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Crystal structure of μ,μ'-bis(trimethylammonio)bis[tetra-μ-trimethylammonio(aquacopper)(triaquaneodynium)] decaperchlorate dihydrate at -50°C

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Abstract. In the crystal structure of μ,μ'-bis(trimethylammonio)bis[μ,μ',μ',μ'''-tetrakistrimethylammonio(aquacopper)(triaquaneodynium)] decaperchlorate dihydrate [*P*-1: a = 15.865(6) Å, b = 15.29(1) Å, c = 12.608(3) Å, α = 105.04(4)°, β = 100.88(4)°, γ = 110.13(4)°], the copper(II) atom shows square pyramidal coordination and the neodynium(III) atom tricapped trigonal prismatic coordination. The cations, anions, coordinated and lattice water molecules are linked by hydrogen bonds into a one-dimensional chain.

Abstrak. Dalam struktur hablur μ,μ'-bis(trimetillammonio)bis[μ,μ',μ',μ'''-tetrakistrimetillammonio-(aquakuprum)(triaquaneodynium)] decaperklorata dwihidrat [*P*-1: a = 15.865(6) Å, b = 15.29(1) Å, c = 12.608(3) Å, α = 105.04(4)°, β = 100.88(4)°, γ = 110.13(4)°], atom kuprum(II) menunjukkan koordinatan piramid empat-segi and atom neodynium(III) koordinatan prima trigon tiga-topi. Kation, anion dan molekul air terkoordinat dan air kekisi disambung oleh ikatan hidrogen untuk membina rantai satu-dimensi.

Introduction

When betaine or trimethylammonioacetate, $(CH_3)_3NCH_2CO_2$, binds to a copper(II) atom, its carboxylate groups are sufficiently activated to permit bindng to hard metal ions; this feature has been exploited in the synthesis of heterometallic copper-lanthanum(III) complexes [1]. The complex $[Cu_{12}Nd_6(OH)_{24}(H_2O)_{12}(C_5H_{11}NO_2)_{12}](ClO_4)_{18}$ crystallizes in the $P4_2/n$ space group (a = 26.841(1) Å, c = 30.056(6) Å). Only the gross features can be ascertained as the crystals that were used in the X-ray measurements decayed significantly during the measurements [2]; the title complex were also deposited from solution along with crystals of this complex. We report, without discussion, the structure of this tetranuclear complex here; the complex is isomorphous with the lanthanum(III) and cerium(III) analogues [3]. Beause the radius of Nd(III) atom is smaller than those of La(III) and Ce(III) atoms, the corresponding Nd-O bonds are somewhat shorter than those of La-O and Ce-O bonds.

Experimental

Diffraction measurements with a purple-colored 0.55 mm x 0.45 mm x 0.35 mm specimen on a CAD-4 diffractometer (Mo-$K\alpha$ radiation, λ = 0.71073 Å) -50°C. The 9323 reflections were measured by ω-2θ scans to up 2θ = 50° (collection range: $-18 \le h \le 17$, $0 \le k \le 18$, $-14 \le l \le 14$); 9281 reflections (R_{int} = 0.15) were independent reflections of which 8820 were above the $I \ge 2\sigma(I)$ cutoff. The raw intensities were reduced to F^2 values [4] for solution [5] and refinement [6]. On convergence, the difference map had a peak larger than 1 eÅ^{-3} near the Nd1 atom. The use of a variation of *DIFABS* [7] in the *PLATON* suite [8] removed this peak, and the H atoms belonging to the water molecules could be located (transmission factors = 0.661 – 0.902). Carbon-bound H atoms were generated and were allowed to ride on their parent C atoms,

