In memory of S. M. Nelson

Copper(I) and Copper(II) Compounds of a Dinucleating, Octadentate Tetrakisbenzimidazole Ligand. Crystal and Molecular Structures of Three Dihalogeno{1,8-bis[bis(1′-methylbenzimidazol-2′-ylmethyl)amino]-3,6-dioxaoctane}dicopper(II) Bis(anion) Compounds (Halogen = F, Cl, or Br; Anion = BF_4, CF_3SO_3, or Cl)†

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Synthesis, spectroscopic characterisation, and single-crystal structure analyses are described for a number of Cu^I and Cu^{II} co-ordination compounds with the ligand 1,8-bis[bis(1′-methylbenzimidazol-2′-ylmethyl)amino]-3,6-dioxaoctane (L). The compounds have the general formulae $Cu_2(L)X_2Y_2 \cdot xS$, Cu(L)Y, $Cu_2(L)(CO)_2Y_2$, $Cu_2(L)(Z)Y_3$, and $Cu_2(L)X_2$, where X = F, Cl, Br, or I; Y = ClO_4, BF_4, CF_3SO_3, Cl, or Br; Z = bridging anion like benzotriazolate; and S = solvent. Single-crystal structures of three Cu^{II} compounds, $[Cu_2(L)F_2][BF_4]_2 \cdot 2H_2O \cdot H_2OBF_3$ (**1**), $[Cu_2(L)Cl_2]Cl_2 \cdot 6H_2O$ (**2**), and $[Cu_2(L)Br_2][CF_3SO_3]_2 \cdot EtOH$ (**3**) have been determined using diffractometer data. All three compounds contain the dinuclear unit $[XCu(L)CuX]^{2+}$ in which the ligand L bridges the two Cu–X fragments. However, the intramolecular Cu • • • Cu distances are very large (*i.e.* larger than 575 pm). The intermolecular Cu • • • Cu contacts are much shorter, being 481, 388—488, and 398—405 pm, for (**1**), (**2**), and (**3**), respectively. Ligand-field, e.s.r., n.m.r., and i.r. spectra have been used to characterise all the compounds. The ligand-field maxima all agree with square-pyramidal Cu^{II} with a CuN_3XO chromophore in which X = F, Cl, or Br, respectively. The e.s.r. spectra indicate that exchange effects (intermolecularly) are important, resulting even in exchange-narrowed signals. Only the compounds $Cu_2(L)(Z)Y_3$ exhibit e.s.r. spectra typical for dinuclear Cu^{II} systems. The observed ν_{CO} bands at *ca.* 2 100 cm^{-1} for the Cu^I–CO adducts agree with end-on CO co-ordination.

Several copper proteins contain dinuclear metal centres, in which the metal ions are predominantly co-ordinated by the imidazole group of histidine.[1,2] Recently, Hol and co-workers[3] have elucidated the crystal structure of deoxy *Panulirus interruptus* haemocyanin, a Type III copper protein which is used for the transport of dioxygen in some molluscs and arthropods. The protein consists of several subunits, each containing two copper ions, which together can bind one molecule of O_2. They have found that each copper ion is surrounded by three imidazole groups, but no accurate distances to the co-ordinating atoms are known yet. The results of various extended *X*-ray absorption fine structure (EXAFS) measurements on other haemocyanins seem to be in accordance with the crystal structure; they indicate the presence of two or three N donors for each copper ion. The Cu–Cu distance is 372 pm, which compares well with those obtained from the EXAFS studies: 340 pm in the deoxy form and 355—367 pm in the oxy forms.[4,5] No definite structure of the oxy Cu^{II} state is known yet.[6] With resonance-Raman studies the O–O band of O_2^{2-} has been detected which agrees with a μ-peroxo group.[7] It is not yet clear whether this bridging group alone is responsible for the very strong antiferromagnetic exchange or that a second bridging group, hydroxide or, less likely, phenolate (from tyrosine), is required. In the crystal structure no evidence for a potential side-chain ligand has been found.[3]

One way to mimic the dinuclear site of haemocyanin with model compounds is to make use of ligand systems which can bind two metal ions and bring them together. This can be accomplished by an internal bridging group, by a multidentate ligand, or a combination of both. The advantage of a multidentate ligand is that the nature of an external bridging group can be varied, which is of great importance in relation to the different bridging groups occurring in Type III proteins in different redox states.

