КРАТКИЕ СООБЩЕНИЯ

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UNEXPECTED C=N BOND CLEAVAGE IN H₃salmp: SYNTHESIS AND STRUCTURES OF [LnNa(salmp)(sal)]₂·6EtOH (Ln = Sm, Er; H₃salmp = 2-BIS(SALICYLIDIENEAMINO)METHYLPHENOL; sal = SALICYLALDEHYDATO)

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The reaction of $LnCl_3$ with Na_3salmp/H_3salmp (H_3salmp = 2-bis(salicylidieneamino)methyl-phenol) affords $[LnNa(salmp)(sal)]_2$ (Ln = Sm(**I**), Er(**II**); sal = salicylaldehydato) complexes being different from the known Ln-salmp complex of $[Sm(salmp)(THF)]_2$. In the reaction, the cleavage of C=N bonds happens in H_3salmp, and the regenerated salicylaldehydato anion arises and takes part in the coordination. Both complexes are characterized by elemental analysis, IR spectroscopy, and X-ray crystallography.

Schiff bases have been widely used to construct metal complexes because they normally contain phenolic hydroxyl groups as well as imine side chains which provide good coordination sites and form versatile structures [1—3]. As a special Schiff base, 2-bis(salicylidieneamino)methylphenol (H_3salmp) has three phenolic hydroxyl groups and two imine short chains [4]. The application of H_3salmp in coordination with transition metals afforded complexes with unique structures and notable properties [5—10]. For example, Holm′s group found that the $salmp^{3-}$ ligand could stabilize ferric complexes in three oxidation states, i.e. $[Fe(salmp)]_2^{0,-,2-}$ containing $Fe^{III}Fe^{III}$, $Fe^{II}Fe^{II}$, and $Fe^{III}Fe^{II}$ [5, 6]. The isolation and structural characterization of the three ferric complexes in different oxidation states clarified the details of chemical interconversions in the reversible electron-transfer reactions. A similar property was also found for the salmp-manganese system [7]. We have successfully introduced the $salmp^{3-}$ ligand into the coordination with lanthanide metals [11, 12]. The $[Sm(salmp)(THF)]_2$ complex was obtained by the reaction of H_3salmp and Cp_3Sm in THF [11]. Tetravalent cerium complex $(salmp)_2Ce_2(O)Na_4(O^tBu)_4(THF)$ was synthesized via the reaction of H_3salmp with $Ce(O^tBu)_4$ [12]. In all cases, the $salmp^{3-}$ group showed considerable stability.

We noticed that the H_3salmp compound can be fully deprotonated to be the $salmp^{3-}$ ligand (such as that in $[Fe(salmp)]_2$ [6]) or partly deprotonated to be the $Hsalmp^{2-}$ anion (such as that in $[Zr(Hsalmp)_2]$ [8]). We wondered whether the coordination style was relevant with the pH value of the solutions in the synthesis. If so, the adjustment of alkaline state of H_3salmp may possibly lead to different types of salmp-metal complexes. Herein we reported that the reaction of Na_3salmp/H_3salmp with $SmCl_3$ in ethanol afforded $[SmNa(salmp)(sal)]_2$ complex (**I**) (sal = salicylaldehydato) rather than previous $[Sm(salmp)(THF)]_2$ [11]. In complex **I**, two deprotonated salicylaldehydato species existed beyond expectation, which implied that in H_3salmp the cleavage of C=N bonds happened in the reaction. Notably the reaction is well reproducible and also applicable for another lanthanide element such as erbium.

Experimental. $LnCl_3 \cdot 6H_2O$ (Ln = Sm, Er) were purchased from Aladdin Industrial Incorporation. H_3salmp was prepared according to the literature method [4]. The FT-IR spectra were recorded on a Perkin Elmer Spectrum BXII spectrometer. Carbon, hydrogen, and nitrogen analyses were carried out by direct combustion on an EA1110-CHNSO elemental analyzer. Lanthanide metal analysis was carried out by the complexometric titration.

