Copper Complexes with Quadridentate Bis(pyrazolyl)thioether Amine and Tris(pyrazolyl)amine Ligands. Structural Characterization of the Complexes $[Cu(NCS)(tpea)][Cu(NCS)_2]$ and $[CuCl(bdma)]Cl{\cdot}2H_2O$ [*]

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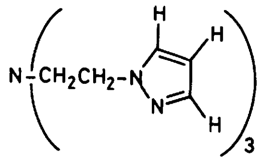
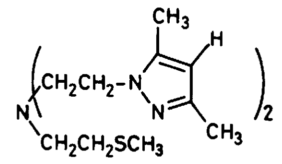
Copper complexes with the two tripod quadridentate ligands tris(2-pyrazolylethyl)amine (tpea) and bis[2-(3′,5′-dimethylpyrazolyl)ethyl](2-methylthioethyl)amine (bdma) having N_4 and N_3S donor sets, respectively, have been synthesized and assigned the following formulae: $[CuX(tpea)]BPh_4$ (X = Cl, Br, or NCS), $[CuCl(tpea)]_2[CuCl_4]$, $[Cu(NCS)L][Cu(NCS)_2]$ (L = tpea or bdma), $[Cu(NCS)(bdma)]BPh_4{\cdot}(CH_3)_2CO$, $[CuCl(bdma)]Cl{\cdot}2H_2O$, and $[CuBr(bdma)]_3[CuBr_3]Br{\cdot}H_2O$. The structures of $[Cu(NCS)(tpea)][Cu(NCS)_2]$ (**1**) and $[CuCl(bdma)]Cl{\cdot}2H_2O$ (**2**) have been solved by *X*-ray diffraction methods. Both compounds crystallize in the monoclinic space group $P2_1/c$ with $Z = 4$ and unit-cell dimensions: (**1**), $a = 18.026(9)$, $b = 8.847(4)$, $c = 16.302(7)$ Å, and $\beta = 113.18(5)°$; (**2**), $a = 17.243(8)$, $b = 10.001(5)$, $c = 14.763(7)$ Å, and $\beta = 109.52(6)°$. The structure of complex (**1**) consists of isolated $[Cu(NCS)(tpea)]^+$ cations, where the copper(II) atom is in an approximately trigonal-bipyramidal environment of five N atoms, and of layers formed by the $[Cu(NCS)_2]^-$ anion, with pseudo-tetrahedral copper(I) atoms. The copper(II) atom in the $[CuCl(bdma)]^+$ cation of (**2**) is in a square-pyramidal environment of one S, one Cl, and three N atoms.

Copper–sulphur co-ordination has attracted increasing attention in recent years because of specific interest in this type of metal–donor atom interaction and because of its role in some copper proteins.[1,2] With the aim of preparing low-molecular-weight models for such copper proteins and of finding conditions under which copper(II) may be co-ordinated by the soft sulphur atom without undergoing reduction to copper(I), some polydentate ligands have been designed and synthesized and their copper(II) compounds have been studied.[3–10]

As a part of our systematic study of co-ordination compounds formed by tripodal ligands containing pyrazole groups as donors[11,12] we have undertaken an investigation on copper complexes formed by the ligand tris(2-pyrazolylethyl)amine (tpea, **I**) and by the novel tripodal ligand bis[2-(3′,5′-dimethylpyrazolyl)ethyl](2-methylthioethyl)amine (bdma, **II**). Copper compounds with the following stoicheiometries were isolated: $Cu_3Cl_6(tpea)_2$, $[CuX(tpea)]BPh_4$ (X = Cl, Br, or NCS), $Cu_2(NCS)_3L$ (L = tpea or bdma), $CuCl_2(bdma){\cdot}2H_2O$, $Cu_4Br_7(bdma)_3{\cdot}H_2O$, and $[Cu(NCS)(bdma)]BPh_4{\cdot}(CH_3)_2CO$. The structures of two of these compounds, $Cu_2(NCS)_3(tpea)$ and $CuCl_2(bdma){\cdot}2H_2O$, have been investigated by *X*-ray diffraction methods.



(I)



(II)

Experimental

Materials.—Tetrahydrofuran (thf) was distilled over $LiAlH_4$ prior to use. All other reagents and solvents were of reagent-grade purity and used as received. The synthesis of the ligand tpea has been described.[13,14]

Synthesis of the Ligand bdma.—Bis(2-chloroethyl)amine (0.2 mol), obtained from the corresponding amine hydrochloride,[15] using a saturated aqueous solution of NaOH (**CAUTION**: the free amine and its hydrochloride cause blistering), was dissolved in thf and added dropwise to a suspension of potassium 3,5-dimethylpyrazolate, in stoicheiometric amount, in anhydrous thf under a nitrogen atmosphere. The mixture was stirred and heated at reflux temperature for 24 h. Potassium chloride was then filtered off, and the solvent evaporated under reduced pressure. The crude bis[2-(3′,5′-dimethylpyrazolyl)ethyl]amine was dissolved in ethanol and finely powdered K_2CO_3 (0.11 mol) was added. 2-Chloroethyl methyl sulphide (Fluka) was then added dropwise with stirring and the mixture was heated under reflux for 24 h. The solution was then filtered and the solvent evaporated under reduced pressure. The crude ligand was obtained as a viscous oil (*ca.* 39 g). Attempts to purify it by distillation under reduced pressure led to decomposition. Therefore the crude ligand was employed to prepare the complex $NiCl_2(bdma)$ which was then decomposed with an excess of KCN. The free ligand was extracted from the resulting aqueous mixture with benzene which was finally distilled off

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[*] Isothiocyanato[tris(2-pyrazolylethyl)amine-$NN^2N^{2'}N^{2''}$]copper(II) di-isothiocyanatocuprate(I) and {bis[2-(3′,5′-dimethylpyrazolyl)-ethyl](2-methylthioethyl)amine-$NN^2N^{2'}S$}chlorocopper(II) chloride dihydrate.

