Inorganica Chimica Acta 362 (2009) 2217-2221

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis, crystal structures and characterization of three novel complexes with *N*-[2-(2-hydroxybenzylideneamino)ethyl]-4-methyl-benzene-sulfonamide as ligand

Shu-Ni Li, Quan-Guo Zhai, Man-Cheng Hu*, Yu-Cheng Jiang

Key Laboratory of Macromolecular Science of Shaanxi Province, School of Chemistry and Materials Science, Shaanxi Normal University, Xi'an, Shaanxi 710062, PR China

ARTICLE INFO

Article history: Received 2 August 2008 Received in revised form 3 October 2008 Accepted 6 October 2008 Available online 14 October 2008

Keywords: N-Tosyl-ethylenediamine Sulfonamide Schiff base Supramolecular architecture Fluorescence

ABSTRACT

Reaction of the N-tosyl-ethylenediamine and salicylaldehyde forms a new sulfonamide Schiff base N-[2-(2-hydroxybenzylideneamino)ethyl]-4-methyl-benzene-sulfonamide (H_2L). Three novel complexes constructed from H_2L , namely, $[M(HL)_2] \cdot xH_2O$ (M = Cu, x = 0 for 1, M = Ni, x = 0 for 2 and M = Zn, x = 1 for 3) have been prepared and characterized *via* X-ray single-crystal diffraction, elemental analysis, X-ray powder diffraction (XRPD), FT-IR, UV–Vis, TGA and photoluminescence measurements. Complex hydrogen bonds, C–H… π and π - π stacking interactions lead 1–3 to present 1-D, 2-D and 3-D supramolecular architectures, respectively.

© 2008 Elsevier B.V. All rights reserved.

Inorganica Chimica Acta

1. Introduction

Metal complexes with Schiff base ligands have played an important role in the development of coordination chemistry due to their preparative accessibility and structural variety [1–3]. Moreover, they have been widely used not only in inorganic and biological field [4–6], but also in catalytic field [7–9]. A great deal of review [3,7,10–12] has been reported in the synthesis, characterization and application of salen like Schiff base with transition metal complexes. However, changes in the electronic, steric and geometric properties of the ligand alter the orbitals at the metal centre and thus affect its properties.

The tetradentate salen ligand is a strong electron donor. Electron withdrawal of the sulfonyl group in the sulfonamide Schiff base causes important changes in both the ligand and the complexes. Over the past 10 years, there have been many reports on transition metal complexes with sulfonamide Schiff base [13,14]. The research mainly focused on two types of sulfonamide Schiff base, one is derived from the condensation of 2-tosylaminobenzal-dehyde and diamines [15–19], and the other is the condensation of N-tosyl-diamine and aldehydes [20–22].

As a part of our going research of project dealing with the coordination chemistry of Schiff base ligands, we recently turn our attention to the study of asymmetric sulfonamide Schiff base in contrast to salen. In this work, a new sulfonamide Schiff base *N*- [2-(2-hydroxybenzylideneamino)ethyl]-4-methyl-benzene-sulfonamide (H_2L) (Scheme 1) was prepared and three novel complexes on the base of this ligand, namely, [M(HL)₂] · xH_2O (M = Cu, x = 0for 1, M = Ni, x = 0 for 2 and M = Zn, x = 1 for 3) have also been prepared and characterized by elemental analysis, X-ray single-crystal diffraction, X-ray powder diffraction (XRPD), FT-IR, UV–Vis, TGA and photoluminescence measurements.

2. Experimental

2.1. Materials

All solvents, $Cu(CH_3COO)_2 \cdot H_2O$, $NiCl_2 \cdot 6H_2O$ and Zn plate were commercial products and used without further purification. N-To-syl-ethylenediamine was synthesized according to the literature method [23].

