Copper Co-ordination Compounds of a Chelating Imidazole–Thioether Ligand. The Molecular Structures of [1,3-Bis(5-methyl-4-imidazolyl)-2- thiapropane]-bis(nitrato)copper(II) and Bis[1,3-bis(5-methyl-4-imidazolyl)-2- thiapropane]-copper(II) Bis(tetrafluoroborate)–ethanol(1/2)

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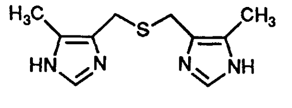
The synthesis and spectroscopic properties of copper compounds with the tridentate ligand 1,3-bis(5-methyl-4-imidazolyl)-2-thiapropane (L) are described. Two series of compounds have been obtained, one green and the other purple. The green series has general formula $[Cu(L)X_2]$, in which X = Cl^-, Br^-, NCS^-, or NO_3^- and $[Cu(L)Cl(BF_4)]$. In these compounds both the ligand and the anions are co-ordinated to the copper(II) ion. The purple series has general formula $[Cu(L)_2]Y_2\cdot nH_2O$, with Y = Cl^-, Br^-, NO_3^-, or BF_4^- and n = 0—3, and $[Cu(L)_2][NCS][NO_3]\cdot H_2O$, with only the ligands L co-ordinated to the copper(II) ion. In all compounds L acts as a tridentate ligand with the thioether sulphur and both imidazole nitrogens co-ordinating. The compound $[Cu(L)(NO_3)_2]$ (**A**) crystallizes in the monoclinic space group $P2_1/n$ with a = 18.060(5) Å, b = 7.063(4) Å, c = 13.229(3) Å, β = 104.13(3)°, for Z = 4. The R' value is 0.032 for 1971 significant reflections. The copper(II) ion has a distorted square-pyramidal geometry with an equatorial N_2S donor set, an equatorial oxygen, and an axial oxygen from the nitrate ions. The Cu–N distances are 1.94 Å, Cu–S 2.37 Å, and the distance of the copper ion to the equatorial oxygen is 1.99 Å and to the axial oxygen 2.41 Å. The compound $[Cu(L)_2][BF_4]_2\cdot 2C_2H_5OH$ (**B**) crystallizes in the monoclinic space group $P2_1/c$ with a = 8.262(2), b = 9.609(3), c = 22.582(5) Å, β = 100.04(2)°, for Z = 2. The R' value is 0.09 for 2 149 independent reflections (including low-intensity reflections). The copper(II) ion has a distorted-octahedral geometry with four equatorial N-donors and two long-distance axial sulphur atoms. The Cu–N distances are 2.00 Å, the Cu–S distances 2.79 Å. Electrochemistry of the two series (1 : 1 and 1 : 2) of copper(II) compounds points to two distinct one-electron reductions in both cases. Only the first copper(II)–copper(I) redox change, which occurs at rather high positive potentials, is chemically reversible. The stability of the copper(II)–copper(I) couple both in the five-co-ordinate $[Cu(L)X_2]^{0/-}$ and six-co-ordinate $[Cu(L)_2]^{2+/+}$ assemblies gives evidence for the relative flexibility and versatility of the tridentate ligand.

In the blue copper protein plastocyanin the Cu^{II} is ligated in a distorted-tetrahedral arrangement of two histidine imidazole nitrogens, a cysteine thiolate sulphur, and a methionine thioether sulphur.[1] The methionine sulphur co-ordinates weakly at a very long distance ($Cu–S_m$ 2.85 Å). The other co-ordination distances are normal. The bond angles around the Cu^{II} are significantly distorted from the ideal tetrahedral values.

There have been considerable research efforts to synthesize chemical analogues of the active site of blue copper proteins.[2] For the modelling of this active site, imidazole- and thioether-containing ligands are relevant. Several N_xS_y donor ligands have been designed so far.[3] One of these is 1,3-bis(5-methyl-4-imidazolyl)-2-thiapropane (L), an N_2S donor ligand. This ligand makes it possible to model the azole and thioether part of the Type I active site. The present paper is devoted to the elucidation of the complexing properties of this ligand, while future work will also incorporate a thiol function to complete the model for the Type I active site.

Co-ordination compounds of the ligand L with copper(II) and various anions have been synthesized and their physicochemical properties, as well as two *X*-ray structures, are described.



L

Experimental

Starting Materials.—The synthesis of the ligand L from thioacetamide and 4-methyl-5-imidazolemethanol hydrochloride has been described in detail elsewhere.[3] Except for copper thiocyanate, all chemicals were commercially available and of sufficient purity. They were used without further treatment. Copper(II) thiocyanate was prepared according to van Rijn.[4]

Synthesis of the Complexes.—The co-ordination compounds of general formula $[Cu(L)X_2]$ were prepared by dissolving the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Crystal and refinement data for the compounds $[Cu(L)(NO_3)_2]$ (**A**) and $[Cu(L)_2][BF_4]_2 \cdot 2C_2H_5OH$ (**B**)

	(**A**)	(**B**)
Formula	$C_{10}H_{18}CuN_6O_6S$	$C_{24}H_{40}B_2CuF_8N_8O_2S_2$
M	409.9	773.9
a/Å	18.060(5)	8.262(2)
b/Å	7.063(4)	9.609(3)
c/Å	13.229(3)	22.582(5)
α/°	90.0	90
β/°	104.13(3)	100.04(2)
γ/°	90.0	90
U/Å^3	1 636.5(8)	1 765.2(7)
T/K	293	293
F(000)	838	798
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Z	4	2
D_c/g cm^{-3}	1.6	1.45
μ/cm^{-1}	14.88	8.03
Crystal dimensions	0.15 × 0.20 × 0.50	0.30 × 0.12 × 0.05
Colour	Green	Purple
habit	Needle	Plate
h values	−23 to 23	−8 to 8
k values	0—9	0—10
l values	0—17	0—23
Scan range, θ/°	2.0—26.0	2—22
Transmission factors	0.93—1.05	0.92—1.05
Intensity variation (%)	5.73	4.21
No. of measured reflections	3 653	2 387
No. of unique reflections	3 497	2 317
No. used in refinement	1 971 [$I > 2\sigma(I)$]	2 149 [$I > \sigma(I)$]
Total no. of parameters	156	273
R^a	0.030	0.17
R'^b	0.032	0.09
Maximum, minimum $\Delta\rho$ excursions, e Å^{-3}	0.39, −0.29	1.05, −1.13

^{a} $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. ^{b} $R' = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]$.

appropriate hydrated metal salt (3 mmol) in warm ethanol (35 cm^3) and adding this solution to a solution of the ligand L (1.5 mmol) in warm ethanol (35 cm^3). After filtration of the hot reaction mixture, the complex crystallized on cooling. In some cases evaporation of some of the solvent was required before crystallization of the co-ordination compound occurred.

