

## Synthesis and Structural Characterization of Trinuclear $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ and $\text{Zn}^{2+}$ - $\text{Eu}^{3+}$ Complexes Based on 2,3-Dihydroxybenzene-1,4-dicarbaldehyde, 1,3-*bis*(Aminoxy)propane with 3-Ethoxysalicylaldehyde

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A novel *bis*(salamo)-type multipledentate chelating ligand  $\text{H}_4\text{L}$  and its three  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Zn}^{2+}$ - $\text{Eu}^{3+}$  complexes have been designed and synthesized and characterized by elemental analyses, IR, UV-visible spectra and  $^1\text{H}$  NMR spectroscopy. The *bis*(salamo)-type compound  $\text{H}_4\text{L}$  shows that the complexation between  $\text{H}_4\text{L}$  and metal ions can afford 1:3 complex  $[\text{M}_3(\text{L})]^{2+}$  or  $[\text{M}'_2\text{M}''(\text{L})]^{3+}$ . The most likely structures of the  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Zn}^{2+}$ - $\text{Eu}^{3+}$  complexes have been suggested.

**Keywords:** *bis*(salamo)-type compound, Synthesis, Characterization.

### INTRODUCTION

Salen-type ligands are easily obtained by the reaction of salicylaldehyde with diamines, coordinated to transition metals in a tetradentate fashion to afford stable mononuclear complexes<sup>1</sup>. Some of these complexes possess multifarious interesting magnetic properties, nonlinear optical materials, catalysts for organic reactions and models of reaction centers of metallo-enzymes<sup>2-5</sup>. In order to improve such functions, chemical modifications of the Salen-type compound, introduction of some functional groups or substitution of some parts with appropriate ones, are effective and inevitable. Thus, we have recently studied *O*-alkyloxime analogue of salen, *N,N'*-*bis*(salicylaldehyde)ethylenediamine, which shows high stability under the conditions where the imine analogues suffer metathesis reaction of the C=N bonds<sup>6</sup>. Herein, we report on the synthesis and characterization of a new *bis*(salamo)-type compound  $\text{H}_4\text{L}$  based on 1,3-*bis*(aminoxy)propane, 2,3-dihydroxybenzene-1,4-dicarbaldehyde and 3-ethoxysalicylaldehyde. The ligand  $\text{H}_4\text{L}$  have the  $\text{O}_6$ -recognition site was occupied by the third metal ions, the  $\text{O}_6$  site of this type of ligand is particularly suitable for transition metals and lanthanides to afford 3d-4f triduclear complexes<sup>7</sup>.

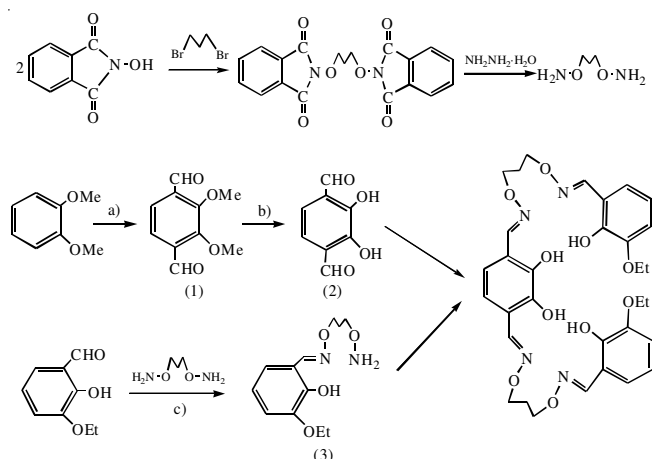
### EXPERIMENTAL

3-Ethoxysalicylaldehyde ( $\geq 98\%$ ), 1,3-dibromopropane, *O*-dimethoxybenzene, TMEDA, *n*-butyllithium, boron tribromide were purchased from Alfa Aesar and used without

further purification. The other reagents and solvents were analytical grade reagents from Tianjin Chemical Reagent Factory. The Methods are the same as literature early<sup>8</sup>.

