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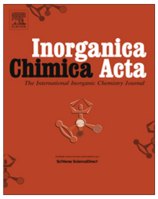

Eight coordination compounds based on a reduced Schiff base tetraaminodiphenol macrocyclic ligand

Ying-Ying Liu [a,b], Jie Liu [a], Jin Yang [a], Bo Liu [b], Jian-Fang Ma [a,*]

[a] *Key Laboratory of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, China*
[b] *Key Laboratory of Preparation and Applications of Environmental Friendly Materials, Ministry of Education, Department of Chemistry, Siping 136000, China*

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ABSTRACT

Eight new compounds, namely, $[Cu_2(L)]\cdot 2NO_3\cdot H_2O$ (**1**), $[Cu(ox)_2]\cdot 0.5(H_6L)\cdot 3H_2O$ (**2**), $[Zn(L)_{0.5}(nds)_{0.5}]$ (**3**), $[Zn_4(L)_2(m\text{-bdc})_2]\cdot 0.5H_2O$ (**4**), $[Cd(L)_{0.5}(ox)_{0.5}(H_2O)]\cdot MeOH\cdot 1.25H_2O$ (**5**), $[Cd(L)_{0.5}(H_2O)_3]\cdot 0.5(p\text{-bdc})\cdot 1.5H_2O$ (**6**), $[Cd_2(L)(btec)_{0.5}(H_2O)_4]\cdot 2.5MeOH\cdot H_2O$ (**7**) and $[Ni_2(L)(btec)_{0.5}(H_2O)]\cdot MeOH\cdot 1.5H_2O$ (**8**) (H_2L = 10,21-dimethyl-3,6,14,17-tetraazatricyclo [17.3.18,12]tetracosa-1(23),8,10,12(24),19,21-hexaene-23,24-diolate, ox = oxalate, nds = 1,5-naphthalenedisulfonate, *m*-bdc = 1,3-benzenedicarboxylate, *p*-bdc = 1,4-benzenedicarboxylate and btec = 1,2,4,5-benzenetetracarboxylate), have been synthesized. In compound **1**, the L ligand coordinates with two Cu(II) atoms to form a $[Cu_2L]^{2+}$ unit. In compound **2**, two ox anions chelate to one Cu(II) atom to form a $[Cu(ox)_2]^{2-}$ unit. The $(H_6L)^{4+}$ acts as a counter ion. The whole structures of **1** and **2** feature three-dimensional (3D) supramolecular architectures connected by weak $Cu\cdots O$ and hydrogen-bonding interactions, respectively. In compounds **3**–**5**, the $[M_2L]^{2+}$ cations are bridged by nds, *m*-bdc and ox anions to form chains, respectively. The chains of **3** and **4** are further linked by hydrogen-bonding interactions into 2D and 3D supramolecular architectures, respectively. In compound **6**, the macrocyclic L anion coordinates to two Cd(II) atoms to form a $[Cd_2L]^{2+}$ cation. The final structure of **6** exhibits a 3D supramolecular architecture linked by hydrogen bonds. In compound **7**, Cd(II) atoms are linked by L anions to form two types of $[Cd_2L]^{2+}$ cations. One type of $[Cd_2L]^{2+}$ cations are bridged by btec anions to generate a polymeric anion chain, whereas the other $[Cd_2L]^{2+}$ cations are free. Further, the polymeric anion chains and the $[Cd_2L]^{2+}$ cations are linked by hydrogen bonds to generate a 2D supramolecular layer. In compound **8**, btec anion bridges the $[Ni_2L]^{2+}$ cations to yield a 2D layer. Thermogravimetric analyses (TGA) for the compounds **1**–**8** have been investigated. In addition, the magnetic property for **1** and the luminescent properties for compounds **3**–**7** have also been studied.

1. Introduction

Schiff base Robson-type macrocycles with additional ligating units, namely, phenoxy oxygen atoms as well as amine nitrogen atoms have potential applications and special coordination abilities with transition metal ions [1]. For this reason, many efforts have been devoted to the design and synthesis of Robson-type macrocycles and their metal complexes [2]. The synthesis of Robson-type macrocyclic ligand is normally achieved by a template Schiff-base condensation of 4-substituted-2,6-diformyl phenols and diamines. Recently, some attention has been focused on the reduced Schiff base macrocycles [3]. Interesting studies in this regard have been reported by Nag [3a–3g] and Martell [3i–3k], who have found that complexes exhibit different coordination properties from corresponding metal ions and amine forms. Besides, the polysulfonate or polycarboxylate anions have significant effects on the structures of coordination compounds. These acids not only display various coordination modes for the large diversity of structures, resulting from completely or partially deprotonated site, but also they can act as hydrogen bond acceptors and donors to assemble intriguing supramolecular architectures [4].