Supplementary data available (No. SUP 56289, 5 pp.): thermal parameters. See Instructions for Authors *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.

Table 1. Analytical data (%) for the complexes

Complex	Found				Calc.			
	C	H	N	Cu	C	H	N	Cu
$[CuCl(tpea)]_2[CuCl_4]$	36.0	4.30	20.9	19.1	36.0	4.20	19.6	19.0
$[CuCl(tpea)]BPh_4$	64.4	6.10	14.1		65.7	5.80	13.8	
$[CuBr(tpea)]BPh_4$	61.5	5.40	12.9		61.9	5.50	12.7	
$[Cu(NCS)(tpea)]BPh_4$	64.9	5.60	15.4	8.35	64.9	5.60	15.1	8.60
$[Cu(NCS)(tpea)][Cu(NCS)_2]$	34.9	3.20	23.3		34.6	3.20	23.4	
$[CuCl(bdma)]Cl{\cdot}2H_2O$	40.1	6.35	13.6	12.4	40.4	6.60	13.8	12.6
$[CuBr(bdma)]_3[CuBr_3]Br{\cdot}H_2O$	33.5	5.25	11.6		33.3	4.90	11.4	
$[Cu(NCS)(bdma)][Cu(NCS)_2]$	38.2	4.75	17.7	19.4	37.7	4.60	17.6	19.9
$[Cu(NCS)(bdma)]BPh_4{\cdot}(CH_3)_2CO$	64.0	6.75	10.3	7.60	64.8	6.65	10.1	7.60

Table 2. Some physical data for the complexes

Complex	Colour	$\mu_{eff.}$ (298 K)	State[a]	$\lambda_{max.}$ with $\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ for solutions in parentheses
$[CuCl(tpea)]_2[CuCl_4]$	Greenish yellow	1.82[b]	d.r.	700 (sh), 960, 1 300br (sh)
			CH_3CN	262 (2 455), 308 (2 685), 463 (363)
			$(CH_3)_2CO$	680 (sh), 870 (631)
			C_2H_5OH	680 (118), 950 (sh)
$[CuCl(tpea)]BPh_4$	Turquoise	1.95	d.r.	650, 950 (sh)
			CH_3CN	312 (2 717), 685 (175), 950 (77)
			$(CH_3)_2CO$	685 (140), 920 (sh)
$[CuBr(tpea)]BPh_4$	Green	1.89	d.r.	650, 950
			CH_3CN	353 (3 070), 680 (393), 970 (97)
			$(CH_3)_2CO$	690 (409), 970 (96)
$[CuBr(tpea)]_3[CuBr_3]Br{\cdot}3H_2O$[c]	Green	1.54[b]	d.r.	675, 925
			CH_3CN	270 (1 510), 355 (1 960), 680 (360), 960 (95)
			$(CH_3)_2CO$	690 (363), 950 (105)
$[Cu(NCS)(tpea)]BPh_4$	Ochre	1.89	d.r.	750, 1 050
			CH_3CN	417 (1 214), 720 (146), 1 000 (sh)
			$(CH_3)_2CO$	425 (944), 715 (150), 1 000 (sh)
$[Cu(NCS)(tpea)][Cu(NCS)_2]$	Green	1.46[b]	d.r.	700, 1 000 (sh)
			CH_3CN	470 (555), 885 (268)
			$(CH_3)_2CO$	475 (547), 880 (262)
			C_2H_5OH	690 (140), 960 (sh)
$[CuCl(bdma)]Cl{\cdot}2H_2O$	Green	1.86	d.r.	675, 1 125
			CH_3CN	305 (5 460), 350 (3 800), 450 (950), 680 (366), 1 080 (81)
$[CuBr(bdma)]_3[CuBr_3]Br{\cdot}H_2O$	Green	1.65[b]	d.r.	675, 1 070
			CH_3CN	355 (2 660), 685 (390), 950 (213)
$[Cu(NCS)(bdma)][Cu(NCS)_2]$	Green	1.29[b]	d.r.	650, 1 000 (sh)
			CH_3CN	345 (3 056), 440 (1 195), 670 (362), 1 000 (sh)
$[Cu(NCS)(bdma)]BPh_4{\cdot}(CH_3)_2CO$	Green	1.85	d.r.	650, 1 000 (sh)
			CH_3CN	345 (3 283), 440 (1 178), 670 (476), 1 000 (sh)

[a] d.r. = Diffuse reflectance. [b] Average value per metal atom. [c] Ref. 21.

under reduced pressure. The ligand was obtained in the form of a colourless oil stable at room temperature, which was employed as such.

