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The Novel Dinuclear Complex Tetraaquahexakis(nitrato-*O*,*O*')bis(2,4,6,8-Tetramethyl-2,4,6,8-Tetraazabicyclo[3.3.0]octane-3,7-Dione-*O*,*O*')dipraseodymium(III): Synthesis and Crystal Structure

E. E. Netreba[a, *], **S. V. Shabanov**[a], **A. A. Velikozhon**[a], **and N. V. Somov**[b]
[a] *Vernadsky Crimean Federal University, Simferopol, Russia*
[b] *Lobachevsky State University, Nizhny Novgorod, Russia*
**e-mail: evgtnu@gmail.com*

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Abstract—A centrosymmetric dinuclear complex, $[Pr(C_8H_{14}N_4O_2)(H_2O)_2(NO_3)_3]_2$ (**I**), was obtained from praseodymium(III) nitrate and the bicyclic bisurea 2,4,6,8-tetramethyl-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione (mebicar, Mc) and structurally characterized (CIF file CCDC no. 1435137). The crystals of complex **I** are triclinic: space group $P\bar{1}$, $a = 9.8967(5)$, $b = 10.3689(5)$, $c = 11.0018(6)$ Å, $\alpha = 74.650(5)°$, $\beta = 68.064(5)°$, $\gamma = 67.257(5)°$, $V = 956.22(10)$ Å^3, $\rho_{calcd} = 1.949$ g/cm^3, $Z = 1$. The praseodymium atom is coordinated to two O atoms of two Mc molecules (related by a center of symmetry), three bidentate nitrate anions, and two water molecules. So its coordination polyhedron has ten vertices; the Pr···Pr distance is 9.8726(7) Å.

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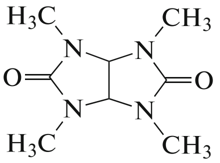
INTRODUCTION

Lanthanide complexes with bicyclic bisurea ligands of the octane series still remain poorly studied. An example is 2,4,6,8-tetramethyl-2,4,6,8-tetraazabicyclo[3.3.0]octane-3,7-dione, or mebicar ($C_8H_{14}N_4O_2$, Mc):



Mebicar exhibits stress-protective, anxiolytic, and nootropic effects and is used in medical practice under the brand name Adaptol. Mebicar mitigates sleep disorders, having no direct somniferous effect; this drug is neither a cholinolytic nor a muscular relaxant, does not impair the motor function, and diminishes nicotine abstinence [1–3]. Mebicar is known to improve the oxygen supply to myocardial tissues, regulate the electrolyte balance of blood plasma and the potassium content of the blood, erythrocytes, and myocardial tissues, promote the protein synthesis, and increase the cellular energy resources [4–6].

Earlier, Tsivadze with coworkers have obtained and described some complexes with mebicar: $[Co(Mc)_2(H_2O)_2Br_2] \cdot 2H_2O$, $[Ni(Mc)_2(H_2O)_2Br_2]$, $[NiMc(H_2O)_4](NO_3)_2$, $[Cu_2(Mc)_3Br_4] \cdot 2H_2O$, $CdCl_2 \cdot Mc \cdot 3H_2O$, $CaCl_2 \cdot 2Mc \cdot H_2O$, $Co(NO_3)_2 \cdot 2Mc \cdot 4H_2O$, $Ni(NO_3)_2 \cdot Mc \cdot 4H_2O$, $CdX_2 \cdot Mc$ (X = Br, I, and NCS), $Cd(NO_3)_2 \cdot 1.5Mc \cdot H_2O$, $ZnCl_2 \cdot Mc$, $ZnI_2 \cdot Mc$, $Ca(NO_3)_2 \cdot 2Mc$, $Cu(NO_3)_2 \cdot 0.5Mc$, and $[Li_2(Mc)_2(H_2O)_4]Br_2$ [7–10]. The above complexes were studied by elemental analysis and IR and Raman spectroscopy; some of them were examined by X-ray diffraction. It was demonstrated that Mc is coordinated to the metal ions through the O atoms of the urea moieties, which is confirmed by the lower frequency of the amide I band and by the higher frequency of the bending vibrations of the methylamino groups.

For this reason, the synthesis and study of metal complexes with this ligand (a hard Lewis base) will elucidate the chemism of its interactions with lanthanide ions and allow determination of the ligand denticity in acetone.