The tetrazamacrocycle ligand H_2L (10,21-dimethyl-3,6,14,17-tetraazatricyclo[17.3.18,12]tetracosa-1(23),8,10,12(24),19,21-hexaene-23,24-diolate, Scheme 1), derived from [2+2] condensation of 4-methyl-2,6-diformylphen with ethylenediamine followed by hydrogenation with $NaBH_4$, is an 18-membered asymmetric macrocycle, of which the coordination hemisphere includes four aliphatic amine groups as well as two phenolic groups. Several complexes based on H_2L ligand with different metal ions and inorganic anions have been reported [5a–5d]. As far as we know, coordination compounds constructed from H_2L in the presence of organic anions have been scarcely investigated so far [5e]. In this work, eight coordination compounds based on the H_2L macrocycle ligand have been synthesized, namely, $[Cu_2(L)]\cdot 2NO_3\cdot H_2O$ (**1**), $[Cu(ox)_2]\cdot 0.5(H_6L)\cdot 3H_2O$ (**2**, $[Zn(L)_{0.5}(nds)_{0.5}]$ (**3**), $[Zn_4(L)_2(m\text{-bdc})_2]\cdot$

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* Corresponding author. Fax: +86 431 85098620.
E-mail address: jianfangma@yahoo.com.cn (J.-F. Ma).

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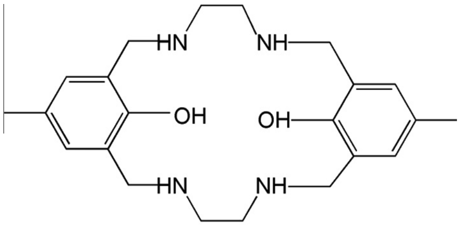

H_2L

Scheme 1. Structure of the macrocyclic ligand H_2L.

$0.5H_2O$ (**4**), $[Cd(L)_{0.5}(ox)_{0.5}(H_2O)]\cdot MeOH\cdot 1.25H_2O$ (**5**), $[Cd(L)_{0.5}(H_2O)_3]\cdot 0.5(p\text{-bdc})\cdot 1.5H_2O$ (**6**), $[Cd_2(L)(btec)_{0.5}(H_2O)_4]\cdot 2.5MeOH\cdot H_2O$ (**7**) and $[Ni_2(L)(btec)_{0.5}(H_2O)]\cdot MeOH\cdot 1.5H_2O$ (**8**) (ox = oxalate, nds = 1,5-naphthalenedisulfonate, *m*-bdc = 1,3-benzenedicarboxylate, *p*-bdc = 1,4-benzenedicarboxylate and btec = 1,2,4,5-benzenetetracarboxylate). The magnetic property for **1** and the luminescent properties for compounds **3–7** have also been studied in the solid state at room temperature.

2. Experimental

2.1. Materials

All reagents and solvents for syntheses were purchased from commercial sources and used as received. The ligand H_2L was synthesized as previously reported method [6].

2.2. General procedures

The C, H and N elemental analysis was conducted on a Perkin-Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Powder X-ray diffraction (XRD) patterns of the samples were collected on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 0.154$ nm) and 2θ ranging from 5° to 35°. The experimental powder XRD patterns are in good agreement with the corresponding simulated ones except for the relative intensity variation because of preferred orientations of the crystals. Therefore, the phase purity of the as-synthesized products is substantiated (Fig. S1 in the Supplementary Data). TGA was performed on a Perkin–Elmer TG-7 analyzer heated from room temperature to 600 °C under nitrogen gas. Temperature-dependent magnetic susceptibility data for polycrystalline compound **1** were obtained on a Quantum Design MPMSXL SQUID magnetometer under an applied field of 1000 Oe over the temperature range of 2–300 K. The photoluminescent data were measured on a FLSP920 Edinburgh Fluorescence Spectrometer.

2.3. Synthesis

2.3.1. Synthesis of $[Cu_2(L)]\cdot 2NO_3\cdot H_2O$ (1)

A mixture of H_2L (0.010 g, 0.026 mmol) in methanol (5 mL) and $Cu(NO_3)_2\cdot 3H_2O$ (0.063 g, 0.026 mmol) in distilled water (5 mL) was stirred for 10 min. The resulting solution was filtered. After one week at room temperature, the red crystals formed were collected, washed with water and methanol and dried in air. The crystals were obtained in a 60% yield. *Anal.* Calc. for $C_{22}H_{32}Cu_2N_6O_9$ ($M_r = 651.62$): C, 40.55; H, 4.95; N, 12.90. Found: C, 40.64; H, 4.83; N, 12.83%. IR data (KBr, cm^{-1}): 3423 (s), 3213 (s), 2920 (m), 2411 (w), 1610 (w), 1471 (s), 1386 (s), 1306 (s), 1255 (s), 1065 (m), 1012 (m), 927 (m), 858 (m), 805 (m), 752 (w), 681 (w), 596 (w).