Quite a number of various ligand systems have been designed, each containing four heterocyclic groups that mimic the co-ordination sphere of Type III copper proteins and hold two copper ions close together. The heterocyclic groups are mainly pyrazole, pyridine, and benzimidazole. They all contain two dipodal N–N′–N moieties with a central amino nitrogen atom and two heterocyclic nitrogen atoms.[8–15]

The ligand 1,8-bis[bis(1′-methylbenzimidazol-2′-ylmethyl)amino]-3,6-dioxaoctane (L)[16] differs from the other ligands in one respect: the long and flexible aliphatic chain between the nitrogen atoms, which also contains two oxygen atoms in the form of ether groups (see Figure 1). Therefore different conformations are possible which may result in different Cu–Cu distances, depending on the presence and kind of bridging anions. This is also schematically depicted in Figure 1.

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

Non-S.I.unit employed: mmHg ≈ 133 Pa.

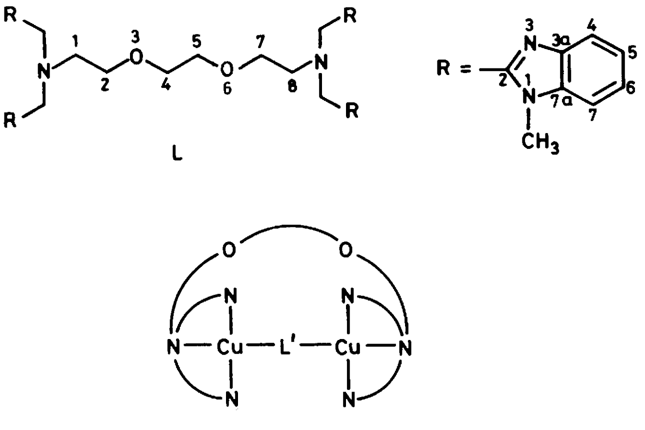

Figure 1. Structural formula of L and the proposed schematical structure of a $[Cu_2(L)(L')]^{3+}$ unit with an intramolecularly bridging anionic group (L′)

In the absence of bridging anions, the so-called 'open form' may be obtained. Both forms have been encountered with dinucleating ligands like L. In this paper mainly the last (open) form will be discussed; these co-ordinations have been characterized by spectroscopic as well as crystallographic means. The ligand itself has been synthesized by the ring-closure reaction of 1,2-diaminobenzene and the tetracarboxylic acid 3,6-dioxaoctane-1,8-diamine-*N*,*N*,*N*′,*N*′-tetra-acetic acid (dodta), followed by a methylation procedure. Crystal structures have been determined for three halide-containing compounds, *viz.* $[Cu_2(L)F_2][BF_4]_2\cdot2H_2O\cdot H_2OBF_3$ (**1**), $[Cu_2(L)Cl_2]Cl_2\cdot6H_2O$ (**2**), and $[Cu_2(L)Br_2][CF_3SO_3]_2\cdot EtOH$ (**3**). The spectroscopic properties of the so-called closed form will be described shortly, as well as related other dinuclear Cu^{II} and Cu^{I} compounds. Part of this work has been reported previously in a preliminary communication.[16]

Experimental

Starting Materials.—Solvents were used without prior purification, except when mentioned otherwise. Most inorganic and organic chemicals were commercially available, of reagent quality, and used as received. The supplier is mentioned when appropriate. Copper(II) trifluoromethanesulphonate (triflate) was prepared from basic copper carbonate and a slight excess of trifluoromethanesulphonic acid in acetonitrile, followed by recrystallization from absolute ethanol.