2.2. Analyses and physical measurements

C, H and N elemental analysis was performed on a Vario EL-III analyzer. Infrared spectra were recorded as KBr pellet on a Nicolet Avatar 360 spectrophotometer in the range 4000–400 cm⁻¹. UV– Vis absorptions were recorded on a SHIMADZU UV-1700 spectrophotometer. Luminescence emission and excitation spectra were recorded with a Perkin–Elmer LS55 luminescence spectrometer at room temperature. Thermogravimetric analysis was performed on Q1000 DSC with a heating rate of 10 °C min⁻¹ under N₂ atmosphere.



^{*} Corresponding author. Tel.: +86 29 85307765; fax: +86 29 85307774. *E-mail address*: hmch@snnu.edu.cn (M.-C. Hu).

^{0020-1693/\$ -} see front matter @ 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2008.10.002



Scheme 1. H₂L.

2.3. Synthesis

2.3.1. N-[2-(2-Hydroxybenzylideneamino)ethyl]-4-methyl-benzenesulfonamide (**H**₂L)

The Schiff base ligand **H**₂**L** was obtained by refluxing the ethanol solution (60 mL) of N-tosyl-ethylenediamine (2.14 g, 0.01 mol) and salicylaldehyde (1.22 g, 0.01 mol). Yellow needle crystals were collected from the solution. M.p. 123.6–124.4 °C. *Anal.* Calc. for C₁₆H₁₈N₂O₃S: C, 60.38; H, 5.660; N, 8.805. Found: C, 60.52; H, 5.487; N, 8.595%.

2.3.2. [Cu(HL)2] (1)

To a THF solution (20 mL) of H_2L (0.318 g, 1 mmol), Cu(CH₃₋COO)₂ · H₂O (0.20 g, 1 mmol) was added slowly. The mixture was stirred for 2 h and the resulting green powder was filtrated and redissolved in DMF. Brown column crystals were obtained after one month. *Anal.* Calc. for C₃₂H₃₄N₄O₆S₂Cu: C, 55.01; H, 4.871; N, 9.169. Found: C, 55.43; H, 4.717; N, 9.306%.

Table 1

Crystal data and structure refinements for complexes 1-3.

Identification code	1	2	3
Empirical formula	C32H34N4O6S2Cu	C32H34N4O6S2Ni	C32H35N4O7S2Zn
Formula weight	698.29	693.46	717.13
Temperature (K)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	orthorhombic
Space group	ΡĪ	P2(1)/c	Pbcn
Unit cell dimensions			
a (Å)	7.6332(8)	16.832(4)	11.1950(18)
b (Å)	10.1629(11)	5.2417(13)	9.9744(16)
<i>c</i> (Å)	10.5240(11)	19.415(5)	29.520(5)
α (°)	94.172(2)	90	90
β(°)	102.5190(10)	111.717(4)	90
γ(°)	99.504(2)	90	90
V (Å ³)	781.04(14)	1591.4(7)	3296.3(9)
Ζ	1	2	9
$D_{\text{calc.}}$ (Mg/m ³)	1.485	1.447	1.445
Absorption coefficient (mm ⁻¹)	0.884	0.791	0.925
F(000)	363	724	1492
Crystal size (mm)	$0.37 \times 0.25 \times 0.20$	$0.38 \times 0.28 \times 0.14$	0.42 imes 0.36 imes 0.20
θ Range for data collection (°)	1.99-25.10	2.15-25.09	2.28-25.10
Limiting indices	$-9 \leqslant h \leqslant 8$	$-20\leqslant h\leqslant 20$	$-13 \leqslant h \leqslant 9$
	$-9 \leqslant k \leqslant 12$	$-5 \leqslant k \leqslant 6$	$-11 \leqslant k \leqslant 11$
	$-12 \leqslant l \leqslant 9$	$-23 \leqslant l \leqslant 21$	$-32 \leqslant l \leqslant 35$
Reflections collected	3969	7418	15287
Independent reflections (R _{int})	2718 (0.0380)	2814 (0.0385)	2933 (0.0325)
Maximum and	0.8773 and	0.8959 and	0.8388 and
minimum transmission	0.7657	0.7536	0.6997
Data/restraints/ parameters	2718/0/205	2814/0/194	2933/1/184
Goodness-of-fit on F^2	1.002	1.003	1.034
R_1 , $wR_2 [I > 2\delta(I)]$	0.0476, 0.1143	0.0415, 0.1166	0.0364, 0.1139
R_1 , wR_2 (all data)	0.0731, 0.1263	0.0542, 0.1273	0.0475, 0.1209
$ ho_{ m fin}(m max/min)$ (e Å ⁻³)	0.345/-0.439	0.448/-0.613	0.433/-0.373