To 5.0 ml of ethanol metallic Na (0.003 g, 0.15 mmol) was added. As metallic Na disappeared, yellow powder of H_3salmp (0.035 g, 0.10 mmol) was added. The mixture was stirred for 10 min to be a red solution (**A**). An ethanol solution (ca. 5 ml) of $SmCl_3 \cdot 6H_2O$ (0.036 g, 0.10 mmol) was poured into a pyrex tube, onto which solution **A** was carefully layered. The tube was sealed up and placed at room temperature for two weeks. Red cubic crystals of **I**·6EtOH (0.046 g, 40 % yield based on Sm) were produced. m.p. > 300 °C. Anal. Calcd. (%) for $C_{68}H_{76}Sm_2N_4Na_2O_{16}$: C 52.62, H 4.94, N 3.61, Sm 19.38. Found (%): C 52.46, H 4.79, N 3.68, Sm 19.32. IR (cm^{-1}): 3413(m), 3013(w), 2972(w), 2871(w), 1645(m), 1619(s), 1534(s), 1472(s), 1451(s), 1409(s), 1315(s), 1272(m), 1180(m), 1150(m), 1122(w), 1045(w), 1022(w), 1006(w), 967(m), 927(w), 898(w), 883(m), 821(m), 760(s), 657(w), 574(m), 463(m).

Complex **II** was prepared by a procedure analogous to that for complex **I**, but $ErCl_3 \cdot 6H_2O$ was used instead of $SmCl_3 \cdot 6H_2O$. Red cubic crystals appeared within two weeks in a yield of 38 %. m.p. > 300 °C. Anal. Calcd. (%) for $C_{68}H_{76}Er_2N_4Na_2O_{16}$: C 51.50, H 4.83, N 3.53, Er 21.09. Found (%): C 51.26, H 4.75, N 3.62, Er 21.12. IR (cm^{-1}): 3412(m), 2853(w), 1624(s), 1533(s), 1485(m), 1445(s), 1405(s), 1385(s), 1341(s), 1276(m), 1186(m), 1148(m), 1124(w), 1028(w), 970(w), 900(w), 884(w), 855(w), 756(m), 658(w), 586(w), 456(w).

Single crystals were selected and mounted on glass fibers. X-ray diffraction data were collected on a Bruker SMART diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å). Unit cell parameters were refined using the CrystalClear program [13]. The structures were solved by direct methods and refined on F^2 by full-matrix least squares calculations using the SHELXS-97 program package [14]. Atom C(34) in complex **I** was treated with disorder over two sites. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed at geometrically idealized positions and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2$—$1.5U_{eq}(C,O)$. Main crystallographic data for complexes **I** and **II** are listed in Table 1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center with CCDC-917522 (**I**) and 882284 (**II**).