To synthesize the co-ordination compounds with general formula $[Cu(L)_2]Y_2$ an analogous procedure was used with the ligand L (6 mmol) dissolved in warm ethanol (35 cm^3). For the preparation of $[Cu(L)_2][NCS][NO_3] \cdot H_2O$ a solution of copper nitrate (3 mmol) in ethanol (35 cm^3) was added to a solution of ammonium thiocyanate (6 mmol) and the ligand L (6 mmol) in warm ethanol (35 cm^3). For the preparation of $[Cu(L)(NCS)_2]$, a solution of L (1.5 mol) in warm ethanol (35 cm^3) was added to a suspension of copper thiocyanate in warm ethanol (35 cm^3).

Analyses.—Metal analyses were carried out complexometrically with ethylenediaminetetra-acetate as the complexing agent.[5] The chloride and bromide analyses of the compounds were performed by potentiometric titrations with a silver–calomel couple.[5] Elemental C, H, and N analyses were performed by the microanalytical laboratory of the University College, Dublin.

Spectroscopic Measurements.—Infrared spectra in the range 4 000—200 cm^{-1} of the samples pelleted in KBr were recorded on a Perkin-Elmer 580 spectrophotometer, solid-state electronic spectra (28 000—5 000 cm^{-1}) on a Perkin-Elmer 330 spectrophotometer, E.p.r. spectra of the powdered copper(II) compounds at *X*-band frequency were obtained with a Varian E3 spectrometer in Leiden at room temperature and at 77 K (liquid nitrogen), spectra of the powdered copper compounds at *Q*-band frequency were obtained with a Varian E-9 equipped with a Bruker ER 061 SR microwave bridge at the University of Amsterdam. *X*-Ray powder diffractograms were recorded on a Guinier-de-Wolff camera using Cu-K_α radiation.

Electrochemical Measurements.—Materials and apparatus for electrochemistry have been described elsewhere.[6] The potentials reported here were measured at room temperature and are referred to the saturated calomel electrode (s.c.e.). Under the ambient experimental conditions the ferrocenium–ferrocene couple was located at +0.40 V.

Crystallographic Data Collection and Structure Refinement.—The diffraction data for $[Cu(L)(NO_3)_2]$ (**A**) and $[Cu(L)_2][BF_4]_2 \cdot 2C_2H_5OH$ (**B**) were collected at room temperature on a four-circle Enraf-Nonius CAD4 diffractometer. Graphite-monochromatized Mo-K_α was used [λ(Mo-K_α) = 0.710 73 Å]. Crystal data and additional details of the data collection and refinement of both structures are presented in Table 1. The intensities of the reflections were corrected for Lorentz and polarization effects. An absorption correction was not applied for (**A**), since μ was only 14.9 cm^{-1} and the relative transmission factors were between 0.93 and 1.05. An empirical absorption correction was applied to the structure of (**B**), using the program DIFABS.[7] The calculations were performed on the Leiden University Amdahl 5860 computer using a local set of computer programs. Scattering factors were taken from ref. 8.

The position of the heavy atom in structure (**A**) was located from the Patterson map. The other non-hydrogen atoms were

Table 2. Fractional co-ordinates for the non-hydrogen atoms

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
(*a*) For $[Cu(L)(NO_3)_2]$ (**A**) [Cu(01) and S(02) × 10^5, others × 10^4]							
Cu(01)	29 032(2)	14 837(7)	51 022(3)	N(23)	2 972(2)	1 836(4)	6 579(2)
S(02)	42 439(6)	10 806(14)	56 477(8)	C(24)	3 669(2)	2 207(6)	7 250(2)
C(10)	4 425(2)	2 723(6)	4 683(3)	C(25)	3 577(2)	2 372(6)	8 232(3)
N(11)	3 124(2)	2 267(6)	2 140(3)	C(26)	4 116(4)	2 777(11)	9 247(4)
C(12)	2 686(2)	1 917(6)	2 782(3)	N(30)	3 333(2)	−2 843(4)	5 112(3)
N(13)	3 106(2)	1 994(4)	3 755(2)	O(31)	3 605(2)	−3 049(4)	4 359(2)
C(14)	3 835(2)	2 411(4)	3 698(3)	O(32)	3 644(2)	−3 515(4)	5 971(2)
C(15)	3 860(2)	2 573(6)	2 686(3)	O(33)	2 720(1)	−1 891(3)	5 020(2)
C(16)	4 491(3)	2 982(8)	2 187(4)	N(40)	1 504(2)	3 122(6)	4 411(2)
C(20)	4 352(2)	2 446(7)	6 841(3)	O(41)	841(2)	3 301(6)	3 942(3)
N(21)	2 815(2)	2 128(6)	8 139(3)	O(42)	1 931(2)	4 466(4)	4 710(2)
C(22)	2 463(2)	1 813(6)	7 147(3)	O(43)	1 774(1)	1 421(4)	4 585(2)
(*b*) For $[Cu(L)_2][BF_4]_2 \cdot 2C_2H_5OH$ (**B**) [Cu(01), C(40), C(41), C(40B), C(41B), O(42B), C(40C), C(41B), and O(42C) × 10^3, others × 10^4]							
Cu(01)	1 000	0	1 000	F(34)	7 027(22)	1 329(21)	6 479(6)
S(02)	12 678(4)	1 027(3)	9 535(1)	B(30B)	5 588(16)	1 240(14)	6 134(6)
C(10)	12 033(16)	200(14)	8 799(5)	F(31B)	4 731(29)	1 674(28)	6 552(7)
N(11)	7 964(12)	−1 203(10)	8 278(4)	F(32B)	4 658(29)	1 355(29)	5 589(7)
C(12)	7 876(15)	−1 096(11)	8 864(5)	F(33B)	6 983(23)	2 015(21)	6 179(8)
N(13)	9 289(11)	−555(8)	9 127(4)	F(34B)	5 992(30)	−101(15)	6 286(8)
C(14)	10 337(13)	−289(11)	8 691(5)	B(30C)	5 641(21)	1 112(16)	6 153(8)
C(15)	9 416(17)	−708(12)	8 175(6)	F(31C)	5 073(42)	703(34)	5 558(8)
C(16)	9 845(19)	−664(15)	7 511(7)	F(32C)	7 198(24)	669(29)	6 308(9)
C(20)	11 876(13)	2 777(11)	9 435(5)	F(33C)	5 626(38)	2 538(18)	6 254(10)
N(21)	7 613(11)	3 753(9)	9 541(4)	F(34C)	4 670(36)	543(32)	6 490(10)
C(22)	7 707(13)	2 444(11)	9 806(5)	C(40)	660(3)	260(3)	785(1)
N(23)	9 215(10)	1 925(8)	9 779(4)	C(41)	522(4)	216(4)	810(1)
C(24)	10 117(13)	2 875(10)	9 498(4)	O(42)	3 838(23)	3 044(23)	7 873(8)
C(25)	9 085(12)	4 040(11)	9 345(4)	C(40B)	675(6)	205(9)	811(3)
C(26)	9 405(12)	5 391(9)	9 019(5)	C(41B)	503(10)	208(13)	824(2)
B(30)	5 562(16)	1 276(14)	6 135(5)	O(42B)	397(5)	182(6)	770(2)
F(31)	4 340(28)	1 104(25)	6 472(6)	C(40C)	538(8)	145(5)	805(3)
F(32)	5 568(27)	206(24)	5 726(7)	C(41C)	649(6)	283(7)	800(2)
F(33)	5 324(25)	2 475(20)	5 825(7)	O(42C)	541(5)	374(3)	765(2)

