Diaquadinitratouranyl(VI) enforces the O(phenoxo)₂O(methoxy)₂ compartment of 3-methoxysalicylaldehyde-diamine ligands to interact with water molecules

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Abstract

This report presents the syntheses, characterization and crystal structures of [{CuL₁₂} ᵃ [(U³O₂] [NO₃]₂ [H₂O]₂] (1), [{CuL₁₂} ᵃ [(U³O₂] [NO₃]₂ [H₂O]₂] 2H₂O (2) and [{CuL₁₂} ᵃ [(U³O₂] [NO₃]₂ [H₂O]₂] 2H₂O (3) derived from three 3-methoxysalicylaldehyde-diamine Schiff base compartmental ligands H₂L₁, H₂L₂ and H₂L₃, in which the diimine moieties come from ethylenediamine, trans-1,2-diaminocyclohexane and ortho-phenylenediamine, respectively. Compounds 2 and 3 crystallize in triclinic crystal system having P1 space group, while compound 1 crystallizes in monoclinic symmetry with space group P2₁/c. The three structures are similar. The two coordinated water molecules in diaquadinitratouranyl(VI) occupy the two trans positions in the hexagonal basal plane of the hexagonal bipyramidal coordination environment. Each of these two water molecules interact, by forming bifurcated hydrogen bonds, with each of the two O(phenoxo)₂O(methoxy)₂ compartments resulting in the stabilization of the [1 × 2 + 1 × 1] trimetallic self-assemblies. The d–d spectra of 1–3 and the corresponding mononuclear copper(II) complexes [CuL₁(H₂O)] [CuL₂(H₂O)] [CuL₃(H₂O)] have been recorded. The previously proposed but little addressed correlation of d–d band position with the displacement of the copper(II) center from the least-squares basal plane has been highlighted, revealing the utilization of this correlation accompanied with the FT-IR data to judge the nature of water molecule in the mononuclear complexes. The unique features in the composition of 1–3 have been discussed.

1. Introduction

The research area of crystal engineering has been extensively explored over the years in terms of the fundamental aspects of the synths and tectons and in terms of the designed syntheses of target aggregates that may have interesting structures or properties or both [1–20]. The individual organic or metallo-organic moieties may be self-assembled to discrete or polymeric topologies either by supramolecular interactions like strong and weak hydrogen bonds and π–π, S···S, metal···metal interactions, etc., or by covalent or coordinate bonds [1–20]. In spite of extensive developments, there are many aspects to be further explored. For example, the definition of some weak interactions is yet not straightforward and is under continuous development [1]. Again, it is yet difficult to predict the nature of aggregate in many cases, particularly for the systems containing metal complexes.

During the last few years we have been exploring the structures and properties of discrete and self-assembled metallo-organic systems derived from 3-ethoxysalicylaldehyde-diamine (H₃L₃) [21–34] and 3-methoxysalicylaldehyde-diamine (H₃L₄) [35–37] Schiff base ligands. While the two types of ligands look closely similar, the structural aspects of the metal compounds are drastically different in most cases. Several homo- and heteronuclear products have been reported so far on reacting mononuclear copper(II)|nickel(II) complexes of both H₃L₃ and H₃L₄ with salts of s-, p-, d- and f-block metal ions [21,22,45]. In the case of the H₃L₄ ligands [21–34], a number of those products are self-assemblies and some of these self-assemblies are stabilized due to bifurcated hydrogen bonds between the O(phenoxo)₂O(ethoxy)₂ compartment and the coordinated water molecules [21–23,25–34]. On the other hand, formation of self-assemblies or water...O(phenoxo)₂O(methoxy)₂ interaction occurs only seldom in the family of large number of homo/heteronuclear products derived from H₃L₄ ligands [12,35–45]. Such drastic difference between the two closely similar ligands looks surprising and therefore we have been continuously exploring this area with the aims including the stabilization of self-assemblies, in general, and systems having water...O₄ hydrogen...
bonds, in particular, derived from the $H_2O$ ligands. We have experienced the stabilization of self-assemblies on reacting mononuclear copper(II)/nickel(II) compounds with uranyl nitrate in the $H_2O$ family, where water $\cdot$ $O_4$ interactions take place [29,30]. To check whether uranyl nitrate will behave differently in comparison to the other second metal salts and thus whether water $\cdot$ $O_4$ interaction would take place in the products, we have now reacted three mononuclear copper(II) compounds, derived from three $H_2O$ ligands ($H_2L^1$, $H_2L^2$ and $H_2L^3$), with uranyl nitrate, where the diamine counterpart in the ligands are ethylenediamine, trans-1,2-diaminocyclohexane and ortho-phenylenediamine, respectively (Scheme 1). Herein we report the syntheses, characterization and crystal structures of the three copper(II)$\cdots$uranyl(VI) systems obtained therefrom, along with the d–d spectra of the three copper(II) precursors and the three copper(II)$\cdots$uranyl(VI) products.