Synthesis of the Complexes.—$[CuX(tpea)]BPh_4$ (X = Cl or Br). The ligand (2.2 mmol) dissolved in ethanol (10 cm^3) was added with stirring at room temperature to a solution of the hydrated copper(II) halide (2.0 mmol) in ethanol (20 cm^3). The addition of $NaBPh_4$ (2.0 mmol) in ethanol (10 cm^3) gave the appropriate products.

$[Cu(NCS)(tpea)]BPh_4$ *and* $[Cu(NCS)(bdma)]BPh_4{\cdot}(CH_3)_2CO$. These compounds were prepared as above starting from a solution of copper(II) thiocyanate obtained by the metathetical reaction of copper(II) chloride with potassium thiocyanate. In the preparation of the bdma complex, $NaBPh_4$ was dissolved in acetone. I.r.: ν(CO) 1 710 cm^{-1}.

$[CuCl(tpea)]_2[CuCl_4]$ *and* $[CuCl(bdma)]Cl{\cdot}2H_2O$. A solution of the ligand (2.0 mmol) in ethanol (10 cm^3) was added to a boiling solution of hydrated copper(II) chloride (2.0 mmol) in ethanol (20 cm^3). The resulting solution was concentrated to about 20 cm^3 and diethyl ether added until crystals separated. I.r.: ν(OH) 3 500, ν(HOH, bend) 1 620 cm^{-1}.

$[Cu(NCS)L][Cu(NCS)_2]$ (L = *tpea or bdma*). To a solution of hydrated copper(II) chloride and of the appropriate ligand prepared as above and cooled to room temperature, a solution of potassium thiocyanate (5.0 mmol) in ethanol–acetone (1:1, 30 cm^3) was added with stirring. The solution was then allowed to evaporate slowly at about 40 °C until crystals separated.

$[CuBr(bdma)]_3[CuBr_3]Br{\cdot}H_2O$. Hydrated copper(II) bromide (2.0 mmol) in ethanol (20 cm^3) and the ligand (2.2 mmol) in acetone–ethanol (15 cm^3) were mixed at room temperature. The resulting solution was allowed to evaporate at about 40 °C until crystals separated.

Recrystallization of some compounds from acetone–ethanol or ethanol–diethyl ether was necessary in order to obtain samples with satisfactory analyses (Table 1).

Physical Measurements.—The apparatus and experimental techniques used for the magnetic measurements and recording of i.r. spectra were as described previously.[16,17] Diffuse reflectance spectra were recorded in the range 450—2 000 nm with a Beckman DK-2A spectrophotometer. Solution spectra in acetone in the range 400—1 750 nm and in acetonitrile in the range 250—1 750 nm were recorded with a Cary 17 spectrophotometer. Magnetic and spectral data are listed in Table 2.

X-*Ray Diffraction Studies.*—[Cu(NCS)(tpea)][Cu(NCS)$_2$]. Crystals of the compound form prisms or elongated plates. A crystal of dimensions 0.10 × 0.40 × 0.80 mm was used for diffraction data collection. Crystal data are presented in Table 3. Intensity data were collected on a Philips PW 1100 automated diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). Unit-cell parameters were derived by least-squares refinement of the angular settings of 24 reflections with $30 < 2\theta < 38°$. Intensity data were collected in the scan mode θ—2θ with a scan width of $(1.10 + 0.30\tan\theta)°$ and scan speed of 6° min^{-1}. Stationary background counts were taken at each end of the scan for fixed 3-s intervals. The intensities of three standard reflections monitored every 120 min showed small fluctuations (<1%) about their mean values but no systematic trend. Diffraction data were corrected for absorption by a numerical procedure,[18] which gave transmission coefficients in the range 0.81—0.45. Lorentz and polarization corrections were applied. The computer program used was SHELX 76.[18]

Table 3. Crystal data and refinement details for the complexes [Cu(NCS)(tpea)][Cu(NCS)$_2$] (**1**) and [CuCl(bdma)]Cl·2H$_2$O (**2**)[a]

	(**1**)	(**2**)
Formula	$C_{18}H_{21}Cu_2N_{10}S_3$	$C_{17}H_{33}Cl_2CuN_5O_2S$
M	600.7	506.0
a/Å	18.026(9)	17.243(8)
b/Å	8.847(4)	10.001(5)
c/Å	16.302(7)	14.763(7)
β/°	113.18(5)	109.52(6)
U/Å^3	2 389.9	2 399.5
D_c/g cm^{-3}	1.669	1.400
μ(Mo-K_α)/cm^{-1}	20.6	12.4
2θ range/°	5—50	5—46
Data recorded	4 662	3 688
Data used [$I > 3\sigma(I)$]	2 518	1 559
Least-squares parameters	329	197
R[b]	0.040	0.044
R'[c]	0.047	0.052
g[d]	0	0.0001

[a] Common features: space group $P2_1/c$; $Z = 4$; λ(Mo-K_α) = 0.710 69 Å; reflection indices ±*h*, *k*, *l*. [b] $\Sigma|F_o - |F_c||/\Sigma F_o$. [c] $[\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. [d] $w = [\sigma^2(F_o) + gF_o^2]^{-1}$.

