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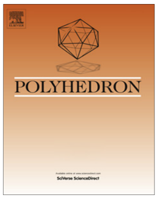

Syntheses, crystal structures and spectroscopy of di/tri/tetranuclear discrete and co-crystalline copper(II)–Na^I/Zn^{II}/Cd^{II} complexes derived from a compartmental ligand: Inconsistency in the shifting of the copper(II) d–d band

Sagarika Bhattacharya, Arpita Jana, Sasankasekhar Mohanta *

Department of Chemistry, University of Calcutta, 92 A.P.C. Road, Kolkata 700 009, India

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The work in this report presents the syntheses, characterization, crystal structures and electronic spectra of the six heteronuclear complexes $[Cu^{II}L^1Na^I(\mu\text{-}BF_4)_2Na^IL^1Cu^{II}]\cdot 2CH_3COCH_3$ (**1**), $[Cu^{II}L^1Na^I(NO_3)(MeOH)]$ (**2**), $[Cu^{II}L^1Zn^{II}(H_2O)_2L^1Cu^{II}](ClO_4)_2$ (**3**), $[Cu^{II}(MeOH)L^1Zn^{II}Cl_2]$ (**4**), $[Cu^{II}L^1Cd^{II}(H_2O)(MeOH)_2](ClO_4)_2$ (**5**) and $[Cu^{II}L^1Cd^{II}Cl_2(MeOH)]\cdot[Cu^{II}(MeOH)L^1Cd^{II}Cl_2]$ (**6**), where H_2L^1 is *N*,*N′*-ethylenebis(3-methoxysalicylaldimine). The crystal systems and space groups are as follows: **1** and **2**, triclinic, $P\bar{1}$; **3** and **6**, monoclinic, $P2_1/c$; **4**, orthorhombic, $P2_12_12_1$; **5**, monoclinic, $C2/c$. While the $N(imine)_2O(phenoxo)_2$ compartment accommodates the copper(II) center, the larger and open $O(phenoxo)_2O(methoxy)_2$ compartment interacts with the second metal ion. Compounds **2**, **4** and **5** are diphenoxo-bridged dinuclear systems, compound **3** is a trinuclear system in which the two $Cu^{II}Zn^{II}$ pairs are monophenoxo-bridged, compound **1** is a tetranuclear system in which two diphenoxo-bridged $Cu^{II}Na^I$ units are interlinked by two tetrafluoroborate moieties, and compound **6** is a $[2\times1+2\times1]$ co-crystal of two dinuclear $Cu^{II}Cd^{II}$ units. The solid state electronic spectra of compounds **1**–**6** and also the mononuclear compound $[Cu^{II}L^1(H_2O)]$ have been recorded in the range 400–800 nm. While correlating the d–d band position with the structural parameters and a previously proposed correlation, some inconsistency has been found, indicating that this area should be explored further.

1. Introduction

Several coordination compounds derived from two very similar compartmental ligand systems, 3-methoxysalicylaldehyde-diamine (H_2L^{OMe}) [1–17] and 3-ethoxysalicylaldehyde-diamine (H_2L^{OEt}) [17–29], have been reported. We have experienced that these two ligand systems are among the best examples that show drastically different structural aspects as a result of only a slight modification in the periphery of the ligand environments [7,8,18–28]. The most stable mononuclear copper(II) compounds derived from the H_2L^{OEt} ligands are inclusion products, $[Cu^{II}L^{OEt}\subset(H_2O)]$, because one water molecule becomes encapsulated in the $O(phenoxo)_2O(ethoxy)_2$ compartment by forming four bifurcated hydrogen bonds [18–20]. In contrast, no such encapsulation takes place in the case of the only structurally characterized mononuclear copper(II) complex, $[Cu^{II}L^1(H_2O)]$, derived from the H_2L^{OMe} system (H_2L^1 = *N*,*N′*-ethylenebis(3-methoxysalicylaldimine); Scheme 1) [1,2]; in this case, a water molecule becomes coordinated to the metal center. Reactions of the mononuclear species $[Cu^{II}L^{OEt}\subset(H_2O)]$ with several metal salts produce systems including interesting examples of two-component co-crystals [17–28]. Most of these co-crystals are stabilized, as in the inclusion products, by four water$\cdots O_4$ bifurcated hydrogen bonds [17–28]. On the other hand, such co-crystallization or such a water$\cdots O_4$ interaction does not occur in the systems (except a single case [8]) obtained on reacting mononuclear copper(II) compounds derived from H_2L^{OMe} ligands with a variety of metal ions [3–17]. However, as a result of our continuous exploration, we have obtained one dinuclear$\cdots$mononuclear co-crystal, derived from a H_2L^{OMe} ligand, in which a water$\cdots O_4$ interaction takes place [8]. We therefore thought to further explore the coordination compounds obtained on reacting mononuclear systems derived from H_2L^{OMe} ligands with other metal ions.

