Dicopper(II) Complexes of a 28-Membered N_8 Macrocycle. Evidence for Proton Transfer from Co-ordinated Secondary Amine to Thiocyanate, leading to Formation of an Isothiocyanic Acid Complex†

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Schiff-base template condensation of 2,6-diacetylpyridine with the diamine 3,3′-diaminodipropylamine on Ag^+, Pb^{2+}, Ca^{2+}, or Sr^{2+} led to binuclear Ag^+ and Pb^{2+} and mononuclear Ca^{2+} and Sr^{2+} complexes of the 28-membered ligand H_2L. A series of binuclear Cu^{II} complexes of this macrocycle, including $[Cu_2(H_2L)(NCS)_4]$, were prepared by transmetallation in acetonitrile solution. A complex of formula $Cu_2(HL)(BPh_4)_3{\cdot}2MeCN$ was prepared from $[Sr(H_2L)][BPh_4]_2$ and $Cu(O_2CMe)_2$ in the presence of excess $NaBPh_4$. This cation was characterised by e.s.r. as a dicopper(II) complex of the singly deprotonated ligand HL^-. The complex $[Cu_2(L)(HNCS)_2][BPh_4]_2{\cdot}1.5MeCN$ was prepared, which showed $\nu_{asym}(NCS)$ at 1 992 cm^{-1}, characteristic of bridging thiocyanate. A single-crystal *X*-ray structure determination was carried out. Crystals were triclinic, space group $P\bar{1}$ with a = 14.695(11), b = 14.051(11), c = 20.721(11) Å, α = 111.5(1), β = 98.8(1), γ = 100.3(1)°, and Z = 2. 3 969 Independent reflections above background have been measured on a diffractometer and the structure refined to R = 0.089. The unit cell contains two independent cations both with imposed $\bar{1}$ symmetry, four BPh_4^- anions and solvent molecules. In both cations the Cu ··· Cu distance is 7.25 Å. Each copper atom is bonded to four nitrogen atoms of the macrocycle and nitrogen of a terminal thiocyanate. The Cu–N–C(S) angles were unusually small at 100(2) and 109(2)°. We believe that the explanation for the correlated phenomenon of small Cu–N–C angle and a low value for the $\nu_{asym}(NCS)$ absorption is that proton transfer has occurred from the co-ordinated NH group to the NCS ion, making this a complex of thiocyanic acid with the macrocyclic ligand being in the doubly deprotonated form L^{2-}.

Recently we have investigated[1] a number of binuclear Cu^{II} complexes where, because of proximity of the paramagnetic centres or intermediacy of a bridging ligand, strong interaction exists between the Cu^{II} centres. This present work describes binuclear Cu^{II} complexes with the macrocycle H_2L (and deprotonated forms) and the hydrogenated ligand L′ (H_2L + 8 H), where the internuclear distance is long and bridging ligands are absent (Figure 1).

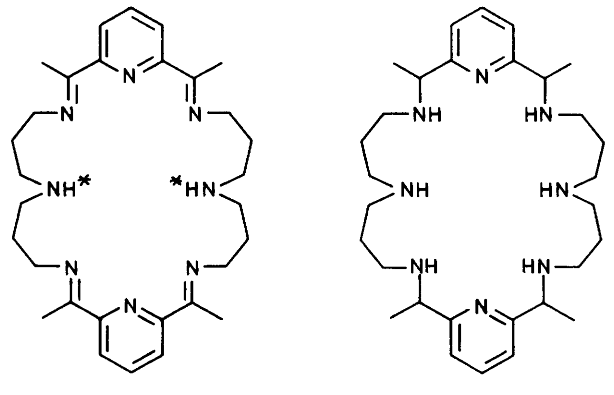
H_2L L′ (H_2L + 8 H)

Figure 1. Hydrogen atoms indicated * are those lost on deprotonation. The ligands HL^- and L^{2-} have lost one and two amino hydrogens respectively

Intriguingly, in one instance preliminary i.r. spectroscopic data implied the existence of a single-atom thiocyanate bridge, but *X*-ray crystallographic structural investigations did not confirm this, suggesting instead formation of an isothiocyanic acid complex.

Isothiocyanic acid (HCNS), being a strong acid of pK_a *ca.* − 1.8, is not expected to co-ordinate to metal ions as the neutral (unionised) acid, although protonation of N-co-ordinated NCS^- in Co^{III} complexes in highly acidic media has been suggested.[2] The thiocyanate ion $(NCS)^-$, on the other hand, is a well known ambidentate ligand capable of co-ordinating in the variety of modes, (a)—(e). A distinctive property of bridging mode (e) is the occurrence of the thiocyanate asymmetric stretch, $\nu_{asym}(NCS)$, below 2 000 cm^{-1} in the i.r. spectrum.[3–5] When a presumed dithiocyanato complex of the ligand under study exhibited $\nu_{asym}(NCS)$ as a strong band at 1 992 cm^{-1} in the Nujol mull spectrum an *X*-ray structure determination was undertaken to discover whether a single-atom bridge could indeed be accommodated in a macrocycle of this size and conformation. As described below, the *X*-ray work showed that the complex does not contain N-only bridging NCS^-. The most plausible explanation of both i.r. and *X*-ray evidence is the existence of terminally N-co-ordinated HNCS.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, Issue 1, 1987, pp. xvii—xx.

Non-S.I. unit employed: G = 10^{-4} T.

