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Towards a system for the systematic structural study of intermolecular interactions in crystals of transition metal complexes†

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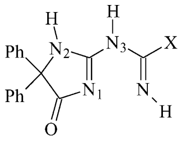
Pseudo-macrocyclic complexes of copper(II), and in one instance nickel(II), incorporating the bidentate ligands methyl *N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)imidocarbamate and *N*,*N*-dimethyl-*N′*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)guanidine are reported and their X-ray structures compared with those previously reported for related complexes of two *N*-(4-oxo- 5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)alkanimidamides. A feature of these complexes is that they are capable of forming hydrogen bonded chains or chains in which adjacent complexes are linked by phenyl 'embraces'. Changes in supramolecular structure arising from small changes in ligand structure or on crystallisation from different solvents are also discussed.

Introduction

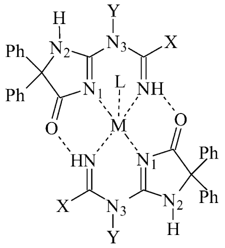
There has been a growing interest in the rational design of crystals incorporating transition metal complexes that are present as metal coordination polymers or for which hydrogen bonding and/or other interactions link coordinated ligands.[1] Such products constitute a category of new materials that show promise for a range of applications that include the uptake or exchange of guest molecules and ions for separation or sensing applications and the potential to act as catalytic frameworks of the 'synthetic zeolite' type. Clearly the need for the targeted design (and synthesis) of new products of this type, displaying specific structures, remains an activity of more than intrinsic interest.

In earlier papers we have described the incorporation of a number of transition metal complexes into supramolecular arrays that incorporate complementary hydrogen bonding motifs.[2–6] In these arrays the complexes occur in two- or three-component subunits, or as chains, which then interact further by hydrogen bonding or other intermolecular interactions to form more elaborate structures. For example, we have previously investigated complexation by selected members of the ligand series listed in Scheme 1—a series that seems well suited for use in a comparative structural study of supramolecular interactions in crystals of transition metal complexes. Thus we have reported the synthesis and structures of the copper(II) complexes **1, 2a** and **2b** (see Scheme 2) containing two bidentate *N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)alkanimidamide ligands.[6]



X = –R, –OR, –NR$_2$, –NHR

Scheme 1



X	Y	L	M^{2+}	other	
Me	–	DMSO	Cu		**1**[ref. 6]
Et	–	–	Cu		**2a**[ref. 6]
Et	–	–	Cu	2DMSO	**2b**[ref. 6]
OMe	H	–	Cu	2ClO$_4^-$, 2MeOH	**3a**
OMe	–	–	Cu	MeOH	**3b**
OMe	–	DMSO	Cu		**3c**
OMe	–	–	Cu	2DMSO	**3d**
NMe$_2$	–	–	Cu	2DMSO	**4a**
NMe$_2$	–	–	Ni	2DMSO	**4b**

Scheme 2

The synthesis of the ligands of the latter type is straightforward and the related ligand derivatives of the type shown in Scheme 1, differing only slightly in steric and electronic properties, are also readily available allowing one to 'tune' the system, with changes being possible both close to and remote from the metallo-rings. Nevertheless, it needs to be noted that one synthetic limitation in the preparation of individual members of such a ligand family is that the diketone precursor must be capable of undergoing a benzilic acid rearrangement; this rules out, for example, the use of butanedione and pyridil.[7,8]

On coordination, ligands of the present type will readily lose a proton from N(3) (see Scheme 1) to form neutral complexes with a suitable metal ion. The generation of neutral complexes will tend to limit additional structural complexity (from hydrogen bonding, solvation and/or steric effects) arising from the presence of counter ions in the crystal.[9] For example, each coordinated ligand in **1, 2a** and **2b** has only one metal bound

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=NH group and in the bis-ligand complexes the hydrogen from this group is hydrogen bonded to the carbonyl group of the second ligand, forming a pseudo-macrocyclic ring (Scheme 2). This neatly removes these hydrogens from being potential hydrogen bond donors to neighbouring molecules or ions. It also means that the self-complementary donor–acceptor (DA) motif encompassing N(2) and N(3) is the only potential (intermolecular) hydrogen bonding group present on the ligand.

The above self-complementary motif can be 'switched off' by protonation of N(3) or by steric influence arising from the presence of a bulky X group (Scheme 1). Such steric interference will always be present when X = $-NR_2$ but will depend on the conformation adopted when X = –OR. The above doublet motif can be expanded to a triplet, DDD or DAD, depending on the protonation present and if X = –NHR and the R group is *syn* with respect to the coordinated imino group.

Whether hydrogen bonding is present or not, phenyl–phenyl interactions, offset face-to-face (OFF), edge-to-face (EF) or more complicated supramolecular motifs such as an $(OFF)(EF)_2$ 'embrace' may occur; it is noted that the energies of such interactions can approach that for hydrogen bonding. Alkyl to π-facial interactions may also occur.[10] Solvent may also play a role in the crystal and will have its own steric requirements; typically it may be present coordinated to the metal or hydrogen bonded to the coordinated ligands or, alternatively, may simply interact with the ligand phenyl groups.

In this paper we present the results of an investigation of structure–function relationships with respect to the supramolecular structures of four complexes (**3a–d**) of methyl-*N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)imidocarbamate in both its neutral and anionic forms, and two (**4a, 4b**) of the anionic form of the ligand *N*,*N*-dimethyl-*N*'-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)guanidine (Scheme 2). In this context we also discuss methoxyiminocimetidine-*N*,*N*′,*N*″,*S*-perchloratocopper(II) perchlorate, **5**, whose X-ray structure was re-determined as part of the present study.

Experimental

4-Oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-ylcyanamide, 6

This was prepared in 66% yield from benzil and dicyandiamide as described previously.[11]

N,*N*-Dimethyl-*N*′-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)guanidine, 7

This was prepared in 85% yield by the reaction of benzil and *N*,*N*-dimethylbiguanide in the presence of sodium ethoxide as reported previously.[12]

Bis(methyl *N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)imidocarbamate)copper(II) perchlorate-2-methanol, 3a, and bis(methyl *N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)imidocarbamato) copper(II)-1-methanol, 3b

$Cu(ClO_4)_2·6H_2O$ (0.095 g, 0.25 mmol) was dissolved in boiling methanol (15 mL) and **6** (0.138 g, 0.5 mmol) was added to the boiling solution. The mixture was heated under reflux for 3 h during which time a deep blue colour developed. The solution was allowed to cool and large blue crystals of **3a** formed. A crystal from this batch was employed for an X-ray structure determination. Pink crystals of a second product, **3b**, also subsequently formed on letting the methanol solution containing the blue crystals of **3a** stand. Over time the blue crystalline solid disappeared and was replaced by the pink. A (pink) crystal from this batch was also employed for a second X-ray structure determination. The methanol solvate present in the crystals was lost on drying over silica gel at room temperature (Found: C, 60.24; H, 4.58; N, 16.60. Calc. for $C_{34}H_{30}CuN_8O_4$: C, 60.21; H, 4.46; N, 16.53%).