2.3.3. [Ni(HL)₂] (2)

To an ethanol solution (25 mL) of H_2L (0.318 g, 1 mmol), NiCl₂ · 6H₂O (0.238 g, 1 mmol) was added as solid slowly. Large amount brown-green precipitation was produced and then filtered. It was collected and washed with ethanol, then redissolved in DMF. Brown-green column crystals were obtained from the filtrate after a week. *Anal.* Calc. for C₃₂H₃₄N₄O₆S₂Ni: C, 55.42; H, 4.940; N, 8.080. Found: C, 55.66; H, 4.835; N, 8.118%.

2.3.4. [Zn(**HL**)₂] · H₂O (**3**)

To a methanol solution (30 mL) of H_2L (0.16 g, 0.5 mmol), 10 mg of tetraethylammonium perchlorate was added as supporting electrolyte. The solution was electrolyzed using a platinum wire as the cathode and Zn plate as the sacrificial anode according to the literature method [13,14,18]. The light yellow precipitation was collected and washed with hot ethanol. It was redissolved in DMF. Yellow block crystals were obtained from the filtrate after two weeks. *Anal.* Calc. for C₃₂H₃₆N₄O₇S₂Zn: C, 37.35; H, 6.730; N, 14.53. Found: C, 37.53; H, 6.640; N, 14.17%.

2.4. Single-crystal X-ray diffraction studies

The crystal determination was performed at room temperature on a Brucker-Smart APEX CCD diffractometer, using graphite monochromated Mo K α radiation (λ = 0.71073 Å). Absorption corrections were made using the sADABS program [24]. The structures were solved by direct methods and refined by full-matrix least squares based on F^2 , using SHELX-97 software [25]. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model except those bonded to the water molecule. The crystal data, experimental details, refinement results and details of structure determinations are shown in Table 1. Selected bond lengths and bond angles are listed in Table S1.

3. Results and discussion

3.1. Crystal structures of $[Cu(HL)_2]$ (1) and $[Ni(HL)_2]$ (2)

The molecular structure of complexes **1** and **2** is presented in Fig. 1. The Cu(II) and Ni(II) ions are tetra-coordinated by the imine nitrogen atoms and phenolate oxygen atoms of two bidentate anionic Schiff base ligands. The $M-N_{imine}$ distance is much longer than $M-O_{phenolate}$ distance in both complexes. The coordination



Fig. 1. Molecular structure of complexes 1 and 2 (H atoms omitted for clarity) (M = Cu(II) and Ni(II) for 1 and 2).



Fig. 2. 1-D chain structure of complex 1 (a) and 2-D layer structure of complex 2 (b).

geometry around Cu(II) and Ni(II) ion is a slightly distorted square planar with the *cis* angles of 92.15(13)° and 87.85(13)° for **1**, and 87.0(10)° and 93.0(10)° for **2**, respectively. Each ligand forms one M–O1–C2–C1–C7–N1 six-membered chelate ring (deviation 0.08 and 0.03 Å for **1** and **2**), and the metal lies deviating from this calculated plane with +0.13 and -0.05 Å for **1** and **2**, respectively. The deviation value of **2** is much small than that of **1**, which may be explained as the larger crystal field stabilization energy (CFSE) of d⁸ configuration of Ni²⁺.

Although complexes **1** and **2** have almost the same coordination geometry, the different electron configuration of Cu²⁺ and Ni²⁺, leads to the much different crystal packing of two complexes. Complex **1** is extended into the final 1-D chain supramolecular structure as shown in Fig. 2a, through weak aromatic π - π stacking interactions between phenyl rings from adjacent organic ligands, with a centre-to-centre distance of about 4.0 Å. In the structure of complex **2**, intermolecular N_{amide}-H···O_{tosyl} hydrogen bond (N···O 2.9345(3) Å) links the molecules into a 1-D chain along the *c*-axis direction (Fig. S1). Then, two weak C6–H6··· π interactions (C···centroid 3.60 Å), link the chains into a 2-D layer structure on *ac* plane (Fig. 2b).

