Crystal structure of bis(guanidinium) (hydrogen triethylenetetramine-hexaacetato)praseodymate(III) hydrate, $C_{18}H_{25}N_4O_{12}Pr \cdot 2CH_6N_3 \cdot 3.5H_2O$

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Abstract

$C_{20}H_{43.50}N_{10}O_{15.50}Pr$, triclinic, $P\bar{1}$ (No. 2), $a = 10.013(2)$ Å, $b = 10.735(2)$ Å, $c = 15.577(4)$ Å, $\alpha = 106.72(2)^\circ$, $\beta = 90.20(2)^\circ$, $\gamma = 93.29(2)^\circ$, $V = 1600.6$ Å³, $Z = 2$, $R_{gt}(F) = 0.042$, $wR_{ref}(F^2) = 0.113$, $T = 293$ K.

Source of material

Within the context of preparation of inorganic materials, the so-called chelate method, involving the low temperature decomposition of solid metal precursors obtained from a solution of the complexed metals has proved to be an advantageous way to get multimetallic oxides [1]. During the search for potential precursors for Pr-based ceramics, the title compound was isolated. Crystals suitable for X ray diffraction analysis were obtained in the same way as for the equivalent Bi complex [2]. $Pr_2(CO_3)_3$ was used as starting reagent instead of Bi oxocarbonate.

Experimental details

All the hydrogen atoms were refined with a common isotropic temperature factor ($U_{iso} = 0.051$ Å²). There are two positions for atom O108; they were included in the refinement and their site occupation factors converge to 0.30 for position A and 0.70 for position B. Only the last one is represented on the figure. The

water molecule labelled O4W lies on a crystallographic center of symmetry. The hydrogen atoms of water molecules were not localized.

Discussion

The structure of the complex $(gu)_2Pr(Htta) \cdot 3.5H_2O$ is presented at the figure. The Htta ligand coordinates the Pr cation by its 6 oxygen and 4 nitrogen atoms resulting in a tenfold coordination. There is no other atom in the coordination sphere. The H atom of the ligand has been localised by comparison of the C—O distances and its position confirmed by a Fourier difference synthesis. It is localised on an oxygen of a terminal carboxylic group (O101). For this oxygen, the coordination distance 2.802(2) Å is significantly longer than the other distances to Pr. The mean value Pr—O, excluding O101, is 2.462(2) Å while the average distance Pr—N is 2.813(2) Å. The carboxylic H atom is involved in a hydrogen bond with O111 of a symmetry related molecule making dimers. The coordination polyhedron is a biccapped square antiprism with O2—O1—N2—O8 as one square face and O11—O5—N3—O12 as the second one. The capping atoms are N1 on one side and N4 on the other side. This coordination polyhedron is the same as that observed in the bis(guanidinium) (hydrogen triethylene-tetraminehexaacetato) lanthanate (III) [3]. It differs however from that observed in the analogous Bi(III) [2], Gd(III) [4] and Dy(III) [3] complexes, which are all characterized by a nine-fold coordination based on a monocapped square antiprism. Within these structures the lower coordination results from the fact that the non-ionized carboxylic acid is not involved in metal coordination.

Table 1. Data collection and handling.