1,8-*Bis*[*bis*(1′-*methylbenzimidazol*-2′-*ylmethyl*)*amino*]-3,6-*dioxaoctane* (L).—A finely ground mixture of dodta (38.0 g, 0.10 mol, Sigma) and 1,2-diaminobenzene (44.0 g, 0.41 mol, Merck) was heated at 180 °C for 3—5 h. After cooling to *ca.* 70 °C the reaction mixture was poured into hot ethanol (500 cm^3), dissolved, and treated with decolourizing carbon. The off-white product precipitated upon cooling (−20 °C) and was recrystallized once from ethanol. The product {1,8-bis[bis(benzimidazol-2′-ylmethyl)amino]-3,6-dioxaoctane} was filtered off, washed with diethyl ether, and dried *in vacuo* at 40 °C (57.9 g, 87%), m.p. 94—104 °C (Found: C, 60.05; H, 6.50; N, 18.40. $C_{38}H_{40}N_{10}O_2\cdot5H_2O$ requires C, 60.15; H, 6.65; N, 18.45%); $\nu_{max.}$ at 3 000 br (N–H), 1 621m, 1 544m, 1 445vs, 1 383m, 1 345s, 1 309m, 1 294m, 1 273vs, 1 249m, 1 215m, 1 154s, 1 126s, 1 114s, 1 085s, 1 074s, 1 050s, 1 028s, 998m, 854m, 756s, 745vs (4 H, $H^{4,5,6,7}$ out-of-plane bending) cm^{-1}; δ_H [$^2H_6$]dimethyl sulphoxide(dmso), 2.79 (4 H, br t, 1,8-CH_2), 3.41 (4 H, s, 4,5-CH_2), 3.54 (4 H, br t, 2,7-CH_2), 4.10 (8 H, s, aryl–CH_2–N), 7.2 (8 H, m, $H^{5,6}$), 7.6 (8 H, m, $H^{4,7}$); δ_C([$^2H_6$]dmso–$CDCl_3$), 52.97 (aryl-CH_2–N), 53.69 (1,8-CH_2), 68.95 (2,7-CH_2),* 70.04 (4,5-CH_2),* 114.85 ($C^{4,7}$), 122.16 ($C^{5,6}$), 138.39 ($C^{3a,7a}$), 152.89 (C^2).

To a suspension of 1,8-bis[bis(benzimidazol-2′-ylmethyl)-amino]-3,6-dioxaoctane (33.4 g, 0.05 mol) in acetone (250 cm^3) finely ground potassium hydroxide (56.0 g, 1 mol) was added at room temperature. Addition of dimethyl sulphoxide (dmso) (100 cm^3) slightly improved the solubility of the components, but also decreased the yield. After 10 min a solution of iodomethane (38.0 g, 0.27 mol, Merck) in acetone (50 cm^3) was added. Immediately heat evolved (cooling was not necessary at this scale) and the product precipitated. The mixture was stirred for 1 h. The product was filtered off, suspended in water (500 cm^3), and filtered again after 1 h. This washing procedure was repeated with absolute ethanol (250 cm^3). The product was dissolved in refluxing chloroform (300 cm^3); the nearly clear solution was filtered and concentrated to 200 cm^3. Upon addition of light petroleum (b.p. 40—60 °C) (100 cm^3) the solution became turbid and was cooled (−20 °C). The product, a white microcrystalline solid, precipitated, was filtered off, and dried (60 °C, 15 mmHg) (28.0 g, 77%), m.p. 225—226 °C (Found: C, 69.15; H, 6.75; N, 19.05. $C_{42}H_{48}N_{10}O_2\cdot\frac{1}{3}H_2O$ requires C, 69.00; H, 6.70; N, 19.15%); $\nu_{max.}$ at 1 618m, 1 515m, 1 480vs, 1 445s, 1 403s, 1 359m, 1 335s, 1 291m, 1 238m, 1 154m, 1 131m, 1 115m, 1 097m, 1 048m, 1 007m, 993m, 868m, 769s, 747vs (4 H, $H^{4,5,6,7}$ out-of-plane bending) cm^{-1}; δ_H($CDCl_3$), 2.84 (4 H, t, *J* 6 Hz, 1,8-CH_2), 3.39 (4 H, s, 4,5-CH_2), 3.48 (12 H, s, CH_3), 3.53 (4 H, t, *J* 6 Hz, 2,7-CH_2), 4.01 (8 H, s, aryl–CH_2–N), 7.2 (12 H, m, $H^{4,5,6}$), 7.7 (4 H, m, H^7); δ_C($CDCl_3$), 29.61 (CH_3), 51.75 (aryl-CH_2–N), 53.84 (1,8-CH_2), 69.95 (2,7-CH_2),* 70.29 (4,5-CH_2),* 109.02 (C^4), 119.76 (C^7), 121.98 (C^5),* 122.68 (C^6),* 136.27 (C^{7a}), 142.51 (C^{3a}), 151.64 (C^2).