The goal of this study was to obtain a complex of praseodymium(III) nitrate (a hard Lewis acid) with mebicar and water molecules, $[Pr(C_8H_{14}N_4O_2)(H_2O)_2(NO_3)_3]_2$ (**I**), and determine its structure.

Table 1. Crystallographic parameters and the data collection and refinement statistics for structure **I**

Parameter	Value
M	1122.41
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell parameters:	
a, Å	9.8967(5)
b, Å	10.3689(5)
c, Å	11.0018(6)
α, deg	74.650(5)
β, deg	68.064(5)
γ, deg	67.257(5)
V, Å^3	956.22(10)
Z	1
ρ_{calcd}, g/cm^3	1.949
μ(MoK_α), mm^{-1}	2.628
F(000)	556
Crystal dimensions, mm	0.12 × 0.10 × 0.06
θ Scan range, deg	3.657–30.499
Ranges of *h*, *k*, *l* indices	$-14 \leqslant h \leqslant 14$ $-14 \leqslant k \leqslant 14$ $-15 \leqslant l \leqslant 15$
Number of measured reflections	19728
Number of unique reflections (R_{int})	5821 (0.0314)
Number of reflections with $I > 2\sigma(I)$	5307
Number of parameters refined	334
Number of constraints	9
R factor ($I > 2\sigma(I)$)	$R_1 = 0.0236$, $wR_2 = 0.0483$
R factor for all reflections	$R_1 = 0.0281$, $wR_2 = 0.0501$
GOOF on F^2	1.038
$\Delta\rho_{max}$, $\Delta\rho_{min}$, *e* Å^{-3}	0.978, –0.407

EXPERIMENTAL

Mebicar prepared as described in [11, 12], $Pr(NO_3)_3 \cdot 6H_2O$ (reagent grade), and acetone (special purity grade) were used.

Synthesis of complex I. A weighed sample of $Pr(NO_3)_3 \cdot 6H_2O$ was dissolved in acetone, and mebicar was added in a molar ratio of 1 : 0.8. The reaction mixture was stirred on a magnetic stirrer for 5–10 min. The resulting solution was filtered and left in a closed vessel for several days for crystallization. The pale green crystals that formed were collected by filtration, washed with acetone, and dried in air. The yield of complex **I** was ~61% (with respect to the ligand). Complex **I** is air-stable.

For $C_{16}H_{36}N_{14}O_{26}Pr_2$

anal. calcd., %:	C, 17.12;	H, 3.23;	N, 17.47.
Found, %:	C, 17.17;	H, 3.25;	N, 17.44.

Elemental analysis of complex **I** was carried out on an EA-3000 analyzer (EuroVector). The IR spectra of mebicar and complex **I** were recorded in the 350–4500 cm^{-1} range on a Bruker Vertex 70 FTIR spectrometer equipped with a diamond crystal-based attachment for the frustrated total internal reflection mode (resolution 4 cm^{-1}, 20 transients).

Single-crystal X-ray diffraction study of complex **I** was carried out on an Oxford Diffraction Gemini S automated diffractometer equipped with a Sapphire III CCD detector (MoK_α radiation, λ = 0.71073 Å) at 296(2) K. The structure was solved by a direct method with the SHELX program package [13] using the embedded WINGX system [14]. The hydrogen atoms were located in a difference electron-density map. Structure **I** was refined anisotropically (for non-hydrogen atoms) on F^2 by the full-matrix least-squares method; constraints were placed on some parameters of the H atoms.

Crystallographic parameters and the data collection and refinement statistics for structure **I** are summarized in Table 1. Selected bond lengths and bond angles in structure **I** are listed in Table 2.

X-ray diffraction data for structure **I** have been deposited with the Cambridge Structural Database (CCDC no. 1435137; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The IR spectra of mebicar and complex **I** show the following characteristic bands (ν, cm^{-1}): 2926, 2884, 2831, 2804 (Me, CH_2); 1701 (C=O, amide **I**); 1454, 1367 (C–N) for Mc; 3487, 3406 (H_2O); 2939, 2889 (Me, CH_2); 1657 (C=O, amide **I**); 1443, 1369 (C–N); 1549, 1289, 1028, 835 (NO_3) for **I**.