with $U = 1.5U_{eq}(C)$; U for the water H atoms were set at 0.05 Å^2. Two of the perchlorate ions are disordered over two positions, and they were refined with Cl-O = 1.41±0.01Å and O···O = 2.30±02 Å; an *ISOR* 0.02 instruction was used for the disordered O atoms. The refinements on 721 variables with 136 restraints converged with a shift-to-error ratio of less than 0.01 to R = 0.028 for 8820 reflections and R = 0.030 for 9281 reflections; S = 0.960 for the weighting scheme, $w^{-1} = \sigma^2(F_o^2) + (0.0473P)^2 + 5.5448P$ where $P = (F_o^2 + 2F_c^2)/3$. Atomic coordinates are listed in Table 1; the structure of the tetranuclear cation is shown as an *ORTEP* [9] plot the the 50% probability level in Figure 1; the geometry of the lanthanum cation is shown in Figure 2..

Acknowledgments

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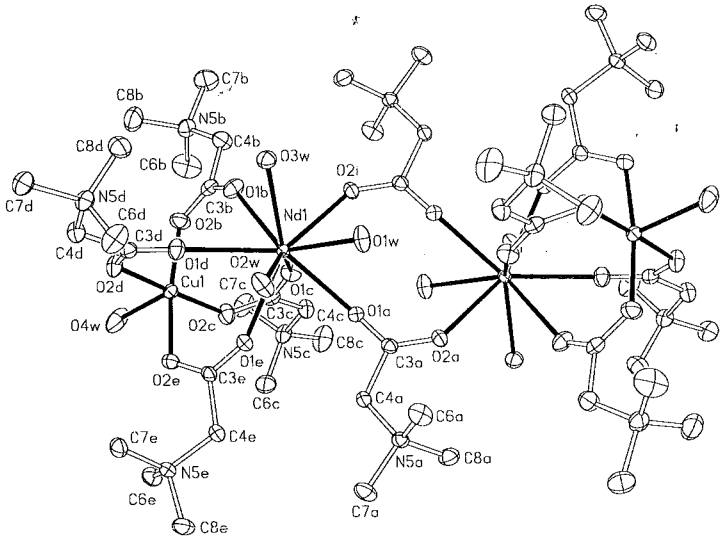

Figure 1. *ORTEP* plot of the μ,μ'-bis(trimethylammonio)bis[μ,μ',μ',μ'''-tetrakistrimethyl-ammonio(aquacopper)(triaquaneodynium)] cation.

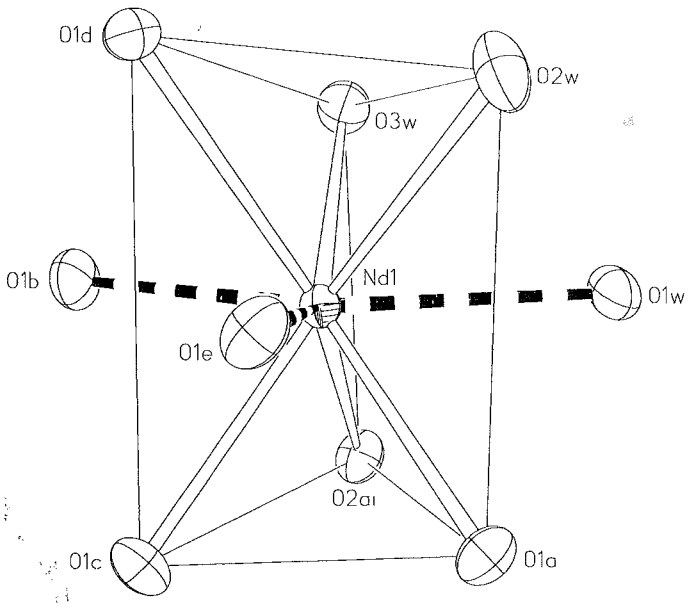

Figure 2. Geometry of the neodynium atom.