The structure was solved by conventional heavy-atom methods (Patterson and Fourier) and refined by full-matrix least squares in which the function $w(|F_o| - |F_c|)^2$ was minimized. The weighting scheme is given in Table 3. The chains of the tripod-like tpea ligand in the cation were found to be affected by orientational disorder about the line passing through the metal atom and the amine nitrogen [N(1)] atom, each of the C atoms bound to N(1) being distributed over two positions. The next C atom in each chain was not affected by disorder. The two orientations of the chains were refined imposing unique N(1)–C and C–C values, a population parameter of 0.62(1) for the most probable orientation being obtained. All the pyrazole H atoms, but not those bound to the disordered C atoms, could be clearly located from ΔF maps. However, all H atoms were incorporated in the model in an idealized geometry with C–H 1.00 Å and each of those belonging to the chains was assigned the population parameter of the respective conformation. All non-hydrogen atoms, including the disordered C atoms, were assigned anisotropic thermal parameters, whereas H atoms were assigned an overall thermal parameter. The final values of the residual indices appear in Table 3. The maximum parameter shift-to-error ratio at convergence was 0.06. The largest peaks on a final difference synthesis were of heights 0.48 (in the region of the disordered chains) and −0.63 e Å^{-3}. Neutral-atom scattering-factor curves were taken from ref. 19 and the anomalous dispersion correction for Cu from ref. 20. The final positional parameters for the non-hydrogen atoms are listed in Table 4.

[CuCl(bdma)]Cl·2H$_2$O. The crystal used was a prism, of dimensions 0.05 × 0.24 × 0.40 mm. Crystal data are listed in Table 3. Unit-cell parameters were derived by least-squares refinement of the angular settings of 24 reflections with $28 < 2\theta < 32°$. The data-collection procedure was as for the

Table 4. Fractional atomic co-ordinates (× 10^4) for [Cu(NCS)(tpea)][Cu(NCS)$_2$][a]

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	1 770(1)	−3 255(1)	2 848(1)
Cu(2)	4 891(1)	1 517(1)	3 572(1)
S(1)	−542(1)	−5 785(2)	869(1)
S(2)	5 774(1)	−2 645(2)	5 501(1)
S(3)	6 086(1)	5 873(2)	2 909(1)
N(1)	2 797(2)	−2 324(5)	3 759(3)
N(2)	1 665(3)	−4 648(5)	3 810(3)
N(3)	2 055(3)	−4 531(5)	4 700(3)
N(4)	1 395(3)	−1 223(5)	2 202(3)
N(5)	1 692(3)	169(5)	2 461(3)
N(6)	2 469(2)	−4 307(5)	2 199(3)
N(7)	3 289(2)	−4 447(5)	2 510(3)
N(8)	786(3)	−4 192(6)	1 990(3)
N(9)	5 384(3)	−319(5)	4 238(3)
N(10)	5 457(3)	3 206(5)	3 295(3)
C(1)[b]	2 638(6)	−2 005(8)	4 578(5)
C(1')[c]	3 153(4)	−2 924(17)	4 694(5)
C(2)	2 592(4)	−3 313(8)	5 140(4)
C(3)	1 907(4)	−5 730(8)	5 114(4)
C(4)	1 407(4)	−6 657(8)	4 486(5)
C(5)	1 262(3)	−5 954(7)	3 684(4)
C(6)[b]	3 019(5)	−896(7)	3 416(7)
C(6')[c]	2 589(10)	−763(8)	3 957(7)
C(7)	2 440(4)	399(7)	3 241(5)
C(8)	1 201(5)	1 215(8)	1 900(5)
C(9)	596(5)	504(9)	1 274(5)
C(10)	727(4)	−1 024(8)	1 460(5)
C(11)[b]	3 466(4)	−3 462(9)	3 999(5)
C(11')[c]	3 459(6)	−2 184(9)	3 425(10)
C(12)	3 821(3)	−3 656(7)	3 315(4)
C(13)	3 502(4)	−5 272(7)	1 958(4)
C(14)	2 827(4)	−5 722(6)	1 270(4)
C(15)	2 193(4)	−5 095(6)	1 445(4)
C(16)	230(3)	−4 838(6)	1 529(4)
C(17)	5 546(3)	−1 275(6)	4 749(3)
C(18)	5 710(3)	4 300(6)	3 120(3)

[a] In this and the following Tables standard deviations on the least significant digits are given in parentheses. Atoms belonging to the cation are labelled in Figure 1; atoms Cu(2), S(2), S(3), N(9), N(10), C(17), and C(18) belong to the anion. [b] Site with occupancy factor 0.62. [c] Site with occupancy factor 0.38.