In the IR spectrum of complex **I**, the band due to ν(C=O (amide **I**)) is shifted by 44 cm^{-1} to the longer wavelengths, which suggests the coordination of Mc to the Pr atom through the O atoms [15]. The IR spectrum also contains the absorption bands due to ν_{s+as}(HOH) of water and a set of bands due to the Mc rings. The free nitrate anion as a planar ion (point group D_{3h}) has four main vibrational frequencies: 1050–1060 (symmetric stretching, ν_s(NO)), 1350–1400 (antisymmetric doubly degenerate stretching, ν_e(NO)), and 810–840 and 710–730 cm^{-1} (bending, δ(NO_3)). The IR spectrum normally shows only ν_e(NO) and two δ(NO_3) [16]. When the nitrate anion

Table 2. Selected bond lengths (Å) and bond angles (deg) in structure **I***

Angle	ω, deg	Angle	ω, deg	Bond	*d*, Å
O(2)N(1)Pr(1)	59.64(10)	O(10)$^{\#}$Pr(1)O(6)	66.73(6)	Pr(1)–O(1)	2.5748(16)
O(1)N(1)Pr(1)	58.25(10)	O(7)Pr(1)O(6)	71.39(5)	Pr(1)–O(2)	2.6058(16)
N(1)O(1)Pr(1)	97.12(12)	O(1)Pr(1)O(6)	134.81(5)	Pr(1)–O(4)	2.6540(17)
N(1)O(2)Pr(1)	95.77(12)	O(2)Pr(1)O(6)	122.07(5)	Pr(1)–O(6)	2.6451(16)
N(2)O(4)Pr(1)	97.14(12)	O(8)Pr(1)O(6)	66.86(5)	Pr(1)–O(7)	2.5542(15)
N(2)O(6)Pr(1)	97.50(12)	O(12)Pr(1)O(4)	72.79(6)	Pr(1)–O(8)	2.6331(17)
N(3)O(7)Pr(1)	98.78(12)	O(13)Pr(1)O(4)	115.64(6)	Pr(1)–O(10)$^{\#}$	2.5502(18)
N(3)O(8)Pr(1)	95.56(12)	O(12)Pr(1)O(10)$^{\#}$	141.62(7)	Pr(1)–O(11)$^{\#}$	2.5012(18)
C(6)O(12)Pr(1)	166.97(16)	O(13)Pr(1)O(10)$^{\#}$	133.38(7)	Pr(1)–O(12)	2.3984(15)
C(1)O(13)Pr(1)	144.07(13)	O(7)Pr(1)O(8)	49.17(5)	Pr(1)–O(13)	2.4372(15)
O(12)Pr(1)O(13)	69.96(5)	O(1)Pr(1)O(8)	153.65(5)		
O(12)Pr(1)N(1)	99.75(6)	O(2)Pr(1)O(8)	109.56(5)		
O(12)Pr(1)O(11)$^{\#}$	76.86(7)	O(12)Pr(1)O(6)	120.24(6)		
O(13)Pr(1)O(11)$^{\#}$	143.04(6)	O(13)Pr(1)O(6)	137.62(6)		
O(11)$^{\#}$Pr(1)O(10)$^{\#}$	69.06(7)	O(11)$^{\#}$Pr(1)O(6)	73.97(6)		
O(12)Pr(1)O(7)	144.62(6)	O(11)$^{\#}$Pr(1)O(8)	133.43(7)		
O(13)Pr(1)O(7)	80.02(5)	O(10)$^{\#}$Pr(1)O(8)	114.28(6)		
O(11)$^{\#}$Pr(1)O(7)	136.40(6)	O(11)$^{\#}$Pr(1)O(4)	67.37(7)		
O(10)$^{\#}$Pr(1)O(7)	73.40(6)	O(10)$^{\#}$Pr(1)O(4)	108.13(7)		
O(12)Pr(1)O(1)	80.44(6)	O(7)Pr(1)O(4)	105.57(5)		
O(13)Pr(1)O(1)	85.78(5)	O(1)Pr(1)O(4)	135.88(5)		
O(11)$^{\#}$Pr(1)O(1)	72.85(6)	O(8)Pr(1)O(4)	67.93(6)		
O(10)$^{\#}$Pr(1)O(1)	73.22(6)	O(6)Pr(1)O(4)	48.02(5)		
O(12)Pr(1)O(2)	117.01(6)	O(13)Pr(1)N(1)	78.26(5)		
O(13)Pr(1)O(2)	71.08(5)	O(11)$^{\#}$Pr(1)N(1)	92.06(6)		
O(11)$^{\#}$Pr(1)O(2)	112.17(6)	O(10)$^{\#}$Pr(1)N(1)	65.29(6)		
O(10)$^{\#}$Pr(1)O(2)	63.60(7)	O(7)Pr(1)N(1)	91.80(5)		
O(7)Pr(1)O(2)	67.55(5)	O(1)Pr(1)N(1)	24.64(5)		
O(1)Pr(1)O(2)	49.20(5)	O(2)Pr(1)N(1)	24.60(5)		
O(12)Pr(1)O(8)	101.75(6)	O(8)Pr(1)N(1)	132.95(5)		
O(13)Pr(1)O(8)	70.79(5)	O(6)Pr(1)N(1)	131.89(5)		