**General procedure:** A synthetic route to the new ligand  $\text{H}_4\text{L}$  is shown in **Scheme-I**. 1,3-*bis*(aminoxy)propane were synthesized according to an analogous method reported earlier<sup>8</sup>. Dilithiation of 1,2-dimethoxybenzene by *n*-butyllithium in the presence of TMEDA followed by the addition of DMF afforded 2,3-dimethoxybenzene-1,4-dicarbaldehyde (**1**) in 29.4 % yield<sup>9</sup>. Demethylation of (**1**) with boron tribromide in dichloromethane obtained 2,3-dihydroxybenzene-1,4-dicarbaldehyde (**2**) in 68.5 % yield<sup>10</sup>. The reaction of 2-[(*O*-1-propyloxyamide)]oxime-6-ethoxyphenol (**3**) with 2,3-dihydroxybenzene-1,4-dicarbaldehyde (**2**) in hot ethanol gave the *bis*(salamo)-type ligand  $\text{H}_4\text{L}$ <sup>8</sup>. Yield, 91.8 %. m.p. 407-408 K.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta/\text{ppm}$ )  $\delta$  2.167 (m,  $J = 6.4$  Hz, 4H,  $\text{CH}_2$ ), 3.91 (s, 6H,  $\text{CH}_3$ ), 4.118 (m,  $J = 6.8$  Hz, 4H,  $\text{CH}_2\text{-O}$ ), 4.320 (m,  $J = 6, 1.6$  Hz, 8H,  $\text{CH}_2\text{-O}$ ), 6.763 (s, 2H, PhH), 6.839 (m, 4H, PhH), 6.906 (dd,  $J = 2.4, 7.2$  Hz, 2H, PhH), 8.180 (s, 2H, N=CH), 8.210 (s, 2H, N=CH), 9.780 (s, 2H, OH), 9.887 (s, 2H, OH).

**Synthesis of  $\text{Cu}^{2+}$  complex:** To a clear solution of  $\text{H}_4\text{L}$  (12.76 mg, 0.02 mmol) in hot methanol (20 mL) was added  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (13.14 mg, 0.06 mmol) in 5 mL of methanol. The resulting solution was left stirring overnight at room temperature to afford a pale brown solid which was filtered off, washed three times with methanol and dried under reduced pressure to give the  $\text{Cu}^{2+}$  complex. Yield: 32.8 %.



**Scheme-I:** Synthetic route to *bis(salamo)*-type compound H<sub>4</sub>L. (a) (i) *n*-BuLi, TMEDA, Et<sub>2</sub>O, (ii) DMF then H<sub>2</sub>O; (b) BBr<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> then H<sub>2</sub>O; (c) EtOH

**Synthesis of Zn<sup>2+</sup> complex:** To a clear solution of H<sub>4</sub>L (12.54 mg, 0.02 mmol) in hot methanol (20 mL) was added Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (13.17 mg, 0.06 mmol) in 3 mL of methanol. The resulting solution was left stirring overnight at room temperature to afford a yellow solid which was filtered off, washed three times with methanol and dried under reduced pressure to give the Zn<sup>2+</sup> complex. Yield: 35.8 %.

**Synthesis of Zn<sup>2+</sup>-Eu<sup>3+</sup> complex:** To a clear solution of H<sub>4</sub>L (12.57 mg, 0.02 mmol) in hot methanol (20 mL) was added Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (8.87 mg, 0.04 mmol) in 3 mL of methanol and added Eu(Pic)<sub>3</sub>·4H<sub>2</sub>O (18.17 mg, 0.02 mmol) in 5 mL of methanol. The resulting solution was left stirring overnight at room temperature to afford an orange solid which was filtered off, washed three times with methanol and dried under reduced pressure to give the Zn<sup>2+</sup>-Eu<sup>3+</sup> complex. Yield: 27.1 %.