Crystal:	yellow parallelepiped, size 0.14 × 0.28 × 0.35 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ :	16.07 cm ⁻¹
Diffractionmeter, scan mode:	Huber, ω
$2\theta_{max}$:	70°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	14088, 14088
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 12067
$N(param)_{refined}$:	552
Programs:	SHELXS-86 [5], SHELXL-93 [6], PLATON [7]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(64A)	2i	0.4498(4)	0.3239(4)	0.5290(3)	0.31(4)
H(64B)	2i	0.3314(4)	0.2900(4)	0.4667(3)	0.31
H(101)	2i	0.356(4)	0.711(4)	0.062(2)	0.051(2)
H(1A)	2i	0.154(4)	0.791(4)	0.235(3)	0.051
H(1B)	2i	0.301(5)	0.760(4)	0.277(3)	0.051
H(2A)	2i	0.090(4)	0.595(5)	0.387(3)	0.051
H(2B)	2i	0.146(4)	0.745(4)	0.391(3)	0.051
H(3A)	2i	-0.010(4)	0.661(4)	0.183(3)	0.051
H(3B)	2i	-0.073(4)	0.694(4)	0.294(3)	0.051
H(4A)	2i	-0.195(4)	0.512(4)	0.220(3)	0.051
H(4B)	2i	-0.099(4)	0.479(4)	0.298(3)	0.051
H(5A)	2i	-0.135(4)	0.365(4)	0.053(3)	0.051
H(5B)	2i	-0.025(4)	0.482(5)	0.079(3)	0.051
H(6A)	2i	-0.139(4)	0.281(4)	0.232(3)	0.051
H(6B)	2i	-0.206(4)	0.251(4)	0.134(3)	0.051
H(7A)	2i	-0.031(4)	0.132(4)	0.082(3)	0.051
H(7B)	2i	-0.116(4)	0.068(4)	0.140(3)	0.051
H(8A)	2i	-0.115(4)	0.095(4)	0.314(3)	0.051
H(8B)	2i	-0.049(4)	0.092(4)	0.284(3)	0.051
H(9A)	2i	0.199(5)	0.002(5)	0.196(3)	0.051
H(9B)	2i	0.111(4)	-0.060(5)	0.126(3)	0.051

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(10A)	2i	0.204(4)	0.064(4)	0.045(3)	0.051
H(10B)	2i	0.297(4)	-0.047(4)	0.056(3)	0.051
H(11A)	2i	0.400(4)	0.167(4)	0.006(3)	0.051
H(11B)	2i	0.501(4)	0.114(4)	0.027(3)	0.051
H(12A)	2i	0.452(4)	0.018(5)	0.170(3)	0.051
H(12B)	2i	0.514(5)	0.127(5)	0.189(3)	0.051
H(52A)	2i	0.293(4)	0.366(4)	-0.031(2)	0.051
H(52B)	2i	0.366(4)	0.480(2)	-0.065(3)	0.051
H(53A)	2i	0.419(4)	0.287(3)	-0.275(2)	0.051
H(53B)	2i	0.449(4)	0.247(2)	-0.196(3)	0.051
H(54A)	2i	0.202(3)	0.182(4)	-0.143(3)	0.051
H(54B)	2i	0.299(4)	0.138(4)	-0.228(2)	0.051
H(62A)	2i	0.472(3)	0.525(4)	0.644(3)	0.051
H(62B)	2i	0.373(4)	0.622(2)	0.635(3)	0.051
H(63A)	2i	0.184(4)	0.569(2)	0.542(3)	0.051
H(63B)	2i	0.184(4)	0.436(3)	0.475(2)	0.051
HW(1A)	2i	0.610(2)	0.173(4)	0.353(3)	0.051
HW(1B)	2i	0.774(3)	0.180(4)	0.379(3)	0.051
HW(2A)	2i	0.677(3)	0.888(5)	0.380(3)	0.051
HW(2B)	2i	0.509(3)	0.885(5)	0.380(3)	0.051

