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Assembly of two supramolecular structures by metal complexes with a urea-based pyridyl ligand

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Abstract

The supramolecular structures of two metal complexes, [CuL_4Cl_2] (**1**) and [ZnL_2Cl_2] (**2**), where L = *N*-(2,6-dimethylphenyl)-*N*′-(3-pyridy1)urea, are reported. Complex **1** features infinite tapes formed by intermolecular N–H· · ·Cl hydrogen bonds with an $R_2^1(6)$ motif, as well as a π–π stacking interaction. The solid-state structure of **2** shows a 2D network held together by two types of N–H· · ·O $R_2^1(6)$ motifs, and there is no significant interaction between the NH groups and the metal-bound Cl^- ions.

Keywords: Pyridyl urea; Hydrogen bonding; π–π Stacking; Copper(II); Zinc(II)

Crystal engineering of inorganic superstructures has become an approach of much interest in the design of molecular materials [1]. In metal-directed assembly the coordination chemistry of metal centers is often dominant, but the non-covalent forces can also play an important role in determining the supramolecular structure and properties of the system [2]. Hydrogen bonding is one of the most efficient and convenient ways to construct supramolecular solid-state architectures with both organic and metal-coordinated systems, and a variety of compounds that are capable of hydrogen bond formation have been developed [3]. Urea-based pyridyl ligands are good candidates in this respect because in these bitopical ligands the urea group can act as hydrogen bond donor and/or acceptor, while the pyridyl function can coordinate with metal ions. Thus, these ligands have the potential of simultaneously binding transition metal ions and forming hydrogen bonds with other components such as anions [4].

Recently we have established a facile synthetic route for urea-containing pyridyl ligands, and prepared a series of mono- and diureas as anion receptors. The co-binding of H^+/oxo-anion by two *N*-dimethylphenyl-*N*′-pyridylurea ligands has been studied and will be reported elsewhere [5]. We further tested the coordination chemistry of *N*-(2,6-dimethylphenyl)-*N*′-(3-pyridyl)urea (L) with transition metals, and herein report the synthesis [6] of two metal complexes [CuL_4Cl_2] (**1**) and [ZnL_2Cl_2] (**2**), and their supramolecular structures [7] based on different hydrogen bond interactions. It is interesting that although both compounds feature $R_2^1(6)$ hydrogen bond motifs [8], the composition of the $R_2^1(6)$ ring is different: the Cu(II) complex contains N–H· · ·Cl bonds, while the Zn(II) complex forms N–H· · ·O contacts.

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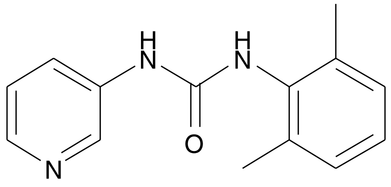