General Procedure for the Synthesis of Co-ordination Compounds with L.—The ligand L (1 mmol) was slurried in refluxing absolute ethanol (40—50 cm^3). The appropriate amount of copper(II) salt was dissolved in absolute ethanol (2—2.1 mmol Cu in 10—15 cm^3) and this solution was added to the ligand suspension. In most cases the colour changed and the ligand dissolved. A new precipitate was simultaneously formed, which was redissolved by subsequent refluxing and stepwise addition of water (5—25 cm^3) and/or ethanol (5—25 cm^3). The warm solution was filtered, if necessary, to remove any remaining insoluble material. Crystallization of the product occurred upon cooling to room temperature or a lower temperature (−20 °C). Partial evaporation of the solvents was also used to induce precipitation. The product was filtered off, washed with a small amount of ethanol and diethyl ether, and dried at room temperature and atmospheric pressure. The yields were around 80% of the theoretical value and were not further optimized. The compounds and their elemental analyses are listed in Table 1. Synthetic details are given below.†

$Cu_2(L)F_2(BF_4)_2\cdot2H_2O\cdot H_2OBF_3$ (**1**). The starting salt was $Cu(BF_4)_2\cdot6H_2O$. An extra amount of water (10 cm^3) was added. The crystalline product did not decompose when dried. Single crystals were obtained from a diluted solution (0.5 mmol L in 25 cm^3 ethanol, 1.0 mmol Cu salt in 15 cm^3 EtOH, 9 cm^3 water). The solution was refluxed for 5 min and cooled to room temperature.

$Cu_2(L)Cl_4\cdot6H_2O$ (**2**). A crystalline product was obtained according to the general procedure with the addition of water (15 cm^3). Single crystals, used for *X*-ray diffraction, were grown

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* These assignments may be interchanged.

† **CAUTION**: Some compounds described in this paper contain perchlorate anions. Although no accidents with perchlorates occurred during the experimental work for this paper, it should be pointed out that the use of perchlorates is hazardous because of the possibility of explosion, especially when the compounds are anhydrous.[17]

Table 1. Co-ordination compounds with L and their elemental analyses (%)[a]

Complex[b]	M	C	H	N	Other
(**1**) $Cu_2(L)F_2(BF_4)_2{\cdot}2H_2O{\cdot}H_2OBF_3$	10.8 (10.7)	43.25 (42.55)	4.70 (4.60)	12.1 (11.8)	20.4 (20.8) F 7.00 (6.75) O 2.65 (2.75) B
(**2**) $Cu_2(L)Cl_4{\cdot}6H_2O$	11.3 (11.5)	45.65 (45.80)	5.50 (5.50)	12.8 (12.7)	13.1 (12.9) Cl
(**3**) $Cu_2(L)Br_2(CF_3SO_3)_2{\cdot}EtOH$	9.5 (9.4)	40.60 (40.75)	4.05 (4.00)	10.40 (10.35)	11.5 (11.8) Br
(**4**) $Cu_2(L)Br_4{\cdot}4H_2O$	10.1 (10.2)	40.65 (40.55)	4.00 (4.55)	11.30 (11.25)	
(**5**) $Cu_2(L)(NO_3)_4{\cdot}2H_2O$	10.7 (11.2)	44.25 (44.40)	4.30 (4.60)	17.15 (17.60)	
(**6**) $Cu_2(L)(ClO_4)_4{\cdot}2H_2O$	9.4 (9.9)	39.15 (39.25)	3.95 (4.10)	10.75 (11.00)	
(**7**) $Cu_2(L)(CF_3SO_3)_4{\cdot}4H_2O$	8.3 (8.7)	37.85 (37.70)	3.35 (3.45)	9.55 (9.55)	
(**8**) $Cu_2(L)Cl_2(CF_3SO_3)_2{\cdot}H_2O$	10.1 (10.3)	42.80 (42.65)	3.80 (4.05)	11.30 (11.30)	
(**9**) $Cu_2(L)(im)(ClO_4)_3{\cdot}H_2O$	10.2 (10.3)	43.00 (43.75)	4.45 (4.30)	13.5 (13.6)	8.55 (8.60) Cl
(**10**) $Cu_2(L)(btz)(CF_3SO_3)_3{\cdot}H_2O$	8.5 (8.8)	42.80 (42.70)	3.90 (3.80)	12.75 (12.70)	
(**11**) $Cu_2(L)(btz)(NO_3)_3{\cdot}6H_2O$		45.75 (45.60)	4.05 (5.00)	18.00 (17.75)	
(**12**) $Cu(L)ClO_4$	7.0 (7.2)	55.80 (56.80)	5.00 (5.45)	15.55 (15.80)	
(**13**) $Cu(L)BF_4$	7.6 (7.3)	56.10 (57.65)	5.30 (5.55)	15.45 (16.00)	
(**14**) $Cu(L)CF_3SO_3$	7.2 (6.8)	53.70 (55.10)	5.05 (5.15)	14.50 (14.95)	
(**15**) $Cu_2(L)Cl_2$	13.7 (13.8)	54.60 (54.65)	4.90 (5.25)	15.25 (15.20)	8.30 (7.70) Cl
(**16**) $Cu_2(L)Br_2$	12.7 (12.6)	49.20 (49.85)	4.90 (4.80)	13.65 (13.85)	15.9 (15.7) Br
(**17**) $Cu_2(L)I_2{\cdot}CH_2Cl_2$	10.8 (10.7)	43.60 (43.35)	4.30 (4.25)	11.60 (11.75)	21.8 (21.3) I
(**18**) $Cu_2(L)(CO)_2(ClO_4)_2$	11.4 (11.5)	47.05 (47.00)	4.50 (4.50)	12.40 (12.45)	

