

Table 1 (continued)

Title	Reference	Retracted by	DOI	Refcode
{ μ -6,6'-Dimethoxy-2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}- μ -nitrate-dinitratoeuropium(III)zinc(II)	Hu <i>et al.</i> (2008)	Author	10.1107/S160053680706151X	MIRPAF
Bis(4-chloro-2-formylphenolato)nickel(II)	Li <i>et al.</i> (2008)	Author	10.1107/S1600536807056309	RISTET
{ μ -6,6'-Dimethoxy-2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}- μ -nitrate-dinitratoerbium(III)zinc(II)	Chen <i>et al.</i> (2008)	Author	10.1107/S1600536808006958	QIXHIP
Bis(2-ethoxy-6-formylphenolato- $\kappa^2 O^1, O^6$)nickel(II)	Han (2008)	Journal	10.1107/S160053680800809X	QIXLIT
{ μ -6,6'-Dimethoxy-2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}- μ -nitrate-dinitratoholmium(III)zinc(II)	Xiao, Sui <i>et al.</i> (2008)	Author	10.1107/S1600536808013743	BIZTUA
{ μ -6,6'-Diethoxy-2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato}-trinitratoholmium(III)nickel(II)	Xiao, Fu <i>et al.</i> (2008)	Author	10.1107/S1600536808013755	BIZVAI
Hydrogen-bonding patterns in the cocrystal terephthalic acid-4,4'-bipyridine (2I)	Wang <i>et al.</i> (2009)	Journal	10.1107/S160053680903236X	DUCZEH
{6,6'-Dimethoxy-2,2'-[ethane-1,2-diylbis(nitrilomethylidyne)]diphenolato-1 $\kappa^4 O^1, O^1, O^6, O^6$:2 $\kappa^4 O^1, N, N, O^1$ } (ethanol-1 κO)- μ -nitrate-1:2 $\kappa^2 O$:O'-dinitrato-1 $\kappa^2 O, O'$ -samarium(III)zinc(II)	Huang <i>et al.</i> (2009)	Journal	10.1107/S1600536809033558	YUCWAV

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A new dinuclear Cu^{II}–Lu^{III} complex
with a salen-type Schiff base ligandYan Sui,^a Yi-An Xiao,^{b*} Xiao-Niu Fang,^a Xi-Rui Zeng^a and Meng-Hua Li^a^aJiangXi Province Key Laboratory of Coordination Chemistry, College of Chemistry and Chemical Engineering, JingGangShan University, 343009 Ji'an, JiangXi, People's Republic of China, and ^bCollege of Life Science, JingGangShan University, 343009 Ji'an, JiangXi, People's Republic of China

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A heteronuclear Cu^{II}–Lu^{III} complex (systematic name: {6,6'-diethoxy-2,2'-[ethane-1,2-diylbis(nitrilomethylidene)]-diphenolato}trinitratolutetium(III)copper(II)), [CuLu(C₂₀H₂₂N₂O₄)(NO₃)₃], with the hexadentate Schiff base compartmental ligand *N,N'*-ethylenebis(3-ethoxysalicylaldehyde) (H₂L), has been synthesized and structurally characterized. The Cu and Lu atoms are doubly bridged by two phenolate O atoms afforded by the Schiff base ligand. No classical intermolecular hydrogen bonds are found. Some weak O···Cu and C–H···O interactions generate a two-dimensional zigzag sheet.

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Key indicators

Single-crystal X-ray study

T = 296 K

Mean $\sigma(C-C)$ = 0.011 Å

R factor = 0.049

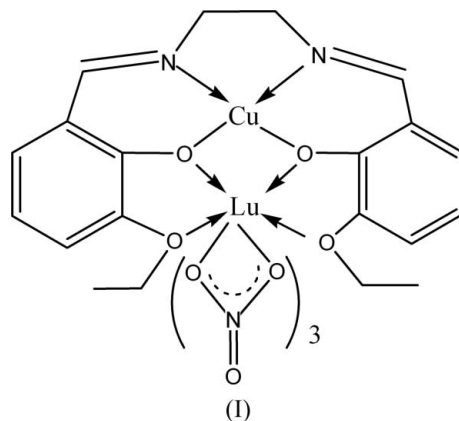
wR factor = 0.137

Data-to-parameter ratio = 15.8

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 agents for magnetic resonance imaging and as stains for fluorescence imaging have prompted considerable interest in the preparation of and magnetic and optical properties of 3d–4f heterometallic dinuclear complexes (Baggio *et al.*, 2000; Caravan *et al.*, 1999; Edder *et al.*, 2000). Recently, some 3d–4f 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 have been relatively few studies to date of Cu^{II}–Lu^{III} dinuclear complexes. As part of our investigation into the structure and applications of 3d–4f heterometallic Schiff base complexes, we report here the synthesis and X-ray crystal structure analysis of the title complex, (I), a new Cu^{II}–Lu^{III} complex with the salen-type Schiff base *N,N'*-ethylenebis(3-ethoxysalicylaldehyde) (H₂L).