3.2. Crystal structure of $[Zn(HL)_2] \cdot H_2O(3)$

Complex **3** consists of a neutral coordination unit $Zn(HL)_2$ and a solvated water molecule (Fig. 3a). The coordination sphere around Zn(II) is completed by the imine nitrogen and deprotonated phenol oxygen of two anionic Schiff base ligands. Zn(II) is in a [ZnN2O2] distorted tetrahedron with the dihedral angle between both N–Zn–O plane of 73.2°. The Zn^{2+} is about -0.29 Å below the calculated plane of Zn10101AN1N1A (deviation +0.79 Å). The bond angles are in the range 94.91(8)–123.89(13)° deviating from the ideal values. The Zn–O $O_{phenolate}$ distance is shorter than Zn–N_{imine} distance.

When viewed from *bc* plane (Fig. S2), weak intermolecular C3– H3···O_{tosyl} hydrogen bonds (C···O 3.428(3) Å) link the molecules into a 1-D chain. Then, two weak C16–H16··· π interactions (C···centroid 3.989(5) Å), one as donor and one as acceptor, link the 1-D chains into a 2-D layer. And the 1-D chains in the layer are packed in the ABAB alternated mode. Then, the solvated water molecules lies in the net by O4–H4B···O_{tosyl} hydrogen bonds (O···O 3.039(6) Å) (Fig. S2). Further, when viewed from *ab* plane (Fig. S3), each [Zn(**HL**)₂] molecule forms four N_{amide}–H···O_{phenolate} intermolecular hydrogen bonds (N···O 2.822(3) Å), forming a 2-D



Fig. 3. (a) Molecular structure of complex **3** (solvated water and H atoms omitted for clarity). (b) 3-D supramolecular structure of complex **3**.

hydrogen bonded (4,4) network. Moreover, each $[Zn(HL)_2]$ molecule also generates four C7–H7… π interactions (C…centroid 3.863(3) Å), which help to stabilize the 2-D network along the *ab* plane (Fig. S4). Finally, all the complex weak interactions link the molecules of **3** into a 3-D supramolecular network (Fig. 3b).

3.3. XRPD and FT-IR spectra

As shown in Fig. S5, complexes **1–3** were characterized *via* X-ray powder diffraction (XRPD) at room temperature. The XRPD pattern measured for the complexes are in good agreement with the results simulated from the single-crystal X-ray data using MERCURY 1.4.2 program, indicating that the compounds were isolated as a single phase.

In the IR spectrum of free ligand **H**₂**L**, the v(O–H) and v(N–H) are at 3439 and 3225 cm⁻¹ (Fig. S6). But complexes **1** and **2** show the absence of the v(O–H) and the presence of the v(N–H), indicating only the deprotonation of O–H group in the coordination complexes. For complex **3**, the band at 3426 cm⁻¹ shows the presence

of the solvated water molecule and the band at 3066 cm⁻¹ indicates the uncoordination mode of the amide N–H. And complexes **1–3** show a negative shift of the N–H band relative to the free ligand. This may be caused by the formation of N–H…O hydrogen bonds. Moreover, the bands at about 1617 cm⁻¹ for **1** and **2**, and 1610 cm⁻¹ for **3** are attributed to v(C=N), showing a lower frequency shift of 15 and 22 cm⁻¹ compared with the free ligand at 1632 cm⁻¹. This suggests the coordination of the ligand to the metals through the imine nitrogen atoms. In addition, two bands at about 1151 and 1320 cm⁻¹ are attributable to the asymmetric and symmetric vibration modes of SO₂ group, respectively [26].