(Dimethyl sulfoxide)bis(methyl *N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)imidocarbamato)copper(II), 3c, and bis(methyl *N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)imidocarbamato)copper(II)-2-dimethyl sulfoxide, 3d

$Cu(ClO_4)_2·6H_2O$ (0.094 g, 0.25 mmol) was dissolved in methanol (15 mL) at room temperature and the solution heated to boiling. Ligand **6** (0.139 g, 0.5 mmol) was added to the boiling solution. The mixture was heated under reflux for 4 h. The solution was removed from the heat and conc. aqueous ammonia (2 mL) was added slowly. A pink powder, which formed immediately, was isolated and washed with methanol (2 × 5 mL) and Et_2O (2 × 5 mL) and air-dried. Yield: 0.074 g, 44%. Drying over silica gel at room temperature gave a solid that analysed as the hemihydrate of bis(methyl *N*-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)imidocarbamato)copper(II) (Found: C, 59.42; H, 4.55; N, 16.31. Calc. for $C_{34}H_{30}CuN_8O_4.\frac{1}{2}H_2O$: C, 59.25; H, 4.49; N, 16.14%). Crystallisation of the pink powder from DMSO gave purple crystals of **3c** mixed with a small amount of a second pink phase **3d**. X-Ray diffraction studies (see later) showed that **3c** was $[Cu(C_{17}H_{15}N_4O_2)_2DMSO]$ and **3d** was $[Cu(C_{17}H_{15}N_4O_2)_2]·2DMSO$.

Bis(*N*,*N*-dimethyl-*N*′-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)guanidino)copper(II)-2-dimethyl sulfoxide, 4a, and bis(*N*,*N*-dimethyl-*N*′-(4-oxo-5,5-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)guanidino)nickel(II)-2-dimethyl sulfoxide, 4b

Complexes **4a** and **4b** were prepared by the same method. The ligand, **7**, (0.321 g, 1 mmol) was dissolved in boiling ethanol (60 mL). To this solution was added an aqueous ammoniacal solution of the hydrated metal chloride (0.5 mmol). A purple precipitate formed immediately and was filtered off when the precipitation was complete. The solid was washed with alcohol (2 × 5 mL) and Et_2O (2 × 5 mL) and air dried. Yields: **4a**, 0.300 g, 43%; **4b**, 0.295 g, 42%. (**4a**, Found: C, 56.05; H, 5.55; N, 16.33. Calc. for $C_{36}H_{36}CuN_{10}O_2·2DMSO$: C, 55.83; H, 5.62; N, 16.28%; **4b**, Found: C, 56.47; H, 5.61; N, 16.35. Calc. for $C_{36}H_{36}NiN_{10}O_2·2DMSO$: C, 56.14; H, 5.65; N, 16.37%.).

Methoxyimino-cimetidine-*N*,*N*′,*N*″,*S*-perchloratocopper(II) perchlorate, 5

This was prepared by the literature procedure[13] and involved the heating a 1 : 1 mixture of cimetidine and copper(II) perchlorate in methanol at reflux temperature.

CAUTION: perchlorate complexes are potentially explosive and appropriate caution should be exercised in their synthesis and handling.

X-Ray structure determinations

Data for the seven crystal structures were collected at 150 K to approximately 0.75 Å resolution, on a Bruker SMART 1000 CCD diffractometer equipped with an Oxford Cryostems cryostat[14] and employed graphite monochromated MoKα radiation (0.71073 Å) from a sealed tube. Data were integrated using SAINT[15] and subsequent computations were carried out with the teXsan,[16] WinGX[17] and XTAL[18] graphical user interfaces. A Gaussian absorption correction[15,19] was applied to compounds **3a, 3c, 4a, 4b** and **5**, and a multi-scan absorption correction[20] based on the method of Blessing[21] was applied to **3b** and **3d**. All structures were solved by direct methods using either SIR97[22] (**3a, 3c, 4a, 4b** and **5**) or SHELXS[23] (**3b** and **3d**) and extended and refined against F^2 using SHELXL97.[23] Final refinement data are listed in Table 1, and details of hydrogen bond geometries are given in Table 3. ORTEP[24] depictions are shown in Figs. 1 and 2. The non-hydrogen atoms were modelled with anisotropic displacement parameters and a riding atom model was used for the hydrogen atoms. Amine hydrogen sites were located and

Table 1 Selected crystallographic data

	3a	3b	3c	3d	4a	4b	5
Formula	$C_{36}H_{40}Cl_2CuN_8O_{14}$	$C_{35}H_{34}CuN_8O_5$	C36H36CuN8O5S	$C_{38}H_{42}CuN_8O_6S_2$	$C_{40}H_{48}CuN_{10}O_4S_2$	$C_{40}H_{48}N_{10}NiO_4S_2$	$C_{11}H_{20}Cl_2CuN_6O_9S$
Molecular weight	943.20	710.24	756.33	834.46	860.54	855.71	546.83
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P21/n$ (#14)[a]	$P\bar{1}$ (#2)	$P21/c$ (#14)	$P21/c$ (#14)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P21/c$ (#14)
a/Å	10.982(2)	8.6598(3)	12.366(3)	15.8052(9)	9.992(3)	9.927(2)	11.6940(13)
b/Å	13.361(3)	9.8301(4)	14.299(3)	16.1700(10)	10.823(3)	10.814(2)	7.3720(8)
c/Å	14.624(3)	10.0256(4)	19.892(4)	16.6035(10)	11.164(3)	11.116(3)	23.655(3)
α/°	90	102.016(2)	90	90	74.218(4)	73.819(4)	90
β/°	105.488(3)	98.708(2)	105.054(3)	111.955(3)	71.368(4)	71.650(3)	94.630(2)
γ/°	90	100.635(2)	90	90	66.793(4)	66.708(3)	90
V/Å^3	2068.0(7)	804.25(5)	3396.6(12)	3935.6(4)	1036.6(5)	1024.0(4)	2032.6(4)
Z	2	1	4	4	1	1	4
T/K	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
μ(MoKα)/mm^{-1}	0.734	0.736	0.762	0.717	0.681	0.630	1.499
$R_1(F)$, $wR_2(F2)$	0.0278, 0.0758	0.0358, 0.0906	0.0379, 0.0795	0.0473, 0.1106	0.0355, 0.0877	0.0410, 0.1012	0.0287, 0.0756

[a] Non-standard setting of $P\,2_1/c$.

modelled with isotropic displacement parameters. Refinement variations are given below for individual structures.