Table 5. Fractional atomic co-ordinates ($\times 10^4$) for $[CuCl(bdma)]Cl{\cdot}2H_2O$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu	2 756(1)	−1 416(1)	1 776(1)	C(4)	4 084(6)	1 175(8)	4 127(6)
S	2 318(2)	252(2)	613(2)	C(5)	3 942(5)	687(7)	3 217(6)
Cl(1)	3 656(2)	−2 092(3)	1 049(2)	C(6)	3 304(6)	908(9)	5 358(6)
Cl(2)	111(2)	−1 905(3)	3 950(2)	C(7)	4 425(5)	920(8)	2 555(7)
O(1)	793(4)	1 020(6)	4 570(5)	C(8)	1 238(5)	−2 709(7)	1 992(6)
O(2)	894(5)	3 085(6)	3 327(5)	C(9)	1 606(5)	−3 808(7)	1 548(6)
N(1)	1 545(4)	−1 334(6)	1 878(4)	C(10)	2 787(5)	−5 335(8)	2 522(6)
N(2)	3 257(4)	−42(6)	2 946(5)	C(11)	3 549(5)	−5 035(7)	3 149(6)
N(3)	2 957(4)	−7(6)	3 700(5)	C(12)	3 646(4)	−3 662(7)	3 166(5)
N(4)	2 969(4)	−3 108(6)	2 564(4)	C(13)	2 346(5)	−6 620(7)	2 214(7)
N(5)	2 439(4)	−4 133(6)	2 167(4)	C(14)	4 355(5)	−2 835(8)	3 757(6)
C(1)	1 521(5)	−485(7)	2 716(5)	C(15)	968(5)	−738(7)	989(6)
C(2)	2 216(5)	−724(7)	3 651(5)	C(16)	1 309(5)	528(7)	695(6)
C(3)	3 463(5)	735(8)	4 432(6)	C(17)	2 037(6)	−595(8)	−528(6)

above NCS derivative with the exception that a scan speed of 3° min^{-1} was used. The intensities of three standard reflections were virtually constant throughout the data collection. Corrections for Lorentz, polarization, and absorption effects were applied, the transmission coefficients ranging from 0.94 to 0.75.

The structure was solved by heavy-atom methods and refined by full-matrix least squares in which the Cu, S, Cl, and O atoms as well as the methyl C atoms were assigned anisotropic thermal parameters, the other C and the N atoms were refined isotropically, and all H atoms were assigned an overall thermal parameter. Hydrogen atoms of the bmda ligand were introduced in calculated positions (C–H 1.00 Å). The water hydrogen atoms, or the maxima in O–H bond densities, were located from ΔF maps and their positions refined by imposing a unique value for all O–H distances and a fixed H–O–H angle of 105°. The final small (0.80 Å) value for the O–H distance is probably caused by fitting the maximum in the O–H bond electron density. The largest shift-to-error ratio at convergence was 0.10 and the largest peaks on a final ΔF map were of heights 0.42 and −0.32 e $Å^{-3}$. The final positional parameters for the non-hydrogen atoms are listed in Table 5.

Table 6. Selected interatomic distances (Å) and angles (°) for $[Cu(NCS)(tpea)][Cu(NCS)_2]$

(*i*) Cation

Cu(1)–N(1)	2.037(4)	Cu(1)–N(8)	1.959(4)
Cu(1)–N(2)	1.061(4)	N(8)–C(16)	1.142(6)
Cu(1)–N(4)	2.059(4)	S(1)–C(16)	1.617(6)
Cu(1)–N(6)	2.151(4)		
N(1)–Cu(1)–N(8)	178.7(2)	N(4)–Cu(1)–N(6)	105.3(2)
N(1)–Cu(1)–N(2)	90.9(2)	N(2)–Cu(1)–N(8)	87.8(2)
N(1)–Cu(1)–N(4)	92.3(2)	N(4)–Cu(1)–N(8)	88.9(2)
N(1)–Cu(1)–N(6)	89.6(2)	N(6)–Cu(1)–N(8)	90.4(2)
N(2)–Cu(1)–N(4)	143.3(2)	Cu(1)–N(8)–C(16)	174.6(5)
N(2)–Cu(1)–N(6)	111.3(2)	N(8)–C(16)–S(1)	178.4(6)

(*ii*) Anion *

Cu(2)–N(9)	1.962(5)	N(9)–C(17)	1.142(6)
Cu(2)–N(10)	1.959(5)	S(2)–C(17)	1.657(5)
Cu(2)–S(2^{I})	2.478(4)	N(10)–C(18)	1.153(6)
Cu(2)–S(3^{II})	2.429(4)	S(3)–C(18)	1.643(6)
S(2^{I})–Cu(2)–S(3^{II})	111.4(1)	Cu(2)–S(2^{I})–C(17^{I})	96.8(4)
S(2^{I})–Cu(2)–N(9)	102.6(2)	Cu(2)–S(3^{II})–C(18^{II})	102.1(4)
S(2^{I})–Cu(2)–N(10)	104.7(2)	Cu(2)–N(9)–C(17)	161.3(4)
S(3^{II})–Cu(2)–N(9)	110.4(2)	Cu(2)–N(10)–C(18)	171.9(5)
S(3^{II})–Cu(2)–N(10)	100.9(2)	N(9)–C(17)–S(2)	179.0(5)
N(9)–Cu(2)–N(10)	126.5(2)	N(10)–C(18)–S(3)	178.0(5)

* Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z: I $1 - x, -y, 1 - z$; II $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$.