Table 1. Analytical (%),[a] i.r., and conductance data for the dicopper(II) complexes

Complex	Yield (%)	N	C	H	Λ^b/S cm^2 mol^{-1}	I.r.		
						ν(NH)	ν(C=N)	ν(NYX⁻) or ν(ClO$_4^-$)
(1) $[Cu_2(H_2L)(H_2O)_4]_2[ClO_4]_4$	50	10.0 (10.05)	32.0 (32.35)	4.40 (4.70)	381	3 245m	1 622m	1 090vs, 622s
(2) $[Cu_2(H_2L)(NCS)_4]$	70	19.25 (19.20)	46.45 (46.6)	5.05 (5.05)	insol	3 170br	1 613m	2 035s, 2 062 (sh)
(3) $[Cu_2(H_2L)(NCSe)_4]$	60	15.7 (15.85)	38.2 (38.4)	4.35 (4.15)	insol	3 145m	1 612m	2 056s, 2 078 (sh)
(4) $[Cu_2(HL)(MeCN)_2][BPh_4]_3$	90	8.35 (8.20)	74.5 (74.75)	6.45 (6.50)	304	3 190w	1 613m	
(5) $[Cu_2(HL)(dmf)_2][BPh_4]_3{\cdot}3H_2O$	70	7.70 (7.75)	71.7 (72.0)	6.90 (6.90)		3 170w	1 620m (sh)	
(6) $[Cu_2(L)(HNCS)_2][BPh_4]_2{\cdot}1.5MeCN$	55	10.75 (11.0)	68.5 (68.3)	6.05 (6.10)	279	3 175mw	1 612m	1 992s
(7) $[Cu_2(L)(HN_3)_2][BPh_4]_2{\cdot}H_2O$	70	14.4 (14.15)	67.55 (67.7)	6.15 (6.30)	insol	3 190w,br	1 612m	2 005ms 1 090vs, 622s
(8) $[Cu_2(L')(H_2O)_4][ClO_4]_4$	40	9.85 (10.0)	32.7 (32.1)	4.90 (5.40)	370	3 210ms		622s

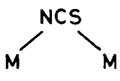
[a] Calculated values in parentheses. [b] 10^{-3} mol dm^{-3} solution in MeCN; insol = insoluble.

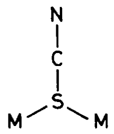
M—NCS

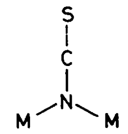
(a)

M—SCN

(b)


(c)


(d)


(e)

Results and Discussion

The macrocycle H_2L was prepared, as described elsewhere,[6] by (2 + 2) Schiff-base template condensation of 2,6-diacetylpyridine with the diamine 3,3′-diaminodipropylamine on Ag^+, Pb^{2+}, Ca^{2+}, or Sr^{2+} in dry methanol leading to binuclear Ag^+, Pb^{2+} but mononuclear Ca^{2+} and Sr^{2+} complexes of the 28-membered ligand H_2L. The dicopper(II) derivatives were easily obtained by transmetallation in acetonitrile solution. The complexes studied are characterised in Table 1. A complex of the reduced ligand (L′) also studied was obtained by direct reaction of its constituents.

The stoicheiometry of the tetraphenylborate salt obtained from $[Sr(H_2L)][BPh_4]_2$ and $Cu(O_2CMe)_2$ in the presence of excess $NaBPh_4$ merits discussion at this stage. This green crystalline complex, which could be obtained either as MeCN or dimethylformamide (dmf) solvate was not (as expected) a tetrakis(tetraphenylborate) salt, but instead analysed to the formula $Cu_2(HL)(BPh_4)_3{\cdot}2$(solvent). No i.r. absorption corresponding to co-ordinated OH^- was observed and the e.s.r. spectrum (see later) demonstrated that the complex was not a mixed-valence Cu^{II}/Cu^{I} salt but a Cu^{II} dimer. Accordingly the cation was formulated as a dicopper(II) complex of the singly deprotonated ligand HL^-.

An increase of acidity of the secondary amino group, >NH, is a well known consequence of co-ordination, in this case leading to deprotonation in the presence of $MeCO_2^-$. The cavity size in this macrocycle is particularly well suited to strong co-ordination of first transition series ions, as evidenced by the existence in the low-spin state of Fe^{II} complexes of H_2L in conjunction with weak-field axial ligands such as Cl^-.[6]

All the complexes listed in Table 1 showed the expected ν(C=N) and pyridine ring absorptions in the i.r. spectrum as a pair of medium-strong bands close to 1 600 cm^{-1}; no absorptions were observed at 1 700 cm^{-1} which might suggest the formation of C=O during the transmetallation reaction. The most variable feature in terms of both intensity and position of the macrocyclic spectrum in this series of complexes is the ν(N–H) absorption which is broadened and shifted in some complexes, indicating hydrogen-bonding interactions.

Table 2. Electronic spectral and magnetic data for the dicopper(II) complexes

Complex	Colour	$\mu_{eff.}$[a]		θ/K	$\nu_{max.}$/cm^{-1} (ε/cm^3 mol^{-1})[b]
		293 K	93 K		
(1)	Blue	1.87	1.81	−10	15 900 (333)
(2)	Green	1.82	1.77	−10	15 900[c]
(3)	Green	1.75	1.71	−18	16 300[c]
(4)	Bottle green	1.85	1.73	−20	16 200 (190)
(6)	Bright green	1.88	1.76	−15	15 100 (280) 16 300[c]
(7)	Pale green	2.02	1.94	−20	
(8)	Blue	1.88	1.80	−15	16 950 (347).

[a] Magnetic moment per metal ion. [b] In MeCN, unless stated otherwise. [c] Nujol mull spectrum.

Infrared spectra and conductivity measurements show that ClO_4^- is ionic, and the pseudohalide is co-ordinated in terminal N-bonding mode, in all the complexes studied. The uniquely low ν_{asym}(NCS) value observed for compound (6) will be discussed later.