2. Experimental

2.1. Materials and physical measurements

All the reagents and solvents were purchased from commercial sources and used as received. The mononuclear products $[CuL^1(H_2O)]$ [35,46], $[CuL^2(H_2O)]$ [36,37] and $[CuL^3(H_2O)]$ [37] were synthesized by the reported procedure. 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 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. $[CuL^1]_2[(UO_2)_{2}(NO_3)_{2}(H_2O)_2]$ (1), $[CuL^2]_2[(UO_2)_{2}(NO_3)_{2}(H_2O)_2]2H_2O (2)$ and $[CuL^3]_2[(UO_2)_{2}(NO_3)_{2}(H_2O)_2]2H_2O (3)$

To a stirred suspension of $[CuL^1(H_2O)][CuL^2(H_2O)][CuL^3(H_2O)]$ (0.102/0.116/0.114 g, 0.25 mmol) in acetonitrile (15 mL), uranyl nitrate hexahydrate (0.125 g, 0.25 mmol) in acetonitrile/acetone (5 mL) for 1 and 3/2 was added. After stirring for 20 mins, the red solution was filtered and the filtrate was kept at room temperature for slow evaporation. After a few days, green (1)/red (2 and 3) crystalline compound containing diffractable single crystals that deposited, were collected by filtration.

Data for 1: Yield: 0.120 g (78%). Anal. Calc. for $C_{36}H_{42}N_{10}$O$_{24}$U$_2$ (FW: 1209.86): C, 35.74; H, 3.33; N, 6.94. Found: C, 35.51; H, 3.16; N, 6.75%. FT-IR(cm$^{-1}$, KBr): $\nu$(H$_2$O), 3221m; $\nu$(C=O), 1640s; $\nu$(uranyl), 1384m and 1281s; $\nu$(uranyl), 945s.

Data for 2: Yield: 0.132 g (77%). Anal. Calc. for $C_{44}H_{56}N_{20}O_{22}$Cu$_2$U (FW: 1354.08): C, 38.99; H, 4.17; N, 6.21. Found: C, 38.75; H, 3.92; N, 6.02%. FT-IR(cm$^{-1}$, KBr): $\nu$(H$_2$O), 3355m; $\nu$(C=O), 1631vs; $\nu$(uranyl), 1385s and 1288m; $\nu$(uranyl), 946m.

Data for 3: Yield: 0.118 g (70%). Anal. Calc. for $C_{44}H_{56}N_{20}O_{22}$Cu$_2$U (FW: 1341.97): C, 39.38; H, 3.31; N, 6.26. Found: C, 39.52; H, 3.48; N, 6.39%. FT-IR(cm$^{-1}$, KBr): $\nu$(H$_2$O), 3216m; $\nu$(C=O), 1609vs; $\nu$(uranyl), 1385s and 1288m; $\nu$(uranyl), 937s.