Results and Discussion

The reactions of hydrated copper(II) salts with the two ligands tpea (**I**) and bdma (**II**) afforded different complexes, depending on the specific salt used and on the mode of operation. When the reactions were performed in the presence of $NaBPh_4$, copper(II) compounds of general formula $[CuX(L)]BPh_4$ (X = Cl, Br, or NCS; L = tpea, X = NCS, L = bdma) were isolated. In the absence of $NaBPh_4$ and when hydrated copper(II) chloride was used, two copper(II) compounds with stoicheiometries $CuCl_2(bdma){\cdot}2H_2O$ and $Cu_3Cl_6(tpea)_2$ were obtained. On the other hand, when hydrated copper(II) bromide or thiocyanate was used under the same conditions, compounds having the stoicheiometries $Cu_4Br_7L_3{\cdot}xH_2O$ (L = tpea, $x = 3$;[21] L = bdma, $x = 1$) and $Cu_2(NCS)_3L$ (L = tpea or bdma) were obtained. The latter derivatives contain both copper(II) and copper(I) as indicated by their stoicheiometry and magnetic moments (Table 2) which are below those usually found for magnetically dilute copper(II) complexes. This had been previously established[21] by a structural investigation of one of these compounds. *X*-Ray diffraction studies were undertaken on the two compounds $Cu_2(NCS)_3(tpea)$ and $CuCl_2(bdma){\cdot}2H_2O$ in order to elucidate their molecular structures which could not be unambiguously assigned on the basis of their stoicheiometry and physicochemical properties. In particular, in the case of $CuCl_2(bdma){\cdot}2H_2O$, both the chlorine atom and the water molecules might compete with the thioether group in the co-ordination sphere. It was also considered interesting to determine the environment of the copper(I) atom in $Cu_2(NCS)_3(tpea)$ in order to compare it with that found in the structure of $Cu_4Br_7(tpea)_3{\cdot}3H_2O$.[21]

The structure of the compound $Cu_2(NCS)_3(tpea)$ is formed of alternating layers of isolated $[Cu(NCS)(tpea)]^+$ cations and polymeric anions with the basic formula $[Cu(NCS)_2]^-$. Values of the bond distances and angles about the metal atoms are listed in Table 6. A view of the cation is given in Figure 1 and the packing in the structure is shown in Figure 2. The copper(II) atom in the cation is co-ordinated by the four N donor atoms of the tpea ligand and by the isothiocyanate N atom in a sort of trigonal-bipyramidal arrangement with the central nitrogen atom [N(1)] of the tripod ligand and the NCS nitrogen atom [N(8)] in the axial positions [N(1)–Cu(1)–N(8) 178.7(2)°]. This arrangement is distorted towards that of a square pyramid with N(6) in the apical position, due to the rather large [N(2)–

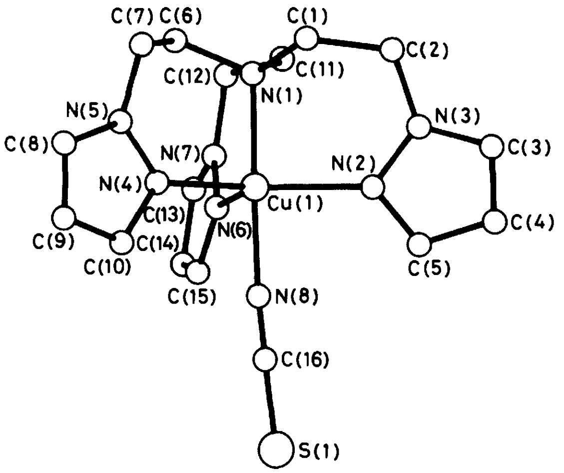

Figure 1. The structure of the $[Cu(NCS)(tpea)]^+$ cation. Only one orientation of the disordered ethyl chains is shown

