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Anion hydrogen bonding from a 'revealed' urea ligand†

Naseem Qureshi,[a] Dmitri S. Yufit,[b] Kirsty M. Steed,[c] Judith A. K. Howard[b] and Jonathan W. Steed*[b]

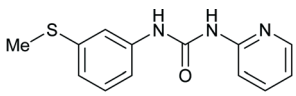
Hydrogen bonding from a urea group to hydrogen bond acceptor anions can adopt either $R_2^1(6)$ or $R_2^2(8)$ motifs depending on the proximity of hydrogen bond acceptor atoms. However, for the sterically bulky and weaker hydrogen bond acceptor triflate anion, hydrogen bond acceptor polymorphism is observed.

Introduction

The scope, geometry, strength and directionality of hydrogen bonding interactions to metal-coordinated anions has generated considerable interest both on a fundamental level[1–8] and in applications such as extraction of halometalate anions in mining processes.[9–11] The directionality, steric constraints and polarization of the M–X bond (in comparison to a spherical halide anion, for example) places considerable constraints on complexed anion hydrogen bonded geometries and hence must be understood in order to inform the design of metal salt ion pair binding hosts. Seminal contributions in the area were the work of Gillon, Orpen and coworkers[4,12,13] and of Brammer and coworkers[2,5,14,15] who showed, for example, that hydrogen bonding from a single NH group of a pyridinium unit to a *cis*-MCl_2 fragment occurs to the centroid of the two chloride ligands. Complexed anion binding by a double hydrogen bond donor group such as the urea functionality can invert this behaviour with both NH donors interacting with a single acceptor atom (the $R_2^1(6)$ motif in graph set nomenclature[16,17]) being particularly common.[1] In this work we report a series of copper(II) complexes of ligand **L** exhibiting hydrogen bonding to anions. In the free state, ligand **L**, while highly polymorphic, consistently adopts an intramolecular $R_2^2(8)$ hydrogen bonded ring motif[18] (Fig. 1) and hence the urea functionality is unavailable for anion hydrogen bonding. We have previously reported the formation of a range of Ag(I) complexes of ligand **L** in which the proximity of the pyridyl nitrogen atom and urea group results in the bonding of contact ion pairs.[19] The coordination mode of copper(II) is very different however and results in significantly different anion binding behaviour.

Results and discussion

The crystal structure of the free ligand **L** is based on an $R_2^2(8)$ hydrogen bonded ring with an unusual *syn*, *anti* conformation of the aryl groups of the *N*,*N*′-diarylurea ligand relative to the urea carbonyl. This feature arises from the formation of a strong intramolecular hydrogen bond to the pyridyl nitrogen atom. Rendering this acceptor unavailable is expected to change the ligand conformation to reveal a more conventional *syn*, *syn* conformation predisposed to the formation of urea α-tape or $R_2^1(6)$ type hydrogen bonds to the urea NH



L

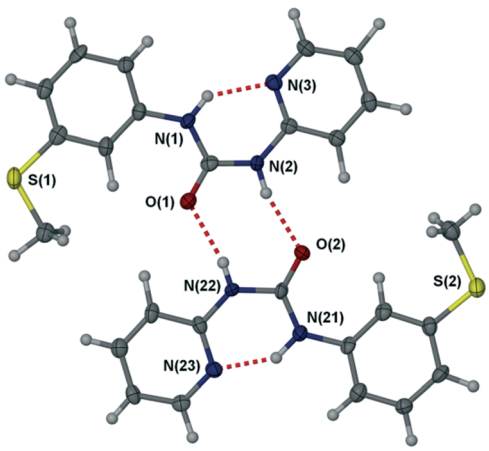


Fig. 1 Intermolecular $R_2^2(8)$ hydrogen bonded ring motif in free ligand **L**.[18]

[a] *Department of Chemistry, Karakoram International University, Gilgit-Baltistan, 15100 Gilgit, Pakistan. E-mail: ngq18@hotmail.com*
[b] *Durham University, South Road, DH1 3LE, UK. E-mail: jon.steed@durham.ac.uk*
[c] *SAgE Faculty, Newcastle University, Devonshire Building, NE1 7RU, UK*

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groups in which both NH donors are aligned in the same direction.[20] This behaviour is exemplified by the single crystal X-ray structure of the protonated ligand $LH^+BF_4^-$ (see Experimental section) in which the *syn*, *syn* ligand displays $NH^+\cdots O$ and $CH\cdots O$ hydrogen bonding to the urea carbonyl group and hydrogen bonding from both urea NH functionalities to the BF_4^- anion giving an $R_2^2(8)$ anion hydrogen bonded motif, Fig. 2.

