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A new dinuclear Cu^{II}–Sm^{III} complex with a salen-type Schiff base ligand

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The title complex (systematic name: diaqua{6,6′-dimethoxy-2,2′-[1,2-ethanediylbis(nitrilomethylidyne)]diphenolato}dinitratosamarium(III)copper(II) nitrate), $[CuSm(C_{18}H_{18}N_2O_4)(NO_3)_2(H_2O)_2]NO_3$, is composed of a discrete dinuclear cation with a salen-type Schiff base ligand and one uncoordinated nitrate anion. The copper and samarium are doubly bridged by two phenolate O atoms provided by the Schiff base ligand. There are some classical intermolecular hydrogen bonds (O—H···O), and some weak O···Cu and N···Cu interactions are also observed. These interactions generate a two-dimensional infinite layer.

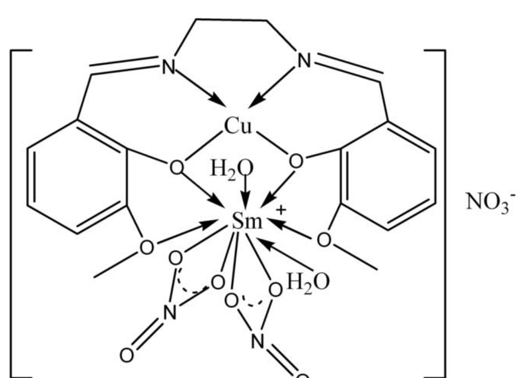
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.006 Å
R factor = 0.028
wR factor = 0.104
Data-to-parameter ratio = 12.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The potential applications of trivalent lanthanide complexes as contrast agent for magnetic resonance imaging and stains for fluorescence imaging have prompted considerable interest in the preparation, magnetic and optical properties of 3*d*–4*f* heterometallic dinuclear complexes (Baggio *et al.*, 2000; Caravan *et al.*, 1999; Edder *et al.*, 2000). Recently, some 3*d*–4*f* heterometallic Schiff base complexes have been synthesized, such as Cu^{II}–Gd^{III}, Ni^{II}–Gd^{III} and Zn^{II}–Ho^{III} heterodinuclear complexes (Brewer *et al.*, 2001; Mohanta *et al.*, 2002; Wong *et al.*, 2002), which exhibit novel magnetic and luminescent properties; however, there are relatively few studies on Cu^{II}–Sm^{III} dinuclear complexes. As part of our investigations into the structure and applications of 3*d*–4*f* heterometallic Schiff base complexes, we report here the synthesis and X-ray crystal structure analysis of the title complex, (I), a new Cu^{II}–Sm^{III} complex with salen-type Schiff base *N*,*N*′-bis(3-methoxysalicylidene) ethylene-1,2-diamine (H_2L).



(I)

Complex (I) crystallizes in the space group $P2_1/n$, with copper and samarium doubly bridged by two phenolate O atoms provided by a salen-type Schiff base ligand. The inner salen-type cavity is occupied by copper(II), while samarium(III) is present in the open and larger portion of the dinucleating compartmental Schiff base ligand. The dihedral angles between the mean planes Cu1/O1/O2 and Sm1/O1/O2 is 5.5 (1)°, suggesting that the bridging group is almost planar; the deviations of atoms from the least squares Cu1/O1/O2/Sm1 plane are 0.0469 (2) Å for Cu, 0.0319 (3) Å for Sm, −0.0397 (4) Å for O1 and −0.0390 (4) Å for O2.

The samarium(III) center in (I) has a decacoordination environment of O atoms. In addition to the phenolate ligands, two methoxy O atoms coordinate to this metal center. Two O atoms from each of the two nitrates and two O atoms from the aqua ligands chelate to samarium to complete the decacoordination. The four kinds of Sm—O bond distances are significantly different, the shortest being the Sm—O(phenolate) and longest the Sm—O(methoxy) separations.

The coordination of copper(II) is square planar. The donor centers are alternatively above and below the mean N_2O_2 plane, with an average deviation from the plane of 0.0117 (4) Å, while Cu1 is just 0.0352 (2) Å below this square plane. One nitrato atom (O5) of a neighboring dinuclear unit occupies the apical position of copper. The Cu—O(nitrate, neighboring) distance is 3.226 (3) Å and the angles of this Cu—O vector with the Cu—N or Cu—O bonds lie between 63.9 (2) and 119.0 (2)°. Thus, although the coordination environment is essentially square planar, it can be considered that one nitrate of a neighboring molecule is semicoordinated to copper(II), resulting in a pseudo-square-pyramidal coordination mode.