3a. The asymmetric unit contains the complex located on an inversion centre, a perchlorate counter ion and a methanol solvate molecule. Distance restraints were used for H(2N) and H(3N).

3b. The non-hydrogen atoms in the asymmetric unit were modelled with anisotropic displacement parameters. Idealised hydrogen positions were calculated for the methanol and allowed to ride on the parent atoms. The methanol solvent was refined as disordered over a crystallographic inversion centre, and the hydroxyl hydrogen atom was geometrically placed in a position so that it was oriented towards the nearest region of high electron density (O1), thus forming a long hydrogen bond. This hydrogen atom was refined as a riding group.

4a. The asymmetric unit contains the complex located on an inversion centre, and a dimethyl sulfoxide solvate molecule. Distance restraints were used for H(2N) and H(4N).

The asymmetric unit contains the complex located on an inversion centre, and a dimethyl sulfoxide solvate molecule. Distance restraints were used for H(2N) and H(4N).

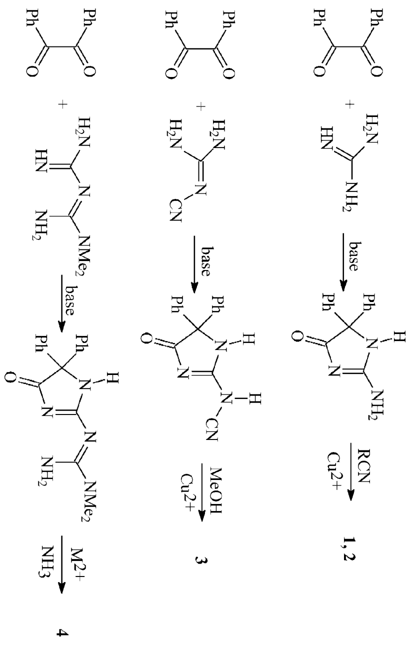
5. The asymmetric unit contains the complex molecule and two perchlorate counter ions. Distance restraints were required for H(11), H(3N) and H(6N).

CCDC reference numbers 265654–265660.

See http://dx.doi.org/10.1039/b503381k for crystallographic data in CIF or other electronic format.

Results and discussion

Crystallographic details for the structurally characterised complexes are listed in Table 1, pertinent geometrical details are given in Table 2 and a summary of hydrogen bond interactions is given in Table 3. More detailed geometric data is available as ESI.† ORTEP[24] depictions are provided in Fig. 1 and Fig. 2. The methods employed for preparation of the ligands and complexes are summarised in Scheme 3.



Scheme 3

Structure **3a** contains a square planar, pseudo-macrocyclic copper(II) complex dication, with the metal residing on an inversion site. The copper–N(imidazole) bonds are slightly longer than for copper–N(imine) (Table 2a) and there is weak perchlorate ion coordination, with O(6) occupying a distorted octahedral site 2.8147(14) Å from the metal centre. Each ligand is approximately planar and the methoxy group lies in the plane in its *syn* conformation, as expected.[25] The ligand atoms N(1), C(1), C(2), N(2), C(3), N(3), C(4), N(4) are approximately coplanar, with minimum and maximum deviations of 0.1668(16) Å and 0.1037(13) Å respectively; the accordingly defined least

Table 2 Selected metal environment geometry details for compounds **3a–d** and **4a** and **4b**. M represents Cu in structures **3a–d** and **4a**, and Ni in **4b**

(a) Coordination bond (M–N) lengths in Å

	M(1)–N(1)	M(1)–N(4)	M(1)–N(5)	M(1)–N(8)
3a[a,b]	2.0396(12)	1.9367(13)	—	—
3b[a]	2.0322(16)	1.9251(16)	—	—
3c[c]	2.0468(17)	1.931(2)	2.0495(18)	1.936(2)
3d	2.034(2)	1.897(2)	2.033(2)	1.908(2)
4a[a]	2.0458(15)	1.9041(17)	—	—
4b[a]	1.9652(18)	1.8679(19)	—	—

(b) Coordination bond angles in °

	N(1)–M(1)–N(4)	N(1)–M(1)–N(5)	N(1)–M(1)–N(8)	N(4)–M(1)–N(5)	N(4)–M(1)–N(8)	N(5)–M(1)–N(8)
3a[a]	88.00(5)	180	91.99(5)	—	180	—
3b[a]	87.67(7)	180	92.33(7)	—	180	—
3c	87.12(8)	176.69(7)	93.16(8)	91.85(8)	171.74(8)	87.41(8)
3d	87.24(9)	174.28(8)	93.32(9)	92.15(8)	175.74(10)	87.71(8)
4a[a]	87.53(7)	180	92.52(7)	—	180	—
4b[a]	88.12(8)	180	91.88(8)	—	180	—

[a] Structures **3a, 3b, 4a** and **4b** all contain the metal atom sited on a crystallographic inversion centre; in these cases N5 is symmetry related by this inversion centre to N1 and N4 is symmetry related to N8. Values are not reported for non-independent values. Note that in these cases angles N(1)–M(1)–N(5) and N(4)–M(1)–N(8) are constrained to be 180°, and N(4)–M(1)–N(5) is constrained to be the same as N(1)–M(1)–N(8). [b] Structure **3a** also contains a perchlorate oxygen atom in an apical coordination site, with a Cu(1)–O(6) bond length of 2.815(2) Å. [c] Structure **3c** also contains an oxygen in an apical coordination site, with a Cu(1)–O(5) bond length of 2.4013(17) Å.

Table 3 Hydrogen bond summary

Donor	Hydrogen	Acceptor	D–H/Å	H–A/Å	D–A/Å	DHA Angle/°
3a						
O(7)	H(7O)	O(3^{a})	0.84	2.10	2.928(2)	167.6
O(7)	H(7O)	O(5^{a})	0.84	2.52	3.022(2)	119.5
N(2)	H(2N)	O(5^{a})	0.806(16)	2.035(17)	2.8278(18)	167.5(18)
N(3)	H(3N)	O(7)	0.797(16)	1.974(17)	2.7633(18)	170.7(18)
N(4)	H(4N)	O(1^{b})	0.80(2)	2.01(2)	2.7576(17)	156.3(19)
3b						
N(4)	H(4N)	O(1^{c})	0.83(3)	1.99(3)	2.748(2)	152(2)
N(2)	H(2N)	N(3^{d})	0.84(3)	2.15(3)	2.987(2)	172(3)
3c						
N(2)	H(2N)	N(7^{e})	0.72(2)	2.23(2)	2.938(3)	170(2)
N(4)	H(4N)	O(3)	0.80(2)	2.05(2)	2.788(2)	153(2)
N(8)	H(8N)	O(1)	0.79(2)	2.07(2)	2.782(3)	150(2)
N(6)	H(6N)	N(3^{f})	0.799(16)	2.144(17)	2.938(3)	173(3)
3d						
N(8)	H(8)	O(1)	0.88	2.03	2.788(3)	144.0
N(4)	H(4)	O(3)	0.88	1.95	2.748(3)	150.0
N(2)	H(2)	O(6)	0.88	1.95	2.777(3)	155.6
N(6)	H(6)	O(5)	0.88	1.92	2.764(3)	160.4

