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Crystal structure of aqua-2,2′,2″-(((nitrilo-κ*N*-tris(ethane-2,1-diyl))tris (azanylylidene-κ^3*N*′,*N*″,*N*‴))tris(methanylylidene))tris (4-chlorophenolato-κ^3*O*,*O*′,*O*″)neodymium(III), $C_{27}H_{26}Cl_3N_4NdO_4$

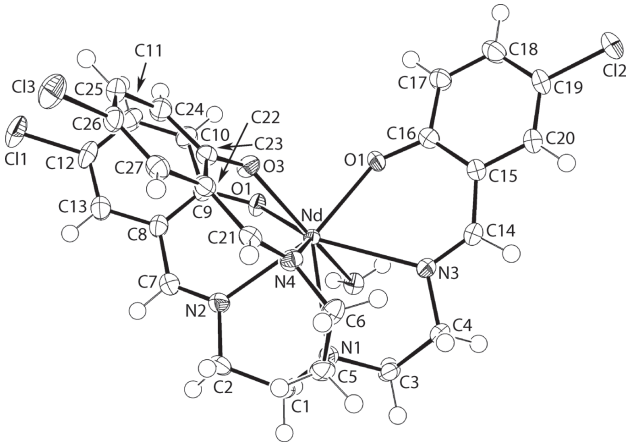

Table 1: Data collection and handling.

Crystal:	Purple prism
Size:	0.16 × 0.12 × 0.05 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	2.18 mm^{-1}
Diffractometer, scan mode:	CCD, φ and ω
θ_{max}, completeness:	30.5°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	25994, 7981, 0.026
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 6843
$N(param)_{refined}$:	358
Programs:	Bruker [1], SHELX [2–4], WinGX/ORTEP [5]

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Abstract

$C_{27}H_{26}Cl_3N_4NdO_4$, monoclinic, $P2_1/c$ (no. 14), $a = 13.6408(1)$ Å, $b = 20.3377(2)$ Å, $c = 10.7272(1)$ Å, $\beta = 109.896(1)°$, $V = 2798.34(5)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0258$, $wR_{ref}(F^2) = 0.0590$, $T = 100(2)$ K.

CCDC no.: 1902338

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The ligand, tris{[(5-chlorosalicylidene)amino]ethyl}amine was prepared from a 1:3 molar ratio of 5-chlorosalicylaldehyde (Sigma-Aldrich) and tris(2-aminoethyl)amine (Sigma-Aldrich) in methanolic solution [6]. Both the ligand (0.56 g, 1 mmol) and triethylamine (0.14 mL, 1.0 mmol) were dissolved in absolute ethanol (25 mL) and refluxed for 1 h. After that, an ethanolic solution (15 mL) of neodymium(III) nitrate hexahydrate (SigmaAldrich; 0.44 g, 1 mmol) was added to the mixture which was further refluxed for 3 h and filtered. The filtrate was evaporated until a precipitate was obtained. The precipitate was recrystallised from ethanol solution and the by-product, triethylammonium chloride, was removed through filtration. Purple needles of the title compound (alternative name: aqua(tris{2-[(5-chloro-2-oxidobenzylidene-κ*O*)amino-κ*N*]ethyl}amine-κ*N*)neodymium(III) suitable for X-ray crystallographic studies were obtained from the slow evaporation of the filtrate. Yield: 0.36 g (50%). M.pt: 430−434 K. IR (cm^{-1}) 1625 (s) ν(C= N), 1526 (m), 1462 (m), 1390 (m) ν(−O−C=C−), 1160 (m) ν(C−O−C).