Table 1

Summary of the crystallographic data for complexes of **I** *and* **II**

| Complex	**I**	**II**
Molecular formula	$C_{68}H_{76}Sm_2N_4Na_2O_{16}$	$C_{68}H_{76}Er_2N_4Na_2O_{16}$
Molecular weight	1552	1585.83
Crystal size, mm	0.35×0.27×0.25	0.32×0.28×0.25
Crystal system; Space group	Triclinic; $P1$	Triclinic; $P1$
a, b, c, Å	11.450(2), 11.727(2), 15.128(3)	11.3169(15), 11.6996(16), 14.967(2)
α, β, γ, deg.	69.61(3), 67.80(3), 66.49(3)	94.232(2), 111.339(2), 112.869(2)
V, Å^3; Z	1677.2(5); 1	1646.4(4); 1
D_{calc}, g/cm^{-3}	1.537	1.599
$F(000)$	786	798
μ(MoK_α), mm^{-1}	1.816	2.615
θ range, deg.	2.83 ~ 25.00	2.04 ~ 27.57
Total / Unique reflections	9573 / 5415 ($R_{int} = 0.0533$)	14151 / 7352 ($R_{int} = 0.0488$)
Goodness of fit on F^2	0.945	1.044
Largest diff. peak and hole, e/Å^{-3})	1.088 and −0.731	1.305 and −1.974
R, wR [$I > 2\sigma(I)$]	$R_1 = 0.0416$, $wR_2 = 0.0660$	$R_1 = 0.0476$, $wR_2 = 0.1109$
R, wR (all data)	$R_1 = 0.0602$, $wR_2 = 0.0702$	$R_1 = 0.0772$, $wR_2 = 0.1421$
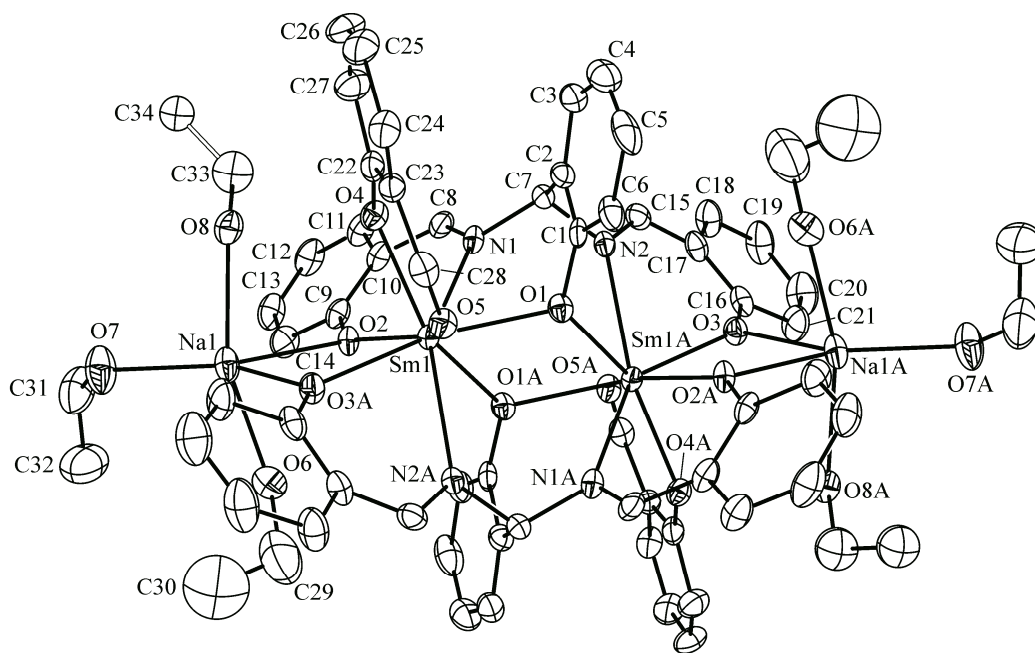
Fig. 1. Molecular structures of **I** and **II** with **I** as a representative, showing 30 % probability ellipsoids with H atoms omitted for clarity

Results and discussion. In order to investigate the effect of the pH value on salmp-lanthanide coordination, we tried the reactions of $LnCl_3$ (Ln = Sm, Er) and Na_3salmp/H_3salmp. The Na_3salmp/H_3salmp system was prepared by the reaction of H_3salmp with 1.5 equivalent of EtONa. Both reactions afforded red crystals as products. They were sensitive to air. In the FT-IR spectra, there are strong absorptions at 1619 cm^{-1} (for **I**) and 1624 cm^{-1} (for **II**), which are consistent with the imine stretching vibration [8, 9]. Also absorption peaks at 1272 cm^{-1} (for **I**) and 1276 cm^{-1} (for **II**) correspond to the salicylidene ring-to-oxygen stretching vibration [8]. These facts demonstrated that H_3salmp had participated in the coordination.