Table 1. Atomic coordinates and equivalent temperature factors

Atom	*x*	*y*	*z*	U_{eq}
Nd1	0.69315(1)	0.12653(1)	0.58825(1)	0.0116(1)
Cu1	0.83525(2)	0.33700(2)	0.86827(3)	0.0147(1)
Cl1	0.55892(6)	-0.44780(6)	0.31707(7)	0.0336(2)
Cl2	0.84630(6)	-0.59873(6)	0.33247(7)	0.0265(2)
Cl3	0.39439(6)	0.00210(6)	0.87772(7)	0.0268(2)
Cl4	0.86674(5)	-0.11560(5)	0.70584(6)	0.0215(2)
Cl5	0.21720(5)	0.24303(6)	0.92204(7)	0.0243(2)
O11 (50%)	0.629(1)	-0.3509(7)	0.382(1)	0.052(5)
O12 (50%)	0.6131(5)	-0.5102(4)	0.2937(6)	0.054(2)
O13 (50%)	0.5059(7)	-0.4877(6)	0.3814(7)	0.064(3)
O14 (50%)	0.5127(7)	-0.4538(6)	0.2095(6)	0.073(2)
O11' (50%)	0.4777(4)	-0.4144(6)	0.3086(6)	0.071(2)
O12' (50%)	0.5512(9)	-0.487(1)	0.2064(7)	0.137(5)
O13' (50%)	0.533(1)	-0.509(1)	0.379(1)	0.131(7)
O14' (50%)	0.638(1)	-0.3581(7)	0.386(1)	0.033(3)
O21 (50%)	0.839(1)	-0.575(1)	0.2325(9)	0.109(6)
O22 (50%)	0.9283(4)	-0.6181(6)	0.3501(6)	0.046(2)
O23 (50%)	0.8601(9)	-0.5152(9)	0.4244(9)	0.057(3)
O24 (50%)	0.7680(4)	-0.6839(5)	0.3198(9)	0.046(2)
O21' (50%)	0.8206(6)	-0.593(1)	0.2225(8)	0.069(4)