Symmetry operators: ^{a} $x - 1/2, -y + 1/2, z - 1/2$; ^{b} $-x + 2, -y, -z + 1$; ^{c} $-x, -y, -z$; ^{d} $-x, -y, -z - 1$; ^{e} $x, -y + 1/2, z - 1/2$; ^{f} $x, -y + 1/2, z + 1/2$.

Donor	Hydrogen	Acceptor	D–H/Å	H–A/Å	D–A/Å	DHA Angle/°
4a						
N(2)	H(2N)	O(2)	0.806(19)	2.115(19)	2.913(2)	171(2)
N(4)	H(4N)	O(1^{a})	0.773(18)	2.084(19)	2.798(2)	154(2)
4b						
N(2)	H(2N)	O(2)	0.840(10)	2.050(11)	2.882(3)	171(3)
N(4)	H(4N)	O(1^{a})	0.837(10)	1.941(15)	2.717(2)	154(3)

Symmetry operators: ^{a} $-x, -y + 1, -z + 1$.

Donor	Hydrogen	Acceptor	D–H/Å	H–A/Å	D–A/Å	DHA Angle/°
5						
N(2)	H(2N)	O(8^{a})	0.77(2)	2.51(2)	3.240(3)	160(2)
N(1)	H(1N)	O(6)	0.819(15)	2.314(18)	3.055(2)	151(2)
N(3)	H(3N)	O(7^{b})	0.806(15)	2.502(19)	3.194(3)	145(2)
N(6)	H(6N)	O(2^{c})	0.788(16)	2.50(2)	3.190(3)	148(2)
N(6)	H(6N)	O(4^{c})	0.788(16)	2.52(2)	3.190(3)	144(2)

Symmetry operators: ^{a} $-x + 1, y + 1/2, -z + 1/2$; ^{b} $x - 1, y, z$; ^{c} $-x + 1, -y, -z$.

squares ligand plane makes an angle of 9.67(4)° with the plane of the four nitrogen donor atoms. The structure also exhibits a long contact between the central metal atom and the perchlorate counterion, forming a [4 + 2] coordination sphere, with Cu(1)–O(6) distance of 2.815(2) Å. Further details of the geometry are listed in Tables 2 and 3.

The supramolecular structure shows the complexity that can attend the inclusion of counter ions in the crystal. The perchlorate ion and a methanol solvent molecule are hydrogen bonded to the protonated nitrogen atoms N(2) and N(3) in a $R^{3}_{3}(10)$ pattern as shown in Fig. 1. This results in an extended layer of pseudo-macrocycles in two different orientations linked into a

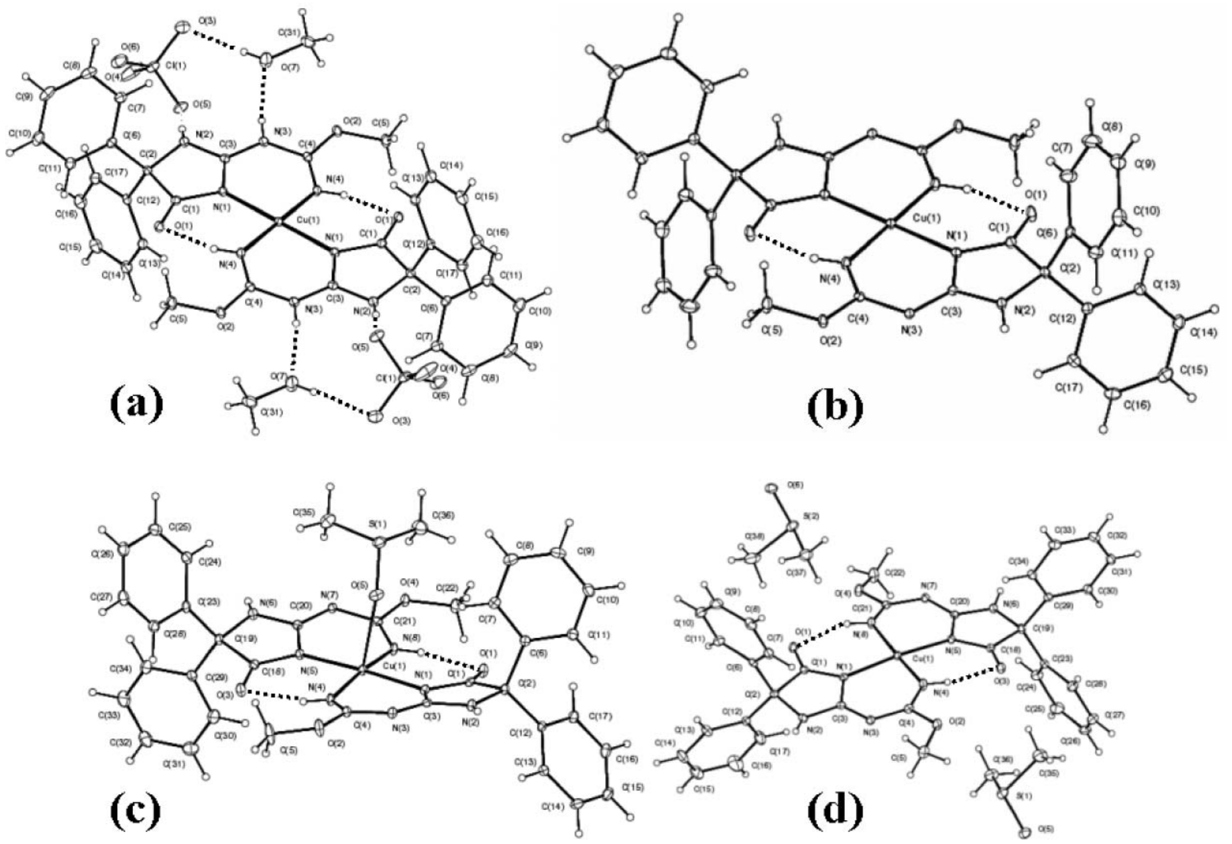


Fig. 1 ORTEP[24] depictions of complexes **3a–3d**, showing 20% displacement ellipsoids. A methanol molecule in **b**, which is disordered over a crystallographic inversion centre, has been omitted. Dotted lines indicate hydrogen bonds.