located with the program AUTOFOUR.[9] The position of the copper ion in (**B**) is determined by symmetry requirements, lying on an inversion centre. The non-hydrogen atoms of the ligand were located with the program AUTOFOUR.[9] The various BF_4 and ethanol positions were deduced from successive Fourier difference maps.

The structures were refined by full-matrix least squares. The refinement was considered to be complete when the changes in the parameters were smaller than one-third of the standard deviation. The positions of the hydrogen atoms of (**A**) were located from Fourier difference maps. The non-hydrogens were refined anisotropically. The positional and isotropic thermal parameters of the hydrogen atoms of (**A**) were refined also. Because of the small size and poor quality of the single crystal of (**B**) not many (953) significant reflections $[I > 2\sigma(I)]$ could be collected. Refinement using these reflections only resulted in large standard deviations in the fractional co-ordinates and isotropic thermal parameters. Therefore, extra reflections with $I < 2\sigma(I)$ were also used in the refinement, which resulted in smaller standard deviations and a lower value for R', but a rather high R value. Only the Cu and S atoms were refined anisotropically. Hydrogen atoms could not be located and were not calculated. The function minimized was $\Sigma w(\|F_o| - |F_c\|)^2$, where $w = 1/\sigma^2(F)$. The fractional co-ordinates of the non-hydrogen atoms of (**A**) and (**B**) are listed in Table 2. Selected bond distances, angles, and hydrogen-bond distances are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

General Considerations.—The copper(II) compounds of the ligand L can be grouped into two series. Those of series I are all green and have either formula $[Cu(L)X_2]$, with X = Cl^-, Br^-, NCS^-, or NO_3^- or $Cu(L)Cl(BF_4)$. In these compounds both the ligand and the anions are co-ordinated to the copper(II) ion. The compounds of series II are all purple and of the formula $[Cu(L)_2]Y_2 \cdot nH_2O$, with Y = Cl^-, Br^-, NO_3^-, or BF_4^- and n = 0—3, and $[Cu(L)_2][NCS][NO_3] \cdot H_2O$. In these compounds only the ligands L are co-ordinated. The spectroscopic characteristics (ligand field and e.p.r.) of the compounds are given in Table 4.

The compounds of series I have identical i.r. spectra, apart from the typical absorption bands of the complex anions. However, *X*-ray powder isomorphism was not observed. Also for the compounds of series II no *X*-ray powder isomorphism was found, despite the very similar i.r. spectra. The characteristic i.r. absorption bands of the anions NCS^- (2 080 cm^{-1}), NO_3^- (1 300 cm^{-1}), and BF_4^- (1 050 cm^{-1}) were present in all respective i.r. spectra.

Description of the Structure of $[Cu(L)(NO_3)_2]$ (**A**).—The asymmetric unit consists of one molecule of $[Cu(L)(NO_3)_2]$. The ORTEP[10] drawing with atomic labelling is given in Figure

1. The copper ion is surrounded by two nitrogens and one sulphur from the ligand L, and two oxygens from the nitrate anions. Relevant bond distances and angles and hydrogen-bond distances are given in Table 3(*a*). From these data it is concluded that the geometry around Cu^{II} is closer to square pyramidal than to trigonal bipyramidal.

The two imidazole nitrogen atoms are co-ordinated in *trans* positions, with a N–Cu–N angle of 57.0°. The O(33) atom is at the apex of the square pyramid at a distance of 2.405(2) Å. The Cu–N distances are 1.939(3) and 1.943(3) Å; the Cu–O(43) distance is 1.987(2) Å and the Cu–S(02) distance is 2.369(1) Å, which is rather short for a copper-to-thioether distance. Short Cu–N distances are also present in previously determined structures of copper(II) compounds with imidazole ligands.[11,12] The short thioether distance is probably caused by the chelating effect of the ligand, whereby the S atom is pulled towards the copper ion by the strongly co-ordinating N atoms. The distance of O(42) to the copper ion is 2.7 Å, which sometimes is regarded as bonding.[12] However, if in this case O(42) is regarded as bonding to Cu^{II}, then it is *trans* with regard to O(33) while the O(33)–Cu–O(42) angle of 133.3° is quite small for *trans* donor atoms. Also, the plane through the four equatorial donor atoms, S(02), N(13), N(23), and O(43) is tetrahedrally distorted [atoms N(13) and N(23) lie 0.24 Å above the least-squares plane, S(02) and O(43) 0.24 Å below the plane] and the copper ion has moved out of the centre of gravity in the direction of O(33). All these factors indicate that O(42) plays a minor role in the co-ordination of the copper ion.