## RESULTS AND DISCUSSION

Colour, yields and elemental analytical results of the newly synthesized *bis(salamo)*-type compound H<sub>4</sub>L and its three complexes are presented in Table-1. Their compositions agree with the general formulae [M<sub>3</sub>(L)(OAc)<sub>2</sub>(H<sub>2</sub>O)] (M = Cu<sup>2+</sup> or Zn<sup>2+</sup>) or [M<sup>1</sup><sub>2</sub>M<sup>2</sup>(L)(OAc)<sub>3</sub>(H<sub>2</sub>O)] (M<sup>1</sup> = Zn<sup>2+</sup>, M<sup>2</sup> = Eu<sup>3+</sup>) and are similar to those reported for M(II) or M(II)-M(III)

complexes with the *bis(salamo)*-type ligand<sup>11-13</sup>. The ligand H<sub>4</sub>L is stable in air and soluble in chloroform, dichloromethane, tetrahydrofuran, benzene, acetone, DMF and DMSO, insoluble in *n*-hexane, ether and water. In addition, all the synthesized complexes are stable in air and soluble in chloroform, dichloromethane, DMF, DMSO, ethanol and methanol, but slightly soluble in ethyl acetate, acetone and acetonitrile.

The molar conductivities of the Cu<sup>2+</sup>, Zn<sup>2+</sup> and Zn<sup>2+</sup>-Eu<sup>3+</sup> complexes at 25 °C of 10<sup>-3</sup> mol L<sup>-1</sup> DMF solution have values of 7.6, 10.5 and 13.7 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, respectively. It can be assumed that all of the three complexes are non-electrolytes<sup>14</sup>.

**IR spectra:** The IR spectra of the *bis(salamo)*-type chelating ligand H<sub>4</sub>L and its corresponding complexes are given in Table-2.

The three complexes have similar IR spectra, which indicate that these complexes have similar structures. The free ligand H<sub>4</sub>L exhibits an Ar-O stretching band at 1263 cm<sup>-1</sup>, which is shifted to lower frequencies by about 7-27 cm<sup>-1</sup> upon complexation. Similarly, a characteristic band of C=N group of the free ligand H<sub>4</sub>L appears at about 1619 cm<sup>-1</sup>, the three complexes show bathochromic shift of C=N stretching band around 1615-1607 cm<sup>-1</sup>. These lowering of energy results from the metal-phenolic oxygen or metal-imine nitrogen interactions upon complexation and are similar to those reported for transition metal complexes with *salamo*-type chelating ligands<sup>8</sup>.

Infrared spectra of the *bis(salamo)*-type chelating ligand H<sub>4</sub>L shows the expected absorption band at 3472 cm<sup>-1</sup>, which is assigned to the stretching vibration band of phenolic hydroxyl group of the free ligand H<sub>4</sub>L. This band disappears in the infrared spectra of the three complexes, indicating the phenolic hydroxyl groups of the three complexes have been deprotonated. Infrared spectra of the three complexes show absorption bands due to the stretching, bending and wagging modes of water at about 3494, 1626 and 545 cm<sup>-1</sup>, respectively, indicating the presence of one coordinated water molecule in the three complexes. This is in agreement with the elemental analytical results.