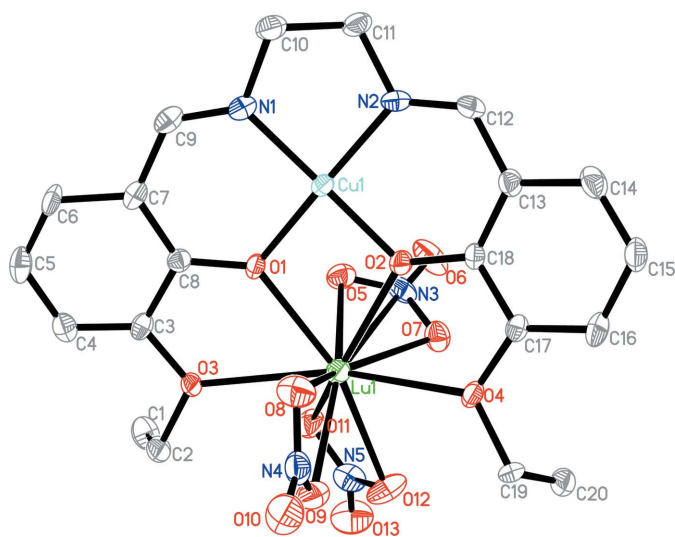


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids. All H atoms have been omitted for clarity.

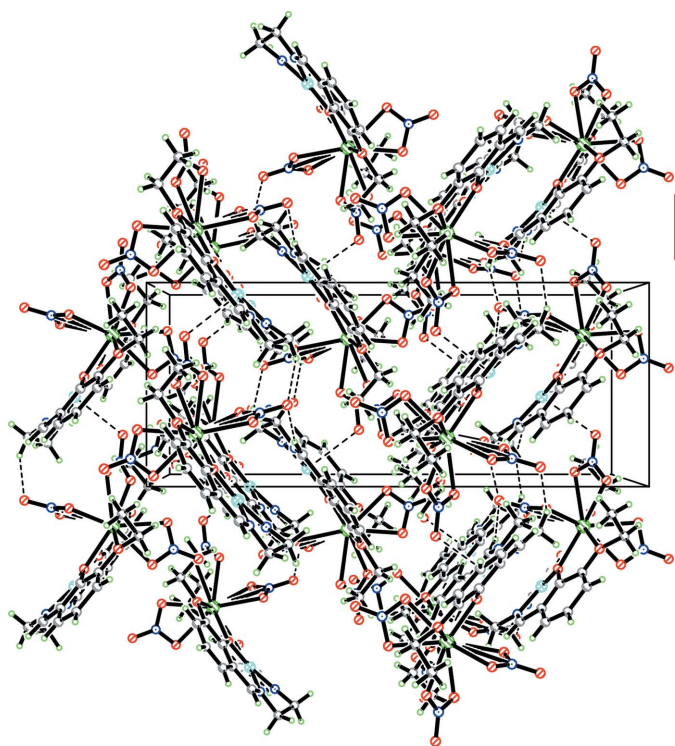


Figure 2
A packing diagram for (I), viewed along the *b* axis. Hydrogen bonds are shown as dashed lines.

Complex (I) crystallizes in the space group $P2_12_12_1$, with the Cu and Lu atoms doubly bridged by two phenolate O atoms provided by a salen-type Schiff base ligand. The inner salen-type cavity is occupied by Cu^{II}, while Lu^{III} is present in the open and larger portion of the dinucleating compartmental Schiff base ligand. The dihedral angle between the mean planes Cu1/O1/O2 and Lu1/O1/O2 is $3.8(2)^\circ$, suggesting that the bridging group is almost planar. The deviations of atoms from the least-squares Cu1/O1/O2/Lu1 plane are

$-0.0319(2)$ Å for Cu, $-0.0224(2)$ Å for Lu, $0.0267(3)$ Å for O1 and $0.0275(2)$ Å for O2.

The Lu^{III} centre in (I) has a decacoordination environment of O atoms. In addition to the phenolate ligands, two ethoxy O atoms coordinate to this metal centre. Two O atoms from each of the three nitrates chelate to Lu to complete the decacoordination. The three kinds of Lu–O bond distances are significantly different, the shortest being the Lu–O(phenolate) and the longest being the Lu–O(ethoxy) separations.

The coordination of Cu^{II} is square-planar. The donor centres are alternately above and below the mean N₂O₂ plane, with an average deviation from the plane of $0.0800(2)$ Å, while Cu1 is just $0.0402(3)$ Å above this square plane.

Adjacent molecules are held together by weak interactions [O13...Cu1 = $3.158(4)$ Å, C1–H1A...O10ⁱ, C1–H1C...O11, C9–H9...O6ⁱⁱ and C11–H11B...O6ⁱⁱⁱ; symmetry codes: (i) $-1 + x, y, z$; (ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, -z$]. These link the molecules into a two-dimensional zigzag sheet (Fig. 2).