Table 3. Selected bond lengths (Å), angles (°), and hydrogen-bond distances (Å)

(*a*)$[Cu(L)(NO_3)_2]$ (**A**)			
Cu(01)–S(02)	2.369(1)	Cu(01)–O(33)	2.405(2)
Cu(01)–N(13)	1.939(3)	Cu(01)–O(43)	1.987(2)
Cu(01)–N(23)	1.943(3)		
S(02)–Cu(01)–N(13)	83.91(9)	N(13)–Cu(01)–O(33)	101.4(1)
S(02)–Cu(01)–N(23)	84.24(9)	N(18)–Cu(01)–O(43)	95.5(1)
S(02)–Cu(01)–O(33)	90.81(6)	N(23)–Cu(01)–O(33)	98.4(1)
S(02)–Cu(01)–O(43)	171.53(8)	N(23)–Cu(01)–O(43)	99.0(1)
N(13)–Cu(01)–N(23)	157.0(1)	O(33)–Cu(01)–O(43)	81.0(1)
O(33) ··· $N(11^{I})$	2.952(5)	O(42) ··· $N(11^{III})$	3.130(5)
O(33) ··· $N(21^{II})$	2.913(5)		
$[Cu(L)_2][BF_4]{\cdot}2C_2H_5OH$ (**B**)			
Cu(01)–S(02)	2.790(8)	Cu(01)–N(23)	1.99(2)
Cu(01)–N(13)	2.03(2)		
S(02)–Cu(01)–N(13)	80.9(7)	S(02)–Cu(01)–$N(23^{IV})$	100.2(6)
S(02)–Cu(01)–N(23)	79.8(6)	N(13)–Cu(01)–N(23)	88.5(9)
S(02)–Cu(01)–$N(13^{IV})$	99.1(7)	N(13)–Cu(01)–$N(23^{IV})$	91.5(9)
N(11) ··· $F(31B^{V})$	3.09(7)	N(21) ··· $F(32B^{VI})$	3.11(8)
N(11) ··· $O(42^{V})$	2.85(6)	N(21) ··· $F(31C^{VI})$	2.9(1)
N(11) ··· $O(42B^{V})$	3.1(1)	F(34C) ··· $O(42^{V})$	3.0(1)
N(11) ··· $O(42C^{V})$	3.2(1)	F(34C) ··· $O(42B^{V})$	3.1(2)
N(21) ··· $F(32^{VI})$	2.95(6)	F(34C) ··· $O(42C^{V})$	2.6(1)

Symmetry relations: I $-x + 0.5, y - 0.5, -z + 0.5$; II $-x + 0.5, y - 0.5, -z + 1.5$; III $-x + 0.5, y + 0.5, -z + 0.5$; IV $2 - x, -y, 2 - z$; V $1 - x, -0.5 + y, 1.5 - z$; VI $1 - x, 0.5 + y, 1.5 - z$.

The imidazole rings are planar, with deviations from the least-squares planes of less than 0.01 Å. The copper ion is at a distance of 0.13 Å from one of these least-squares planes and at 0.02 Å from the other. The two imidazole rings in the ligand L are nearly coplanar, with an angle between the two planes of 11.4°. The nitrate ions are planar, with deviations from the least-squares planes of less than 0.01 Å. The nitrate ions are almost perpendicular to each other, with an angle between the two planes of 87.7°.

The molecules are chained together by hydrogen bridges. The

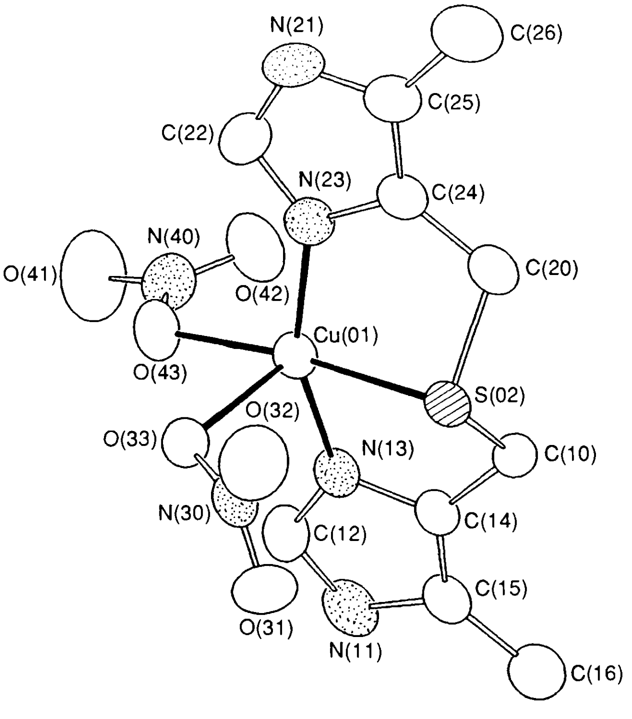


Figure 1. ORTEP projection of $[Cu(L)(NO_3)_2]$ with the atomic labelling. For clarity the hydrogen atoms are omitted

Table 4. Visible–near-i.r. absorption bands (× 10^{-3} cm^{-1}) and e.p.r. data (G = 10^{-4} T) for the copper co-ordination compounds with the ligand L

Compound	Visible–near-i.r.	E.p.r.
$[Cu(L)Cl_2]$ *	15.5, 12.5	$g_{1a} = 2.17, g_{2a} = 2.13, g_{3a} = 2.02$ $g_{1b} = 2.21, g_{2b} = 2.09$
$[Cu(L)Br_2]$	14.8, 11.5	$g_1 = 2.14, g_2 = 2.01$
$[Cu(L)(NCS)_2]$	16.7, 13.5	$g_{\parallel} = 2.28, g_{\perp} = 2.08$
$[Cu(L)(NO_3)_2]$	16.0	$g_{\parallel} = 2.22, g_{\perp} = 2.08$
$[Cu(L)Cl(BF_4)]$	15.6	$g_1 = 2.14, g_2 = 2.09, g_3 = 2.06$
$[Cu(L)_2]Cl_2$	19.5, 15.3, 12.7	$g_{\parallel} = 2.20, g_{\perp} = 2.10, A_{\parallel} = 175$ G
$[Cu(L)_2]Br_2{\cdot}2H_2O$	19.5, 15.2, 13.2	$g_{iso} = 2.09$
$[Cu(L)_2][NCS][NO_3]{\cdot}H_2O$	19.5, 15.2, 12.7	$g_{\parallel} = 2.28, g_{\perp} = 2.07$
$[Cu(L)_2][NO_3]_2$	19.8, 15.0, 13.0	$g_{\parallel} = 2.25, g_{\perp} = 2.07$
$[Cu(L)_2][BF_4]_2$	19.4, 15.1, 12.6	$g_{\parallel} = 2.27, g_{\perp} = 2.07, A_{\parallel} = 170$ G

* The *Q*-band e.p.r. spectra at 45 K indicate two independent isomeric species: rhombic and inverted axial (see text).