The observation of a medium intensity band close to 16 000 cm^{-1} in the electronic spectrum of the complexes (Table 2) is consistent with orthogonal (tetragonal, square pyramidal, or octahedral) geometry around the copper atom, indicating co-ordination of water in the tetraperchlorate salts.

Magnetic data indicate the operation of a weak exchange interaction between the paramagnetic centres; the Curie-Weiss plots lie close to linear, with θ values ranging from −10 to −20 K. Attempts to fit the data to the Bleaney-Bowers equation yielded $-J$ values around 15—20 cm^{-1}; however, these values may only be taken as an indication of the upper limit of the interaction, because no data were available below 93 K from which to derive an accurate value of J.

E.S.R. Spectra.—E.s.r. parameters (Table 3) derived for the complexes confirm the inference of electronic spectra that Cu^{2+} ions are in a square-based co-ordination environment, with $g_\perp$ and $g_\parallel$ values lying in the range expected[7] for tetragonally extended or square-pyramidal geometry.

Table 3. E.s.r. parameters for the dicopper(II) complexes

	$g_\perp$		$g_\parallel$		
Complex	Solid	Glass[a]	Solid	Glass[a]	$A_\parallel$/G
(1)	2.05	2.07[b]	2.14	2.21[b]	81
(2)	2.07	2.07	2.16	2.21	77
(3)	2.05	2.08	2.17	2.20	82
(4)	2.07	2.08	2.20	2.21	78
(5)	2.08	2.08[b]	2.21	2.21[b]	78
(6)	2.06	2.07	2.20	2.19	82
(8)	2.09	2.09	2.20	2.23	80

[a] In Me_2SO–MeOH. [b] In dmf.

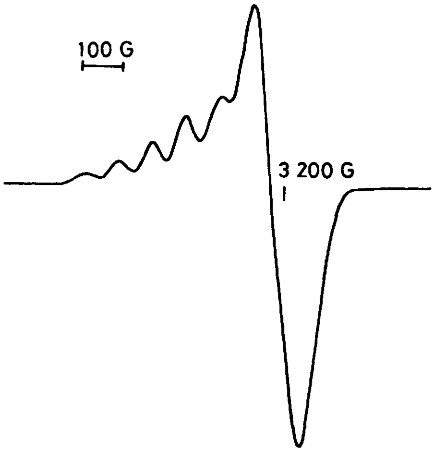


Figure 2. E.s.r. spectrum of polycrystalline (**4**): $g = 2$; hyperfine splitting, $A_\parallel = 78$ G

When studied as glasses in dmf or Me_2SO–MeOH, or as polycrystalline tetraphenylborate salts, hyperfine splitting is apparent on the $g_\parallel$ signal (Figure 2). The axial-type spectrum shows, in the parallel signal, five lines of relative intensity 1:2:3:4:3, the remainder of the signal being overlapped by the more intense $g_\perp$ component. Because no parallel lines appear on the high-field side of the perpendicular signal where any possible eighth or ninth component would be clear of interference, the five lines are interpreted as the first five lines of a seven-line $g_\parallel$ pattern, with relative intensity 1:2:3:4:3:2:1. The hyperfine splitting constant $A_\parallel$ is in the range typically observed for Cu^{II} dimers.[8]

All the complexes in Table 3 show the same hyperfine splitting pattern in frozen solution. Although some spectra are better resolved than others, in all cases five lines of approximate 1:2:3:4:3 intensity ratio are discernible on the low-field 'wing' of the $g_\parallel$ signal. The small hyperfine coupling constant (80 G) provides clear evidence of interaction between the metal centres in all these complexes. Examination of the 1 500—1 600 G region of the spectrum of the most soluble complex, of formula $Cu_2(H_2L)(ClO_4)_4{\cdot}4H_2O$, at high sensitivity provides further corroboration: the forbidden $\Delta m = 2$ 'half-band' signal appears weakly. This is also split into seven lines with a hyperfine splitting (74 G) just slightly less than that observed for the $\Delta m = 1$ signal. Similar seven-line half-band signals were observed for most of the complexes in Table 3, with the exception of the very insoluble tetrathiocyanato or tetraselenocyanato complexes. The observation of the half-band signal for polycrystalline $[Cu_2(HL)(MeCN)_2][BPh_4]_3$ (Figure 3) proves that this is a Cu^{II} dimer and not a mixed-valence Cu^{II}/Cu^{I} complex.

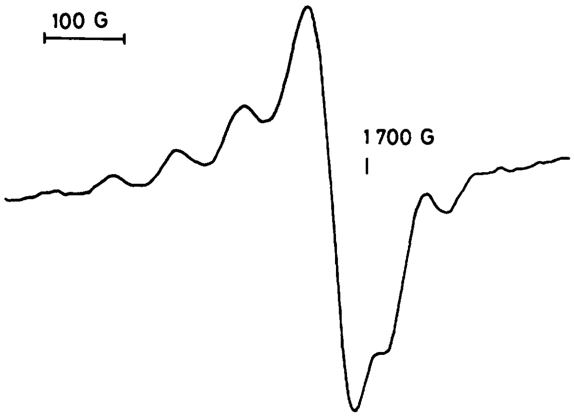


Figure 3. E.s.r. spectrum of polycrystalline (**4**): $g = 4$; at high sensitivity ($\times 10^3$); hyperfine splitting, $A_\parallel = 77$ G

Despite this evidence of interaction between paramagnetic centres, there is no pronounced anisotropy in the $g = 2$ signal constituting a recognisable 'triplet' spectrum. In particular, no more than one, perhaps broadened, $g_\perp$ signal was ever observed. A small (*ca.* 30 G) splitting of each component of the $g_\parallel$ signal was indeed observed in the better resolved frozen solution spectra (Figure 4). We think it possible that this represents the zero-field splitting ($2D_2$) arising from interaction with the second Cu^{II} ion in the macrocycle. A zero-field splitting of this order is to be expected from a purely dipolar interaction at the likely internuclear distance of 7—8 Å for a pair of Cu^{II} ions oriented at an angle of *ca.* 45—50° to the field direction (considered 90° to the CuN_4 planes), according to equation (1).[9] On the basis of

$$D_{d\text{-}d} = 0.75\, g^2\beta^2(1 - 3\cos^2\theta)/r_{12}^3 \qquad (1)$$

the structure determination which follows, the values for θ and r_{12} from (1) seem to present a reasonable approximation to the geometry in this series of Cu^{II} dimers.