L

Reaction of ligand L with $CuCl_2 \cdot 2H_2O$ affords the 1:4 metal complex $[CuL_4Cl_2]$ (**1**). This complex crystallizes in the monoclinic space group $P2_1/n$. The coordination geometry of the metal center is typical Jahn–Teller distorted octahedral. The pyridyl N donors of four ligands are coordinated to the Cu(II) atom in the equatorial plane, while two chlorine atoms are located in the axial positions. The Cu–Cl bond length of 2.775 Å is significantly longer than the normal Cu–Cl bonds in the equatorial planes or in the tetrahedral complexes, thus falling into the catalog of weaker contacts [9]. For instance, these two types of Cu–Cl bond have been found to be 2.30/2.33 Å and 2.79 Å in $(NH_4)_2[CuCl_4]$ [9b]. The axial Cu–Cl bond lengths of similar 4 + 2 complexes with nitrogen donor ligands, $[Cu(L^N)_4Cl_2]$, have been reported to be still longer, in the range 2.80–3.08 Å [9c]. The Cu(II) center in **1** resides at an inversion center. Within a molecule, the four ureidopyridyls are arranged into two pairs, each including two *cis*-oriented ligands. Such a pair is linked by an intramolecular N–H···O hydrogen bond (N(5)···O(1), 2.943(2) Å, ∠N(5)–H(5A)···O(1), 158.5°) between one of the urea NH groups and the carbonyl oxygen from the other ligand (Fig. 1a). The disubstituted aryl moieties of the *cis*-pair of ligands are nearly parallel to each other (dihedral angle 6.76°), but they stay out of significant π–π stacking because of the lack of efficient overlapping between them. Instead, this slippage of the two planes leads to a favorable arrangement for a strong N–H···π interaction to form between the unbound NH group [N(6)H(6A)] and the aryl ring [C(7)–C(12)] from the other ligand within a *cis*-pair (Fig. 1a). The H···Cg (Cg represents the centroid of the aryl ring) distance of this N–H···π interaction is 2.66 Å, the N···Cg distance 3.40 Å, the perpendicular distance of H atom to the plane 2.64 Å, with a N–H···Cg angle of 144.2° [10]. The typical N–H···O $R_2^1(6)$ synthon of urea moieties [11], which includes both NH groups, is absent in this complex.

In the extended structure, each of the axial Cl atoms forms two intermolecular N–H···Cl hydrogen bonds N(2)···Cl(1), 3.187(2) Å, ∠N(2)–H(2A)···Cl(1), 124.0°; (N(3)···Cl(1), 3.368(2) Å, ∠N(3)–H(3A)···Cl(1), 141.2°) in an $R_2^1(6)$ motif with the urea moiety of a neighboring molecule. Two adjacent CuL_4Cl_2 units are held together by two of the $R_2^1(6)$ rings, complemented by a rather strong π–π stacking interaction between two perfectly parallel (dihedral angle 0.0°) pyridine rings (centroid-centroid separation 3.42 Å, vertical displacement between ring centroids 1.14 Å) [10]. Thus, the complex is packed into an infinite tape along the crystallographic *a* axis (Fig. 1b). Such tapes are parallel to each other in the *b* direction, and are arranged in a zigzag fashion along the *c* axis. Notably, the cadmium(II) complex of a similar ligand, $[CdL'_4Cl_2] \cdot 2H_2O \cdot 2MeCN$ (L′ = *N*-(*p*-tolyl)-*N*′-(3-pyridyl)urea) [4d], has been reported in which the enclathrated water molecules act as bridging ligands between the Cl atom and the urea group, thus breaking the intramolecular N–H···O hydrogen bond. Another difference is that in the Cu(II) complex reported here the metal-coordinated Cl atoms form merely N–H···Cl $R_2^1(6)$ rings, while in the Cd(II) complex the Cl atoms also interact with the crystalline water molecules.