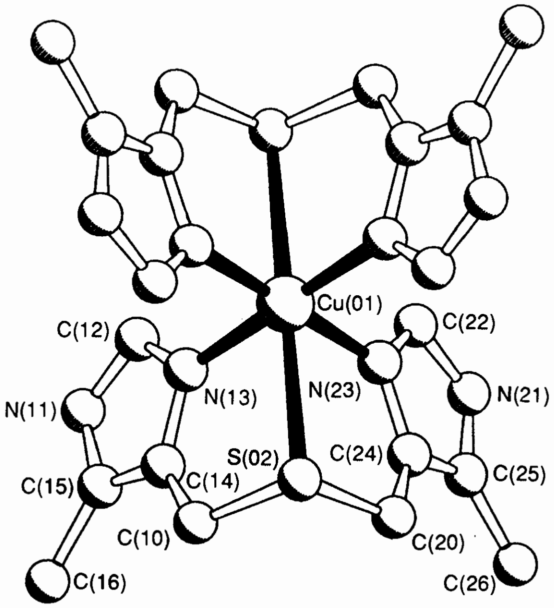


Figure 2. PLUTO projection and atomic labelling of the cation $[Cu(L)_2]^{2+}$. For clarity the disordered BF_4^- anions and ethanol molecules are omitted

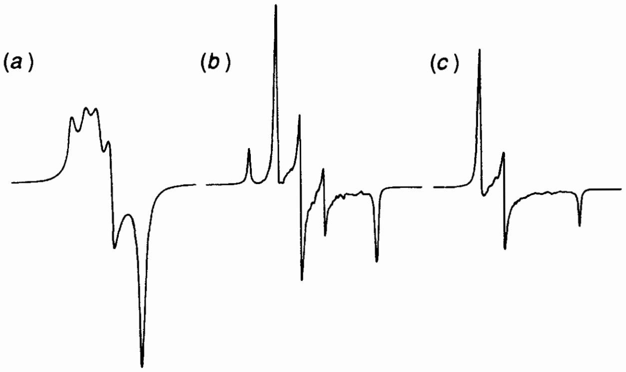


Figure 3. The e.p.r. spectra of $[Cu(L)Cl_2]$: (*a*) *X*-band of powdery material, (*b*) *Q*-band of powdery material, (*c*) *Q*-band of crystalline material

hydrogen atoms of the imidazole-nitrogen atoms N(11) and N(21) bridge to the co-ordinating oxygen atom [O(33)] of other molecules, forming a two-dimensional network.

Description of the Structure of $[Cu(L)_2][BF_4]_2 \cdot 2C_2H_5OH$ (**B**).—A PLUTO[13] drawing of the cation $[Cu(L)_2]^{2+}$, also showing the atomic numbering scheme, is depicted in Figure 2. The asymmetric unit of the monoclinic cell consists of half a molecule. The copper(II) ion is surrounded by two ligands, each tridentately co-ordinated, with two imidazole nitrogens and the thioether sulphur atom. Relevant bond distances and bond angles are given in Table 3(*b*). The copper ion lies on a centre of symmetry, which implies that the two ligands are facially co-ordinated, with the two thioether sulphur atoms in *trans* positions. The geometry of the copper ion is elongated octahedral: the equatorial plane is formed by the four imidazole nitrogens; the thioether sulphur atoms occupy the axial positions at rather large distances.

The imidazole rings are planar, with deviations from the least-squares planes being less than 0.02 Å. The bond distances and angles in the ligand are normal. The BF_4^- anions and the ethanol molecules are not co-ordinated, and are strongly disordered positionally. Both the anion and the ethanol molecule have been refined in three positions with varying occupation factors. However, additional partially occupied sites are present, as the final Fourier difference map still contains some rather high peaks. No further attempts to resolve this phenomenon were undertaken.

Spectroscopic Results for Series I.—The stoicheiometry of the compounds of group I has been established from the copper and halogen determinations, which were indicative for one ligand co-ordinated to the metal ion. From the *X*-ray powder photographs it has been established that there is no *X*-ray isomorphism within this group. The visible–near-i.r. spectra of these green compounds appear to be very similar and are indicative of a square-pyramidal or elongated-octahedral geometry for the copper ion. The square-pyramidal geometry of the copper(II) ion in $[Cu(L)(NO_3)_2]$ is confirmed by the structure determination (see above). The visible–near-i.r. and e.p.r. data for the copper bromide and thiocyanate compounds are indicative of a distorted square-pyramidal geometry. This is also the case for the mixed-anion compound $Cu(L)Cl(BF_4)$, in which the apical position can be occupied either by the tetrafluoroborate anion or by a bridging chloride ion from a neighbouring molecule. In the latter case the compound may be dinuclear, as in $[\{Cu(L^1)Cl\}_2][ClO_4]_2$[6], [$L^1$ = 1,5-bis(4-imidazolyl)-3-thiapentane], or polynuclear.[14,15] A square-pyramidal geometry of the copper ion, in which the equatorial plane is formed by the ligand and one chloride ion, with the other chloride ion occupying the apical position, is also observed in the crystal structure of $[Cu(L)Cl_2]$.[16] Unfortunately, the crystal structure of this compound could not be refined adequately, due to the poor quality of the single crystal. Better crystals could not be obtained due to the poor solubility. The *X*-band e.p.r. spectrum of the powdery precipitate of $[Cu(L)Cl_2]$ was quite difficult to interpret [Figure 3*a*)]. Therefore, a *Q*-band e.p.r. spectrum has been recorded, which reveals the presence of two independent copper species [Figure 3(*b*)]. The ratio in which the two species are present in the precipitate of different syntheses is quite constant, as deduced from the fact that the *X*- and *Q*-band spectra are very well reproducible. Initially it was presumed that these two species corresponded to the two independent molecules of $[Cu(L)Cl_2]$, present in the asymmetric unit of the crystal structure.[16] However, the e.p.r. spectrum of the microcrystalline product shows the presence of only one of the two species, namely the rhombic one [Figure 3(*c*)]. This implies that the second species must be another allotrope.