As the water molecule in the above mentioned mononuclear compound $[Cu^{II}L^1(H_2O)]$ is coordinated, the coordination environment of the copper(II) center is distorted square pyramidal and, as usual, the copper(II) center is shifted from the $N(imine)_2O(phenoxo)_2$ plane towards the axial atom, by 0.198 Å [2]. On the other

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* Corresponding author. Tel.: +91 33 9433883751.
E-mail address: sm_cu_chem@yahoo.co.in (S. Mohanta).

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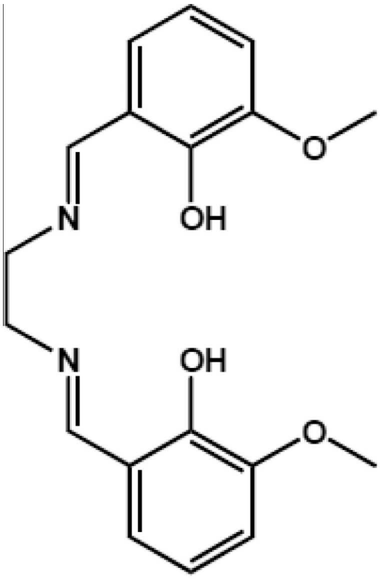

H_2L^1

Scheme 1. Chemical structure of the Schiff base ligand.

hand, in the previously reported products obtained from the reactions of [$Cu^{II}L^1(H_2O)$] with metal salts, the copper(II) centers coordinated with the N_2O_2 compartment adopt a distorted square planar geometry in most cases and a distorted square pyramidal geometry in some cases [3–17]. In any case, the displacement of the copper(II) center from the N_2O_2 plane will be different from that in the mononuclear complex. So, the copper(II)–second metal ion complexes may be very good systems to explore and correlate the shift of the d–d band position of copper(II) as a function of the displacement of the metal ion from the basal plane, if the second metal ion is diamagnetic. Such a spectroscopic concept has been proposed but not practically explored further [30,31].

With the above mentioned twofold aims, we have isolated six compounds on reacting [$Cu^{II}L^1(H_2O)$] with $NaBF_4$, $NaNO_3$,[1] $Zn(ClO_4)_2\cdot 6H_2O$, $ZnCl_2$, $Cd(ClO_4)_2\cdot xH_2O$ and $CdCl_2\cdot H_2O$. Herein, we report the syntheses, characterization, crystal structures and electronic spectroscopy of the six compounds obtained from those reactions.

2. Experimental

Caution! Perchlorate complexes of metal ions are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.

2.1. Materials and physical methods

All the reagents and solvents were purchased from commercial sources and were used as received. The mononuclear product [$Cu^{II}L^1(H_2O)$] was synthesized by the reported procedure [1,2]. Elemental (C, H and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. IR spectra were recorded in the region 400–4000 cm^{-1} on a Bruker-Optics Alpha–T spectrophotometer, with the samples as KBr disks. Diffuse reflectance spectra of the solid compounds were recorded with a Hitachi U-3501 UV–Vis–NIR spectrophotometer using its integrating sphere set up.

2.2. Syntheses

2.2.1. [$Cu^{II}L^1Na^I(\mu\text{-}BF_4)_2Na^IL^1Cu^{II}$]$\cdot 2CH_3COCH_3$ (**1**)

To a stirred acetone (5 mL) suspension of [$Cu^{II}L^1(H_2O)$] (0.102 g, 0.25 mmol), $NaBF_4$ (0.028 g, 0.25 mmol) in acetone solution (5 mL) was added dropwise. Immediately after addition, the suspension became clear and the color of the solution changed from green to red. It was stirred for 15 min, filtered to remove any suspended particles and kept at room temperature for slow evaporation. After 1–2 days, a red colored crystalline compound, containing single crystals suitable for X-ray diffraction, started to deposit. The compound was collected by filtration and washed with cold acetone. Yield: 0.105 g (75%). *Anal.* Calc. for $C_{42}H_{48}N_4O_{10}B_2F_8Cu_2Na_2$ (1115.52): C, 45.22; H, 4.34; N, 5.02. Found: C, 45.51; H, 4.16; N, 5.25%. FT-IR (cm^{-1}, KBr): 1708w [ν(acetone)], 1627vs [ν(C=N)], 1082s, 1030s [$\nu(BF_4)$].