To understand more about the coordination, we characterized the crystal products by X-ray crystallography. The molecular structures of **I** and **II** are shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. It is obvious that salmp^{3-} ligands are involved in these complexes. Complexes **I** and **II** are isostructural. The salmp^{3-} ligand acts as a bridge linking two Ln^{3+} ions. Two salmp^{3-} anions coordinate two Ln^{3+} cations via double bridges to form dinuclear complexes, similar to those in [Sm(salmp)(THF)]$_2$ [11]. The adjustment of the alkaline state of H_3salmp does not lead to the occurrence of any partly deprotonated anions such as H_2salmp$^-$ or Hsalmp^{2-}. Surprisingly, salicylaldehydato

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*Selected bond lengths* (Å) *and angle* (deg.) *for complexes of* **I** *and* **II**

Bond	**I**	**II**	Bond	**I**	**II**
Ln(1)—O(1)	2.366(3)	2.307(4)	Ln(1)···Ln(1A)	3.8491(11)	3.7510(7)
Ln(1)—O(1A)	2.365(4)	2.307(4)	Ln(1)···Na(1)	3.661(2)	3.657(3)
Ln(1)—O(2)	2.318(4)	2.249(5)	Na(1)—O(2)	2.378(4)	2.358(6)
Ln(1)—O(3A)	2.325(3)	2.274(5)	Na(1)—O(3)	2.303(4)	2.294(6)
Ln(1)—O(4)	2.367(3)	2.311(4)	Na(1)—O(6)	2.425(5)	2.478(6)
Ln(1)—O(5)	2.492(4)	2.435(5)	Na(1)—O(7)	2.312(5)	2.453(7)
Ln(1)—N(1)	2.635(4)	2.565(6)	Na(1)—O(8)	2.453(4)	2.311(7)
Ln(1)—N(2A)	2.664(4)	2.575(6)			

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Angle	I	II	Angle	I	II
O(1)—Ln(1)—O(1A)	71.11(12)	71.22(17)	O(2)—Ln(1)—O(4)	90.52(12)	91.48(17)
O(1)—Ln(1)—O(2)	138.09(12)	139.66(17)	O(2)—Ln(1)—O(5)	146.51(12)	146.98(16)
O(1)—Ln(1)—O(3)	121.70(12)	124.93(17)	O(2)—Ln(1)—N(1)	71.44(12)	73.11(18)
O(1)—Ln(1)—O(3A)	145.94(12)	145.45(17)	O(2)—Ln(1)—N(2A)	110.97(12)	108.67(18)
O(1)—Ln(1)—O(4)	98.22(11)	97.70(16)	O(3A)—Ln(1)—O(4)	83.17(12)	81.78(18)
O(1)—Ln(1)—O(5)	73.73(12)	72.56(16)	O(3A)—Ln(1)—O(5)	74.71(13)	74.32(16)
O(1)—Ln(1)—N(1)	71.60(12)	72.55(17)	O(3A)—Ln(1)—N(1)	139.75(13)	137.63(17)
O(1)—Ln(1)—N(2A)	88.64(12)	88.58(17)	O(3A)—Ln(1)—N(2A)	69.81(12)	71.82(18)
O(1A)—Ln(1)—O(4)	149.91(12)	147.37(17)	O(4)—Ln(1)—O(5)	70.88(12)	73.13(16)
O(1A)—Ln(1)—O(5)	128.52(12)	128.02(15)	O(4)—Ln(1)—N(1)	74.73(12)	72.35(17)
O(1A)—Ln(1)—N(1)	75.20(12)	75.04(16)	O(4)—Ln(1)—N(2A)	138.90(13)	140.41(18)
O(1A)—Ln(1)—N(2A)	70.38(13)	71.43(17)	O(5)—Ln(1)—N(1)	126.09(12)	126.11(17)
O(2)—Ln(1)—O(1A)	80.95(12)	80.01(16)	O(5)—Ln(1)—N(2)	72.42(13)	71.66(17)
O(2)—Ln(1)—O(3A)	75.63(13)	74.67(17)	N(1)—Ln(1)—N(2)	144.39(13)	145.38(17)