Reaction of ligand **L** with a range of copper(II) salts in polar solvent mixtures results in crystals of the following complexes that were analysed by X-ray crystallography: $[\{Cu(\mathbf{L})(\mu\text{-}Cl)Cl\}_2]$ (**1**), $[Cu(\mathbf{L})_2Br_2]$ (**2**), $[Cu(\mathbf{L})_2(NO_3)_2]$ (**3**) and $[Cu(\mathbf{L})_2(CF_3SO_3)_2]$ (**4**). The triflate complex **4** exists in two polymorphic modifications, forms A and B, depending on the crystallization solvent. In each case **1**–**4** the copper(II) ion is chelated by the pyridyl nitrogen and urea carbonyl oxygen atoms to give a 6-membered chelate ring. Cu–O distances range from 1.95–1.98 Å and Cu–N 2.00–2.04 Å, consistent with related structures such as $[Cu(N,N'\text{-di-2-pyridylurea})_2(NO_3)_2]$,[21] $[Cu(1\text{-benzyl-3-(2-pyridinyl)urea})_2Cl_2]$ (ref. 22) and a series of dinuclear stacked analogues reported by us previously.[23] Complexes **2**–**4** are all closely related (albeit not isomorphous) mononuclear 1 : 2 M : L complexes, exhibiting a Jahn–Teller distorted octahedral copper(II) centre with long axial bonds to the anionic ligands. In contrast the chloride complex **1** is a 1 : 1 complex exhibiting a chloride bridged dimeric structure, making the anionic ligands somewhat less accessible for hydrogen bonding. Since all complexes were formed from similar concentrations of mixtures of 1 : 1 stoichiometry the different stoichiometry of product in the case of **1** is likely to arise from the better ligating ability of chloride for copper(II).

In all complexes **1**–**4** the urea aryl substituents adopt a *syn*, *syn* conformation and hence the urea NH groups point away from the metal centre and are co-aligned. Despite the bridged structure, complex **1** exhibits an $R_2^2(8)$ hydrogen bonding interaction with both chloride ligands acting as hydrogen bond acceptors, Fig. 3. This interaction mode contrasts with a range of *trans* dihalide complexes of the related ligand *N*,*N'*-*p*-tolyl-3-pyridylurea which tends to form $R_2^1(6)$ interactions as a result of the exposed nature of the terminal halide ligands. Complex **1** is similar, however, to the *cis*-dihalide complex $[Zn(N,N'\text{-}p\text{-tolyl-3-pyridylurea})_2Cl_2]$ and to $LH^+BF_4^-$ (Fig. 2).[1]

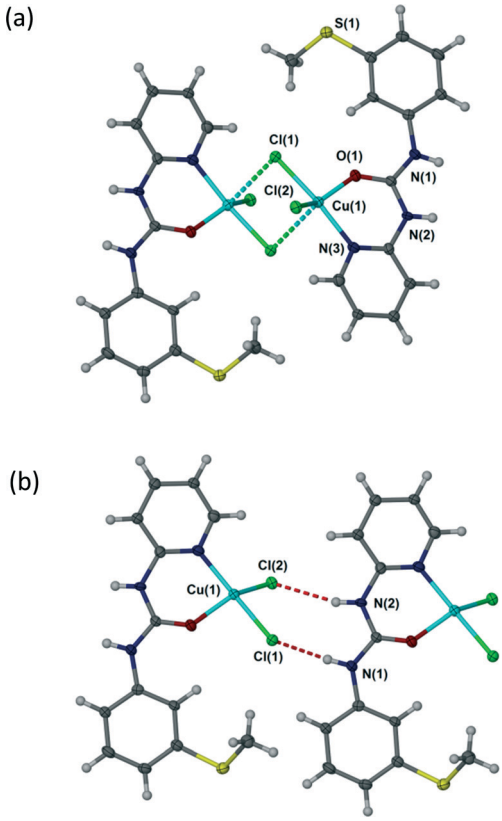

Fig. 3 (a) Dimeric structure of $[\{Cu(L)(\mu\text{-}Cl)Cl\}_2]$ (**1**) – long axial Cu–Cl interactions shown as dotted lines. (b) $R_2^2(8)$ hydrogen bond motif in **1** (one half of the chloride-bridged dimer is shown for clarity). Selected distances (Å): N(1)···Cl(1) 3.156(6), N(2)···Cl(2) 3.371(6).