Dithiocyanato Bis(tetraphenylborate) Complex.—Although polycrystalline e.s.r. spectra of this complex are broad, and no further splitting of hyperfine lines corresponding to zero-field splitting is observed, there is no indication that zero-field splitting is larger than that observed (30 G) in sharper spectra obtained with other members of the series. So it was puzzling that the i.r. spectrum of this complex exhibited a ν_{asym}(NCS) absorption at 1 992 cm^{-1}.* With the exception of thiocyanate co-ordinated to metals in high oxidation states,[10] ν_{asym}(NCS) frequencies below 2 000 cm^{-1} have been observed previously only where the N atom of NCS^- bridges two metal ions as in mode (e).[3–5] The existence of a single-atom Cu–N–Cu bridge would imply much more substantial interaction between the paramagnetic centres than that observed experimentally. Accordingly an *X*-ray crystallographic structure determination was undertaken to establish the structure of the complex.

Crystal Structure of (**6**).—The unit cell contains two independent cations, for which we propose the formula

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* In the mull spectrum only; in MeCN solution the frequency observed was 2 080 cm^{-1} and in KBr disc peaks at both 1 990 and 2 080 cm^{-1} were observed.

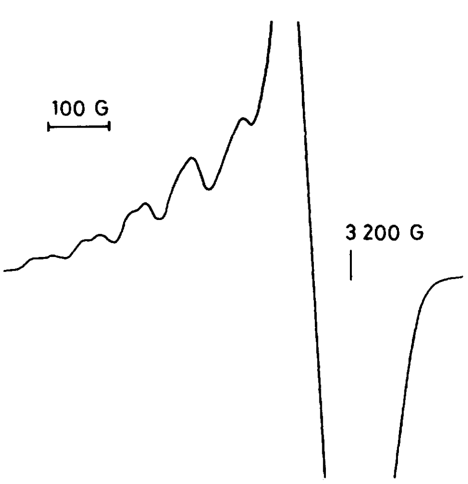

Figure 4. Frozen solution e.s.r. spectrum of (**5**): $g = 2$; zero-field splitting, $2D_2 = ca.\ 30$ G

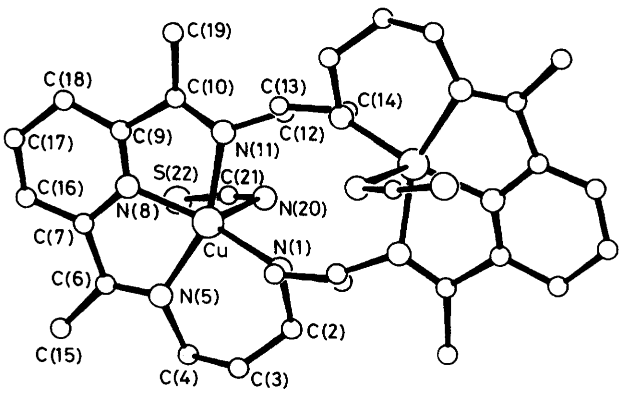

Figure 5. Structure of the [Cu$_2$(L)(HNCS)$_2$]$^{2+}$ cation

Table 4. Details of structures containing the Cu=N(thiocyanate) moiety with the smallest Cu–N–C angles (in ascending order)

Structure	Ref.	Cu–N–C/°	Cu–N/Å
(**6**)	*a*	100(2) 109(2)	2.31 2.33
(**9**) [Cu^{II}(en)$_2$(NCS)]Br^{b}	*c*	102.5	2.674
(**10**) [Cu$^{II}_3$(μ-dapo)$_2$(Hdapo)$_2$][NCS]$_4$^{d}	*e*	120.6	2.696
(**11**) [Cu^{II}(L″)(NCS)]PF$_6$^{f}	*g*	122.6	2.383
(**12**) [{Cu(L‴)$_2$(NCS)}$_2$(μ-NCS)$_2$]^{h}	*i*	142.8	2.205

[a] This work. [b] en = Ethylenediamine. [c] N. V. Pervukhina, N. V. Podberezskaya, and V. N. Kirichenko, *Zh. Strukt. Khim*, 1982, **23**, 130. [d] Hdapo = 1,3-diaminopropan-2-ol. [e] R. Kiverkas, A. Pajunen, and K. Smolander, *Finn. Chem. Lett.*, 1977, 256. [f] L″ = 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene. [g] A. Elia, E. C. Lingafelter, and V. Schomaker, *Acta Crystallogr., Sect. C*, 1984, **40**, 1313. [h] L‴ = 2*H*-5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine. [i] J. G. Haasnoot, W. L. Dreissen, and J. Reedijk, *Inorg. Chem.*, 1984, **23**, 2803.