* The symmetry operation is $^{\#}$ $1 - x, 1 - y, -z$.

is coordinated, its symmetry can lower to C_s and C_{2v}. As a result, the IR spectrum contains six intense bands at 970–1040 (fully symmetric vibrations), 1550–1410 and 1290–1250 (antisymmetric stretching manifested as two intense bands), 830–800 (out-of-plane vibrations), and 780–700 and ~680 cm^{-1} (in-plane bending manifested as two bands) [17, 18]. The IR spectrum of complex **I** exhibits absorption bands at 1549, 1289, 1028, and 835 cm^{-1}. This suggests that the nitrate anions are coordinated to the metal center in a chelating bidentate fashion.

According to X-ray diffraction data, structure **I** is a centrosymmetric dinuclear complex of the Pr^{3+} cation with two mebicar molecules (related by a center of symmetry), bidentate nitrate anions, and two water molecules (Fig. 1). The coordination polyhedron of the praseodymium atom comprises ten vertices; the Pr···Pr distance is 9.8726(7) Å.

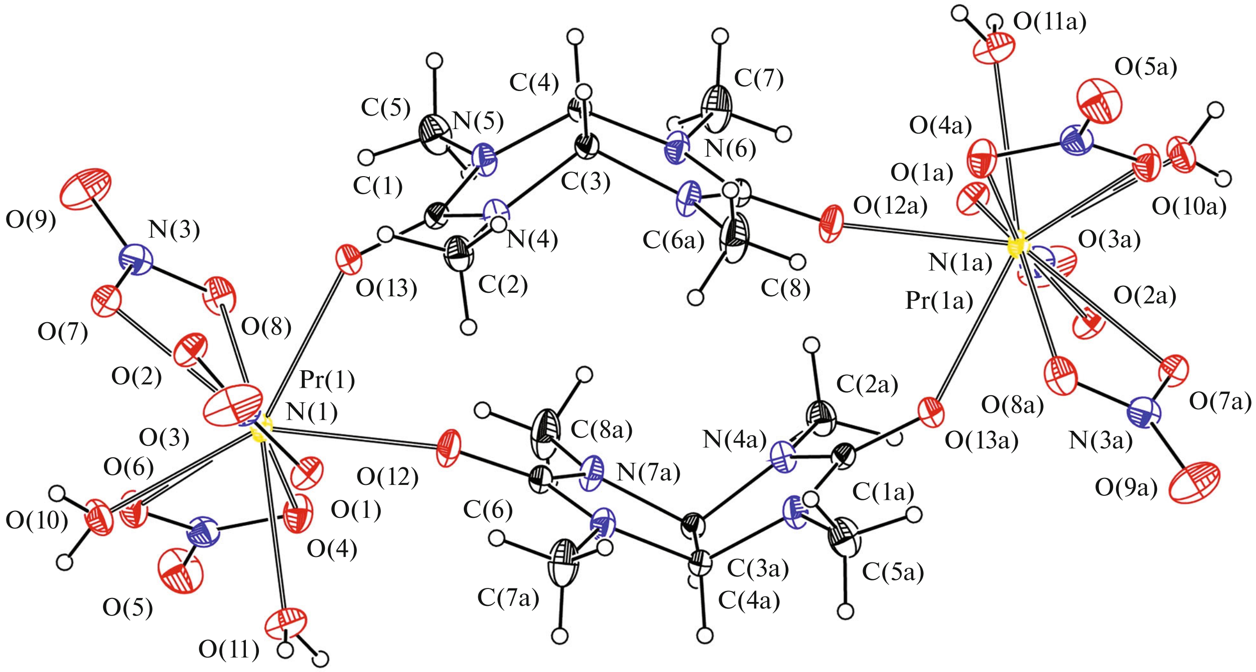


Fig. 1. Fragment of structure **I** with atomic displacement ellipsoids for the non-hydrogen atoms (50% probability).