In contrast to the chloride complex, the bromide complex **2** exhibits long bonds to mutually *trans* axial bromide ligands and as a result hydrogen bonding is of the $R_2^1(6)$ type in which each bromide anion acts as an acceptor to two NH hydrogen bond donors of similar length, Fig. 4, in a way that is related to the *N*,*N'*-*p*-tolyl-3-pyridylurea analogues.[1] The nitrate salt **3** also exhibits long, *trans* diaxial coordination of the anions however because the anion itself is polyatomic with adjacent pairs of oxygen atoms the hydrogen bonded geometry

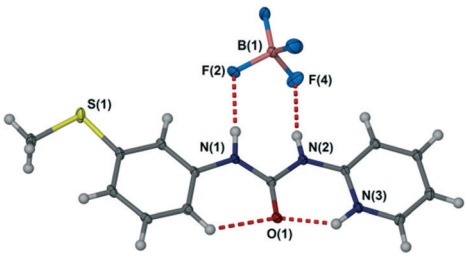

Fig. 2 *Syn*, *syn* conformation of protonated **L** in $LH^+BF_4^-$ and the $R_2^2(8)$ hydrogen bond motif to the BF_4^- anion. Selected hydrogen bonded distances (Å): N(1)···F(2) 2.870(2), N(2)···F(4) 2.824(2), N(3)···O(1) 2.645(2), C(5)···O(1) 2.940(2).

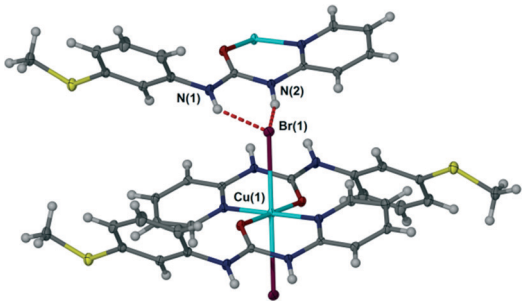

Fig. 4 $R_2^1(6)$ motif in bromide complex **2**. Selected distances (Å): N(1)···Br(1) 3.3399(16), N(2)···Br(1) 3.2871(15).

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is $R_2^2(8)$ with a single *syn*, *syn* urea group interacting with an 'NO_2' group comprising the coordinated oxygen atom O(2) and one uncoordinated atom O(4). The remaining nitrate oxygen atom O(3) does not form any short interactions and the closest contact is to a pyridyl CH atom (Fig. 5).

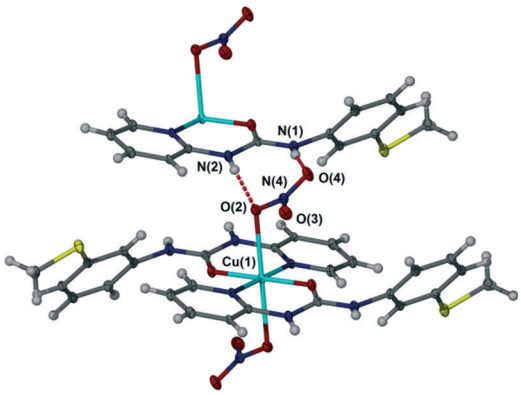

Fig. 5 $R_2^2(8)$ hydrogen bond motif in nitrate complex **3**. Selected distances (Å): N(1)···O(2) 2.817(3), N(2)···O(4) 2.810(3).

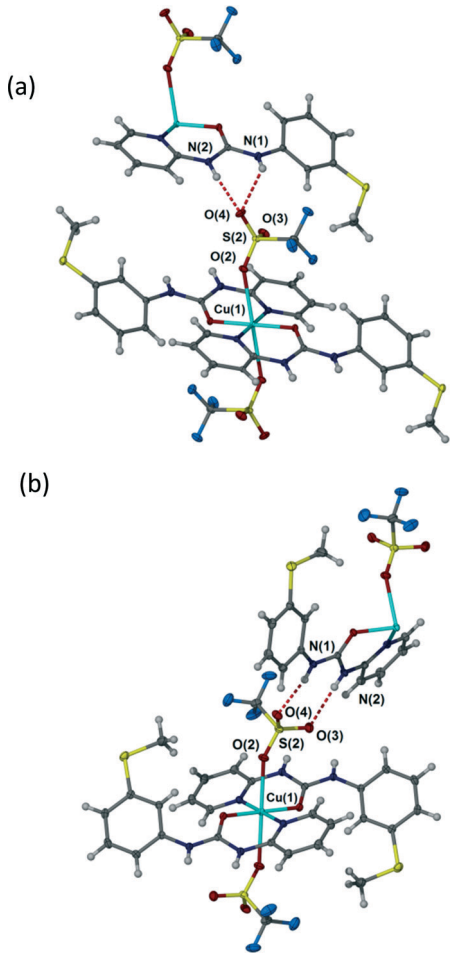

Fig. 6 Hydrogen bonding in triflate complex **4** (a) highly unsymmetrical $R_2^1(6)$ interaction in Form A, selected distances (Å): N(1)···O(4) 3.255(5), N(2)···O(4) 2.892(5). (b) $R_2^2(8)$ interaction in Form B. Selected distances (Å): N(1)···O(4) 2.825(2), N(2)···O(3) 2.982(3).