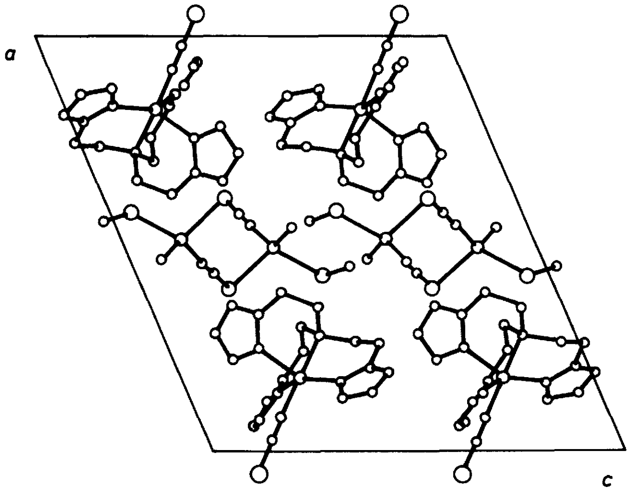

Figure 2. Unit-cell contents of $[Cu(NCS)(tpea)][Cu(NCS)_2]$ projected down *b*

Cu(1)–N(4) 143.3(2)°] angle in the equatorial plane of the bipyramid and to elongation of the opposite bond [Cu(1)–N(6) 2.151(4) Å], with respect to the other two Cu–N bonds in the equatorial plane [2.060(4) Å, mean]. The NCS ligand in the cation is almost linear [Cu(1)–N(8)–C(16) 174.6(5)°]. An essentially square-pyramidal geometry about the metal atom was found for the $[CuL(H_2O)]^{2+}$ cation formed by the same tpea ligand.[22] In spite of a few differences in individual values, the mean of the four Cu–N distances (2.064 Å) in that cation is close to that (2.077 Å) of the Cu–N bonds formed by the tpea ligand in the present compound. Each copper(I) atom in the polymeric anion is co-ordinated by two N and two S atoms of four NCS groups in a pseudo-tetrahedral environment (Table 6). It shares two NCS groups with a mirror-related copper(I) atom and is linked to two additional copper(I) centres through the other two NCS groups. Such Cu atoms and NCS groups are arranged in sheets parallel to the (100) planes, at $x = \frac{1}{2}$. There are no unusually short contacts between these sheets and the cations in the structure. A layer structure for the polymeric $[Cu(NCS)_2]^-$ anion was also found in $Cu_2(NCS)_3(NH_3)_3$,[23] but with a different arrangement of the NCS groups which, in contrast to the present case, are also involved in interactions between the anionic and cationic sites.

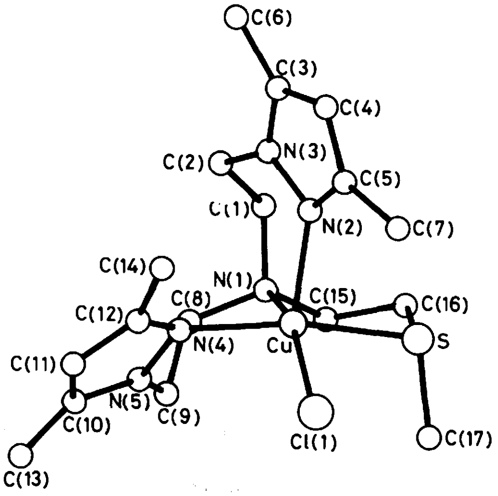

Figure 3. The structure of the $[CuCl(bdma)]^+$ cation

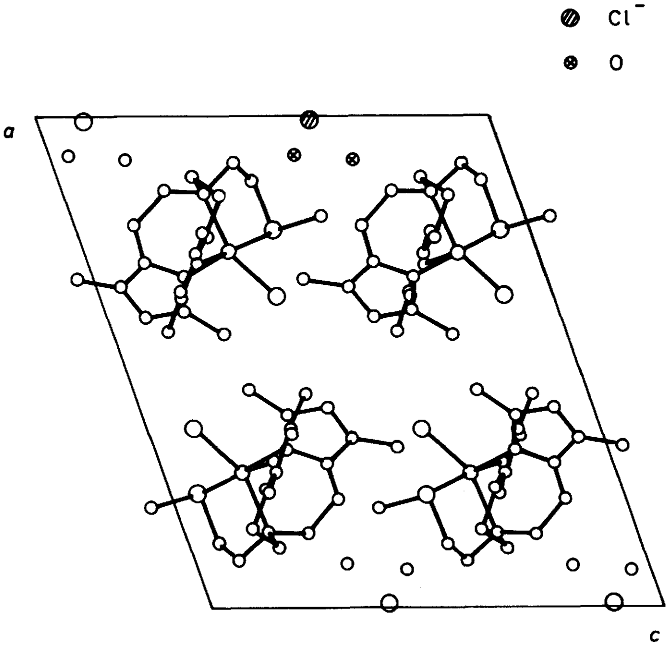

Figure 4. Unit-cell contents of $[CuCl(bdma)]Cl{\cdot}2H_2O$ projected down *b*

The structure of the compound $CuCl_2(bdma){\cdot}2H_2O$ consists of $[CuCl(bdma)]^+$ cations, Cl^- anions, and interposed water molecules which form hydrogen bonds with each other and with the Cl^-. Values of the bond distances and angles are listed in Table 7. A view of the structure of the cation is given in Figure 3 and the packing is shown in Figure 4. The co-ordination geometry in the cation is approximately square pyramidal, with N(2) in the apical position and N(1), N(4), S, and Cl(1) defining the base of the pyramid. The metal atom lies 0.38 Å above the least-squares plane through the four basal donor atoms. The Cu–N and Cu–Cl bond lengths are in the normal range. The Cu–S bond distance [2.332(3) Å] is in agreement with that [2.322(2) Å] found in $[CuL'(H_2O)(OClO_3)]^+$,[6] where L′ is the tridentate bis[2-(5′,6′-dimethylbenzimidazol-2′-yl)ethyl] sulphide ligand having a N_2S donor set, and with that [2.359(4) Å] found in $[CuL''(o\text{-}SC_6H_4CO_2)]$ where L″ = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane.[24] The S atom shows a preference for a basal site of the square pyramid, both in the present cation and in $[CuL'(H_2O)(OClO_3)]^+$.[6] Although the co-ordination geometry in $[CuL''(o\text{-}SC_6H_4CO_2)]$ is better

Table 7. Selected interatomic distances (Å) and angles (°) for $[CuCl(bdma)]Cl \cdot 2H_2O$