[Cu$_2$(L)(HNCS)$_2$]$^{2+}$, with crystallographically imposed centres of symmetry and four independent BPh$_4^-$ anions together with solvent MeCN molecules. The two cations have similar conformations; cation A is shown in Figure 5. The packing of the cations in the unit cell is shown in Figure 6. Cu ··· Cu distances are 7.25 and 7.25 Å between atoms in the same macrocycle and 6.20, 7.21, and 7.54 Å between atoms in different macrocycles. In the cations, the copper atoms are five-co-ordinate being bonded to four nitrogen atoms of the macrocycle in an approximate square plane [Cu–N bond lengths (Å): in A, N(1) 1.99(1), N(5) 2.07(1), N(8) 1.91(1), N(11) 2.07(2); in **B**, N(1) 2.02(1), N(5) 2.07(1), N(8) 1.91(1), N(11) 2.10(1)] and a thiocyanate in an axial position [A, 2.31(2); **B**, 2.33(2) Å]. The square planes are considerably distorted from ideal as is apparent from the bond angles.

The most interesting feature of the structure is the unusually small value of the Cu–N–C angles at 109(2) and 100(2)°. As stated above, we believe that this result, which parallels a similarly unusual ν_{asym}(NCS) frequency, is due to hydrogen transfer from the macrocycle to the thiocyanate resulting in an hydrothiocyanate complex.

However, it is interesting to note that there are close intermolecular contacts between N(1A) and N(20B) and between N(1B) and N(20A), both of 3.49 Å. When hydrogen atoms are placed in trigonal positions on the thiocyanate nitrogen atoms, N(20A) and N(20B) respectively, the calculated N(1) ··· H–N(20) angles are 160 and 162°. If they are placed on N(1) in tetrahedral positions the N(1)–H ··· N(20) angles are 162 and 160°. So whichever nitrogen the hydrogen is bonded to, it will be positioned close to the N ··· N vector and a strong N–H ··· N hydrogen bond will be formed. As stated in the Experimental section, we were unable to locate the position of the hydrogen atom. This is not too surprising in view of the large number of atoms in the structure. However it may indicate some disorder in the hydrogen position between the two possible sites.

What is clear, however, is that the dimensions of the Cu–NCS moiety are unique. We searched the Cambridge Data Centre files for Cu–N(thiocyanate) groups and found 80 examples from 38 structures. The mean Cu–N–C angle was 160.8° and the mean Cu–N distance was 2.055 Å. Details of the structures with the smallest Cu–N–C angles are given in Table 4, where the names of the ligands are listed, as a footnote. There are only four other structures with angles less than 150°. There is a high inverse correlation between increasing Cu–N distance and decreasing Cu–N–C angle as is apparent from the Table and the mean values. Indeed structures (**9**) and (**10**) (Table 4) have very large Cu–N distances that may represent only a weak interaction. In (**12**) the small angles are a consequence of the thiocyanate groups bridging the metal atoms. Therefore the only structure that is similar to our own is (**11**) (Table 4) where the thiocyanate is in the axial site of a square pyramid formed by the four donor nitrogen atoms of the macrocycle. However there is a weak interaction between copper atoms and sulphur atoms of adjacent thiocyanates (3.22 Å) in the vacant axial position to form a weak polymeric chain. In (**6**) there are similar contacts in the axial position for the copper atoms of 3.56 and 3.81 Å (see Figure 6). However (**11**) has no hydrogen atoms bonded to the axial nitrogens which can be transferred to the thiocyanate group. The ν_{asym} value for (**11**) was not reported.

For the unique compound (**6**) (Table 1) we believe that the explanation for the correlated phenomenon of small Cu–N–C angle and low ν_{asym}(NCS) value is that proton transfer has occurred from the co-ordinated NH group to the NCS ion, making this a complex of thiocyanic acid with the macrocyclic ligand being in the deprotonated form. The ν_{asym}(NCS) absorption of isothiocyanic acid is observed as a strong band at 1 980 cm^{-1} in inert solvents, moving to higher frequencies on hydrogen bonding, so 1 992 cm^{-1} is a reasonable frequency at which to observe co-ordinated isothiocyanic acid, particularly when involved in hydrogen bonding.

As we have noted already in the case of the tris(tetraphenylborate) salt, strong co-ordination of –NH in the equatorial plane of the Cu^{II} co-ordination polyhedron has a marked effect on the acidity of the –NH group. In addition to the co-

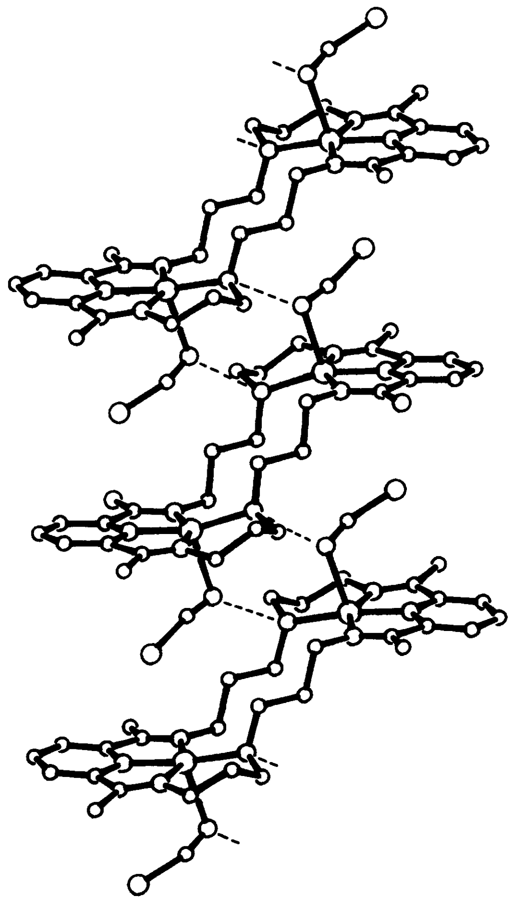

Figure 6. The packing of the $[Cu_2(L)(HNCS)_2]^{2+}$ cations showing the N–H ··· N interactions as dotted lines