Experimental details

The C-bound H atoms were geometrically placed (C−H = 0.95−0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The O-bound H-atoms were located in difference Fourier maps but were refined with a distance restraint of O−H = 0.84+−0.01 Å, and with $U_{iso}(H)$ set to $1.5U_{equiv}(O)$. Owing to poor agreement, two reflections, i.e. (1 0 0) and ($\bar{1}$4 17 3), were removed from the final cycles of refinement. The maximum and minimum electron density peaks of 1.13 and 0.78 e Å^{-3}, respectively, were located 0.80 and 1.33 Å from the Nd and H17 atoms, respectively.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Nd	0.05622(2)	0.61064(2)	0.40249(2)	0.01016(3)
Cl1	0.60937(4)	0.56005(3)	0.83944(6)	0.02975(14)
Cl2	−0.42199(5)	0.71835(4)	0.60792(6)	0.03063(14)
Cl3	0.47697(5)	0.88849(3)	0.67008(6)	0.02568(12)
O1	0.16097(11)	0.53052(7)	0.55077(14)	0.0146(3)
O2	−0.04437(11)	0.61118(7)	0.53981(14)	0.0138(3)
O3	0.17656(11)	0.67202(8)	0.56006(14)	0.0155(3)
O4W	−0.02914(12)	0.50248(8)	0.32709(14)	0.0146(3)
H1W	−0.0784(15)	0.4987(14)	0.356(2)	0.022*
H2W	0.0079(18)	0.4703(9)	0.361(2)	0.022*
N1	0.00753(13)	0.61455(9)	0.13345(17)	0.0136(3)
N2	0.20733(14)	0.57302(10)	0.32562(17)	0.0163(4)
N3	−0.14468(13)	0.63584(9)	0.26254(17)	0.0140(3)
N4	0.08638(14)	0.72383(9)	0.30762(17)	0.0143(3)
C1	0.07921(17)	0.56754(12)	0.1020(2)	0.0182(4)
H1A	0.070210	0.570987	0.006652	0.022*
H1B	0.060774	0.522165	0.119093	0.022*
C2	0.19230(17)	0.58064(13)	0.1837(2)	0.0214(5)
H2A	0.237834	0.549390	0.158250	0.026*
H2B	0.211592	0.625807	0.166528	0.026*
C3	−0.10032(16)	0.58985(11)	0.0754(2)	0.0150(4)
H3A	−0.103058	0.543818	0.104023	0.018*
H3B	−0.120921	0.590099	−0.022481	0.018*
C4	−0.17747(16)	0.63102(12)	0.1162(2)	0.0159(4)
H4A	−0.181854	0.675632	0.077803	0.019*
H4B	−0.247515	0.610721	0.081206	0.019*
C5	0.01757(17)	0.68092(11)	0.0815(2)	0.0168(4)
H5A	−0.038607	0.687042	−0.005026	0.020*
H5B	0.085101	0.683811	0.066363	0.020*
C6	0.01154(17)	0.73578(11)	0.1743(2)	0.0169(4)
H6A	0.027280	0.778355	0.140489	0.020*
H6B	−0.059892	0.738134	0.178029	0.020*
C7	0.29957(17)	0.55877(12)	0.4017(2)	0.0181(4)
H7	0.351231	0.553503	0.361412	0.022*
C8	0.33250(16)	0.54988(11)	0.5454(2)	0.0159(4)
C9	0.26150(16)	0.53619(10)	0.6128(2)	0.0148(4)
C10	0.30384(17)	0.52836(11)	0.7516(2)	0.0180(4)
H10	0.258652	0.517502	0.799166	0.022*
C11	0.40906(17)	0.53602(11)	0.8205(2)	0.0198(4)
H11	0.435202	0.531886	0.914289	0.024*
C12	0.47624(17)	0.54979(12)	0.7518(2)	0.0203(5)
C13	0.43954(17)	0.55525(12)	0.6160(2)	0.0192(4)
H13	0.486882	0.562684	0.569892	0.023*
C14	−0.21906(16)	0.65046(12)	0.3047(2)	0.0182(4)
H14	−0.284811	0.658750	0.238603	0.022*
C15	−0.21532(16)	0.65594(11)	0.4412(2)	0.0167(4)
C16	−0.13137(16)	0.63308(10)	0.5511(2)	0.0136(4)
C17	−0.14311(17)	0.63510(12)	0.6769(2)	0.0178(4)
H17	−0.088962	0.618149	0.751531	0.021*
C18	−0.23074(18)	0.66091(12)	0.6945(2)	0.0208(5)
H18	−0.236272	0.662149	0.780373	0.025*
C19	−0.31137(17)	0.68524(12)	0.5857(2)	0.0208(5)
C20	−0.30457(18)	0.68177(13)	0.4608(2)	0.0228(5)
H20	−0.360955	0.697033	0.386853	0.027*
C21	0.15556(16)	0.76880(11)	0.3534(2)	0.0143(4)
H21	0.152702	0.805744	0.298139	0.017*
C22	0.23772(16)	0.76818(11)	0.4823(2)	0.0141(4)
C23	0.24552(16)	0.71832(11)	0.5779(2)	0.0144(4)
C24	0.33087(17)	0.72199(11)	0.6986(2)	0.0169(4)
H24	0.340138	0.687993	0.762316	0.020*
C25	0.40041(16)	0.77319(12)	0.7260(2)	0.0181(4)
H25	0.455684	0.775017	0.808781	0.022*
C26	0.38976(16)	0.82262(11)	0.6320(2)	0.0174(4)
C27	0.31042(16)	0.82021(11)	0.5118(2)	0.0159(4)
H27	0.304467	0.853806	0.448093	0.019*