In the 1580-1406 cm<sup>-1</sup> region, the observed bands are attributed to aromatic C=C vibrations bands. In the region of 500-100 cm<sup>-1</sup>, where we expect to observe metal-ligand stretching frequencies of the three complexes, two new absorption bands are observed in the regions of 467-457 and 436-425 cm<sup>-1</sup>, respectively, which are assigned to (M-N) and (M-O)

TABLE-1  
COLOUR, YIELDS AND ELEMENTAL ANALYTICAL RESULTS OF *bis(SALAMO)*-TYPE LIGAND H<sub>4</sub>L AND ITS METAL COMPLEXES

Compound	Colour	Yield (%)	m.f. (m.w.)	Elemental analysis (%): Found (Calcd.)		
				C	H	N
H <sub>4</sub> L	White	91.8	C <sub>32</sub> H <sub>38</sub> N <sub>4</sub> O <sub>10</sub> (638.7)	60.11 (60.18)	6.05 (6.00)	8.79 (8.77)
[Cu <sub>3</sub> (L)(OAc) <sub>2</sub> (H <sub>2</sub> O)]	Brown	32.8	C <sub>36</sub> H <sub>42</sub> Cu <sub>3</sub> N <sub>4</sub> O <sub>15</sub> (961.4)	44.81 (44.98)	4.58 (4.40)	5.72 (5.83)
[Zn <sub>3</sub> (L)(OAc) <sub>2</sub> (H <sub>2</sub> O)]	Yellow	35.8	C <sub>36</sub> H <sub>42</sub> Zn <sub>3</sub> N <sub>4</sub> O <sub>15</sub> (966.9)	44.85 (44.72)	4.18 (4.36)	5.78 (5.79)
[Zn <sub>2</sub> Eu(L)(OAc) <sub>3</sub> (H <sub>2</sub> O)]	Orange	27.1	C <sub>38</sub> H <sub>45</sub> Zn <sub>2</sub> EuN <sub>4</sub> O <sub>17</sub> (1112.5)	40.87 (41.02)	4.11 (4.08)	5.17 (5.04)

TABLE-2  
MOST IMPORTANT IR BANDS FOR THE *bis(SALAMO)*-TYPE LIGAND H<sub>4</sub>L AND ITS METAL COMPLEXES (cm<sup>-1</sup>)

Compound	v(O-H)	v, δ and ρ(H <sub>2</sub> O)	v(C=N)	v(Ar-O)	v(M-N)	v(M-O)	v(C=C) <sub>benzene ring</sub>
H <sub>4</sub> L	3472	-	1619	1263	-	-	1537, 1472, 1406
[Cu <sub>3</sub> (L)(OAc) <sub>2</sub> (H <sub>2</sub> O)]	-	3494, 1626, 545	1610	1236	467	425	1571, 1514, 1409
[Zn <sub>3</sub> (L)(OAc) <sub>2</sub> (H <sub>2</sub> O)]	-	3498, 1625, 551	1615	1245	467	428	1572, 1503, 1412
[Zn <sub>2</sub> Eu(L)(OAc) <sub>3</sub> (H <sub>2</sub> O)]	-	3497, 1625, 554	1607	1256	457	436	1580, 1524, 1415

TABLE-3  
UV-VISIBLE SPECTRAL DATA FOR THE *bis*(SALAMO)-TYPE LIGAND H<sub>4</sub>L AND ITS METAL COMPLEXES

Compoune	C ( $\times 10^{-5}$ mol L <sup>-1</sup> )	First band	Second band	Third band
		$\lambda_{\max 1}$ (nm)	$\lambda_{\max 2}$ (nm)	$\lambda_{\max 3}$ (nm)
H <sub>4</sub> L	2.50	273	304	318
[Cu <sub>3</sub> (L)(OAc) <sub>2</sub> (H <sub>2</sub> O)]	2.50	283	304	318
[Zn <sub>3</sub> (L)(OAc) <sub>2</sub> (H <sub>2</sub> O)]	2.50	270	322	-
[Zn <sub>2</sub> Eu(L)(OAc) <sub>3</sub> (H <sub>2</sub> O)]	2.50	262	327	-