2.3.2. Synthesis of $[Cu(ox)_2]\cdot 0.5(H_6L)\cdot 3H_2O$ (2)

$CuCl_2\cdot 3H_2O$ (0.049 g, 0.23 mmol) and H_2L (0.010 g, 0.026 mmol) were dissolved in 5 mL of methanol and placed in a 25 mL screw-capped tube. A mixture of 1:2 water/MeOH (5 mL) was applied as a buffer layer, and a water solution (5 mL) of H_2ox (0.029 g, 0.23 mmol) and NaOH (0.020 g, 0.5 mmol) was layered on top. Blue block crystals were obtained at the interface after one month in a 40% yield. *Anal.* Calc. for $C_{30}H_{44}Cu_2N_4O_{24}$ ($M_r = 971.77$): C, 37.08; H, 4.56; N, 5.77. Found: C, 37.14; H, 4.67; N, 5.85%. IR data (KBr, cm^{-1}): 3392 (s), 3172 (s), 2911 (s), 2683 (w), 1590 (s), 1470 (s), 1373 (m), 1343 (s), 1257 (s), 1162 (w), 1064 (m), 1018 (m), 972 (w), 864 (w), 804 (m), 762 (m), 680 (w), 596 (w).

2.3.3. Synthesis of $[Zn(L)_{0.5}(nds)_{0.5}]$ (3)

A mixture of $Zn(OAc)_2\cdot 2H_2O$ (0.050 g, 0.25 mmol), H_2L (0.050 g, 0.13 mmol), NaOH (0.020 g, 0.50 mmol), 1,5-$Na_2nds\cdot 2H_2O$ (0.049 g, 0.15 mmol) in *N,N′*-dimethylformamide (18 mL) was kept at 80 °C

Table 1
Crystal data and structure refinements for compounds **1–8**.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Formula	$C_{22}H_{32}Cu_2N_6O_9$	$C_{30}H_{48}Cu_2N_4O_{24}$	$C_{16}H_{18}ZnN_2O_4S$	$C_{60}H_{69}Zn_4N_8O_{12..50}$	$C_{13}H_{23.5}CdN_2O_{6.25}$	$C_{30}H_{52}Cd_2N_4O_{15}$	$C_{29.5}H_{51}Cd_2N_4O_{13.5}$	$C_{28}H_{40}Ni_2N_4O_{9.5}$
Formula weight	651.62	975.80	399.75	1363.71	420.24	933.56	902.54	702.06
Space group	$P2_1/c$	$P\bar{1}$	*Pbca*	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.753(4)	10.049(1)	16.739(2)	10.220(3)	11.094(2)	10.290(5)	11.848(4)	10.336(4)
b (Å)	14.752(5)	10.853(1)	9.557(4)	17.019(7)	13.237(3)	10.551(6)	11.980(4)	12.175(6)
c (Å)	13.844(3)	11.194(1)	20.295(4)	18.574(6)	15.332(3)	10.573(7)	16.172(5)	12.760(5)
α (deg.)	90	117.721(2)	90	70.492(13)	90	61.81(3)	70.674(4)	97.378(16)
β (deg.)	110.100(5)	102.109(2)	90	83.894(10)	100.022(3)	80.96(3)	77.724(5)	105.934(14)
γ (deg.)	90	102.6000(10)	90	74.857(12)	90	73.06(2)	74.770(4)	98.935(18)
V (Å^3)	2637.7(13)	2938.8(17)	983.86(19)	3246.7(16)	2217.2(8)	967.6(10)	2070.0(10)	1500.4(11)
Z	4	1	8	2	4	1	2	2
D_{calc} (g cm^{-3})	1.641	1.647	1.636	1.541	1.259	1.602	1.448	1.554
$F(000)$	1344	506	1648	1410	854	476	920	736
Observed reflection/unique	15814/6129	6042/4371	29462/3699	28406/12975	13257/5163	9494/4393	11145/7661	14826/6757
R_{int}	0.0273	0.0137	0.0868	0.0558	0.0222	0.0207	0.0279	0.0551
Goodness-of-fit (GOF) on F^2	1.019	1.150	1.052	1.027	1.033	1.073	0.982	1.034
R_1, wR_2 [$I > 2\sigma(I)$]	0.0333, 0.0788	0.0448, 0.1362	0.0423, 0.0890	0.0535, 0.1029	0.0461, 0.1414	0.0299, 0.0773	0.0598, 0.1589	0.0498, 0.1154
R_1, wR_2 (all data)	0.0527, 0.0868	0.0546, 0.1424	0.0692, 0.0976	0.1033, 0.1202	0.0606, 0.1547	0.0326, 0.0785	0.1055, 0.1870	0.0777, 0.1294