2.2.2. [$Cu^{II}L^1Na^I(NO_3)(MeOH)$] (**2**)

This was prepared following the reported procedure[1].

2.2.3. [$Cu^{II}L^1Zn^{II}(H_2O)_2L^1Cu^{II}$]$(ClO_4)_2$ (**3**), [$Cu^{II}(MeOH)L^1Zn^{II}Cl_2$] (**4**), [$Cu^{II}L^1Cd^{II}(H_2O)(MeOH)_2$]$(ClO_4)_2$ (**5**) and [$Cu^{II}L^1Cd^{II}Cl_2(MeOH)$]$\cdot$[$Cu^{II}(MeOH)L^1Cd^{II}Cl_2$] (**6**)

These compounds were prepared by a similar method to that of **1**, by reacting [$Cu^{II}L^1(H_2O)$] in methanol solution with the appropriate second metal salt. The metal salts used are as follows: $Zn(ClO_4)_2\cdot 6H_2O$ for **3**, $ZnCl_2$ for **4**, $Cd(ClO_4)_2\cdot xH_2O$ for **5**, $CdCl_2\cdot H_2O$ for **6**.

Data for **3**: Yield: 0.107 g (79%). *Anal.* Calc. for $C_{36}H_{40}N_4O_{18}Cl_2Cu_2Zn$ (1080.12): C, 40.03; H, 3.73; N, 5.19. Found: C, 39.82; H, 3.48; N, 5.39%. FT-IR (cm^{-1}, KBr): 3398w [$\nu(H_2O)$], 1643vs [ν(C=N)], 1085vs, 624m [$\nu(ClO_4)$].

Data for **4**: Yield: 0.095 g (68%). *Anal.* Calc. for $C_{19}H_{22}N_2O_5Cl_2CuZn$ (558.23): C, 40.84; H, 3.97; N, 5.02. Found: C, 40.51; H, 3.76; N, 5.35%. FT-IR (cm^{-1}, KBr): 1630vs [ν(C=N)].

Data for **5**: Yield: 0.150 g (77%). *Anal.* Calc. for $C_{20}H_{28}N_2O_{15}Cl_2CuCd$ (783.31): C, 30.64; H, 3.60; N, 3.58. Found: C, 30.75; H, 3.82; N, 3.72%. FT-IR (cm^{-1}, KBr): 3422w [$\nu(H_2O)$], 1629s [ν(C=N)], 1082vs, 626m [$\nu(ClO_4)$].

Data for **6**: Yield: 0.120 g (79%). *Anal.* Calc. for $C_{19}H_{22}N_2O_5Cl_2CuCd$ (605.26): C, 37.67; H, 3.66; N, 4.63. Found: C, 37.52; H, 3.48; N, 4.39%. FT-IR (cm^{-1}, KBr): 1630vs [ν(C=N)].

2.3. Crystal structure determination of **1**–**6**

The crystallographic data of compounds **1** and **3**–**6** are summarized in Table 1, while that of **2** is summarized in Table S1. The diffraction data of **1**–**6** were collected on a Bruker APEX-II CCD diffractometer at 296 K with data collection and reduction using the Bruker APEX2 program packages and Bruker SAINT, respectively [32]. All the data were corrected for Lorentz-polarisation effects. Multi-scan absorption corrections were made for all the cases using the program SADABS [33]. The structures of **1**–**6** were solved by direct and Fourier methods using the SHELXTL-97 programs [34]. The structures were refined by full-matrix least-squares based on F^2 using SHELXL-97 [35].

During the development of the structures it became apparent that a few atoms in **2**, **3** and **6** were each disordered over two sites. The disordered atoms were two coordinated oxygen atoms O6 and O8 of the nitrate moiety in **2**, four oxygen atoms O6, O7, O8 and O9 of the perchlorate moiety in **3** and one carbon atom C38 of a meth-

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[1] The synthesis and structure of the compound [$Cu^{II}L^1Na^I(NO_3)(MeOH)$] (**2**) was published previously in Ref. [14]. However, we have re-prepared this compound for the purpose of electronic spectroscopic studies and it was characterized by single crystal X-ray structure determination. The re-determined structure of this compound is discussed here to compare it with other structures in this manuscript. Crystallographic information (Table S1), crystal structure (Fig. S1) and bond lengths and angles (Table S2) are shown/listed in the Supplementary Information.