ordination effect, it may be that the non-polar environment affects the relative acidity of secondary –NH and isothiocyanic acid causing their usual (aqueous) Brönsted acidities to be reversed. It should be noted in this connection that the perchlorate analogue, $[Cu_2(H_2L)(NCS)_2][ClO_4]_2$,[11] shows a normal NCS^- frequency (at 2 095 cm^{-1}) with no evidence for isothiocyanic acid formation. The tetrathiocyanato complex, $[Cu_2(H_2L)(NCS)_4]$, also shows ν_{asym}(NCS) absorptions in the normal range for terminal N-bonded NCS^-.

A similar behaviour to (**6**) was noted in the case of the presumed diazido complex (**7**). This showed a sharp i.r. absorption (in the Nujol mull spectrum only) at 2 005 cm^{-1}. In KBr disc a broad absorption at 2 240 cm^{-1} dominates this region of the spectrum. As it seemed possible, by analogy with complex (**6**), that this was a complex of the highly explosive hydrazoic acid, HN_3, little work was done on this product.

While both the low value for ν_{asym} and the small Cu–N–C angle are consistent with heavier weighting of canonical forms such as N=C=S and $^-$N–C=S which permit bonding of the nitrogen to both Cu^{2+} and H^+, no evidence is found for this in the dimensions of the –NCS group in (**6**). However we note from our literature survey of thiocyanato-complexes that there is little or no correlation between –NCS dimensions and either type of bonding [types (a)—(e) inclusive] or ν_{asym}(NCS). Indeed no significant lengthening of the N–C bond in >N(CS) bridging [type (e)] compared with terminal –NCS was noted.[3,5]

There does not in general appear to be any good correlation between ν(NCS) and N=C bond length, as a comparison of HNCS with a selection of co-ordinated terminal NCS complexes shows. Possibly the origin of the unusually low ν_{asym}(NCS) in >N(CS) bridged complexes lies more in the absence of strong adjacent-bond interaction between motions in the M–N and N–C bonds. Such interaction is maximised when these oscillators are linearly arranged, as is normally the case with isothiocyanato complexes. The existence of a π-bonding system covering all four atoms M–N–C–S also implies strong adjacent-bond interaction. In the >N(CS) bonding mode, where M–N and N–C oscillators are arranged at angles closer to 90 than 180°, adjacent-bond interactions (and the M–N bonding which enhances them) are minimised.

Experimental

Preparation of the Ligands.—Macrocycle H_2L. The ligand H_2L was prepared, as described previously,[6] by template condensation of 2,6-diacetylpyridine with 3,3′-diaminodipropylamine on Group 2A metal ions or on Ag^+.

Macrocycle L′. This reduced ligand was obtained by BH_4^- reduction of $[Pb_2(H_2L)(NCS)_4]$ whose preparation is described in ref. 6. The reduction was carried out as described elsewhere.[12]

Preparation of the Complexes.—$[Cu_2(H_2L)(H_2O)_4][ClO_4]_4$. This complex was prepared on a millimolar scale by refluxing $Cu(ClO_4)_2\cdot 6H_2O$ (1 mmol) with $[Ag_2(H_2L)][ClO_4]_2$ (0.5 mmol) in acetonitrile–methanol (2:1, 100 cm^3) for *ca.* 30 min. Bright saxe-blue crystals were obtained on cooling.

$[Cu_2(HL)(MeCN)_2][BPh_4]_3$. To a solution of $[Sr(H_2L)][BPh_4]_2$ (1 mmol) in acetonitrile (50 cm^3) was added excess $NaBPh_4$ (*ca.* 1 g) and $Cu(O_2CMe)_2\cdot H_2O$ (2 mmol) in dry acetonitrile (50 cm^3). The $Sr(O_2CMe)_2$ precipitate was filtered off and the resulting blue-green solution concentrated to *ca.* 30 cm^3 on a rotary evaporator. The complex crystallised out as bottle-green crystals and could be recrystallised from acetonitrile. Recrystallisation from dimethylformamide yielded the product $[Cu_2(HL)(dmf)_2][BPh_4]_3\cdot 3H_2O$.

$[Cu_2(H_2L)(NCX)_4]$ (X = S *or* Se). To $[Cu_2(HL)(MeCN)_2][BPh_4]_3$ or $[Cu_2(H_2L)(H_2O)_4][ClO_4]_4$ (0.5 mmol) dissolved in acetonitrile (*ca.* 40 cm^3) was added, in slight excess, a methanol solution of LiNCS or KNCSe respectively. The pseudohalide complex crystallised out rapidly as small, bright green crystals.

$[Cu_2(L)(HNCS)_2][BPh_4]_2\cdot 1.5MeCN$ *and* $[Cu_2(L)(HN_3)_2][BPh_4]_2\cdot H_2O$. To $[Cu_2(HL)(MeCN)_2][BPh_4]_3$ (0.5 mmol) in acetonitrile (*ca.*30 cm^3) was added a slight deficit (0.9 mmol) of an alcoholic solution of LiNCS or NaN_3 respectively, and the complex allowed to crystallise. The green needles of the HCNS complex were stable in the solid state, while the blue-green needles of the HN_3 complex turned brownish on standing, particularly in light. As the HN_3 complex is potentially explosive, few measurements were carried out on this compound.

$[Cu_2(L')(H_2O)_4][ClO_4]_4$. To $Cu(ClO_4)_2\cdot 6H_2O$ (1 mmol) was added L′ (0.5 mmol) in methanol (*ca.* 150 cm^3). A deep blue solution was obtained from which the product crystallised on standing.