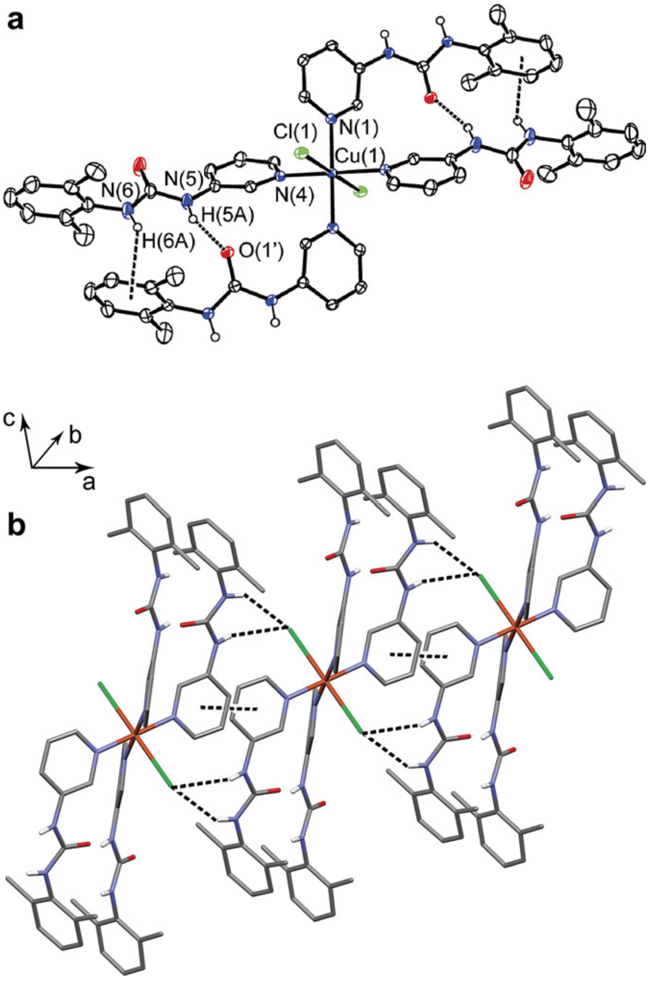

Fig. 1. (a) ORTEP drawing of a $[CuL_4Cl_2]$ (**1**) molecule, showing the intramolecular N–H···O and N–H···π interactions (thermal ellipsoid at 30% probability level); (b) Part of a tape structure formed by intermolecular N–H···Cl ($R_2^1(6)$ motif) and π–π stacking interactions. Non-urea hydrogen atoms omitted for clarity. Selected bond lengths (Å): Cu(1)–N(1) 2.079(2), Cu(1)–N(4) 2.077(2), Cu(1)–Cl(1) 2.7747(6).

The zinc(II) complex $[ZnL_2Cl_2]$ (**2**), obtained by the reaction of L with $ZnCl_2$, has a different structure from the copper(II) analog. While **1** shows a metal to ligand ratio of 1:4, the Zn:L ratio of compound **2** is 1:2. In contrast to the elongated octahedral configuration of the Cu(II) complex, the zinc center is four-coordinated by two ureidopyridyl ligands and two Cl atoms with a tetrahedral geometry. In a complex molecule of **2**, the orientation of the two ligands is in a "*syn*" fashion, and the Cl–Zn–Cl angle is considerably widened (125.63(6)°), as shown in Fig. 2a.

The two ligand arms of each [ZnL_2Cl_2] unit participate in intermolecular contacts with adjacent molecules. The urea NH groups of one ligand form two N–H···O hydrogen bonds with one carbonyl group of another molecule, resulting in an $R_2^1(6)$ ring, while the other ligand of the same ZnL_2Cl_2 unit donates two N–H···O bonds to a third molecule, also with an $R_2^1(6)$ motif. Each of the hydrogen-bonded rings is further expanded along the *a* axis to generate the urea tape synthon (i.e., the $C(4)R_2^1(6)$ motif [8]), which is frequently seen in diarylureas [11]. This is in contrast to the absence of N–H···O bonds in complex **1**. It is noteworthy that the two $C(4)R_2^1(6)$ tapes are different from the viewpoints of orientation and geometry. First, one of them is constructed by ligands which are roughly *anti*-parallel to each other (Fig. 2b, motif #1), while the other includes staggered ligand molecules (Fig. 2b, motif #2). Second, the hydrogen bond parameters are different (motif #1: N(6)–H(6A)···O(2), 2.795(4) Å, 154.3°; N(5)–H(5A)···O(2), 2.885(4) Å, 149.0°; motif #2: N(2)–H(2A)···O(1), 2.962(3) Å, 140.2°; N(3)–H(3A)···O(1), 2.748(3) Å, 148.5°). Along the *c* axis, the two types of urea tapes repeat alternatively, forming a hydrogen-bonded two-dimensional network in *ac* plane (Fig. 2b), and these sheets are arranged parallel to each other in the *b* direction. Interestingly, the chloride ions act as coordination ligands rather than hydrogen bond acceptors in this complex: they do not form efficient intermolecular hydrogen bonding interactions with the NH units (the shortest N–H···Cl contact is 3.406 Å, but the ∠N–H···Cl angle is too acute, at 68.1°). This differs significantly from the copper(II) complex **1** and a ZnL'_2Cl_2 compound [4d], both of which feature two N–H···Cl bonds of either $R_2^1(6)$ or $R_2^2(8)$ motif.