Experimental

H₂L was prepared by the 2:1 condensation of 3-ethoxysalicylaldehyde and ethylenediamine in methanol. Complex (I) was obtained by the treatment of copper(II) acetate monohydrate (0.168 g, 1 mmol) with H₂L (0.356 g, 1 mmol) in methanol solution (100 ml) under reflux for 3 h, and then for another 3 h after the addition of lutetium(III) nitrate hexahydrate (0.469 g, 1 mmol). The reaction mixture was cooled and the resulting precipitate was filtered off, washed with diethyl ether and dried *in vacuo*. Single crystals of (I) suitable for X-ray analysis were obtained by slow evaporation at room temperature of a methanol solution. Analysis calculated for C₂₀H₂₂CuLuN₅O₁₃: C 30.84, H 2.85, Cu 8.16, N 8.99, Lu 22.46%; found: C 30.47, H 2.85, Cu 8.17, N 9.03, Lu 22.53%. IR (KBr, cm⁻¹): 1642 (C=N), 1384, 1490 (nitrate).

Crystal data

[CuLu(C₂₀H₂₂N₂O₄)(NO₃)₃]
M_r = 778.94
Orthorhombic, $P2_12_12_1$
a = $8.5948(3)$ Å
b = $13.8147(4)$ Å
c = $21.1553(7)$ Å
V = $2511.87(14)$ Å³

Z = 4
D_x = 2.060 Mg m⁻³
Mo *K*α radiation
 μ = 4.83 mm⁻¹
T = $296(2)$ K
Block, red
 $0.16 \times 0.14 \times 0.11$ mm

Data collection

Bruker APEXII area-detector diffractometer
 φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.478, *T_{max}* = 0.602

18360 measured reflections
5736 independent reflections
4572 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
 θ_{\max} = 27.5°

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.137$
S = 1.01
5736 reflections
364 parameters
H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0975P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 1.53 e \text{ \AA}^{-3}$
 $\Delta\rho_{\min} = -2.40 e \text{ \AA}^{-3}$
Extinction correction: APEX2 (Bruker, 2004)
Extinction coefficient: 0.0025 (4)
Absolute structure: Flack (1983), with 2476 Friedel pairs
Flack parameter: 0.156 (16)

Table 1

Selected geometric parameters (Å, °).

Cu1–N1	1.898 (7)	Lu1–O4	2.605 (5)
Cu1–N2	1.906 (6)	Lu1–O5	2.524 (6)
Cu1–O1	1.901 (5)	Lu1–O7	2.507 (6)
Cu1–O2	1.896 (5)	Lu1–O8	2.508 (7)
Lu1–O1	2.398 (5)	Lu1–O9	2.470 (6)
Lu1–O2	2.355 (5)	Lu1–O11	2.495 (6)
Lu1–O3	2.653 (5)	Lu1–O12	2.578 (6)
N1–Cu1–N2	86.3 (3)	O5–Lu1–O4	114.4 (2)
N1–Cu1–O1	95.6 (3)	O5–Lu1–O12	105.3 (2)
O1–Cu1–N2	172.6 (3)	O7–Lu1–O3	132.38 (18)
O2–Cu1–N1	177.6 (3)	O7–Lu1–O5	49.8 (2)
O2–Cu1–N2	94.1 (2)	O7–Lu1–O8	146.6 (2)
O2–Cu1–O1	84.3 (2)	O7–Lu1–O12	71.9 (2)
O1–Lu1–O3	60.13 (16)	O8–Lu1–O3	80.2 (2)
O1–Lu1–O4	121.95 (17)	O8–Lu1–O4	77.5 (2)
O1–Lu1–O5	69.8 (2)	O8–Lu1–O5	141.1 (2)
O1–Lu1–O7	113.56 (18)	O8–Lu1–O12	113.5 (2)
O1–Lu1–O8	72.7 (2)	O9–Lu1–O3	79.0 (2)
O1–Lu1–O9	114.5 (2)	O9–Lu1–O4	78.3 (2)
O1–Lu1–O11	113.2 (2)	O9–Lu1–O5	162.8 (2)
O1–Lu1–O12	160.9 (2)	O9–Lu1–O7	131.5 (2)
O2–Lu1–O1	64.84 (18)	O9–Lu1–O8	50.3 (2)
O2–Lu1–O3	124.87 (17)	O9–Lu1–O11	94.4 (2)
O2–Lu1–O4	62.09 (17)	O9–Lu1–O12	64.8 (2)
O2–Lu1–O5	74.0 (2)	O11–Lu1–O3	69.67 (18)
O2–Lu1–O7	73.50 (19)	O11–Lu1–O4	122.25 (18)
O2–Lu1–O8	81.0 (2)	O11–Lu1–O5	69.2 (2)
O2–Lu1–O9	123.2 (2)	O11–Lu1–O7	72.1 (2)
O2–Lu1–O11	140.5 (2)	O11–Lu1–O8	137.9 (2)
O2–Lu1–O12	132.8 (2)	O11–Lu1–O12	49.6 (2)
O4–Lu1–O3	155.1 (2)	O12–Lu1–O3	102.2 (2)
O5–Lu1–O3	90.07 (19)	O12–Lu1–O4	77.1 (2)

H atoms were positioned geometrically and treated as riding on their parent atoms, with C–H distances of 0.97 (methylene) and 0.96 Å (methyl), and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms or $1.2U_{\text{eq}}(\text{C})$ 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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