Physical Measurements.—E.s.r. spectra of the dicopper complexes were obtained as undiluted powders or as glasses in Me_2SO–MeOH or dmf, using a Varian E9 instrument. Other physical measurements were made as described in earlier papers.[13]

X-Ray Crystallography.—Crystals of (**6**) were prepared as described above.

Crystal data. $[Cu_2(L)(HNCS)_2][BPh_4]_2\cdot 1.5MeCN$, $C_{83}H_{88.5}B_2Cu_2N_{11.5}$, M = 1 460.0, triclinic, space group $P\bar{1}$, a = 14.695(11), b = 14.051(11), c = 20.721(11) Å, α = 111.5(1),

Table 5. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	−1 395(1)	1 819(1)	5(2)	C(002)	7 309(23)	4 386(23)	3 288(28)
N(20A)	−1 057(10)	3 227(13)	325(17)	C(003)	6 603(15)	4 645(21)	3 363(30)
C(21A)	−1 432(16)	3 817(17)	259(23)	N(004)	4 819(23)	684(26)	6 729(36)
S(22A1)	−2 234(8)	4 642(7)	499(12)	C(005)	4 766(28)	49(25)	7 234(84)
S(22A2)	−1 907(13)	4 648(11)	32(19)	C(006)	4 714(46)	−554(53)	7 579(77)
N(1A)	−370(7)	1 285(8)	−982(11)	B(1)	3 993(13)	4 266(16)	2 742(17)
C(2A)	−131(9)	1 597(11)	−1 983(14)	C(31)	4 122(11)	3 724(15)	3 661(14)
C(3A)	−620(9)	1 432(13)	−2 604(13)	C(32)	4 629(11)	3 855(13)	4 023(18)
C(4A)	−1 324(10)	2 176(12)	−2 132(14)	C(33)	4 733(11)	3 341(21)	4 726(18)
N(5A)	−1 798(9)	2 157(9)	−1 059(12)	C(34)	4 362(16)	2 631(16)	4 983(18)
C(6A)	−2 482(11)	2 480(11)	−679(16)	C(35)	3 860(13)	2 474(17)	4 606(22)
C(7A)	−2 865(10)	2 424(10)	415(14)	C(36)	3 773(11)	3 011(17)	3 938(18)
N(8A)	−2 401(7)	2 151(8)	860(13)	C(41)	4 320(14)	5 237(13)	2 813(17)
C(9A)	−2 656(10)	2 045(9)	1 859(19)	C(42)	5 047(12)	5 275(17)	2 396(15)
C(10A)	−2 077(13)	1 779(11)	2 200(18)	C(43)	5 286(14)	6 077(23)	2 509(20)
N(11A)	−1 448(9)	1 562(9)	1 430(13)	C(44)	4 770(21)	6 915(20)	3 130(24)
C(12A)	−820(9)	1 263(11)	1 634(12)	C(45)	4 062(17)	6 945(19)	3 571(19)
C(13A)	−616(9)	194(10)	1 571(12)	C(46)	3 831(12)	6 126(22)	3 432(17)
C(14A)	148(7)	−221(12)	1 225(12)	C(51)	3 137(11)	4 556(12)	3 018(21)
C(15A)	−2 891(10)	2 888(12)	−1 248(15)	C(52)	2 591(14)	4 751(12)	4 035(18)
C(16A)	−3 593(9)	2 577(11)	1 007(16)	C(53)	1 895(18)	5 074(15)	4 268(21)
C(17A)	−3 846(11)	2 444(14)	1 980(19)	C(54)	1 690(12)	5 176(15)	3 390(31)
C(18A)	−3 390(11)	2 190(11)	2 454(15)	C(55)	2 240(17)	4 970(14)	2 366(26)
C(19A)	−2 260(9)	1 761(13)	3 329(15)	C(56)	2 950(13)	4 673(13)	2 174(20)
Cu(2)	1 137(1)	3 212(1)	531(2)	C(61)	4 471(9)	3 569(15)	1 543(18)
N(20B)	818(9)	1 795(10)	122(13)	C(62)	4 609(10)	2 545(17)	1 334(19)
C(21B)	1 259(11)	1 303(16)	96(18)	C(63)	4 975(9)	1 947(13)	301(20)
S(22B)	1 868(4)	415(5)	161(7)	C(64)	5 253(9)	2 310(16)	−564(17)
N(1B)	100(7)	3 930(9)	1 318(11)	C(65)	5 118(10)	3 345(17)	−366(19)
C(2B)	−288(10)	3 724(13)	2 365(16)	C(66)	4 755(10)	3 895(15)	636(19)
C(3B)	71(10)	3 851(13)	3 114(14)	B(2)	2 131(14)	339(15)	4 571(22)
C(4B)	746(11)	3 053(15)	2 853(17)	C(71)	1 734(14)	−566(14)	4 734(19)
N(5B)	1 304(11)	3 020(10)	1 843(14)	C(72)	2 164(11)	−1 493(18)	4 192(17)
C(6B)	1 956(13)	2 771(12)	1 698(18)	C(73)	1 887(15)	−2 276(13)	4 354(17)
C(7B)	2 501(13)	2 719(11)	583(21)	C(74)	1 211(17)	−2 194(18)	5 086(22)
N(8B)	2 156(8)	2 916(9)	−45(18)	C(75)	780(11)	−1 292(22)	5 623(16)
C(9B)	2 540(12)	2 868(11)	−1 073(22)	C(76)	1 038(13)	−490(15)	5 459(16)
C(10B)	2 073(10)	3 119(11)	−1 646(17)	C(91)	2 550(14)	305(13)	5 383(19)
N(11B)	1 399(10)	3 316(8)	−1 030(11)	C(92)	2 151(12)	744(15)	6 486(23)
C(12B)	841(10)	3 578(11)	−1 415(13)	C(93)	2 464(16)	666(15)	7 181(20)
C(13B)	743(9)	4 633(11)	−1 480(13)	C(94)	3 178(18)	187(18)	6 849(26)
C(14B)	5(8)	5 019(11)	−1 423(12)	C(95)	3 536(15)	−232(17)	5 775(30)
C(15B)	2 260(11)	2 477(14)	2 461(16)	C(96)	3 244(14)	−202(15)	5 025(19)
C(16B)	3 226(14)	2 527(13)	152(20)	C(81)	1 545(14)	1 366(15)	4 924(15)
C(17B)	3 618(10)	2 492(13)	−911(20)	C(82)	892(15)	1 585(20)	4 942(17)
C(18B)	3 279(11)	2 659(11)	−1 565(15)	C(83)	451(12)	2 475(23)	5 253(17)
C(19B)	2 396(10)	3 119(14)	−2 777(14)	C(84)	737(18)	3 241(17)	5 513(17)
N(001)	7 873(17)	4 264(27)	3 200(28)	C(85)	1 385(18)	3 123(21)	5 460(19)
				C(86)	1 834(18)	2 132(20)	5 167(18)