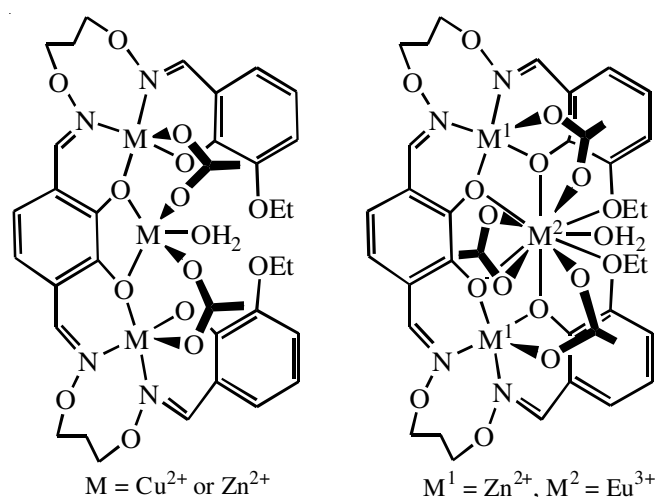
stretching bands, respectively<sup>8</sup>. These bands are not present in that of the free ligand H<sub>4</sub>L.

**UV-visible spectra:** The UV-visible spectral data of the *bis*(salamo)-type ligand H<sub>4</sub>L and its three Cu<sup>2+</sup>, Zn<sup>2+</sup> and Zn<sup>2+</sup>-Eu<sup>3+</sup> complexes in  $2.5 \times 10^{-5}$  mol L<sup>-1</sup> chloroform solution are presented in Table-3.

The *bis*(salamo)-type ligand H<sub>4</sub>L exhibits three intense peaks at around 273, 304 and 318 nm. The former absorption peak at about 273 nm can be assigned to the  $\pi$ - $\pi^*$  transition of the benzene rings, while the middle peak at 304 nm can be attributed to the intra-ligand  $\pi$ - $\pi^*$  transition of the C=N bonds and the latter peak at 318 nm can be assigned to the n- $\pi^*$  transition of the substitutional group to benzene rings<sup>8,15</sup>. Upon the addition of Cu<sup>2+</sup>, Zn<sup>2+</sup> or Zn<sup>2+</sup> and Eu<sup>3+</sup> ions, the absorption peak of 273 nm with moderate bathochromic or hypochromatic shifts and the band at 304 nm only show a bathochromic shift of the peak extending to 304-327 nm<sup>15</sup>.

## Conclusion

A novel *bis*(salamo)-type chelating ligand H<sub>4</sub>L and its Cu<sup>2+</sup>, Zn<sup>2+</sup> and Zn<sup>2+</sup>-Eu<sup>3+</sup> complexes have been designed and synthesized, respectively and characterized by elemental analyses, IR and UV-visible spectra. The most likely structures of the Cu<sup>2+</sup>, Zn<sup>2+</sup> and Zn<sup>2+</sup>-Eu<sup>3+</sup> complexes have been suggested.