network by hydrogen bonding and electrostatic (weak) coordination interactions with the perchlorate ions and methanol. The layers are 'linked' to one another by centrosymmetric methyl–π facial interactions between ligands; the average C(methyl)–C(phenyl) distance is 3.79 Å. The complexes so linked form chains quasi-parallel to the *a*-axis. It is worth noting that the most advantageous intermolecular C–C distance is not the sum of the van der Waals radii (3.4 Å) but some 0.3–0.4 Å longer. For offset face-to-face interactions the distance is even greater. In fact, the intermolecular potential becomes zero, or slightly destabilising, at the van der Waals distance.[26]

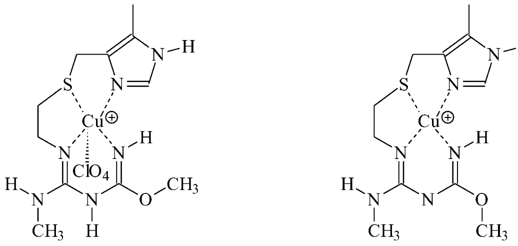
Structure **3b** forms spontaneously at the expense of **3a** when the latter is allowed to stand in the crystal growth solution. Like **3a, 3b** contains square planar copper(II), with each copper at an inversion site, but this time each complex is neutral. The least squares ligand plane makes an angle of 5.24(6)° with the plane of the four nitrogen donor atoms (see also Table 2b). The supramolecular structure, however, is much simpler than before and much simpler too than that of the apparently similar **2a**. The latter contains three crystallographically distinct complexes and two different chains intricately interlocked.[6] The DA (donor–acceptor) hydrogen bonding motif is self-complementary so that in **3b** chains of complexes, linked by $R^2_2(8)$ patterns, form quasi-parallel to the *c*-axis (Fig. 3).

The formation of the chains results in the methoxy group being in its *syn* conformation instead of being *anti* as would be expected for the corresponding anionic ligand. The methyl group is twisted 8° out of the plane of the ligand. It is also interesting that the conformations of the phenyl rings are quite different from those present in **1, 2a** and **2b**. In the present case one of the phenyl groups forms a C(11)H···O(2) interaction (3.36 Å, 165°) while the other makes a π-facial interaction with the terminal methyl group (average C–C distance: 4.05 Å). This suggests that the twisting of the chains observed for **2a** reflect the steric requirements of the ethyl side chain. The phenyl groups are further involved in OFF and EF interactions between the chains.

The methanol in the crystal, which lies on an inversion site and is disordered, is not coordinated or involved in hydrogen bonding but lies amongst the phenyl rings as shown in Fig. 4.

The change of conformation from that expected for the above system prompted us to re-determine the structure of **5**, in which hydrogen bonding might be expected to occur but for which the crystal data only, but not the atomic coordinates, were available in the Cambridge Structural Database.[27] From the structure it is clear that the methoxy methyl conformation is *syn*, as is expected for the coordinated neutral ligand (protonated on N(3)) and different from the *anti* conformation observed for the anionic ligand **6**[28] (Scheme 4). The N-methyl group is *anti*; all the hydrogen bonds are rather long (Table 3). The supramolecular structure is depicted in Fig. 5.

When **2a** was crystallised from DMSO, the hydrogen bonded chains did not re-form but instead crystals of **2b** grew from the solution.



5

6[28]

Scheme 4

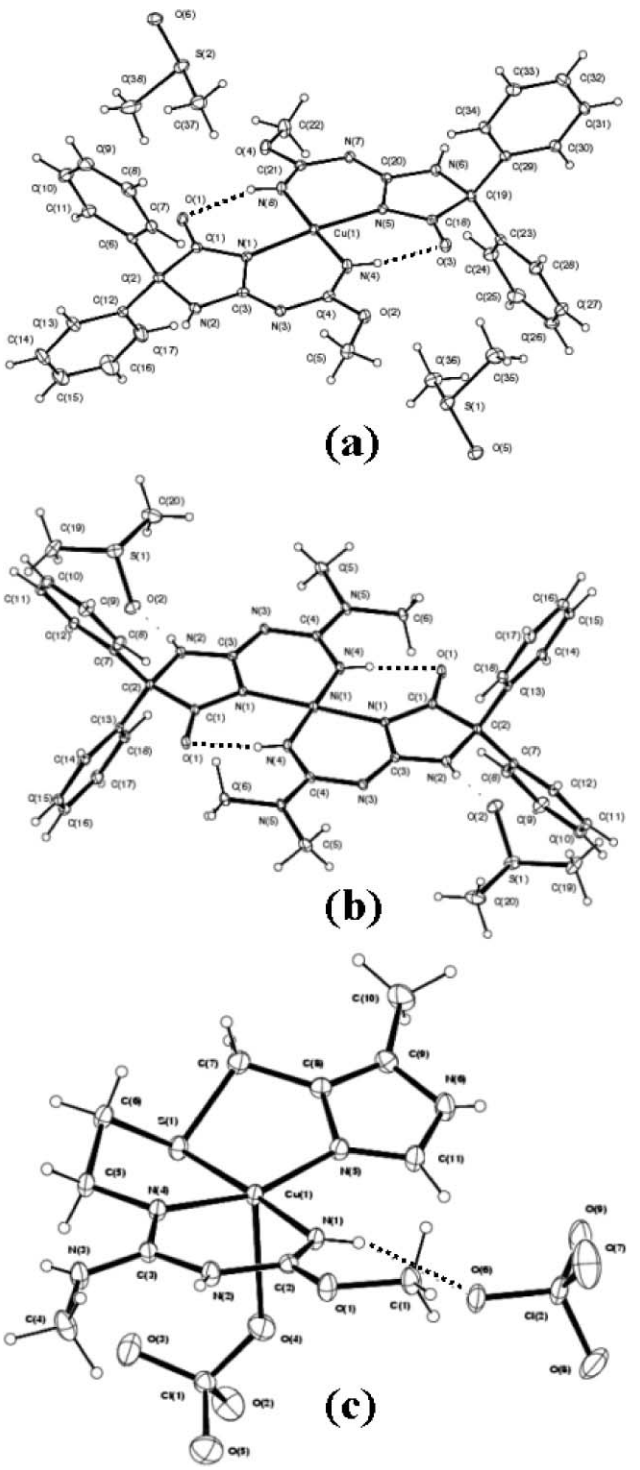


Fig. 2 An ORTEP[24] depiction of complexes **4a, 4b** and **5** showing 20% displacement ellipsoids. Dotted lines indicate hydrogen bonds.

