries were generated using the program *POLYHEDFIT* (Rudert, 1991) and their spatial orientations were systematically varied to fit their edges with the actual atoms as close as possible. This was checked *via* the distances d_i (i = 1–10) between comparable points in the observed and ideal polyhedra. For the best orientation $\Delta = \Sigma_i d_i^2/10$ (i = 1–10) was 0.269 Å^2 for a BCSAP geometry and 0.983 Å^2 for a 46Dod. Therefore the coordination polyhedron can better be described by a BCSAP than a 46Dod. The distortion of this type of coordination polyhedron is probably caused by the constraints introduced at the edges [O(2)—O(4), O(5)—O(6) and O(8)—O(9)] occupied by chelates.

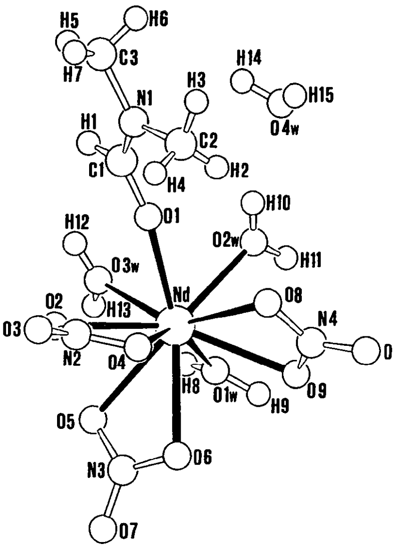
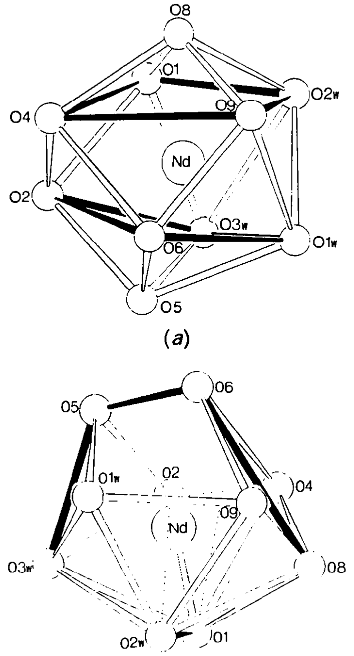


Fig. 1. A *SCHAKAL88* (Keller, 1988) perspective view of the [Nd(C_3H_7NO)(NO_3)$_3$(H_2O)$_3$].H_2O structure.



(*a*)

(*b*)

Fig. 2. The neodymium coordination polyhedra described as (*a*) a BCSAP and (*b*) a 46Dod.

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Structure of Tetrakis(cyclopentadienyl)uranium(IV) Acetate Dioxide*

BY J. REBIZANT, M. R. SPIRLET† AND C. APOSTOLIDIS

Commission of the European Communities, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, *D*-7500 *Karlsruhe* 1, *Germany*

AND B. KANELLAKOPULOS

Institut für Heisse Chemie, Kernforschungszentrum Karlsruhe, Postfach 3640, *D*-7500 *Karlsruhe* 1, *Germany*

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Abstract. $[U(C_5H_5)(CH_3CO_2)_2]_4O_2$, $M_r = 2 \times 858.43$, triclinic, $P\bar{1}$, $a = 9.354\,(4)$, $b = 12.988\,(5)$, $c = 19.613\,(7)$ Å, $\alpha = 82.74\,(3)$, $\beta = 98.24\,(3)$, $\gamma = 102.89\,(4)°$, $V = 2287.6$ Å^3, $Z = 4$, $D_x = 2.492$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 134.501$ cm^{-1}, $F(000) = 1544$, $T = 295\,(1)$ K, $R = 0.043$ for 3390 reflections $[I > 3\sigma(I)]$. In this tetrameric complex, each U^{IV} atom is seven coordinated in a distorted pentagonal-bipyramidal geometry. The bridging between U atoms occurs through acetate and oxide O atoms. The cyclopentadienyl ligands occupy the apical coordination sites of the bipyramids.

Introduction. Acetate ions can function as both monodentate and bidentate ligands but the crystallochemical factors which favour one of these two coordinations are not known. The title compound is a product obtained while attempting to synthesize tris(cyclopentadienyl)uranium acetate.

Within the large series of cyclopentadienyl complexes of uranium(IV), the title compound is the first observed where the uranium(IV) exhibits a coordination number of seven. Its characterization and structure analysis by single-crystal X-ray diffraction is reported here.

Experimental. $[U(C_5H_5)(CH_3CO_2)_2]_4O_2$ was obtained from partial hydrolysis of $[U(C_5H_5)_3(CH_3CO_2)]$ in tetrahydrofuran solution. Recrystallization in *n*-pentane yielded green prismatic single crystals. The selected specimen (0.30 × 0.30 × 0.40 mm) was sealed in a thin-walled glass capillary under an inert atmosphere. X-ray diffraction data were measured with an Enraf–Nonius CAD-4 X-ray diffractometer using graphite-monochromated Mo $K\alpha$ radiation and θ–2θ scans. The unit-cell dimensions were determined from 25 reflections in the range $4 \le 2\theta \le 44°$. No systematic absences were detected. Intensity data were collected in the range $4 \le 2\theta \le 45°$, h $-11 \rightarrow 0$, k $-15 \rightarrow 15$, l $-23 \rightarrow 23$; 5947 unique reflections were collected, 3390 of which were considered observed $[I \ge 3\sigma(I)]$ and used in refinement. The intensities of three standard reflections measured at 30 min intervals showed no deviations from the mean. The intensities were corrected for Lorentz–polarization effects. Empirical absorption corrections were also applied using the program *DIFABS*

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[*] Octa-μ-acetato-di-μ-oxo-tetrakis[(cyclopentadienyl)uranium-(IV)].

[†] On leave from University of Liège, Belgium.

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