Depending on crystallization conditions (see Experimental section) the triflate complex **4** exists in two polymorphic modifications, A and B. Forms A and B differ in a very interesting way in the context of the preceding discussion. The coordination complex **4** itself in both polymorphs is a 1 : 2 M : L species with unidentate *trans* diaxial triflate anions. However, in form A the anion adopts a highly unsymmetrical $R_2^1(6)$ hydrogen bonding interaction with an adjacent urea group with NH···O distances of 2.89 and 3.23 Å (Fig. 6a) while in Form B the polyatomic anion forms an $R_2^2(8)$ interaction involving symmetrical hydrogen bonding to the two uncoordinated sulfonyl oxygen atoms (Fig. 6b), hydrogen bonded distances 2.83 and 2.98 Å. The fact that the triflate salt thus does not seem to exhibit a strong preference for a particular hydrogen bonding geometry may be attributed to the relatively diffuse negative charge of the $-SO_3^-$ group and the steric constraints of the $-CF_3$ group which are absent in the nitrate analogue.

Conclusions

Coordination to copper(II) forces a *syn*, *syn* conformation for the *N*,*N*′-diaryl urea ligand and allows the mode of interaction to coordinated anions to be explored. In the case of strong hydrogen bond acceptors in which two acceptor atoms are adjacent to one another as in the "$CuCL_2$" unit of complex **1** and in nitrate complex **3** the $R_2^2(8)$ motif is formed. Mononuclear anions result in an $R_2^1(6)$ arrangement as in the bromide complex **2**. For the weaker acceptor, sterically bulky triflate anion both arrangements appear to be almost equienergetic resulting in anion hydrogen bond acceptor polymorphism in complex **4**.

Experimental

X-ray crystallography

Suitable single crystals were grown by slow evaporation. Crystallographic measurements were carried out on a Rigaku R-AXIS Spider IP diffractometer (compounds **1** and **2**) and on a Bruker SMART CCD 6000 diffractometer (all other compounds) using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at the temperature of 120(2) K, maintained by open flow N_2 Cryostream (Oxford Cryosystems) cryostates. Structures were solved using direct methods with and refined by full-matrix least squares on F^2 for all data using SHELXTL and OLEX2 software.[24,25] All non-hydrogen atoms were refined with anisotropic displacement parameters; H-atoms were located on the difference map and refined isotropically. Molecular graphics were produced using the programs X-Seed[26] and POV-Ray.[27] Crystal data and parameters of refinement are listed in Table 1. Crystallographic data for the structures has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-1476704–1476709.

Synthesis

The Ligand 1-(3-methylsulfanyl-phenyl)-3-pyridin-2-yl-urea (**L**) was prepared as previously described.[19]

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Table 1 Crystal data and structure refinement data

Compound	LHBF$_4$	1	2	3	4A	4B
Empirical formula	$C_{13}H_{14}SON_3BF_4$	$C_{13}H_{13}N_3OCuCl_2S$	$C_{26}H_{26}N_6O_2CuBr_2S_2$	$C_{26}H_{26}N_8CuS_2O_8$	$Cu(C_{13}H_{13}N_3OS)_2(CF_3SO_3)_2$	
Formula weight	347.14	393.76	742.01	706.21	880.33	
Temperature	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a/Å	6.6282(3)	7.7680(16)	7.8394(16)	8.9556(3)	8.2365(3)	12.6428(3)
b/Å	10.3741(5)	9.1578(18)	8.1920(16)	21.6859(9)	9.6360(3)	9.0531(2)
c/Å	11.1178(5)	10.466(2)	12.372(3)	7.1433(4)	11.5943(4)	15.2733(4)
α/°	96.700(10)	90.77(3)	104.40(3)	90.00	110.59(2)	90.00
β/°	92.305(10)	98.75(3)	92.42(3)	98.90(1)	97.00(2)	99.138(10)
γ/°	99.927(10)	95.52(3)	116.28(3)	90.00	103.85(2)	90.00
Volume/Å^3	746.47(6)	732.1(3)	679.3(2)	1370.6(1)	814.57(5)	1725.94(7)
Z	2	2	1	2	1	2
ρ_{calc} mg mm^{-3}	1.544	1.786	1.814	1.711	1.795	1.694
μ, m mm^{-1}	0.266	1.999	3.937	1.018	1.023	0.966
F(000)	356	398	371	726	447	894
Reflections collected	9369	9240	17 441	13 846	10 725	23 373
Independent reflections/R_{int}	3948/0.0420	2846/0.0990	4319/0.0336	3301/0.0534	4645/0.0374	5028/0.0524
Data/restrains/parameters	3948/0/264	2846/0/192	4319/0/179	3301/0/253	4645/0/242	5028/0/293
Goodness-of-fit on F^2	1.099	1.036	1.021	1.063	0.874	1.020
R_1 indexes [$I > 2\sigma(I)$]	0.0479	0.0864	0.0268	0.0405	0.0641	0.0391
wR_2 indexes [all data]	0.1324	0.2519	0.0627	0.1069	0.1662	0.1084