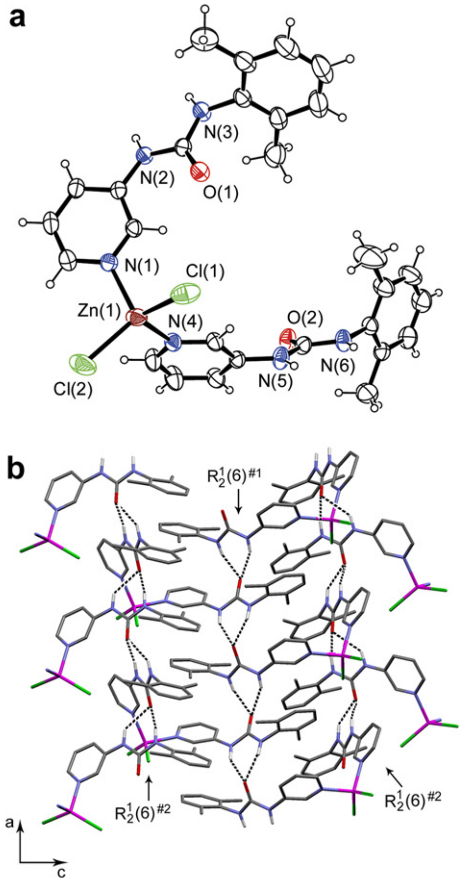

Fig. 2. (a) ORTEP drawing of a [ZnL_2Cl_2] (**2**) molecule, showing the *syn*-arranged ligand arms (thermal ellipsoid set at 30% probability level); (b) The hydrogen-bonded 2D network in the *ac* plane with two different types of N–H···O $R_2^1(6)$ motifs. Non-urea hydrogens and some ligands are omitted for clarity. Selected bond lengths (Å): Zn(1)–N(1) 2.068(3), Zn(1)–N(4) 2.070(2), Zn(1)–Cl(1) 2.212(1), Zn(1)–Cl(2) 2.204(1).

IR spectra of the two complexes are consistent with hydrogen bond formation. It is known that upon association by hydrogen bonding the urea NH stretch frequencies would decrease (e.g. from above 3400 to around 3200 cm^{-1} [12]). In the present work, the NH-stretch of **1** (3378 cm^{-1}) is considerably higher than that of **2** (3287 cm^{-1}), which may be attributed to the different hydrogen bond types in the two complexes. As described above, complex **1** has a combination of N–H···Cl, N–H···π and N–H···O interactions, while in **2** all the NH groups are involved in the stronger N–H···O bonds and thus displays less NH stretch. Furthermore, the NH stretch of complex **2** is almost identical to the hydrated ligand $L \cdot H_2O$ (3285 cm^{-1}), whose solid-state structure also features N–H···O hydrogen bonds between the NH groups and the enclathrated water [5].

In conclusion, we report the supramolecular structures of two metal complexes with a urea-based pyridyl ligand and chloride ion. Both complexes contain $R_2^1(6)$ hydrogen bond motifs that are further extended to an infinite tape (**1**) or a 2D sheet structure (**2**). However, the metal-bound Cl atoms in **1** are involved in intermolecular N–H···Cl bonds, while in **2** they do not participate in any N–H···Cl interactions.

Acknowledgement

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Appendix A. Supplementary material

CCDC 634820 and 634821 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.01.026.