Cu–Cl(1)	2.266(2)	Cu–N(4)	2.016(6)
Cu–S	2.332(3)	S–C(16)	1.806(8)
Cu–N(1)	2.143(6)	S–C(17)	1.801(8)
Cu–N(2)	2.150(6)		
Cl(1)–Cu–N(1)	151.9(2)	Cl(1)–Cu–N(2)	114.6(2)
N(1)–Cu–S	86.6(2)	Cl(1)–Cu–N(4)	90.1(2)
N(1)–Cu–N(2)	93.4(2)	S–Cu–N(2)	94.5(2)
N(1)–Cu–N(4)	89.2(2)	S–Cu–N(4)	167.7(2)
Cl(1)–Cu–S	88.2(1)	N(2)–Cu–N(4)	97.3(2)

described as approximately trigonal bipyramidal,[24] the S atom is still involved in the largest angle [135.4(3)°] in the equatorial plane. The Cl^- anion and the water molecules in the present structure form a two-dimensional network of hydrogen bonds, essentially parallel to the (100) planes. The H atoms bound to O(1) are directed toward two Cl^- ions related by an inversion centre, whereas the H atoms of O(2) are directed toward a third Cl^- and toward O(1) respectively. The O(1) ··· O(2) distance [2.81(1) Å] is comparable to those existing in ice (2.75—2.80 Å).[25]

Among the other compounds reported here, that with stoicheiometry $Cu_2(NCS)_3(bdma)$ may be assigned the formula $[Cu(NCS)(bdma)][Cu(NCS)_2]$ on the basis of the similarity in composition and magnetic moment with the tpea analogue, whose structure was described above. For similar reasons, the compound $Cu_4Br_7(bdma)_3 \cdot H_2O$ is assigned the formula $[CuBr(bdma)]_3[CuBr_3]Br \cdot H_2O$ and the same sort of structure as that of the tpea analogue.[21] The spectrum of the compound $Cu_3Cl_6(tpea)_2$ (Table 2) is dominated by an intense band at 960 nm with a shoulder centered at about 1 300 nm. These absorptions may be assigned to the distorted tetrahedral $[CuCl_4]^{2-}$ species[26] so that this compound may be formulated as $[CuCl(tpea)]_2[CuCl_4]$.

The reflectance spectra of all the compounds, except that of $[CuCl(tpea)]_2[CuCl_4]$, are similar in the range 450—2 000 nm. These spectra are either characterized by two distinct bands or by one band and a well separated shoulder at lower energies, respectively occurring in the 650—750 and 900—1 100 nm ranges (Table 2). In view of these spectral similarities it may be assumed that the compounds whose structures cannot be assigned on the basis of the analogy in stoicheiometry with compounds of known structure also contain mononuclear five-co-ordinate species $[CuX(L)]^+$ with structures generally similar to those found in the $[Cu(NCS)(tpea)]^+$ and $[CuCl(bdma)]^+$ cations. The *d–d* electronic spectra of the bdma complexes in acetonitrile solution are similar to those of the solid compounds. Therefore substantial structural changes apparently do not occur on going from the solid compounds to their solutions in acetonitrile. The near-u.v. spectra of the same compounds are characterized by an intense band in the range 345—355 nm (Table 2) which is assigned as a thioether $\sigma(S) \rightarrow Cu^{II}$ ligand-to-metal charge-transfer (l.m.c.t.) transition, according to the assignments reported for other thioether–copper complexes.[3–6,10] The presence of this absorption confirms that the sulphur atom is co-ordinated to the metal atom even in acetonitrile solution. All the complexes with the ligand tpea have strictly similar *d–d* spectra in acetone or acetonitrile solutions, which in turn generally agree with those of the solid compounds. The same five-co-ordinate $[CuX(tpea)]^+$ cations should therefore be present in the solutions as in the solid compounds. In the case of the complex $[CuCl(tpea)]_2[CuCl_4]$ the medium-intensity absorptions of the $[CuCl_4]^{2-}$ anion disappear in ethanol solution and the spectrum of the five-co-ordinate cation emerges.

For some thiolatocopper(II) complexes and for the so-called 'blue copper proteins' an unusually intense [$\varepsilon = (3—5) \times 10^3$ $dm^3\ mol^{-1}\ cm^{-1}$] band was found in the visible region at about 600 nm.[8,9,27] The assignment of this band either as *d–d* or charge transfer (c.t.) in character has been a matter of debate.[5,9,10,24,27] The comparison between the *d–d* electronic spectra of the two series of complexes reported here shows that substitution of one S for a N donor atom in the co-ordination sphere has no remarkable consequences on the intensities and positions of the *d–d* transitions. In particular, the band at about 650 nm in the spectra of the bdma complexes does not borrow much intensity from the strong c.t. at about 350 nm. As a consequence it seems unlikely that the band at about 600 nm of the copper proteins may be a *d–d* transition reinforced by an intensity-stealing mechanism. This band is probably also not due to a thioether-to-copper c.t. transition which, as mentioned above, is considered to occur at higher energies. The present results, therefore, support the view[9,10,27] that the intense band at *ca.* 600 nm in the spectra of the blue copper proteins is due to a thiolate $S \rightarrow Cu^{II}$ l.m.c.t. transition.

Acknowledgements

Thanks are expressed to Mr. S. Seniori Costantini for technical assistance and to the Istituto Studio Stereochimica Energetica Composti Coordinazione Institute, Consiglio Nazionale Ricerche, Florence, for use of instruments.

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Received 12*th March* 1985; *Paper* 5/419