Fluoroboric acid salt HL$^+$BF$_4^-$. Ligand **L** (0.30 g, 0.116 mmol) was dissolved in THF (4 ml) and added to a solution of copper(II) tetraflouoroborate hexahydrate (0.40 g, 0.155 mmol) in THF (4 ml). The mixture was refluxed under nitrogen for 19 h, filtered and left to evaporate slowly over several days resulting in the formation of crystals suitable for X-ray diffraction analysis. IR (ν/cm^{-1}) 711 (br), 1054 (br), 1619 (s), 1673 (s), 2925 (w), 3081 (m), 3206 (br).

[{Cu(L)(μ-Cl)Cl}$_2$] (1). Ligand **L** (0.30 g, 0.116 mmol) was dissolved in THF (2 ml) and added to a solution of copper(II) chloride (0.20 g, 0.118 mmol) in MeOH (2 ml). The mixture was left to slowly evaporate for few days resulting in a formation of green crystals suitable for X-ray analysis. IR (ν/cm^{-1}) 1387 (s), 1535 (s), 1578 (s), 1608 (s), 1709 (s), 3129 (w, br), 3278 (w, br).

[Cu(L)Br$_2$] (2). Ligand **L** (0.30 g, 0.116 mmol) was dissolved in THF (2 ml) and added to a solution of copper(II) bromide (0.19 g, 0.116 mmol) in distilled water (1 ml). The mixture was left to slowly evaporate resulting in a formation of green crystals suitable for X-ray analysis. IR (ν/cm^{-1}) 1478 (s), 1535 (s), 1613 (m), 1660 (s), 3026 (w) and 3325 (vw).

[Cu(L)(NO$_3$)$_2$] (3). Ligand **L** (0.30 g, 0.116 mmol) was dissolved in THF (2 ml) and added to a solution of copper nitrate (0.22 g, 0.116 mmol) in THF : H_2O (1 : 1 v/v, 2 ml). The mixture was left to slowly evaporate resulting in a formation of green crystals suitable for X-ray analysis. IR (ν/cm^{-1}) 1030 (m, NO_3), 1231 (vs), 1414, (m) 1478, (m) 1529 (m), 1668 (m), 3027 (br).

[Cu(L)(CF$_3$SO$_3$)$_2$] (4) (Form A). Ligand **L** (0.12 g, 0.046 mmol) in THF (2 ml) was mixed with copper trifluromethanesulfonate (0.168 g, 0.046 mmol) in methanol : H_2O (1 : 1 v/v, 2 ml) and the mixture allowed to evaporate slowly resulting in a formation of green crystals suitable for X-ray diffraction analysis. IR (ν/cm^{-1}) 1227 (s), 1438 (s), 1548 (s), 1585 (s), 1651 (s), 3282 (br).

[Cu(L)(CF$_3$SO$_3$)$_2$] (4) (Form B). Ligand **L** (0.30 g, 0.116 mmol) was dissolved in THF (2 ml) and mixed with copper(II) trifluromethanesulfonate (0.19 g, 0.116 mmol) in methanol : acetonitrile (1 : 1 v/v, 2 ml) and the mixture was left to evaporate slowly. This resulted in the formation of crystals suitable for X-ray diffraction analysis. IR (ν/cm^{-1}) 1411 (s), 1467 (s), 1531 (s), 1579 (s), 1612 (s), 1718 (s), 3199 (m), 3279 (m).

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