O22' (50%)	0.830(1)	-0.526(1)	0.410(1)	0.100(6)
O23' (50%)	0.802(1)	-0.6918(7)	0.335(1)	0.169(7)
O24' (50%)	0.9432(7)	-0.573(2)	0.352(2)	0.23(1)
O31	0.3208(2)	0.0049(2)	0.7928(2)	0.049(1)
O32	0.4039(2)	0.0656(2)	0.9885(2)	0.043(1)
O33	0.4810(2)	0.0348(2)	0.8510(3)	0.047(1)
O34	0.3669(2)	-0.0972(2)	0.8755(3)	0.057(1)
O41	0.9047(2)	-0.0105(2)	0.7282(2)	0.041(1)
O42	0.9357(2)	-0.1535(2)	0.6888(2)	0.041(1)
O43	0.8400(2)	-0.1334(2)	0.8031(2)	0.044(1)
O44	0.7857(2)	-0.1658(2)	0.6054(2)	0.039(1)
O51	0.2107(3)	0.1689(3)	0.8203(3)	0.056(1)
O52	0.1248(2)	0.2242(3)	0.9287(3)	0.057(1)
O53	0.2725(2)	0.2377(2)	1.0210(2)	0.043(1)
O54	0.2594(2)	0.3378(2)	0.9130(3)	0.059(1)
O1*w*	0.6052(2)	-0.0350(2)	0.4186(2)	0.026(1)
O2*w*	0.7746(2)	0.0134(2)	0.5602(2)	0.029(1)
O3*w*	0.7498(2)	0.1522(2)	0.4210(2)	0.022(1)
O4*w*	0.9014(2)	0.4533(2)	1.0421(2)	0.044(1)
O5*w*	0.6944(2)	-0.1588(2)	0.3532(2)	0.035(1)
O1*a*	0.5601(1)	0.0131(2)	0.6238(2)	0.019(1)
O2*a*	0.4397(1)	-0.1362(2)	0.5396(2)	0.019(1)
C3*a*	0.5181(2)	- 0.0764(2)	0.6107(2)	0.016(1)
C4*a*	0.5707(2)	-0.1081(2)	0.6971(3)	0.019(1)
N5*a*	0.5334(2)	-0.2174(2)	0.6791(2)	0.017(1)
C6*a*	0.5364(3)	-0.2753(2)	0.5652(3)	0.027(1)
C7*a*	0.5962(2)	-0.2301(2)	0.7735(3)	0.026(1)
C8*a*	0.4343(2)	-0.2560(3)	0.6860(3)	0.026(1)
O1*b*	0.7486(2)	0.3010(2)	0.6045(2)	0.025(1)
O2*b*	0.8079(2)	0.4192(2)	0.7806(2)	0.027(1)
C3*b*	0.7678(2)	0.3848(2)	0.6736(3)	0.020(1)
C4*b*	0.7324(2)	0.4475(2)	0.6176(3)	0.026(1)
N5*b*	0.7746(2)	0.5572(2)	0.6807(2)	0.024(1)
C6*b*	0.7514(3)	0.5855(3)	0.7902(3)	0.045(1)
C7*b*	0.7318(3)	0.5990(3)	0.6002(4)	0.039(1)
C8*b*	0.8792(3)	0.5995(3)	0.7040(4)	0.042(1)
O1*c*	0.6246(2)	0.2172(2)	0.7155(2)	0.024(1)
O2*c*	0.7151(2)	0.3100(2)	0.8970(2)	0.025(1)
C3*c*	0.6378(2)	0.2647(2)	0.8175(3)	0.018(1)
C4*c*	0.5501(2)	0.2669(2)	0.8465(3)	0.022(1)
N5*c*	0.5629(2)	0.3302(2)	0.9666(2)	0.023(1)
C6*c*	0.6019(3)	0.2934(3)	1.0550(3)	0.033(1)
C7*c*	0.6248(3)	0.4378(2)	0.9943(3)	0.033(1)
C8*c*	0.4666(3)	0.3209(3)	0.9717(4)	0.040(1)
O1*d*	0.8782(1)	0.2206(2)	0.6725(2)	0.022(1)
O2*d*	0.9516(1)	0.3576(2)	0.8310(2)	0.022(1)
C3*d*	0.9488(2)	0.2943(2)	0.7406(2)	0.018(1)
C4*d*	1.0462(2)	0.3190(2)	0.7269(3)	0.022(1)
N5*d*	1.0534(2)	0.2624(2)	0.6147(2)	0.021(1)
C6*d*	1.0213(3)	0.1536(3)	0.5957(3)	0.034(1)
C7*d*	1.1560(2)	0.3050(3)	0.6216(3)	0.028(1)
C8*d*	0.9974(2)	0.2772(3)	0.5161(3)	0.031(1)
O1*e*	0.7485(2)	0.1120(2)	0.7761(2)	0.022(1)

O2*e*	0.8488(2)	0.2381(2)	0.9360(2)	0.023(1)
C3*e*	0.7983(2)	0.1478(2)	0.8786(2)	0.017(1)
C4*e*	0.7929(2)	0.0713(2)	0.9370(2)	0.019(1)
N5*e*	0.8722(2)	0.1016(2)	1.0441(2)	0.017(1)
C6*e*	0.8726(2)	0.1810(2)	1.1434(3)	0.023(1)
C7*e*	0.9652(2)	0.1355(2)	1.0204(3)	0.024(1)
C8*e*	0.8572(2)	0.0102(2)	1.0763(3)	0.026(1)

U_{eq} is defined as one-third the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 2. Selected bond distances (Å) and angles (°)