Adjacent molecules are held together by classical intermolecular hydrogen bonds (Table 2) and weak interactions [N3···Cu1 3.535 (8) and O7···Cu1 2.587 (4) Å]; these link the molecules into a two-dimensional infinite layer (Fig. 2).

Experimental

H_2L was prepared by 2:1 condensation of 3-methoxysalicylaldehyde and ethylenediamine in methanol. Complex (I) was obtained by the treatment of copper(II) acetate monohydrate (0.168 g, 1 mmol) with H_2L (0.328 g, 1 mmol) in methanol solution (100 ml) under reflux for 3 h and then for another 3 h after the addition of samarium(III) nitrate hexahydrate (0.444 g, 1 mmol). The reaction mixture was cooled and the resulting precipitate was filtered, washed with diethyl ether and dried *in vacuo*. Single crystals suitable for X-ray analysis were obtained by slow evaporation at room temperature of a methanol solution. Analysis calculated for $C_{18}H_{22}CuN_5O_{15}Sm$: C 28.36, H 2.91, Cu 8.34, N 9.19, Sm 19.72%; found: C 28.47, H 2.85, Cu 8.28, N 9.25, Sm 19.77%. IR (KBr, cm^{-1}): 1638 (C=N), 1385, 1490 (nitrate).

Crystal data

$[CuSm(C_{18}H_{18}N_2O_4)(NO_3)_2(H_2O)_2]NO_3$
M_r = 762.30
Monoclinic, $P2_1/n$
a = 9.1526 (3) Å
b = 21.6121 (7) Å
c = 13.4409 (4) Å
β = 108.196 (1)°
V = 2525.75 (14) Å^3
Z = 4
D_x = 2.005 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 3.23 mm^{-1}
T = 296 (2) K
Block, red
0.28 × 0.17 × 0.15 mm

Data collection

Bruker APEX-II area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.528, T_{max} = 0.622
16313 measured reflections
4906 independent reflections
4310 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 26.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.104
S = 1.00
4906 reflections
379 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.084P)^2 + 0.4122P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.81 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Sm1—O1	2.417 (2)	Sm1—O9	2.659 (3)
Sm1—O2	2.462 (2)	Sm1—O11	2.503 (3)
Sm1—O3	2.670 (3)	Sm1—O12	2.466 (3)
Sm1—O4	2.647 (3)	Cu1—N1	1.908 (3)
Sm1—O5	2.674 (3)	Cu1—N2	1.912 (3)
Sm1—O6	2.640 (3)	Cu1—O1	1.920 (3)
Sm1—O8	2.541 (3)	Cu1—O2	1.908 (3)
O1—Sm1—O2	64.23 (8)	O8—Sm1—O5	69.25 (10)
O1—Sm1—O3	61.97 (9)	O8—Sm1—O6	72.22 (11)
O1—Sm1—O4	123.77 (8)	O8—Sm1—O9	48.52 (10)
O1—Sm1—O5	69.28 (9)	O9—Sm1—O3	76.73 (10)
O1—Sm1—O6	71.26 (9)	O9—Sm1—O5	99.38 (10)
O1—Sm1—O8	136.76 (10)	O11—Sm1—O3	75.18 (11)
O1—Sm1—O9	129.48 (10)	O11—Sm1—O4	93.15 (11)
O1—Sm1—O11	72.61 (10)	O11—Sm1—O5	133.95 (9)
O1—Sm1—O12	131.91 (10)	O11—Sm1—O6	136.53 (12)
O2—Sm1—O3	123.48 (8)	O11—Sm1—O8	149.67 (12)
O2—Sm1—O4	59.58 (8)	O11—Sm1—O9	124.93 (10)
O2—Sm1—O5	67.10 (9)	O12—Sm1—O3	84.61 (11)
O2—Sm1—O6	110.26 (8)	O12—Sm1—O4	82.24 (11)
O2—Sm1—O8	109.11 (9)	O12—Sm1—O5	158.53 (11)
O2—Sm1—O9	157.62 (10)	O12—Sm1—O6	128.16 (11)
O2—Sm1—O11	73.67 (10)	O12—Sm1—O8	89.33 (11)
O2—Sm1—O12	121.57 (11)	O12—Sm1—O9	65.37 (11)
O3—Sm1—O5	107.35 (9)	O12—Sm1—O11	65.65 (10)
O4—Sm1—O3	165.20 (9)	N1—Cu1—N2	86.14 (15)
O4—Sm1—O5	87.27 (9)	N1—Cu1—O1	93.79 (14)
O4—Sm1—O9	103.66 (10)	N2—Cu1—O1	178.59 (14)
O6—Sm1—O3	66.95 (9)	O2—Cu1—N1	177.06 (13)
O6—Sm1—O4	127.11 (9)	O2—Cu1—N2	94.68 (13)
O6—Sm1—O5	47.82 (8)	O2—Cu1—O1	85.32 (11)
O6—Sm1—O9	66.36 (10)	Cu1—O1—Sm1	105.71 (10)
O8—Sm1—O3	121.29 (9)	Cu1—O2—Sm1	104.40 (11)
O8—Sm1—O4	65.42 (9)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O12—H12A···O14^{i}	0.82 (5)	1.95 (3)	2.714 (4)	154 (5)
O12—H12B···O14	0.83 (2)	1.96 (2)	2.783 (5)	169 (4)
O11—H11A···O13	0.82 (4)	1.96 (3)	2.767 (5)	166 (7)
O11—H11B···O7^{ii}	0.81 (2)	2.02 (2)	2.819 (4)	167 (5)