$\beta = 98.8(1)$, $\gamma = 100.3(1)^\circ$, $U = 3\,804.6$ Å^3, $D_m = 1.28(3)$ g cm^{-3}, $Z = 2$, $D_c = 1.27$ g cm^{-3}, $F(000) = 1\,534$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, $\mu = 6.90$ cm^{-1}.

A crystal of approximate size 0.30 × 0.30 × 0.20 mm was mounted on a Stoe Stadi-2 diffractometer and data collected *via* variable-width ω scan. Background counts were 20 s and the scan rate of 0.033° s^{-1} was applied to a width of $(2.0 + \sin\mu/\tan\theta)^\circ$. 9 163 Independent reflections with $2\theta < 50^\circ$ of which 3 969 with $I > 2\sigma(I)$ were used in subsequent refinement. Neither an absorption nor an extinction correction was applied. The structure was determined by heavy-atom methods. There were two independent $[Cu_2(L)(HNCS)_2]^{2+}$ units in the unit cell, each containing a crystallographically imposed centre of symmetry. The two independent BPh_4^- anions in the asymmetric unit have no imposed symmetry. One MeCN solvent molecule [N(004), C(005), C(006)] was given an occupation factor of 0.5. Positions were located for S(22A) and their occupancy factors were refined to 0.65 and 0.35 respectively.

In view of the amount of significant data available and the large number of parameters, only the copper and sulphur atoms were refined anisotropically. Hydrogen atoms were placed in geometric positions and their thermal parameters only were refined. Calculations were performed using full-matrix least squares with a weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$. Scattering factors were taken from ref. 14. Calculations were performed using SHELX 76 [15] on the Amdahl V7A computer at the University of Reading. The final *R* value was 0.089 ($R' = 0.090$) $\{R = \Sigma|\Delta F|/|F_o|,\ R' = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. In view of the importance of locating a hydrogen atom on the thiocyanate group, special effort was put into this. However, no conclusive evidence could be found. Final atomic co-ordinates are given in Table 5 and bond lengths and angles in the metal co-ordination spheres are given in Table 6.

Table 6. Dimensions in the co-ordination spheres (distances in Å, angles in °)

	Molecule	
	A	B
Cu(1)–N20)	2.314(20)	2.329(17)
Cu(1)–N(1)	1.993(11)	2.022(12)
Cu(1)–N(5)	2.072(21)	2.066(23)
Cu(1)–N(8)	1.912(13)	1.909(16)
Cu(1)–N(11)	2.073(19)	2.098(15)
N(1)–Cu(1)–N(20)	85.2(6)	91.3(6)
N(5)–Cu(1)–N(20)	96.2(8)	98.6(7)
N(5)–Cu(1)–N(1)	99.6(6)	96.8(7)
N(8)–Cu(1)–N(20)	103.7(6)	106.7(6)
N(8)–Cu(1)–N(1)	171.2(6)	161.9(6)
N(8)–Cu(1)–N(5)	78.3(7)	79.4(10)
N(11)–Cu(1)–N(20)	92.2(8)	89.1(6)
N(11)–Cu(1)–N(1)	103.7(7)	103.9(7)
N(11)–Cu(1)–N(5)	155.9(7)	157.7(8)
N(11)–Cu(1)–N(8)	77.8(8)	78.4(10)

Dimensions in the thiocyanate

C(21A)–N(20A)	1.11(4)	C(21A)–N(20A)–Cu(1)	109(2)
S(22A1)–C(21A)	1.78(3)	C(21B)–N(20B)–Cu(2)	100(2)
S(22A2)–C(21A)	1.60(4)	S(22A1)–C(21A)–N(20A)	165(2)
C(21B)–N(20B)	1.06(3)	C(22A2)–C(21A)–N(20A)	166(2)
C(22B)–C(21B)	1.71(3)	C(22B)–C(21B)–N(20B)	171(2)

Conclusions

The series of Cu^{II} dimers studied displays weak interaction between Cu^{2+} ions separated by 7—8 Å. The secondary amine function deprotonates readily when co-ordinated leading to formation of complexes of the singly and doubly deprotonated macrocycle. In the latter case, the proton may transfer to the counter ion, resulting in the first authentic example of a complex containing co-ordinated isothiocyanic acid.

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