2.3. Crystallographic studies

The crystallographic data of these three compounds are summarized in Table 1. Diffraction data of 1 was collected on a Bruker APEX-II CCD diffractometer at 296 K, while that of 2 and 3 were collected on a Bruker SMART diffractometer at 296 and 293 K, respectively. Data of 1–3 were processed with Bruker SAINT program packages [47]. The data were corrected for Lorentz-polarization effects. Multi-scan absorption correction were made for 1–3 using the program SADABS [47]. The structures of 1, 2 and 3 were solved by direct and Fourier methods using Bruker SHELXTL and SHELXS-97 programs [48], and refined by full-matrix least-squares based on $F^2$ using SHELXL-97 [49]. In 2 the cyclohexyl group of the diimine moiety which sits astride a 2-fold rotation axis was found to be disordered over two positions, the sum of the occupancies of the two sets of water molecules for each of 1, KBr: $\nu$(U:O), 1384m and 1281s; $\nu$(C=O), 1385s and 1288m; $\nu$(C=O), 946m.

The crystal structures of 1–3 are shown in Figs. 1–3, respectively. The structures of the three compounds are similar, each

![Scheme 1. Chemical structures of ligands.](image-url)
contain two mononuclear [Cu^{II}L][Cu^{II}L] moieties and one [UO_2(NO_3)_2(H_2O)_2] moiety. In 2 and 3 each, there are two water molecules as solvent of crystallization. Of the N(imine)_2O(phenoxo)_2 and O(phenoxo)_2O(methoxy)_2 compartments of one ligand, the former is occupied by the copper(II) center, while the later compartment interacts with one of the two coordinated water molecules in [UO_2(NO_3)_2(H_2O)_2], the second coordinated water molecule of which interacts with the O4 compartment of the second mononuclear [Cu^{II}L][Cu^{II}L] moiety; the type of interaction is bifurcated hydrogen bonds between each of the water hydrogen atoms and one phenoxo and one methoxy oxygen atoms. Clearly, two [Cu^{II}L][Cu^{II}L] moieties are self-assembled by the [UO_2(NO_3)_2(H_2O)_2] moiety through its two water molecules, which are situated almost linearly in the coordination environment of the uranium center. The self-assembly in 1–3 may be called as supramolecular dimeric of the two mononuclear [Cu^{II}L][Cu^{II}L] moieties by the [UO_2(NO_3)_2(H_2O)_2] moiety as the tecton. Again, as two mononuclear copper(II) and one mononuclear uranyl moieties are crystalized in a single crystal, these compounds are [1 × 2 + 1 × 1] trimetallic self-assemblies.

The geometries of the bifurcated water–O(phenoxo)/O(methoxo) hydrogen bonds responsible for the generation of self-assembly are listed in Table 2. The donor–acceptor contacts lie in the range 2.666–2.988 Å and the donor–H acceptor angles vary in between 122.66 and 160.80°, indicating that the hydrogen bonds are either moderate or strong.

The bond lengths and angles for the copper(II) centers in 1–3 are listed in Table S1, while the ranges of the bond angles along with some metrical parameters are compared in Table 3. The Cu–N/O bond lengths (1.83–1.96 Å), cisoid angles (83.78(11)–93.71(17)°) and transoid angles (169.65(10)–177.39(17)°) in the environment of all the copper(II) centers in 1–3 are not very different and are in the ranges observed in the previously published compounds derived from 3-methoxysalicylaldehyde-diamine ligands. From the least-squares Ni(imine)_2O(phenoxo)_2 basal planes, both the deviation of the constituent atoms and the displacement of the copper(II) center are small, less than 0.1 Å (vide infra and Table 3).