Symmetry codes: $-x, -y+1, -z$ for **I**; $-x+2, -y+1, -z+1$ for **II**.

anions occurred and participated in the coordination. Since there was not any salicylaldehyde in the reactants, it should come from the cleavage of C=N groups in H₃salmp. This phenomenon has not been found previously as far as we know in the synthesis processes for the reported salmp-metal complexes such as Zr(Hsalmp)₂ [8], Zr(Hsalmp)(Fdsp) [8] (H₂Fdsp = *N,N'*-di(3-fluorosalicylidene)-1,2-phenylenediamine), M₂(salmp)₂ (M = Fe [5], Mn [7]), [Et₄N]₂[M₂(salmp)₂] (M = Fe [5], Mn [7]), [Et₄N][M₂(salmp)₂] (M = Fe [5, 6], Mn [7]), [Et₄NH][M₃(O)(salmp)(salox)₂(Hsalox)] (M = Ti, V, Cr, Mn, Fe, Co) [9] (H₂salox = salicylaldoxime), [Et₄NH][Fe₃(O)(salmp)₂(salox)₃] [10], [Sm(salmp)(THF)]₂ [11], and (salmp)₂Ce₂(O)Na₄(O^{t}Bu)₄(THF) [12], H₃salmp compound showed considerable stability under diverse conditions. We supposed that Ln³⁺ ions could contribute to the cleavage of C=N bonds in H₃salmp. The reactions are described in Equation (1).

$$\text{(1)}$$
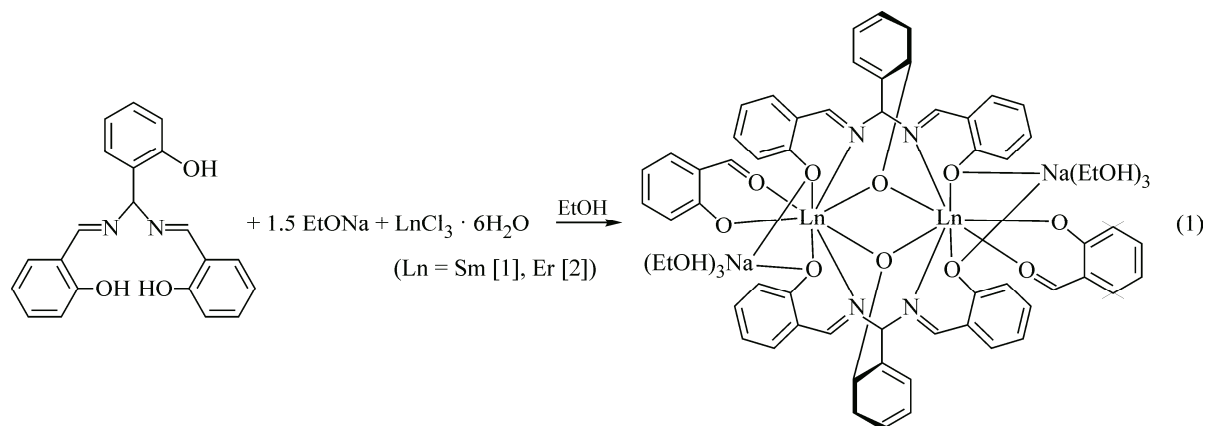
In complex **I** (Fig. 1), each of the Sm³⁺ ions is eight-coordinated by six O atoms (four from two salmp³⁻ anions and two from a salicylaldehydato anion) and two N atoms (from two salmp³⁻ anions). In complex **I**, the Sm···Sm distance (3.8491(11) Å) is comparable with that in [Sm(salmp)(THF)]₂ (3.8057(4) Å) [11]. When the 0.059 Å difference in ionic radius between 8-coordinate Sm³⁺ (1.079 Å) and 7-coordinate Sm³⁺ (1.02 Å) is taken into account [15], the Sm—O(salmp) bond length in **I** (av. 2.344 Å) is comparable with that in [Sm(salmp)(THF)]₂ [11] (2.291 Å). The O(1)—Sm(1)—O(1A)