The neutral complexes of type **3**, which have methoxy instead of ethyl groups, behave differently to the above. The major crystalline form, **3c**, contains hydrogen bonded chains. There is also a small amount of a second phase, **3d**, formed (Table 2). This minor phase resembles **2b** in that it consists of discrete three-component units made up of the complex and two molecules of DMSO hydrogen bonded to the protons on N(2) and N(6). This behaviour is also consistent with the postulate that it will be more difficult to accommodate the ethyl group than the methoxy group in the hydrogen bonded chains.

Interestingly each copper ion in **3c** is five coordinate, with a DMSO molecule occupying its apical site. This arrangement resembles that present in **1**. The maximum and minimum

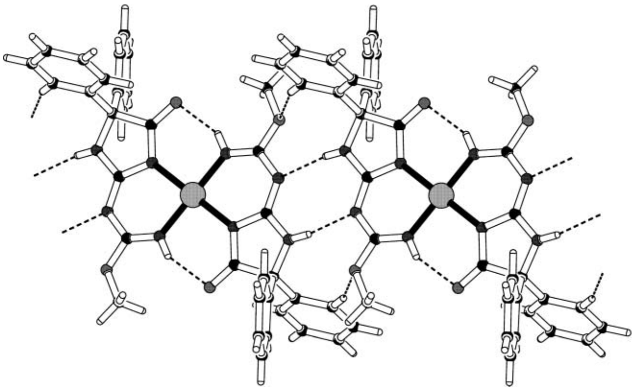


Fig. 3 A PLATON[29] depiction of part of a chain in **3b** and the interactions between neighbouring complexes within a chain.

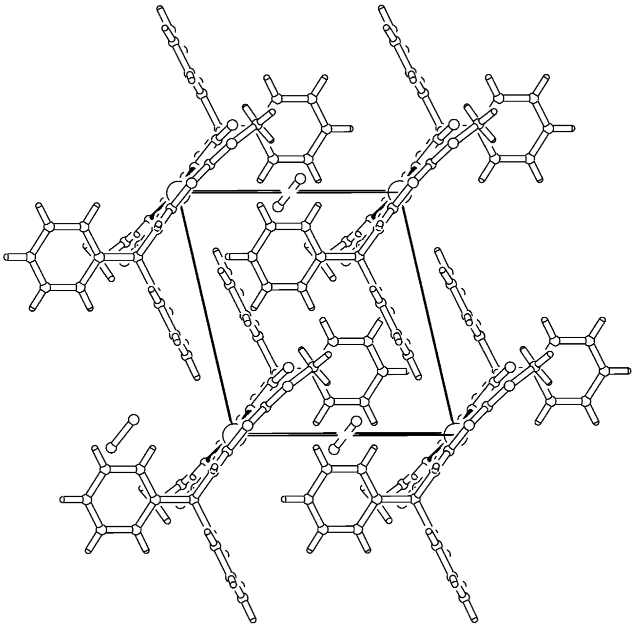


Fig. 4 A PLATON[29] depiction of the unit cell of **3b**, viewed down the *c*-axis. The hydrogen atoms of the disordered methanol molecules are not shown.

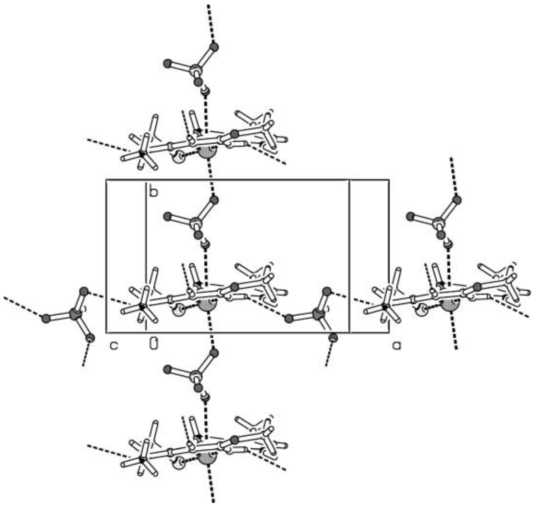


Fig. 5 A PLATON[29] depiction of **5** showing the complex–perchlorate chains quasi-parallel to the *b*-axis and the long hydrogen bonded NH · · · O chains quasi-parallel to the *a*-axis.

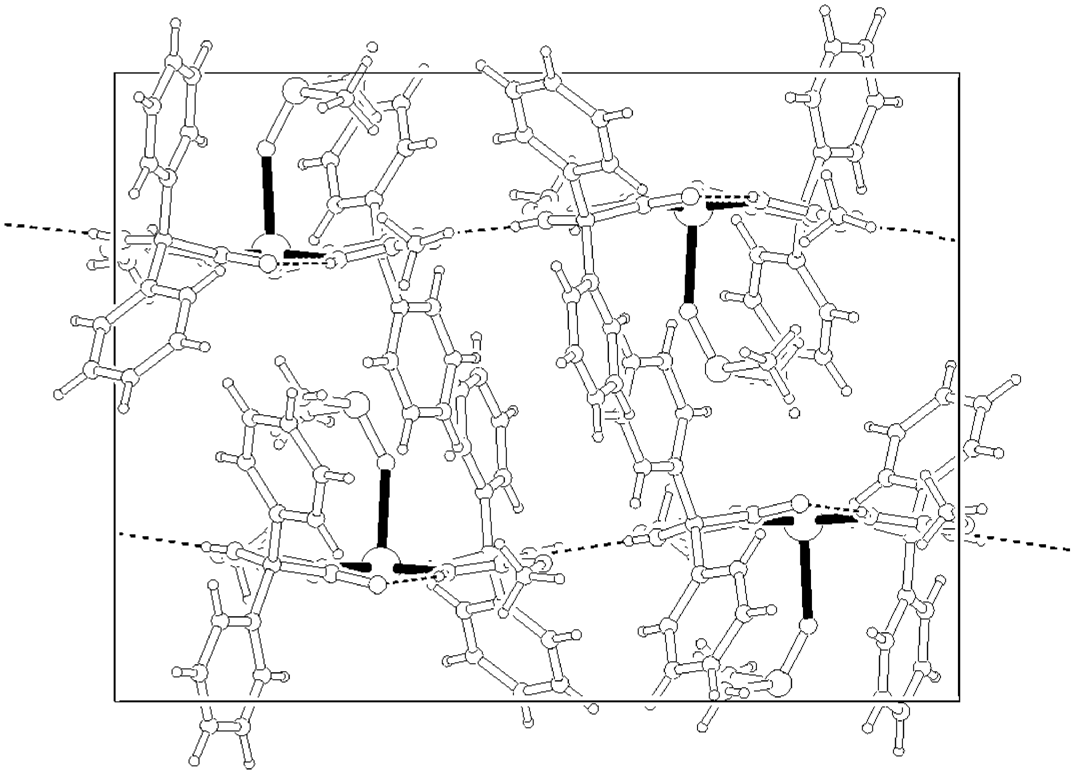
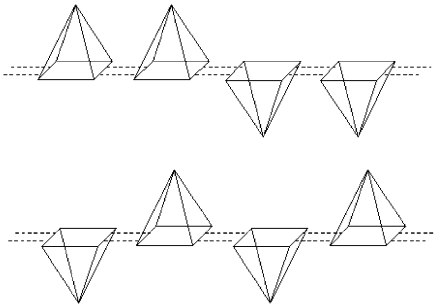