Spectroscopic Results for Series II.—The copper(II) compounds of series II are all purple, their stoicheiometry $[Cu(L)_2]X_2 \cdot nH_2O$ being inferred from the metal and halogen determinations. The compounds show many similarities, although no *X*-ray powder isomorphism is encountered. The visible–near-i.r. spectra are nearly identical for all compounds, and show some remarkable features: the low-energy part is indicative of a *trans* elongated-octahedral geometry, which is confirmed by the crystal-structure determination of $[Cu(L)_2][BF_4]_2$ (see above, Figure 2). The spectra of all the 1:2 copper compounds show an additional absorption at about 19 800 cm^{-1}, which is rather high for a copper *d–d* transition. However, the low absorption coefficient ($\varepsilon = 34\ dm^3\ mol^{-1}\ cm^{-1}$ as a 10^{-2} mol dm^{-3} solution in dimethyl sulphoxide) suggests that this absorption does not originate from a charge-transfer transition. A similar absorption in the high-energy region has been observed for the related compound $[Cu(L^2)_2][ClO_4]_2$ with L^2 = 1,3-bis(5-phenyl-2-imidazolyl)-2-thiapropane.[17] The crystal structure of the latter compound is very similar to the structure of $[Cu(L)_2][BF_4]_2$. Therefore, the additional absorption band has to be assigned to a *d–d* transition, due, probably, to a small distortion of the axial ligand-field symmetry. The

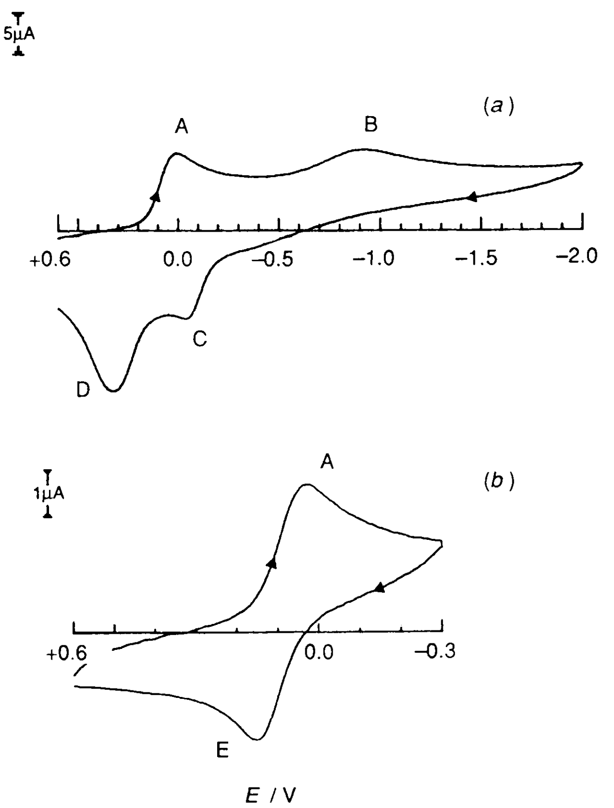


Figure 4. Cyclic voltammograms recorded at a platinum electrode on a deaerated dimethyl sulphoxide solution containing $[Cu(L)(NO_3)_2]$ (1.88×10^{-3} mol dm^{-3}) and NEt_4ClO_4 (0.1 mol dm^{-3}). Scan rate: (*a*) 0.2, (*b*) 0.02 V s^{-1}

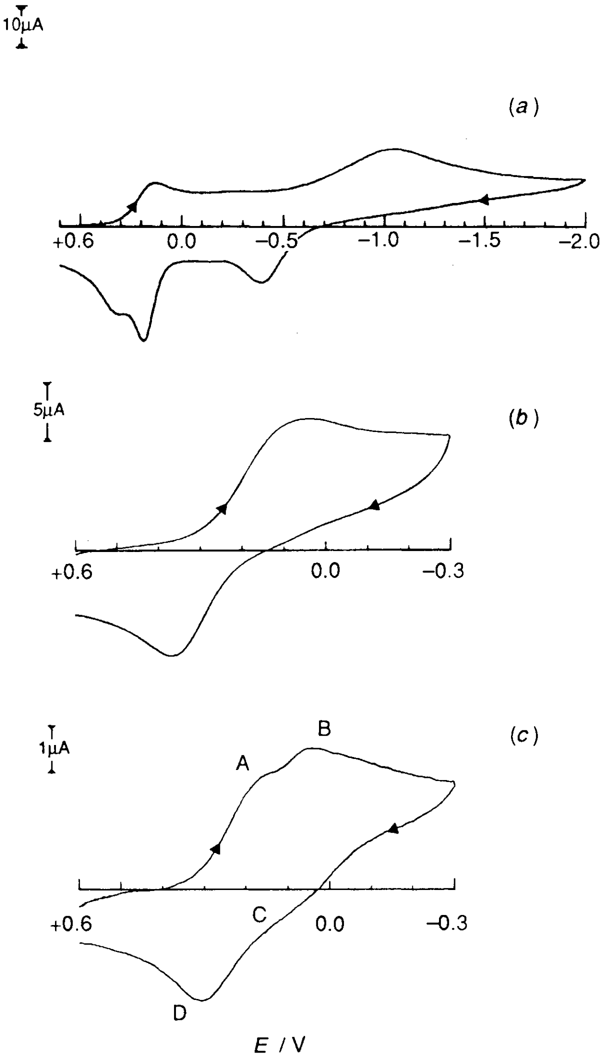


Figure 5. Cyclic voltammograms recorded at a platinum electrode on a deaerated dimethyl sulphoxide solution containing $[Cu(L)Cl_2]$ (1.97×10^{-3} mol dm^{-3}) and NEt_4ClO_4 (0.1 mol dm^{-3}). Scan rate: (*a*), (*b*) 0.2; (*c*) 0.02 V s^{-1}

powder e.p.r. spectra of all compounds have axial symmetry, in some cases with a slight indication of rhombicity, in agreement with the elongated-octahedral geometry. Single-crystal ligand-field and e.p.r. measurements would be required to confirm this tentative assignment.