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## REFERENCES

1. S. Akine, T. Taniguchi and T. Nabeshima, *Inorg. Chem.*, **43**, 6142 (2004).
2. (a) A. Bencini, C. Benelli, A. Caneschi, R.L. Carlin, A. Dei and D. Gatteschi, *J. Am. Chem. Soc.*, **107**, 8128 (1985); (b) M. Sasaki, K. Manseki, H. Horiuchi, M. Kumagai, M. Sakamoto, H. Sakiyama, Y. Nishida, M. Sakai, Y. Sadaoka, M. Ohba and H. Okawa, *J. Chem. Soc., Dalton Trans.*, 259 (2000); (c) J.-P. Costes, F. Dahan and A. Dupuis, *Inorg. Chem.*, **39**, 165 (2000).
3. T. Katsuki, *Coord. Chem. Rev.*, **140**, 189 (1995).
4. T.K. Saha, V. Ramkumar and D. Chakraborty, *Inorg. Chem.*, **50**, 2720 (2011).
5. (a) T.-T. Tsou, M. Loots and J. Halpern, *J. Am. Chem. Soc.*, **104**, 623 (1982); (b) M.F. Summers, L.G. Marzilli, N. Bresciani-Pahor and L. Randaccio, *J. Am. Chem. Soc.*, **106**, 4478 (1984).
6. S. Akine, T. Taniguchi and T. Nabeshima, *Chem. Lett.*, **30**, 682 (2001).
7. (a) W.-K. Wong, H. Liang, W.-Y. Wong, Z. Cai, K.-F. Li and K.-W. Cheah, *New J. Chem.*, **26**, 275 (2002); (b) O. Margeat, P.G. Lacroix, J.-P. Costes, B. Donnadiou, C. Lepetit and K. Nakatani, *Inorg. Chem.*, **43**, 4743 (2004); (c) W.-K. Lo, W.-K. Wong, J. Guo, W.-Y. Wong, K.-F. Li and K.-W. Cheah, *Inorg. Chim. Acta*, **357**, 4510 (2004); (d) S. Akine, W.K. Dong and T. Nabeshima, *Inorg. Chem.*, **45**, 4677 (2006).
8. (a) W.K. Dong, X.N. He, H.B. Yan, Z.W. Lv, X. Chen, C.Y. Zhao and X.L. Tang, *Polyhedron*, **28**, 1419 (2009); (b) W.K. Dong, Y.X. Sun, C.Y. Zhao, X.Y. Dong and L. Xu, *Polyhedron*, **29**, 2087 (2010); (c) W.K. Dong, L. Wang, Y.X. Sun, J.F. Tong and J.C. Wu, *Chinese J. Inorg. Chem.*, **27**, 372 (2011); (d) W.K. Dong, C.Y. Zhao, Y.X. Sun, X.L. Tang and X.N. He, *Inorg. Chem. Commun.*, **12**, 234 (2009); (e) W.K. Dong and Y.J. Ding, *Cryst. Res. Technol.*, **43**, 321 (2008); (f) W.K. Dong, Y.X. Sun, Y.P. Zhang, L. Li, X.N. He and X.L. Tang, *Inorg. Chim. Acta*, **362**, 117 (2009); (g) W.K. Dong, Y.X. Sun, X.N. He, J.F. Tong and J.C. Wu, *Spectrochim. Acta A*, **76**, 476 (2010); (h) W.K. Dong, Y.X. Sun, G.H. Liu, L. Li, X.Y. Dong and X.H. Gao, *Z. Anorg. Allg. Chem.*, **638**, 1370 (2012); (i) J.A. Faniran, K.S. Patel and J.C. Bailar Jr., *J. Inorg. Nucl. Chem.*, **36**, 1547 (1974); (j) W.K. Dong, Y.X. Sun, S.J. Xing, Y. Wang and X.H. Gao, *Z. Naturforsch.*, **67b**, 197 (2012); (k) W.K. Dong, S.J. Xing, Y.X. Sun, L. Zhao, L.Q. Chai and X.H. Gao, *J. Coord. Chem.*, **65**, 1212 (2012); (l) L.Q. Chai, G. Wang, Y.X. Sun, W.K. Dong, L. Zhao and X.H. Gao, *J. Coord. Chem.*, **65**, 1621 (2012).
9. G.P. Crowther, R.J. Sundberg and A.M. Sarpeshkar, *J. Org. Chem.*, **49**, 4657 (1984).
10. S. Akine, T. Taniguchi and T. Nabeshima, *Tetrahedron Lett.*, **42**, 8861 (2001).
11. S. Akine, T. Taniguchi and T. Nabeshima, *J. Am. Chem. Soc.*, **128**, 15765 (2006).
12. S. Akine, T. Taniguchi and T. Nabeshima, *Inorg. Chem.*, **43**, 6142 (2004).
13. S. Akine, T. Taniguchi and T. Nabeshima, *Angew. Chem. Int. Ed.*, **41**, 4670 (2002).
14. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
15. H.E. Smith, *Chem. Rev.*, **83**, 359 (1983).