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$.

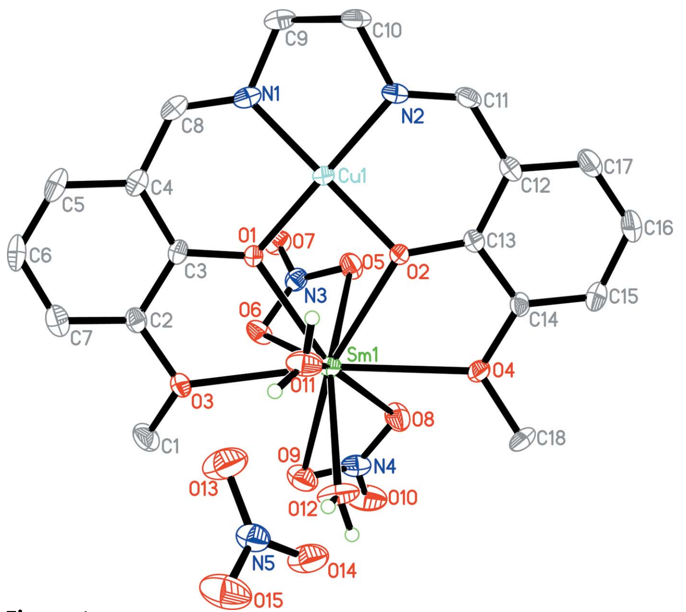


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids. All the H atoms bound to C atoms have been omitted for clarity.

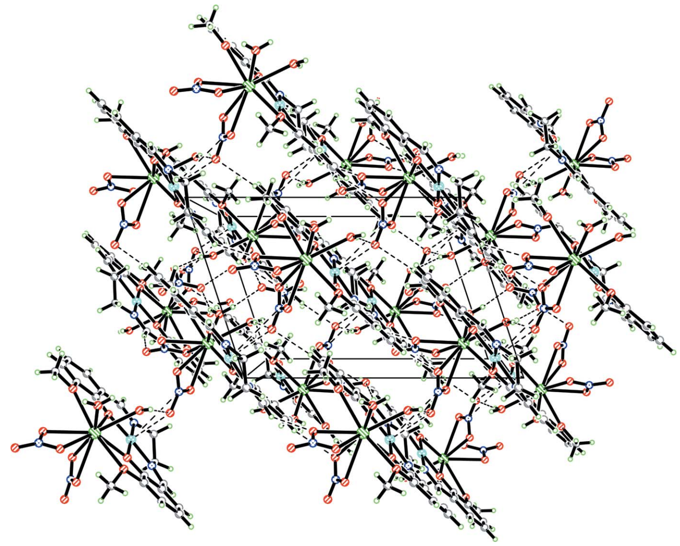


Figure 2
The packing of (I), viewed along the *b* axis. Hydrogen bonds are shown as dashed lines.

Water H atoms were found in a difference Fourier map and refined with the following restraints: H···O = 0.85 (2) H···H = 1.35 (2) Å whilst maintaining a H—O—H bond angle of 107.5°. The other H atoms were positioned geometrically and treated as riding on their parent atoms, with C—H distances of 0.93 (aromatic), 0.97 (methylene) and 0.96 Å (methyl), and with U_{iso}(H) values of $1.5U_{eq}$(C) for methyl H atoms and $1.2U_{eq}$(C) for other H atoms.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *APEX2*; program(s) used to refine structure: *APEX2*; molecular graphics: *APEX2*; software used to prepare material for publication: *APEX2*.

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