Electrochemistry.—Series I. Figure 4 shows the cyclic voltammetric response exhibited by $[Cu(L)(NO_3)_2]$ in dimethyl sulphoxide solution. Two subsequent reduction steps are displayed in correspondence to peaks A and B. The number of electrons involved in each step could not be determined experimentally by controlled-potential electrolysis ($E_w = -0.3$ V), because of the occurrence of electrode-poisoning effects. Nevertheless, comparison with the peak height of an equimolar solution of ferrocene indicated that the reduction process proceeds through two successive one-electron redox changes. The first $Cu^{II}L \longrightarrow Cu^{I}L$ step is chemically reversible [Figure 4(*b*), $i_{p_E}/i_{p_A} = 1$], but electrochemically quasi-reversible ($\Delta E_p = 131$ mV). The second electron transfer $Cu^{I}L \longrightarrow Cu^{0}L$ is irreversible. It is probably accompanied by demetallation of the complex, as is illustrated by the reoxidation of copper metal to free Cu^+ and Cu^{2+} ions as shown by the presence of peaks C and D, respectively.

Analysis[18] of the cyclic voltammetric response of the peak system A/E with scan rate v points to the occurrence of a quasi-reversible one-electron reduction, followed by a reversible chemical reaction: E_{p_A} shifts cathodically with v; the parameter $i_{p_A} v^{-\frac{1}{2}}$ tends to decrease about 10% for a ten-fold increase in scan rate, and i_{p_E}/i_{p_A} progressively decreases from 1 at 0.02 V s^{-1} to 0.5 at 1.0 V s^{-1}. In addition, some adsorption of the electrogenerated copper(I) complex on the electrode surface must occur, because in macroelectrolysis the current rapidly drops to zero.

A qualitatively similar electrode mechanism seems to be operative for $[Cu(L)Br_2]$ and $[Cu(L)Cl(BF_4)]$. In these cases, however, electrode-poisoning phenomena do not occur, which made it possible to ascertain, by macroelectrolysis, that the first reduction process of $[Cu(L)Br_2]$ is a one-electron, chemically reversible step ($E_w = -0.4$ V). In contrast, the poor solubility of $[Cu(L)Cl(BF_4)]$ prevented quantitative assessments.

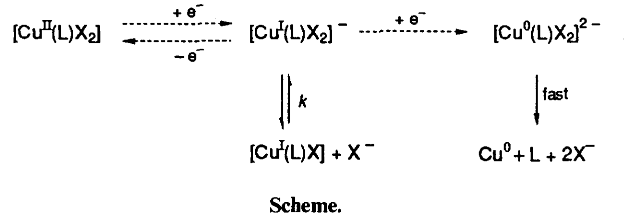
A further aspect of the electrochemistry of some compounds of this series is revealed by Figure 5, which refers to $[Cu(L)Cl_2]$. The two responses in (*a*) and (*b*) seem similar to those shown in Figure 4. However, it is clearly visible from (*c*) that the rounding of the reduction peak in (*b*) is really due to the overlapping, caused by scan rate, of two peaks, A and B. This correlates with the solid-state e.p.r. evidence, which gives support to the presence of two species, with slightly different Cu^{II}–Cu^{I} redox potentials ($E^{0'}_{A/D} = +0.23$, $E^{0'}_{B/C} = +0.08$ V). A similar response is displayed also by $[Cu(L)Br_2]$. The redox potentials reported in Table 5, thus have to be considered as the average of two close-spaced reductions for these compounds.

Attempts to clarify the nature of the chemical equilibrium following the copper(II)–copper(I) step were not completely

Table 5. Electrochemical parameters for the cathodic reduction of the complexes in dimethyl sulphoxide solution

Complex	$E^{0'}$(Cu^{II}–Cu^{I})/V	$\Delta E_p{}^a$/mV	E_p(Cu^{I}–Cu^{0})^a/V
$[Cu(L)Cl_2]$	+0.21[b]	308	−1.05
$[Cu(L)Br_2]$	+0.20[b]	280	−1.60
$[Cu(L)(NCS)_2]$	+0.19	320	−0.93
$[Cu(L)(NO_3)_2]$	+0.10	209	−0.90
$[Cu(L)Cl(BF_4)]$	+0.15[c]	440	−1.06
$[Cu(L)_2]Cl_2$	*d*		*d*
$[Cu(L)_2]Br_2{\cdot}2H_2O$	+0.10	115	−1.20
$[Cu(L)_2][NCS][NO_3]{\cdot}H_2O$	+0.14	151	−1.12
$[Cu(L)_2][NO_3]_2$	*d*		*d*
$[Cu(L)_2][BF_4]_2$	+0.08	193	−1.13

[a] Measured at 0.2 V s^{-1}. [b] Mean value between two overlapping reductions (see text). [c] Approximate value at very low current, caused by insolubility. [d] Fast decomposition in dimethyl sulphoxide solution (see text).



Scheme.

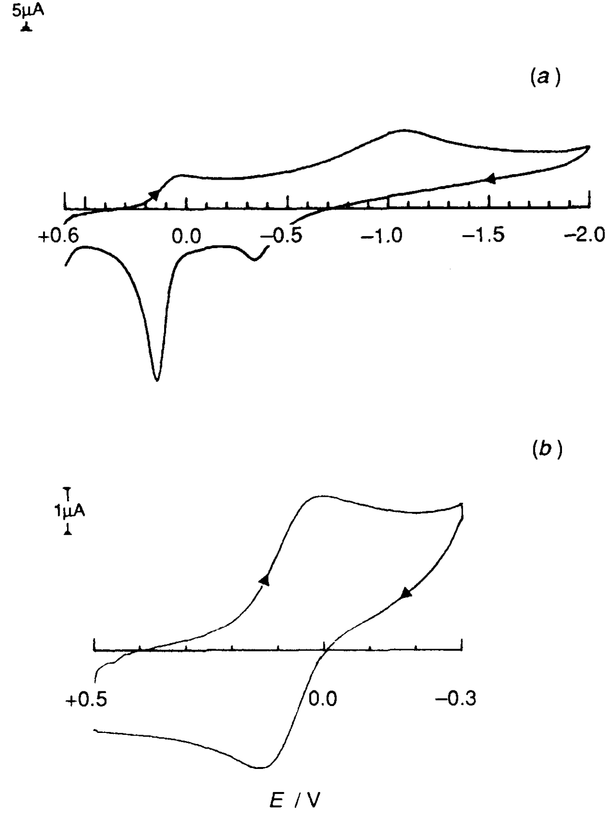


Figure 6. Cyclic voltammograms recorded at a platinum electrode on a deaerated dimethyl sulphoxide solution containing $[Cu(L)_2][BF_4]_2$ (1.17×10^{-3} mol dm^{-3}) and NEt_4ClO_4 (0.1 mol dm^{-3}). Scan rate 0.1 V s^{-1}

