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Crystal structure of aqua-2,2′,2″-(((nitrilo-κN-tris(ethane-2,1-diyl))tris(azanylylidene-κ3N′,N″,N‴))tris(methanylylidene))tris(4-chlorophenolato-κ3O,O′,O″)neodymium(III), C_{27}H_{26}Cl_{3}N_{4}NdO_{4}

Abstract

C_{27}H_{26}Cl_{3}N_{4}NdO_{4}, monoclinic, P2_{1}/c (no. 14), a = 13.6408(1) Å, b = 20.3377(2) Å, c = 10.7272(1) Å, β = 109.896(1)°, V = 2798.34(5) Å³, Z = 4, R_{wp}(F) = 0.0258, wR_{ref}(F²) = 0.0590, T = 100(2) K.

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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 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_{eq}(O). Owing to poor agreement, two reflections, i.e. (1 0 0) and (I4 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.
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 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 tripod 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 N₉O₆ donor set defines a square anti-prism with one face defined by the Nd—O bond shorter than the Nd—N(amine) bond [2.7335(17) Å].

Comment

Within each class of bond, the Nd—O(phenoxy) bonds [2.2850(15)—2.3384(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(phenoxy) hydrogen bonding is apparent [O4w—H1w···O1: H1w···O1 = 1.84(2) Å, O4w···O1 = 2.647(2) Å with angle at H1w = 162(3)° and O4w···H2w···O2: H2w···O2 = 1.941(4) Å,
O4w ··· O2ii = 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 {···HOH···ONdO} ring. As these hydrogen bonds occur across a centre of inversion, a dimeric supramolecular aggregate ensues.

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References