The bond distances and the ranges of the bond angles of uranium are listed in Table 4. The bond distances involving the uranium center in 1–3 follows the order: U–O(nitrate) (2.505(6)–2.538(5) Å) > U–O(water) (2.387(4)–2.393(3) Å) > U–O(uranyl) (1.750(2)–1.760(4) Å). The coordination environment around U is distorted hexagonal bipyramidal in which the pyramidal positions are occupied by the two uranyl oxygen (O8 and O8A/O8B) atoms;
the three trans (opposite) sets in the hexagonal basal plane are: water oxygen atoms O9 and O9A/O9B, two nitrate oxygen atoms O5 and O5A/O5B and O7 and O7A/O7B. The four transoid angles in the hexagonal bipyramidal coordination environment are practically 180° and the uranium center is perfectly pocketed in the least-squares O6 basal plane. On the other hand, the ranges of the angles not involving the trans (opposite) ligand centers in the basal plane (49.37(13)–130.63(13)°; 1–3) and also involving the pyramidal and basal atoms (86.22(10)–93.78(10)°; 1–3) along with the wide range of bond distances (1.750(2)–2.538(5) Å; 1–3) together with the average deviation (0.023–0.142 Å; 1–3) of the six constituent oxygen atoms from the least-squares O6 basal plane indicate the significant distortion of the hexagonal bipyramidal coordination environment.

3.2. Significant aspects

As already mentioned, several homo/heteronuclear metal complexes have been reported on reacting mononuclear copper(II)/nickel(II) compounds derived from both H2L6O3Me and H2L6O3Et ligands [12,21–45]. In the H2L6O3Et ligand family, some of those complexes are discrete, while some others are self-assemblies including those in which water–O(phenoxo)2O(ethoxy)2 bifurcated hydrogen bonds are responsible for the formation of self-assemblies [21–23,25–34]. For example, the self-assembled self-assemblies having water–OH interactions are formed when the second metal salts are: LiClO4, NaNO3, Na(dicynamide), NaBPh4, Mg(ClO4)2, 6H2O, Mg(NO3)2·6H2O, Cu(ClO4)2·6H2O, Ni(ClO4)2·6H2O, Co(ClO4)2·6H2O, Fe(ClO4)2·6H2O, Mn(ClO4)2·6H2O, Zn(ClO4)2·6H2O, Cd(ClO4)2·XH2O, AgClO4·xH2O, UO2(NO3)2·6H2O [21–23,25–34]. In contrast, considering all the homo/heteronuclear complexes [12,35–45] having not only copper(II)/nickel(II) in the N(imine)2O(phenoxo)2 compartment but also any transition metal ion in this compartment, there is only one example in which water–O4 interaction and subsequent formation of self-assemblies takes place [37]. This single odd member, a tetrametallic [2 × 1 + 1 × 2] CuII3Mn11+1 self-assembly with composition ([CuII6L3Mn3(H2O)9]([CuII6L3]2[ClO4]2)2H2O, has been obtained on reacting copper(II) mononuclear complex derived from a H2L6O3Me ligand, H2L6Et, with Mn(II)ClO4. In the H2L6O3Et family, we have reported five complexes on reacting copper(II)/nickel(II) mononuclear compounds with UO2(NO3)2·6H2O [29,30]. Three (say, I, II and III) of those compounds are [1 × 2 + 1 × 1] trimetallic self-assemblies of composition ([CuII6L3Mn3(H2O)9]([CuII6L3]2[ClO4]2)2H2O) [30], the fourth (say, IV) is a [1 × 1 + 1 × 1] self-assembly with composition ([CuII3NiL6O8]([CuII6O2]2[NO3]2)2(H2O)2) [30] and the fifth (say, V) is a hexametallic [2 × 1 + 1 × 4] self-assembly with composition ([UO2]2[CuII3Li6O8]2(C2H4)2(NO3)2)4[ClO4]2·(C2H3OH) [29]. In V, water–O4 interaction takes place but the interacting water molecules are not coordinated to the uranium centers. However, in I–IV, as in I–III, the formation of self-assemblies takes place due to the bifurcated hydrogen bonds between the O3 com-

Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>D–H–A</th>
<th>D–A</th>
<th>H–A</th>
<th>D–H–A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O9A–HBD A–O1</td>
<td>2.988</td>
<td>2.363</td>
<td>138.52</td>
</tr>
<tr>
<td>2</td>
<td>O9A–HBD B–O1</td>
<td>2.706</td>
<td>2.011</td>
<td>149.24</td>
</tr>
<tr>
<td>3</td>
<td>O9A–HBD C–O1</td>
<td>2.747</td>
<td>1.912</td>
<td>156.78</td>
</tr>
<tr>
<td>4</td>
<td>O9A–HBD D–O1</td>
<td>2.909</td>
<td>2.293</td>
<td>126.65</td>
</tr>
</tbody>
</table>

Fig. 2. Crystal structure of ([CuII6L3]2([UO2]2(NO3)2(H2O)3])2H2O (2). The two solvent molecules of crystallization and hydrogen atoms, except those of the two coordinated water molecules, are omitted for clarity. Symmetry code: A, x, y, –1 + z; B, 1 – x, 1 – y, –z; C, 1 – x, 1 – y, 1 – z.

Fig. 3. Crystal structure of ([CuII6L3]2([UO2]2(NO3)2(H2O)3])2H2O (3). The two solvent molecules of crystallization and hydrogen atoms, except those of the two coordinated water molecules, are omitted for clarity. Symmetry codes: A, x, y, –1 + z; B, 1 – x, 1 – y, –z; C, 1 – x, 1 – y, 1 – z.
water · O₄ interaction and subsequent self-assembly and formation of self-assemblies have been just a rare phenomenon previously in the copper(II)/nickel(II)–second metal ion complexes derived from H₂L³Me, that has become very much possible in the presence of the [U(VI)O₂(NO₃)₂(H₂O)₂] as the tecton.

3.3. Electronic spectroscopy

The compounds 1–3 are practically insoluble in common organic solvents except in N,N-dimethylformamide (dmf). However, while dissolving in dmf, the color changed to the typical color of the corresponding mononuclear complex. In fact from the dmf solution of the compounds 1–3, the corresponding mononuclear compound separates out. Therefore, it was not possible to record the spectra of 1–3 in solution and so we recorded diffuse reflectance spectra of the solid compounds 1–3 in the range 400–800 nm. We have also recorded diffuse reflectance spectra of the three corresponding mononuclear copper(II) compounds in the same wave length range. Each of these three compounds exhibit one d–d band, typical of copper(II) center, centered at 630, 567 and 605 nm for [CuL³(H₂O)], [CuL²(H₂O)] and [CuL¹(H₂O)], respectively, and at 575, 566 and 607 nm, respectively, for the Cu²⁺–UO₂–Cu³⁺ compounds 1–3. The spectra of the six compounds are shown in Fig. 4, while the λₘₐₓ values and the shifting amount of the copper(II) d–d band in 1–3 in comparison to that in [CuL¹(H₂O)].

A proposition was published regarding the shifting of the d–d band of copper(II) in square planar/square pyramidal environment [50–53], the absorbance values in Fig. 4 are in arbitrary unit. It is worth mentioning that, as usual for diffuse reflectance spectra [50–53], the absorbance values in Fig. 4 are in arbitrary unit.

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A proposition was published regarding the shifting of the d–d band of copper(II) in square planar/square pyramidal environment [50,54,55]. According to this proposition, the more the displacement of the copper(II) center from the least-squares basal plane the less the d–d band energy. The displacement of the metal center and average deviation of the constituent atoms, forming the basal plane, from the least-squares basal plane are listed in Table 3, which also lists the ranges of the trans and cis angles. While no comment could be made from the ranges of the cis angles, the other three parameters indicate that the square planar geometry of copper(II) is distorted in the order 1 > 2 > 3. However, the order of the λₘₐₓ values of 3 > 1 > 2 could not be rationalized from the dₓₐ values because the difference in the dₓₐ values in these three systems are rather small, ranging between 0.020 and 0.087 Å, and also probably due to the change of the dinamo moiety in the three complexes. On the other hand, the blue shifting of the d–d band position in the Cu²⁺–UO₂–Cu³⁺ compound 1 by 55 nm in comparison to the corresponding mononuclear compound [CuL¹(H₂O)] can be well correlated to the decrease of the dₓₐ value in 1.