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Pr	2i		0.22666(1)	0.37087(1)	0.214104(8)	0.02695(6)	0.02026(5)	0.02092(6)	0.00219(3)	0.00107(3)	0.00638(4)
N(1)	2i		0.1306(2)	0.6267(2)	0.2711(2)	0.046(1)	0.0266(9)	0.0255(9)	0.0087(8)	0.0074(8)	0.0107(7)
C(1)	2i		0.2107(4)	0.7234(3)	0.2395(2)	0.071(2)	0.023(1)	0.033(1)	0.006(1)	0.016(1)	0.0101(9)
C(101)	2i		0.2639(3)	0.6646(2)	0.1477(2)	0.045(1)	0.025(1)	0.028(1)	0.0038(9)	0.0046(9)	0.0104(8)
O(1)	2i		0.2648(3)	0.5486(2)	0.1140(2)	0.062(1)	0.0244(8)	0.040(1)	0.0038(8)	0.016(1)	0.0082(8)
O(101)	2i		0.3151(2)	0.7535(2)	0.1125(2)	0.060(1)	0.0267(8)	0.035(1)	0.0027(8)	0.0123(9)	0.0126(7)
C(2)	2i		0.1514(3)	0.6601(3)	0.3690(2)	0.052(2)	0.030(1)	0.024(1)	0.011(1)	0.009(1)	0.0071(9)
C(102)	2i		0.2958(3)	0.6369(3)	0.3886(2)	0.050(2)	0.030(1)	0.030(1)	0.001(1)	0.001(1)	0.0053(9)
O(2)	2i		0.3463(2)	0.5404(2)	0.3348(2)	0.040(1)	0.0304(9)	0.035(1)	0.0033(7)	-0.0027(8)	-0.0009(7)
O(102)	2i		0.3553(3)	0.7142(3)	0.4539(2)	0.067(2)	0.058(2)	0.050(2)	0.007(1)	-0.011(1)	-0.017(1)
C(3)	2i		-0.0110(3)	0.6267(3)	0.2438(2)	0.051(2)	0.039(1)	0.035(1)	0.020(1)	0.003(1)	0.016(1)
C(4)	2i		-0.0908(3)	0.5005(3)	0.2356(2)	0.036(1)	0.049(2)	0.033(1)	0.015(1)	0.0062(9)	0.015(1)
N(2)	2i		-0.0358(2)	0.3857(2)	0.1713(2)	0.0295(9)	0.038(1)	0.0286(9)	0.0051(8)	0.0005(7)	0.0155(8)
C(5)	2i		-0.0428(3)	0.3934(3)	0.0782(2)	0.038(1)	0.047(2)	0.030(1)	0.008(1)	-0.0010(9)	0.020(1)
C(105)	2i		0.0568(3)	0.3094(2)	0.0177(2)	0.038(1)	0.029(1)	0.025(1)	-0.0041(8)	-0.0015(8)	0.0129(8)
O(105)	2i		0.0303(2)	0.2677(2)	-0.0633(1)	0.051(1)	0.049(1)	0.0247(9)	-0.0051(9)	-0.0052(8)	0.0088(8)
O(5)	2i		0.1654(2)	0.2922(2)	0.0546(1)	0.0371(9)	0.0300(8)	0.0259(8)	0.0033(7)	0.0016(6)	0.0092(6)
C(6)	2i		-0.1152(3)	0.2682(3)	0.1770(2)	0.028(1)	0.050(2)	0.043(2)	-0.000(1)	0.001(1)	0.025(1)
C(7)	2i		-0.0441(3)	0.1421(3)	0.1437(2)	0.036(1)	0.038(1)	0.037(1)	-0.008(1)	-0.006(1)	0.015(1)
N(3)	2i		0.0773(2)	0.1396(2)	0.1982(2)	0.036(1)	0.0250(9)	0.031(1)	-0.0027(7)	0.0001(8)	0.0111(7)
C(8)	2i		0.0386(3)	0.1352(3)	0.2888(2)	0.046(1)	0.033(1)	0.034(1)	-0.002(1)	0.005(1)	0.016(1)
C(108)	2i		0.0280(3)	0.2688(3)	0.3559(2)	0.054(2)	0.039(1)	0.031(1)	-0.000(1)	0.008(1)	0.015(1)
O(8A)	2i	0.31(4)	-0.059(1)	0.277(2)	0.415(1)	0.029(6)	0.070(7)	0.044(6)	-0.007(3)	0.004(3)	0.024(5)
O(8B)	2i	0.69	-0.016(3)	0.2709(9)	0.4300(9)	0.20(1)	0.054(3)	0.051(4)	-0.013(6)	0.067(6)	0.011(3)
O(8)	2i		0.0841(2)	0.3666(2)	0.3395(1)	0.0403(9)	0.0312(8)	0.0281(8)	0.0025(7)	0.0060(7)	0.0105(7)
C(9)	2i		0.1499(3)	0.0216(2)	0.1537(2)	0.044(1)	0.0210(9)	0.037(1)	-0.0026(9)	0.002(1)	0.0090(9)
C(10)	2i		0.2459(3)	0.0429(2)	0.0842(2)	0.045(1)	0.0207(9)	0.033(1)	-0.0009(9)	0.000(1)	0.0047(8)
N(4)	2i		0.3515(2)	0.1453(2)	0.1250(2)	0.0340(9)	0.0220(8)	0.031(1)	0.0026(7)	0.0024(7)	0.0088(7)
C(11)	2i		0.4338(3)	0.1779(3)	0.0561(2)	0.041(1)	0.026(1)	0.031(1)	0.0032(9)	0.0093(9)	0.0040(9)
C(111)	2i		0.5030(3)	0.3123(2)	0.0908(2)	0.032(1)	0.027(1)	0.031(1)	0.0029(8)	0.0042(8)	0.0091(8)
O(111)	2i		0.5991(2)	0.3399(2)	0.0466(2)	0.041(1)	0.042(1)	0.033(1)	-0.0037(8)	0.0156(9)	0.0081(9)
O(11)	2i		0.4598(2)	0.3894(2)	0.1598(1)	0.0386(9)	0.0273(8)	0.0351(9)	-0.0015(7)	0.0109(7)	0.0033(7)
C(12)	2i		0.4372(3)	0.1054(3)	0.1887(2)	0.040(1)	0.031(1)	0.045(2)	0.009(1)	-0.001(1)	0.014(1)
C(112)	2i		0.3904(3)	0.1481(3)	0.2844(2)	0.045(1)	0.033(1)	0.038(1)	0.006(1)	-0.007(1)	0.013(1)
O(12)	2i		0.3311(2)	0.2524(2)	0.3085(1)	0.050(1)	0.037(1)	0.0319(9)	0.0124(8)	-0.0052(8)	0.0098(8)
O(112)	2i		0.4152(4)	0.0808(3)	0.3348(2)	0.113(3)	0.066(2)	0.048(2)	0.037(2)	-0.001(2)	0.031(1)
C(51)	2i		0.3412(3)	0.3101(3)	-0.1566(2)	0.038(1)	0.034(1)	0.041(1)	0.003(1)	0.001(1)	0.016(1)
N(52)	2i		0.3296(3)	0.3940(3)	-0.0770(2)	0.054(2)	0.039(1)	0.043(1)	-0.004(1)	0.006(1)	0.013(1)
N(53)	2i		0.4170(3)	0.3401(3)	-0.2177(2)	0.051(2)	0.040(1)	0.044(1)	-0.000(1)	0.009(1)	0.014(1)
N(54)	2i		0.2752(4)	0.1926(3)	-0.1746(2)	0.060(2)	0.037(1)	0.057(2)	-0.004(1)	0.009(1)	0.013(1)
C(61)	2i		0.3232(4)	0.4557(4)	0.5543(2)	0.049(2)	0.051(2)	0.034(1)	-0.003(1)	-0.001(1)	0.013(1)