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[6] *Synthesis*: *[CuL$_4$Cl$_2$]* ***(1)*** : A solution of L (50.2 mg, 0.21 mmol) in acetonitrile/methanol (1:1 v/v, 4 mL) was added to an aqueous solution (2 mL) of $CuCl_2 \cdot 2H_2O$ (17.7 mg, 0.10 mmol) under stirring. The resulting greenish solution was allowed to evaporate at room temperature for about 2 weeks to yield dark green crystals (60%). M.p.: 201–202 °C. Anal. Calc. for $C_{56}H_{60}N_{12}O_4CuCl_2$ (1099.62): C, 61.17; H, 5.50; N, 15.29%; Found: C, 60.99; H, 5.55; N, 15.20%. IR (KBr, ν/cm^{-1}): 3378 (N–H), 3064, 1703 (C=O), 1590, 1514, 1485, 805, 786. *[ZnL$_2$Cl$_2$]* ***(2)***: L (50.2 mg, 0.21 mmol) and $ZnCl_2$ (13.6 mg, 0.10 mmol) were stirred in acetone/ethanol (1:1 v/v, 6 mL) for 3 h at room temperature. The mixture was filtered, and the filtrate was allowed to evaporate for several days to give colorless block crystals. Yield: 58%. M.p.: 236–237 °C. Anal. Calc. for $C_{28}H_{30}Cl_2N_6O_2Zn$ (618.89): C, 54.34; H, 4.89; N, 13.58%; Found: C, 54.01; H, 4.46; N, 13.39%. ^{1}H NMR (DMSO-d_6, 400 MHz, ppm): $\delta = 9.00$ (s, 1H, NH), 8.61 (d, 1H, $J = 2.4$ Hz, Py-H2), 8.14 (d, 1H, $J = 3.6$ Hz, Py-H6), 7.91 (dt, 1H, $J = 8.4$, 4.0 Hz, Py-H4), 7.88 (s, 1H, NH), 7.31 (dd, 1H, $J=$ 8.4, 4.8 Hz, Py-H5), 7.07 (s, 3H, Ar), 2.08 (s, 6H, $2CH_3$). IR (KBr, ν/cm^{-1}): 3287 (N–H), 3036, 1640 (C=O), 1561, 1480, 1424, 1228, 770, 697.

[7] *Crystal data for **1***: $C_{56}H_{60}Cl_2CuN_{12}O_4$, monoclinic, space group $P2_1/n$, $a = 8.448(1)$ Å, $b = 13.820(2)$ Å, $c = 23.201(3)$ Å, $\beta = 100.149(1)°$, $V = 2666.2(5)$ Å^3, $Z = 2$, $D_{calc} = 1.370$ g cm^{-3}, $F(000) = 1150$, $\mu = 0.569$ mm^{-1}, $T = 293(2)$ K, 13,139 reflections collected, 4739 independent ($R_{int} = 0.0289$), $R_1 = 0.0353$, $wR_2 = 0.0853$ [$I > 2\sigma(I)$]. *Data for **2***: $C_{28}H_{30}Cl_2N_6O_2Zn$, orthorhombic, space group *Pbca*, $a = 8.5346(6)$ Å, $b = 24.382(2)$ Å, $c = 29.434(2)$ Å, $V = 6124.9(8)$ Å^3, $Z = 8$, $D_{calc} = 1.342$ g cm^{-3}, $F(000) = 2560$, $\mu = 1.011$ mm^{-1}, $T = 293(2)$ K, 34,252 reflections collected, 6560 independent ($R_{int} = 0.0661$), $R_1 = 0.0451$, $wR_2 = 0.1070$ [$I > 2\sigma(I)$]. Diffraction data were collected on a Bruker SMART APEX II diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). An empirical absorption correction using SADABS was applied for the data. The structures were solved by direct methods using the SHELXS-97 program. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 by the use of the program SHELXL-97, and hydrogen atoms were included in idealized positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached.

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