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**Table 3**
The comparison of the d–d band position and the geometries of the copper(II) centers in 1–3 and the corresponding mononuclear systems.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>λₘₐₓ (nm)</th>
<th>Δλₘₐₓ (nm)</th>
<th>In the N(imine)²O(phenoxo)₂ plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CuL³(H₂O)]</td>
<td>630</td>
<td>–</td>
<td>dₓₐ (Å) dₓₐ (Å) cis Angles (°) trans Angles (°)</td>
</tr>
<tr>
<td>[[CuL²(H₂O)]</td>
<td>575</td>
<td>55</td>
<td>0.087 0.077 83.78(11)–92.44(10) 167.30(9)</td>
</tr>
<tr>
<td>[[CuL¹(H₂O)]</td>
<td>567</td>
<td>–</td>
<td>0.053 0.046 84.16(12)–92.74(11) 173.28(12)–176.89(10)</td>
</tr>
<tr>
<td>[[CuL¹(H₂O)]</td>
<td>566</td>
<td>1</td>
<td>0.020 0.023 84.07(19)–93.71(17) 176.61(18)–177.39(17)</td>
</tr>
<tr>
<td>[[CuL¹(H₂O)]</td>
<td>605</td>
<td>–</td>
<td>0.00</td>
</tr>
<tr>
<td>[[CuL¹(H₂O)]</td>
<td>607</td>
<td>2</td>
<td>0.00</td>
</tr>
</tbody>
</table>

**Table 4**
Bond lengths (Å) and bond angles (°) in the coordination environments of uranium(VI) in 1–3. See captions of Figs. 1–3 for Symmetry codes.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Bond lengths</th>
<th>Bond angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>U1–O5 2.532(2)</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>U1–O7 2.553(2)</td>
<td>180.0</td>
</tr>
<tr>
<td></td>
<td>U1–O8 1.752(2)</td>
<td>180.0</td>
</tr>
<tr>
<td></td>
<td>U1–O9 2.391(2)</td>
<td>180.0</td>
</tr>
<tr>
<td>2</td>
<td>U1–O5 2.533(3)</td>
<td>179.991(1)</td>
</tr>
<tr>
<td></td>
<td>U1–O7 2.519(3)</td>
<td>180.0</td>
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<td></td>
<td>U1–O8 1.757(2)</td>
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<tr>
<td></td>
<td>U1–O9 2.393(3)</td>
<td>180.0</td>
</tr>
<tr>
<td>3</td>
<td>U1–O5 2.505(6)</td>
<td>180.0</td>
</tr>
<tr>
<td></td>
<td>U1–O7 2.538(5)</td>
<td>180.0</td>
</tr>
<tr>
<td></td>
<td>U1–O8 1.760(4)</td>
<td>180.0</td>
</tr>
<tr>
<td></td>
<td>U1–O9 2.387(4)</td>
<td>180.0</td>
</tr>
</tbody>
</table>