Table 3. Continued.

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
N(62)	2i		0.3898(4)	0.5358(4)	0.6227(2)	0.054(2)	0.067(2)	0.045(2)	0.007(2)	−0.013(1)	0.002(2)
N(63)	2i		0.2030(4)	0.4848(4)	0.5309(2)	0.057(2)	0.054(2)	0.047(2)	0.002(1)	−0.015(1)	0.009(1)
N(64)	2i		0.3741(4)	0.3433(4)	0.5116(3)	0.071(2)	0.063(2)	0.069(3)	0.010(2)	−0.015(2)	−0.001(2)
OW(1)	2i		0.7032(4)	0.1970(5)	0.3446(3)	0.065(2)	0.112(3)	0.100(3)	0.004(2)	0.012(2)	0.052(3)
OW(2)	2i		0.5933(9)	0.9015(6)	0.3490(3)	0.229(7)	0.103(4)	0.071(3)	0.077(5)	−0.008(4)	−0.002(3)
OW(3)	2i		0.3037(8)	0.9962(6)	0.4785(4)	0.239(8)	0.111(4)	0.086(4)	−0.018(5)	−0.015(4)	0.031(3)
OW(4)	2i	0.50	0.025(2)	0.059(2)	0.508(2)	0.31(2)	0.20(2)	0.31(2)	0.19(2)	0.23(2)	0.19(2)

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