The nearly planar conjugated five-membered heterocycles of mebicar are shaped like a butterfly or a "slightly opened book." The dihedral angle between their planes is 57.21(2)°. The MOC bond angles differ considerably: Pr(1)O(13)C(1), 144.04(1)°; Pr(1)O(12)C(6), 166.98(2)°. The OMO angles involving the carbonyl groups of the ligand are equal (69.96(6)°). Obviously, the MOC angle in the complex is most flexible. The carbonyl O(12) and O(13) atoms are coplanar with and bound to the heterocycles. The distances between the coordinated water molecules and the praseodymium cation are nearly equal: Pr(1)–O(10*w*), 2.5502(18) Å; Pr(1)–O(11*w*), 2.5012(18) Å.

The methyl C atoms are arranged differently relative to the planes of the bicyclic framework; all methyl groups are oriented outside. The C(2), C(5), and C(7) atoms deviate substantially from the planes of the heterocycles with respect to the internal part of the bicyclic framework (by 0.219(3), 0.184(4), and 0.3(4) Å, respectively); the deviation of the C(8) atom is small (0.089(5) Å). The polyhedra of the N atoms are shaped like nearly regular triangles coplanar (within ~0.1 Å) with the.

In the ring containing the N(4) and N(5) atoms, the O–C–N–C fragments are nonplanar; the torsion angles O(13)C(1)N(4)C(2) and O(13)C(1)N(5)C(5) are 8.83(2)° and –5.92(2)°. In the ring containing the N(7) and N(6) atoms, the torsion angles O(12)C(6)N(6)C(7) and O(12)C(6)N(7)C(8) are 13.62(2)° and –2.55(2)°, respectively.

Table 3. Geometrical parameters of the hydrogen bonds in structure **I***

D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
O(11)–H(1)···O(3)^{i}	0.73(4)	2.03(4)	2.727(4)	163(3)
O(11)–H(2)···O(4)^{ii}	0.82(5)	2.42(5)	3.220(3)	168(4)
O(10)–H(3)···O(7)^{iii}	0.77(4)	2.19(4)	2.902(3)	154(4)
O(10)–H(4)···O(6)^{iii}	0.71(4)	2.30(5)	2.936(3)	152(5)

* The symmetry operations are ^{i} 1 – *x*, 2 – *y*, –1 – *z*; ^{ii} 2 – *x*, 1 – *y*, –1 – *z*; ^{iii} 2 – *x*, 2 – *y*, –1 – *z*.

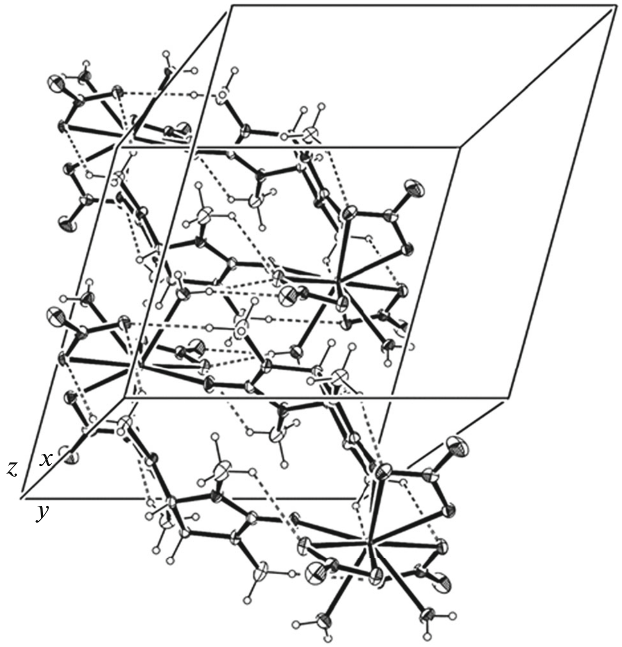


Fig. 2. Crystal packing of complex **I** in the [100] plane (fragment).

In the crystal, the molecules of complex **I** are united through hydrogen bonds (Table 3, Fig. 2).

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