conclusive. At first the most reliable pathway was believed to be that shown in the Scheme. However, cyclic voltammetric tests performed either on $[Cu(L)Cl_2]$ or $[Cu(L)Br_2]$ in the presence of a saturated dimethyl sulphoxide solution of NEt_4Cl or NEt_4Br showed no variations in the diagnostic electrochemical features. So, discarding the involvement of the co-ordinated anions, one possible speculation is that, upon one-electron reduction, one of the three donor atoms of the ligand (possibly the weakest bound sulphur atom) may tend to leave the copper centre. As an example of this type of reorganization, the five-co-ordinated copper(II)–thioether complex $[Cu(L^3)]^{2+}$, (L^3 = 1,4,7,10,13-pentathiacyclopentadecane) upon one-electron reduction, gives rise to the copper(I) complex $[Cu(L^4)]^+$, in which one of the sulphur atoms is no longer co-ordinated.[19] On the other hand, the occurrence of a chemical equilibrium between a five- and a four-co-ordinate copper(I) species is supported by the preference of copper(I) for tetrahedral (or pseudo-tetrahedral) geometries and by a significantly high departure from pure electrochemical reversibility for the present copper(II)–copper(I) reduction, as measured by a mean ΔE_p value of about 300 mV at 0.2 V s^{-1}, which means that a rather elevated reorganizational energy is involved. Non-stereodynamic one-electron transfers involve constant ΔE_p values of 60 mV.[20,21]

It is interesting that in the case of the rather similar complexes $[Cu(L^1)X_2]$ this complication did not arise.[6] In such cases the smaller strain induced by the presence of two six-membered chelate rings, possibly makes the assembly more flexible, and may stabilize the five-co-ordination of the copper(I) centre. Accordingly, the ΔE_p value at 0.2 V s^{-1} averages to 130 mV.[6]

Series II. As a typical example of the redox behaviour of the complexes of series II, Figure 6 shows the cyclic voltammetric pattern exhibited by $[Cu(L)_2][BF_4]_2$ just after its dissolution in dimethyl sulphoxide. The reduction pathway once again proceeds through a first quasi-reversible Cu^{II}–Cu^{I} step, followed by a second irreversible Cu^{I}–Cu^{0} step. At variance with the complexes of series I, the first one-electron addition does not seem complicated by subsequent chemical reactions, even if it must be taken into account that an extended electrochemical investigation is prevented by the occurrence of decomposition of these complexes in Me_2SO. The first chemically reversible reduction is progressively substituted by an irreversible reduction at $E_p = -0.4$ V. This decomposition is particularly rapid for $[Cu(L)_2]Cl_2$ and $[Cu(L)_2][NO_3]_2$ (see Table 5 for a summary of the redox potentials for the complexes of series II). All complexes of series II contain the tetragonally distorted octahedral cation $[Cu(L)_2]^{2+}$. The unexpected differences in redox potentials for these compounds suggest some kind of interaction of the cation in solution with the different counter ions, which is also indicated by the different rates of self-decomposition.

One interesting aspect is the stability [within the lifetime of the copper(II) species] of the Cu^{I}–N$_4$S$_2$ assembly. Even if the quasi-reversibility of the relevant redox change introduces some stereochemical reorganization, it seems likely that the substantial octahedral geometry of the framework is retained. A similar copper(I) co-ordination compound can be postulated only in the reduction of the 1:2 copper–cimetidine complex[22] which in an aqueous medium (pH 7.8) occurs just at +0.11 V.[23]

Comparison of the Complexes with Related Compounds.— Similar to $[Cu(L)(NO_3)_2]$ the compounds $[Cu(L^4)(H_2O)(OClO_3)]ClO_4$ with L^4 = 1,5-bis(5,6-dimethyl-2-benzimidazolyl)-3-thiapentane[24] and $[Cu(L^5)(MeOH)(H_2O)][ClO_4]_2$ with L^5 = 1,5-bis(2-benzimidazolyl)-3-thiapentane[25] also have two co-ordinating nitrogen atoms, one sulphur atom, and two oxygen atoms in a distorted square-pyramidal arrangement around the copper(II) ion.

The environment of the copper ion in $[Cu(L)_2]^{2+}$ is similar to that in the compound $[Cu(L^6)_2][ClO_4]_2$ with L^6 = 1-thia-4,7-diazacyclononane[26] with a distorted-octahedral N_4S_2 chromophore with the two sulphur atoms *trans*-co-ordinated at long distances.

The molecular structure of $[Cu(L)_2][BF_4]_2{\cdot}2C_2H_5OH$ is comparable to the compound $[Cu(L^2)_2][ClO_4]_2{\cdot}5CH_3OH$.[17] The co-ordination geometry of both compounds can be described as an elongated octahedron with four equatorial N atoms, normal Cu–N distances of about 2.0 Å, and axial thioether sulphur atoms at a rather large Cu–S distance of about 2.8 Å.

Surprisingly, a previous crystal-structure determination of a 1:2 L compound, *viz.* $[Ni(L)_2]SiF_6{\cdot}5H_2O$, showed a *cis* distorted-octahedral geometry for the central metal ion.[27] However, *trans* distorted-octahedral $[Ni(L)_2]^{2+}$ complexes have also been obtained.[28] In these compounds, the geometry of the nickel ions is expected to be similar to that of the copper ion in $[Cu(L)_2][BF_4]_2$, as is described in this paper.

Conclusion

Two series of copper(II) compounds have been obtained with the ligand L, namely the green 1:1 compounds with essentially square-pyramidal geometry for the copper ion, and purple 1:2 compounds with elongated-octahedral geometry. Both the 1:1 and the 1:2 compounds are quite stable. This is illustrated by the observation that the strong donor anion thiocyanate resides in a non-co-ordinating lattice position in the compound $[Cu(L)_2][NCS][NO_3]{\cdot}H_2O$.

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