3.4. UV-Vis absorption and fluorescence studies

The UV–Vis absorption spectra of the ligand in ethanol, complex **1**, **2** and **3** in DMF were given in Fig. 4. The absorption band at 359 nm for free ligand shift to 364, 405 and 365 nm in complexes **1**, **2** and **3**, respectively. The red shift indicates the coordination of C=N to the metal. The band at 321 nm for ligand still appears in complex **2** but disappear in complexes **1** and **3**. These bands in the UV wavelength region can be assigned to the intraligand $\pi \rightarrow \pi^*$ transition of C=N group. Moreover, there exist weak d–d transition at about 599 nm for complex **1**, and about 653 and 767 nm for complex **2**. However, complex **3** has no bands in the visible range because of the d¹⁰ configuration of Zn²⁺.

Solid state fluorescence spectra show that the ligand and the complexes have the similar excitation at 212 nm and emission at 361 nm at room temperature (Fig. S7). The only difference is that the chelation of the metal ion to HL⁻ decrease the fluorescence intensity of the complexes comparing with the ligand.

The solution fluorescence properties of the ligand and its complexes **1**, **2** were studied at room temperature in DMF solutions $(10^{-4} \text{ mol } \text{L}^{-1})$ (Fig. 5). The emission spectra of the ligand $(\lambda = 443 \text{ nm})$ and complex **3** $(\lambda = 451 \text{ nm})$ are similar, but the excitation of complex **3** $(\lambda = 309 \text{ nm})$ is strong red-shifted compared to the ligand $(\lambda = 249 \text{ nm})$. This may be explained that the electron density of C=N group is decreased when the metal coordinating to the ligand. It also can be seen that the emission intensity of complex **3** is much stronger than that of the ligand. This is in general called as chelation enhanced fluorescence intensity. However, complex **2** shows a fluorescence quenching in solution. For fluorescence character of the complexes in the solid and the solution, no emission can be assigned to the MLCT or LMCT transition. Thus, the emission of the complexes and the ligand can be assigned to intraligand $\pi \rightarrow \pi^*$ fluorescence [27,28].



Fig. 4. UV–Vis spectra of H₂L and complexes 1–3.



Fig. 5. Solution fluorescence spectra of $H_2L,\ \mbox{complexes}\ 2$ and 3 at room temperature.

3.5. Thermogravimetric analysis

The TG/DSC curves are provided in Fig. S8. The TG curves of complexes **1** and **2** show almost one stage weight loss corresponding to the decomposition of the ligand. And the residue is NiO (exptl. 10.78%, calc. 10.65%) for complex **2**. Complex **3** lose the solvated water at the temperature of about 20–300 °C. Then the ligand decomposition takes place and the TG curve shows a rapidly weight loss at about 350 °C. The residue should be ZnO (exptl. 10.82%, calc. 11.35%).

4. Conclusion

In this paper, we have reported the synthesis, crystal structure and characterization of three novel metal–organic coordination complexes with sulfonamide Schiff base ligands. The potentially tridentate Schiff base acts as bidentate ligand in the three complexes because of the presence of the tosyl group. The hydrogen bonds, weak C–H··· π and π ··· π interactions in the crystals link the similar coordination unit to form 1-D, 2-D and 3-D supramolecular structures.

Acknowledgement

We thank the National Natural Science Foundation of China (Nos. 20801033 and 20871079).

Appendix A. Supplementary material

CCDC 694915, 694916 and 694917 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.10.002.