Nd1-O1*a*	2.430(2)	Cu1-O2*b*	1.975(2)
Nd1-O2*a*i	2.473(2)	Cu1-O2*d*	1.931(2)
Nd1-O1*b*	2.442(3)	Cu1-O2*c*	1.932(2)
Nd1-O1*c*	2.495(2)	Cu1-O2*e*	1.971(2)
Nd1-O1*d*	2.634(3)	Cu1-O4*w*	2.211(3)
Nd1-O1*e*	2.460(2)		
Nd1-O1*w*	2.526(3)		
Nd1-O2*w*	2.486(3)		
Nd1-O3*w*	2.512(2)		
O1*w*···O1*a*ii	2.728(4)		
O1*w*···O5	2.782(5)		
O2*w*···O5	2.870(4)		
O2*w*···O41	2.855(4)		
O3*w*···O23'iii	2.81(1)		
O3*w*···O24iii	3.048(9)		
O3*w*···O31i	2.817(4)		
O4*w*··· O21i	2.84(1)		
O4*w*···O21'i	2.94(1)		
O4*w*···O2*d*i	2.812(4)		
O5*w*···O11	2.90(1)		
O5*w*···O14'	3.03(1)		
O5*w*···O51iv	2.882(6)		
O1*a*-Nd1-O2*a*i	79.31(8)	O2*b*-Cu1-O2*c*	89.0(1)
O1*a*-Nd1-O1*b*	134.23(8)	O2*b*-Cu1-O2*d*	90.7(1)
O1*a*-Nd1-O1*c*	68.09(9)	O2*b*-Cu1-O23	171.6(1)
O1*a*-Nd1-O1*d*	140.41(7)	O2*b*-Cu1-O4*w*	98.4(1)
O1*a*-Nd1-O1*e*	71.29(8)	O2*c*-Cu1-O2*d*	176.7(1)
O1*a*-Nd1-O1*w*	68.64(9)	O2*c*-Cu1-O2*e*	88.7(1)
O1*a*-Nd1-O2*w*	95.52(9)	O2*c*-Cu1-O4*w*	87.8(1)
O1*a*-Nd1-O3*w*	139.07(8)	O2*d*-Cu1-O2*e*	91.1(1)
O2*a*i-Nd1-O1*b*	75.08(9)	O2*d*-Cu1-O4*w*	95.5(1)
O2*a*i-Nd1-O1*c*	73.06(8)	O2*e*-Cu1-O4*w*	89.6(1)
O2*a*i-Nd1-O1*d*	139.00(7)		
O2*a*i-N1d-O1*e*	143.32(7)		
O2*a*i-Nd1-O1*w*	70.57(9)		
O2*a*i-Nd1-O2*w*	132.92(8)		
O2*a*i-Nd1-O3*w*	76.22(7)		
O1*b*-Nd1-O1*c*	68.44(8)		
O1*b*-Nd1-O1*d*	68.03(9)		
O1*b*-Nd1-O1*e*	110.75(9)		

O1*b*-Nd1-O1*w*	132.96(9)
O1*b*-Nd1-O2*w*	129.54(9)
O1*b*-Nd1-O3*w*	68.82(8)
O1*c*-Nd1-O1*d*	107.80(9)
O1*c*-Nd1-O1*e*	75.88(8)
O1*c*-Nd1-O1*w*	127.25(8)
O1*c*-Nd1-O2*w*	147.88(8)
O1*c*-Nd1-O3*w*	132.20(8)
O1*d*-Nd1-O1*e*	69.67(8)
O1*d*-Nd1-O1*w*	124.75(8)
O1*d*-Nd1-O2*w*	66.77(9)
O1*d*-Nd1-O3*w*	74.32(8)
O1*e*-Nd1-O1*w*	116.05(9)
O1*e*-Nd1-O2*w*	72.64(8)
O1*e*-Nd1-O3*w*	140.35(7)
O1*w*-Nd1-O2*w*	64.20(8)
O1*w*-Nd1-O2*w*	72.47(8)
O2*w*-Nd1-O3*w*	78.42(8)

i = 1 - *x*, -*y*, 1 - *z*; ii = 1 - *x*, -*y*, 2 - *z*; iii = *x*, 1 + *y*, *z*; iv = 1 + *x*, *y*, 1 + *z*.