Fig. 6 A PLATON[29] depiction of the unit cell of **3c**, viewed down the *a*-axis.

deviations of the four nitrogen donor atoms from their least squares plane are 0.046(3) and 0.036(2) Å and Cu(1) lies 0.0932(10) Å from the plane. The least squares ligand plane make angles of 10.82(6)° and 12.63(6)° with the plane of the nitrogen donor atoms. The hydrogen bonded chains have a slightly wave-like disposition relative to the *c*-axis (Fig. 6) and the orientation of the coordination pyramids in the chains has a different pattern from that in **1** (Scheme 5).



Scheme 5

The hydrogen bonds in **3c** are slightly shorter than those in **1** but similar to those in **3b**. The orientation of the phenyl groups is different from that in **3b**; they interact with others from neighbouring chains as well as with the DMSO methyl groups of adjacent complexes. Adjacent chains appeared linked by DMSO methyl to phenyl π-facial interactions and by phenyl EF and OFF interactions.

Structure **3d**, at least superficially, resembles that of **2b**, in that the complexes are not linked into chains but rather form three-component systems with DMSO molecules acting as hydrogen bond acceptors. The copper coordination is approximately square planar, with the maximum and minimum deviation of the nitrogen donor atoms from their least squares plane being 0.094(3) and 0.078(3)Å; Cu(1) lies 0.0229(10) Å from the plane. The least squares ligand planes subtend angles of 6.44(7)° and 3.60(6)° with the nitrogen donor plane. The conformation of the methoxy group is now *anti* as expected for the presence of an anionic ligand (and contrasts with the *syn* conformation observed in **3b** and **3c**).

The three-component unit in **2b** is interesting in that the two 'ends' of the unit differ with respect to the orientation of the hydrogen bonded DMSO, the X side chain conformation as well as the orientation of the phenyl groups. In the absence of hydrogen bonding between complexes, chains linked by phenyl–phenyl interactions are formed. Two such types of interaction alternate: a centrosymmetric CH–π facial dimer interaction and an OFF(EF)$_2$ embrace.

Although the two ends of the three-component unit of **3d** are crystallographically distinct, both DMSO molecules in the unit are oriented in a similar manner, with the DMSO methyl groups pointing back towards the centre of the complex and with one of the methyl groups of each DMSO making a methyl–π-facial phenyl contact within the unit. The methoxy methyl group is in the *anti* conformation. This arrangement is similar to that found in **2b** which is associated with the OFF(EF) embrace; in the present case, the same motif is observed and leads to the formation of chains running quasi-parallel to the *a*-axis. The motif is not centrosymmetric. The chains are illustrated in Fig. 7 and a space-filling model of the motif is shown in Fig. 8. Between the chains there are further methyl–π facial interactions involving both DMSO molecules, C(37), and methoxy, C(5), methyl groups and again both faces of the benzene ring interact with methyl groups.

The crystal structures of **4a** and **4b** show them to be isostructural (Tables 1, 2 and 3). The metal ions again have square planar geometries with the metal ions located at inversion sites. In both complexes the least squares ligand planes make angles of 6.11(6)° (**4a**) and 7.73(7)° (**4b**) with the nitrogen donor

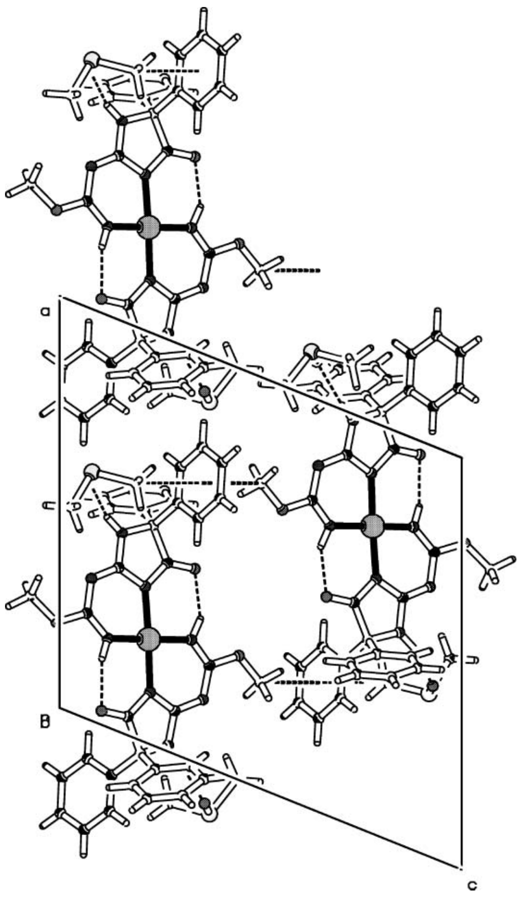
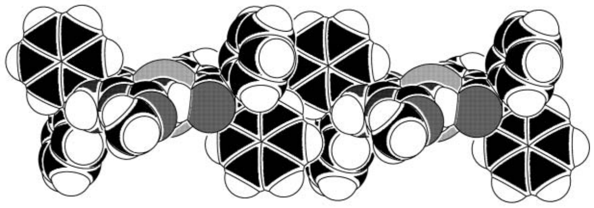


Fig. 7 A PLATON[29] depiction of **3d** looking down the *b*-axis. Chains, quasi-parallel to the *a*-axis, formed by (OFF)(EF)$_2$ interactions and the methyl–π facial–methyl interactions between neighbouring chains are also shown.