(71.10(12)°) bond angle in **I** is smaller than that in [Sm(salmp)(THF)]$_2$ (73.11(8)°). Correspondingly, the Sm(1)—O(1)—Sm(1A) angle in **I** (108.90(12)°) is larger than that in [Sm(salmp)(THF)]$_2$ (106.89(8)°) [11]. The Sm(1)—O(4) bond length (2.367(3) Å) is close to that of Sm—O(salmp) (av. 2.344 Å). The Sm(1)—O(5) bond (2.492(4) Å) is much longer than the Sm(1)—O(4) bond (2.367(3) Å), and comparable with those in Sm(sal)$_3$(phenanthroline) (2.4714(18) Å to 2.4977(16) Å) [16]. The Er···Er (3.7510(7) Å) and Er—O(phenolate) (av. 2.289 Å) distances in **II** are in accordance with those in complex **I**, when the difference of the ionic radii is taken into account. The radii of eight-coordinated Sm^{3+} and Er^{3+} are 1.079 Å and 1.004 Å, respectively [15].

In summary, the reactions of LnCl$_3$ and Na$_3$salmp/H$_3$salmp afforded [LnNa(salmp)(sal)]$_2$ (Ln = Sm, Er) complexes. It is confirmed that in H$_3$salmp the cleavage of C=N bonds happened in the reaction.

REFERENCES

1. *Yang X., Jones R.A., Huang S.* // Coord. Chem. Rev. – 2014. – **273**. – P. 63 – 75.
2. *Büunzli J.C.G.* // Chem. Rev. – 2010. – **110**. – P. 2729 – 2755.
3. *Radecka-Paryzek W., Patroniak V., Lisowski J.* // Coord. Chem. Rev. – 2005. – **249**. – P. 2156 – 2175.
4. *Nabulsi N.A.R., Fronczek F.R., Gandour R.D.* // Acta Crystallogr. – 1988. – **C44**. – P. 1086 – 1089.
5. *Snyder B.S., Patterson G.S., Abrahamson A.J. et al.* // J. Am. Chem. Soc. – 1989. – **111**, N 14. – P. 5214 – 5223.
6. *Achim C., Bominaar E.L., Staples R.J. et al.* // Inorg. Chem. – 2001. – **40**, N 17. – P. 4389 – 4403.
7. *Yu S.B., Wang C.P., Day E.P. et al.* // Inorg. Chem. – 1991. – **30**, N 21. – P. 4067 – 4074.
8. *Illingsworth M.L., Schwartz L.J., Jensen A.J. et al.* // Polyhedron. – 2002. – **21**, N 2. – P. 211 – 218.
9. *Chaudhuri P., Hess M., Weyhermuller T. et al.* // Inorg. Chem. Commun. – 1998. – **1**, N 2. – P. 39 – 42.
10. *Bill E., Krebs C., Winter M. et al.* // Chem. Eur. J. – 1997. – **3**, N 2. – P. 193 – 201.
11. *Li L., Zhou Y., Yuan F.G.* // Acta Crystallogr. – 2012. – **E68**. – P. m603 – m604.
12. *Zhang M.M., Zhou Y., Yuan F.G. et al.* // Chin. J. Struct. Chem. – 2014. – **33**, N 2. – P. 258 – 262.
13. *Rigaku.* CrystalClear. Rigaku Corporation. – Tokyo, Japan, 2004.
14. *Sheldrick G.M.* // Acta Crystallogr. – 2008. – **A64**. – P. 112 – 122.
15. *Shannon R.D.* // Acta Crystallogr. – 1976. – **A32**. – P. 751 – 767.
16. *Zhong Y., Yang J., Hu L.* // Acta Crystallogr. – 2013. – **E69**. – P. m430.