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1 We have redetermined the single crystal structure of [CuL¹(H₂O)]. Tables for crystallographic information (Table S2) and bond lengths/angles (Table S3) and crystal structure (Fig. S1) of this compound are listed/shown in Electronic supplementary information (ESI).
A water molecule in the mononuclear system (0.087 Å) by 0.117 Å in comparison to the mononuclear system (0.204 Å)⁴. Clearly, this correlation is possible as the structure of [CuLI\(_2\)(H\(_2\)O)] is known¹. It may be noted that it has been not possible in spite of our many attempts to prepare single crystals of the mononuclear compounds [CuLI\(_2\)(H\(_2\)O)] and [CuLI\(_2\)(H\(_2\)O)]. However, the coordinated or noncoordinated nature of the water molecule in these two mononuclear compounds can be understood from the comparison of their d–d band position with those of the corresponding Cu\(^{II}\)–\(\cdot\)\(\cdot\)\(\cdot\)UO\(_2\)–Cu\(^{0}\) compounds. If the water molecule is coordinated, the Cu center should be shifted towards the apical water molecule and so the \(d_{Cu}\) value should be reasonably greater than that in the Cu\(^{II}\)–\(\cdot\)\(\cdot\)\(\cdot\)UO\(_2\)–Cu\(^{0}\) compound for which the copper(I) center is square planar. In that case, the d–d band position in the Cu\(^{II}\)–\(\cdot\)\(\cdot\)\(\cdot\)UO\(_2\)–Cu\(^{0}\) compounds should be reasonably blue shifted in comparison to the corresponding mononuclear complexes. But, the d–d band positions of 2 and [CuLI\(_2\)(H\(_2\)O)] are practically same, as are the d–d band positions of 3 and [CuLI\(_2\)(H\(_2\)O)], indicating that the water molecule in these two mononuclear compounds is not coordinated, at least. So, the water molecule may be either encapsulated in the O\(_6\) compartment or it may be solvent of crystallization. In the former case, the two water stretching vibrations should appear separately, for later those should not be separated and should appear as a broad band. In fact, well resolved separation of the asymmetric and symmetric stretching vibrations take place in [CuLI\(_2\)(H\(_2\)O)] (\(v_{as} = 3537\) cm\(^{-1}\), \(v_{s} = 3502\) cm\(^{-1}\)) and [CuLI\(_2\)(H\(_2\)O)] (\(v_{as} = 3505\) cm\(^{-1}\), \(v_{s} = 3462\) cm\(^{-1}\)), indicating the encapsulated nature of the water molecules.

4. Conclusions

Three copper(I)–uranil(VI)–copper(I) compounds have been reported in the 3-methoxyalocyclicadheyde–diamine (H\(_2\)OMe) ligand family. In the midst of so many dissimilarities between these two closely similar ligand types, H\(_2\)OMe and 3-ethoxysalicyl-adheyde–diamine (H\(_2\)OMe), this report describes that the both ligand systems are more or less similar in terms of the self-assembly formation when the second metal salt is uranyl nitrate. We would like to address the situation as that diaquadintratouranyl(VI) enforces the O\(_{phenoxyo\}_{2}O\)(methoxy\(_{2}\)) compartment of 3-methoxyalocyclicadheyde-diamine ligands to interact with water molecules and generates the self-assemblies. A previously proposed correlation of the d–d band position with the shifting of the copper(I) center from the basal plane of the square planar/square pyramidal coordination environment has been highlighted here [54,55], revealing nice matching of the blue shifting of the structurally characterized systems. The correlation has been explained here as useful to judge the nature of water molecule in the mononuclear systems for which structure determination has not been possible and such identification from the d–d band position is in line with the FT-IR data. As spectral properties of metal complexes are in general an important area, the spectral correlation observed here deserves importance [56]. Although a spectroscopic correlation has been established and found useful in the set of small number of compounds presented here, the applicability of this correlation in more complexes should be checked to consider this as straightforward. It may be argued that this correlation is a little bit simplistic since other factors like different donor properties of the ligands may play a role in this respect. Density functional theoretical calculation on the correlation proposed here and on the role of donor properties of the ligands as well as other structural parameters would certainly be helpful to facilitate the proposal and to understand the in-depth scenario of the dependency of \(\lambda_{\text{max}}\) values on possible factors.

Acknowledgements

Financial support from the Government of India through Department of Science and Technology (Project No. SR/SI/IC-42/2011) and Council for Scientific and Industrial Research (Fellowship to S. Bhattacharya and A. Jana) are gratefully acknowledged. Crystal data of 1 was collected at the DST (Government of India)–FIST funded Single Crystal X-ray Diffraction Facility at the Department of Chemistry, University of Calcutta.

Appendix A. Supplementary material

CCDC 926210–926212 contains the supplementary crystallographic data for 1–3. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.ica.2013.05.017.

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