Comment

The structural chemistry of lanthanide complexes is diverse as they can often display various coordination numbers and flexible coordination geometries. A stand-out potential application for lanthanide complexes relates to their luminescent characteristics owing to their sharp emission bands, colour tuneability and long-lived emission states [7], therefore making them potential materials as organic light-emitting devices (OLED's). Tripodal lanthanide complexes have been well characterized since the 1990's [8] and as part of an on-going study investigating related tripodal lanthanide(III) complexes [9], the crystal and molecular structures of the title neodymium(III) complex is described.

The molecular structure is shown in the figure (70% displacement ellipsoids) and comprises a heptadentate tris{[5-chlorosalicylidene)amino]ethyl}amine) trianion which coordinates *via* the three phenolate-oxygen, three imine-nitrogen and tertiary amine-nitrogen atoms. The eighth position is occupied by the aqua ligand. The ensuing N_4O_4 donor set defines a square anti-prism with one face defined by the O1, O4w, N1 and N2 atoms, while the other is defined by the O2, O3, N3 and N4 atoms. Systematic variations are noted in the bond lengths with the Nd—O bonds being uniformly shorter than the Nd—N bonds. Within each class of bond, the Nd—O(phenoxide) bonds [2.2850(15)—2.3834(14) Å] are shorter than the Nd—O(aqua) bond [2.4916(15) Å]. In the same way, the Nd—N(imine) bonds [2.5829(18)—2.6882(17) Å] are shorter than the Nd—N(amine) bond [2.7335(17) Å].

The most closely related structure in the literature is that of the cerium(III) derivative, isolated as its hemi-methanol solvate. As would be expected, the mode of coordination of the ligand and distorted coordination geometry mimics that found in the title complex [10]. In addition, there are other examples with a slightly modified ligand [11].

In the crystal, water-O—H···O(phenoxide) hydrogen bonding is apparent [O4w—H1w···O1^{i}: H1w···O1^{i} = 1.84(2) Å, O4w···O1^{i} = 2.647(2) Å with angle at H1w = 162(3)° and O4w—H2w···O2^{ii}: H2w···O2^{i} = 1.941(19) Å,

O4w$\cdots$O2^{ii} = 2.723(2) Å with angle at H2w = 156(2)° for symmetry operation i: $-x$, $1-y$, $1-z$]. Each hydrogen atom of one water molecule hydrogen bonds to one of a pair of adjacent phenoxide atoms of another molecule to close a six-membered {$\cdots$HOH$\cdots$ONdO} ring. As these hydrogen bonds occur across a centre of inversion, a dimeric supramolecular aggregate ensues.

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