References

- [1] A.D. Garnovskii, A.L. Nivorozhkin, V.I. Minkin, Coord. Chem. Rev. 126 (1993) 1.
- [2] V. Alexande, Chem. Rev. 95 (1995) 273.
- [3] S. Yamada, Chem. Rev. 190–192 (1999) 537.
- [4] M. Lanznaster, A. Neves, A.J. Bortoluzzi, A.M.C. Assumpcao, I. Vencato, S.P. Machado, S.M. Drechsel, Inorg. Chem. 45 (2006) 1005.
- [5] T. Ueno, T. Koshiyama, M. Ohashi, K. Kondo, M. Kono, A. Suzuki, T. Yamane, Y. Watanabe, J. Am. Chem. Soc. 127 (2005) 6556.
- [6] T. Ueno, T. Koshiyama, S. Abe, N. Yokoi, M. Ohashi, H. Nakajima, Y. Watanabe, J. Organomet. Chem. 692 (2007) 142.
- [7] K.C. Gupta, A.K. Sutar, Coord. Chem. Rev. 252 (2008) 1420.
- [8] N.S. Venkataramanan, G. Kuppuraj, S. Rajagopal, Coord. Chem. Rev. 249 (2005) 1249.
- [9] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189.
- [10] M. Calligaris, G. Nardin, L. Randaccio, Coord. Chem. Rev. 7 (1972) 385.
- [11] D.J. Darensbourg, R.M. Mackiewicz, A.L. Phelps, D.R. Billodeaux, Acc. Chem.
- Res. 37 (2004) 836. [12] H. Miyasaka, A. Saitoh, S. Abe, Coord. Chem. Rev. 251 (2007) 2622.
- [12] H. Miyasaka, A. Saroh, S. Abe, Coord. Circlin. Rev. 231 (2007) 2022.[13] M. Bernal, J.A. García-Vázquez, J. Romero, C. Gómez, M.L. Durán, A. Sousa, A.
- Sousa-Pedrares, D.J. Rose, K.P. Maresca, J. Zubieta, Inorg. Chim. Acta 295 (1999) 39.
- [14] A.M. García-Deibe, J.S. Matalobos, M. Fondo, M. Vázquez, M.R. Bermejo, Inorg. Chim. Acta 357 (2004) 2561.
- [15] J. Mahia, M.A. Maestro, M. Vázquez, M.R. Bermejo, A.M. Gonzalez, M. Maneiro, Acta Crystallogr., Sect. C 56 (2000) 347.
- [16] J. Mahia, M.A. Maestro, M. Vázquez, M.R. Bermejo, J. Sanmartín, M. Maneiro, Acta Crystallogr., Sect. C 55 (1999) 1545.
- [17] J. Mahia, M.A. Maestro, M. Vàzquez, M.R. Bermejo, A.M. Gonzalez, M. Maneiro, Acta Crystallogr., Sect. C 56 (2000) m492.
- [18] J. Sanmartín, A.M. García-Deibe, M. Fondo, F. Novio, N. Ocampo, M.R. Bermejo, Inorg. Chim. Acta 359 (2006) 3156.
- [19] L. Rodríguez, E. Labisbal, A. Sousa-Pedrares, J. Romero, J.A. García-Vázquez, A. Sousa, Z. Anorg. Allg. Chem. 633 (2007) 1832.
- [20] E. Labisbal, L. Rodriguez, A. Vizoso, M. Alonso, J. Romero, J.A. García-Vázquez, A. Sousa- Pedrares, A. Sousa, Z. Anorg. Allg. Chem. 631 (2005) 2107.
- [21] H.-W. Yang, Y.-Z. Li, X. Pan, J.-T. Sun, C.-J. Zhu, Acta Crystallogr., Sect. E 62 (2006) 01982.
- [22] E. Labisbal, L. Rodríguez, A. Sousa-Pedrares, M. Alonso, A. Vizoso, J. Romero, J.A. García-Vázquez, A. Sousa, J. Organomet, Chem. 691 (2006) 1321.
- [23] M.T. Barros, F. Sineriz, Tetrahedron 56 (2000) 4759.
- [24] G.M. Sheldrick, SADABS, Program for Area Detector Adsorption Correction, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.
- [25] G.M. Sheldrick, SHEIXL 97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [26] K. Nakamoto, Translated by Deru Huang, Renging Wang, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd ed., Chemical Industry Press, Beijing, 1986.
- [27] G. Yu, S.-W. Yin, Y.-Q. Liu, Z. Shuai, D. Zhu, Inorga. Chim. Acta 359 (2006) 2246.
- [28] S. Basak, S. Sen, C. Marschner, J. Baumgartner, S.R. Batten, D.R. Turner, S. Mitra, Polyhedron 27 (2008) 1193.