Offset π facial and edge to face interactions in **3b**



A centrosymmetric pair of CH-π facial interactions in **4a**

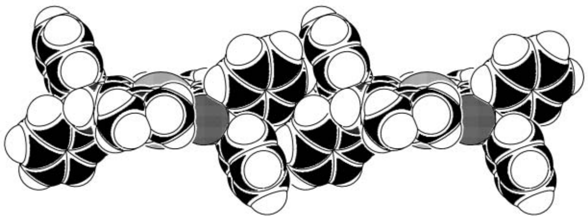


Fig. 8 A PLATON[29] depiction (CPK-style) of the two four-phenyl motifs linking complexes into chains in **3b** and **4a**. DMSO molecules are not shown.

planes. Although potential complementary doublet motifs are present, the formation of hydrogen bonded chains is inhibited by steric interference from the ligand-NMe$_2$ groups. The complexes form three-component units with DMSO molecules hydrogen bonded to the proton on N(2), with the orientation of the DMSO molecules differing from that in **3d**. In **4**, the DMSO methyl groups are oriented away from the metal (in the same manner as the disordered DMSO methyl groups in **2b** and there are no methyl–phenyl–π-facial contacts within the three component units).

Instead of hydrogen bonded chains, the complexes form chains linked by centrosymmetric pairs of aromatic CH · · · π-facial interactions as shown in Fig. 8 and Fig. 9. The interactions are of the same type as observed in **2b**. In addition, each of the remaining six faces of the four phenyl rings in the motif has a methyl group (–NMe from a ligand, C(5), the *anti* methyl, or –SMe from a DMSO molecule C(19)) interacting with it (Fig. 10).

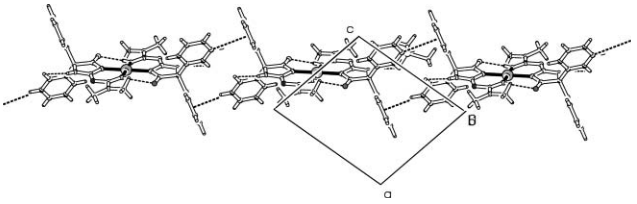


Fig. 9 A PLATON[29] depiction of one of the chains of complexes for **4a** linked by the synthon consisting of a centrosymmetric pair of aromatic CH to π-facial interactions.

Concluding remarks

The structures of six pseudo-macrocyclic complexes of similar ligands that possess potential self-complementary hydrogen bonding doublet DA motifs have been examined. Where linking of these motifs is not prevented by solvation of the motif or by the steric requirements of the ligand, the complexes form chains involving $R^2_2(8)$ hydrogen bond patterns. When hydrogen bonding is not possible, phenyl embraces link the complexes together. In all cases, the chains are offset from one another in the crystal rather than forming 'channels'. The rational modification of the alignment of these chains by making small structural changes to the ligand remains a goal of planned future studies.

Other points of interest arising from the studies include: (i) Hydrogen bonded chains in which the hydrogen bonded ligands of adjacent complexes are approximately coplanar (**1a, 3b, 3c**) were observed but the steric requirements of the ligands can also cause twisting of the chains (**2a**). (ii) The five coordinate complexes **1a** and **3c** show different 'orientational' motifs within the chains. (iii) Where hydrogen bonding of the neutral complexes is not possible because of solvation (**2b, 3d**) or the steric requirements of the ligand (**4**), the complexes yield chains involving the phenyl substituents in (OFF)(EF)$_2$ embraces or involve centrosymmetric aromatic CH to π-facial interactions, or both. (iv) Complexes of different ligands differ in the ease with which the hydrogen bonded form can be isolated from a solution of the strong hydrogen bond acceptor, DMSO (**2a, 2b** and **3c, 3d**). (v) Variation of the solvent or conditions of crystallisation can also give rise to different supramolecular structures (**3a, 3b, 3c, 3d**) with molecules of the respective solvents incorporated in different ways. Finally, (iv) it is noted that methyl groups attached to heteroatoms (O, N, S) exhibit a tendency to form CH to π-facial contacts with ligand phenyl rings.

Acknowledgements

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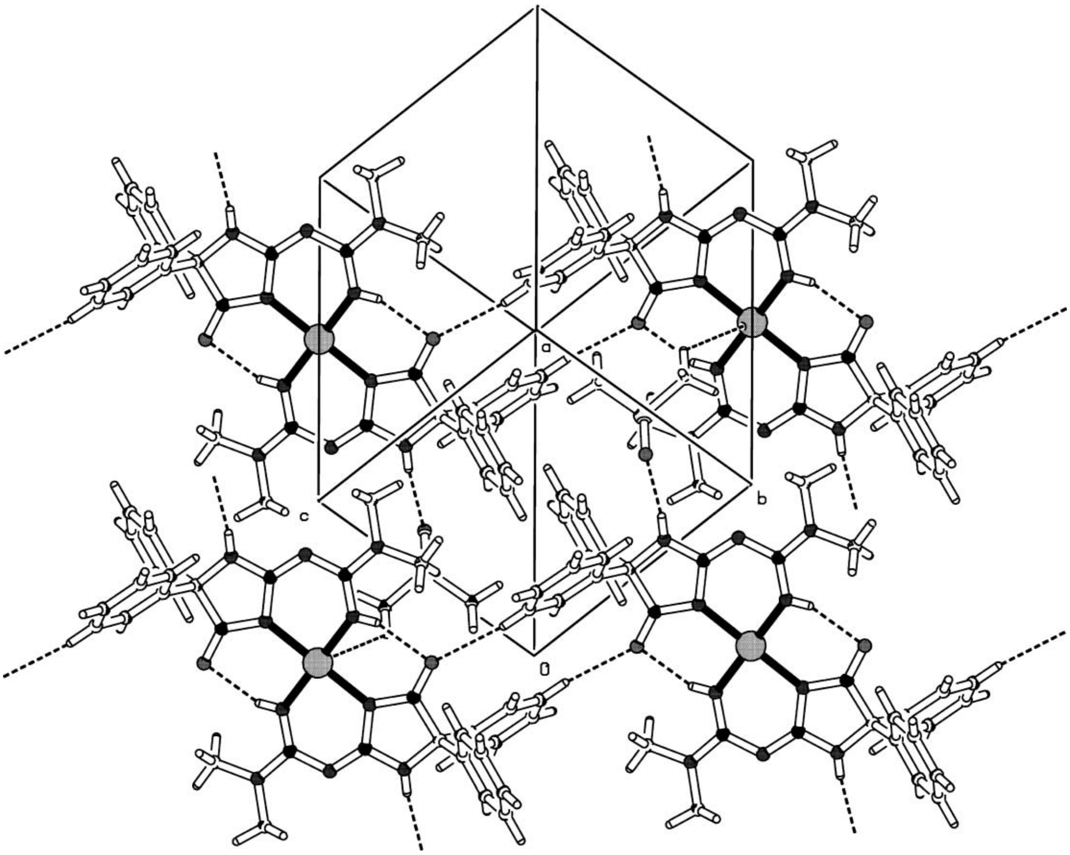

Fig. 10 A PLATON[29] depiction of **4a** showing the intermolecular interactions. For clarity, only two DMSO molecules are shown.

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