[a] Calculated values are given in parentheses. [b] L = $C_{42}H_{48}N_{10}O_2$, im = imidazolate ($C_3H_3N_2$), btz = benzotriazolate ($C_6H_4N_3$).

from a four-fold diluted solution. A small tray was placed in a closed vessel containing absolute ethanol. The fluids were not in direct contact with each other, but diffusion in the vapour phase was allowed to occur. The crystals became opaque and lost their lustre when they were dried.

$Cu_2(L)Br_2(CF_3SO_3)_2{\cdot}EtOH$ (**3**) *and* $Cu_2(L)Cl_2(CF_3SO_3)_2{\cdot}H_2O$ (**8**). These compounds crystallized from a solution, prepared according to the general procedure, containing the halide and triflate anions in a starting ratio of 1:1. An extra amount of ethanol (Cl, 20 cm^3; Br, 10 cm^3) was added. Single crystals of $Cu_2(L)Br_2(CF_3SO_3)_2{\cdot}EtOH$ were grown from a solution containing a three-fold excess of triflate. The crystals became opaque and lost their lustre when they were dried.

$Cu_2(L)Br_4{\cdot}4H_2O$ (**4**). This compound was insoluble in ethanol-containing mixtures. The general procedure worked out well with methanol and the addition of water (10 cm^3).

$Cu_2(L)(NO_3)_4{\cdot}2H_2O$ (**5**), $Cu_2(L)(ClO_4)_4{\cdot}2H_2O$ (**6**), *and* $Cu_2(L)(CF_3SO_3)_4{\cdot}4H_2O$ (**7**). In each case water (10 cm^3) was added. The crystals became opaque when dried.

$Cu_2(L)(im)(ClO_4)_3{\cdot}H_2O$ (**9**, Him = *imidazole*). A solution of $Cu_2(L)(ClO_4)_4$ (1 mmol) was prepared as described above (no excess of copper salt) in 96% ethanol (60 cm^3) and water (5 cm^3). Imidazole (1 mmol) was dissolved in ethanol (5 cm^3) and treated with a solution of sodium hydroxide (1 cm^3, 1 mol dm^{-3}). The azolate solution was added to the copper compound, whereupon a light blue product precipitated immediately. This product was not soluble upon refluxing or after addition of water and ethanol.

$Cu_2(L)(btz)(CF_3SO_3)_3{\cdot}H_2O$ (**10**, Hbtz = *benzotriazole*) *and* $Cu_2(L)(btz)(NO_3)_3{\cdot}6H_2O$ (**11**). A solution of sodium benzotriazolate was added to the copper compound as described above. A crystalline product was obtained after cooling [(**10**)]. The blue colour of the solution intensified. Precipitation of compound (**11**) occurred after concentration of the solution to 10 cm^3 and addition of water (10 cm^3).

General Procedure for the Synthesis of Copper(I) *Co-ordination Compounds with* L.—All reactions and manipulations were carried out in an inert atmosphere of nitrogen gas in Schlenk-type glassware connected to a standard dual nitrogen-vacuum rack. Commercially available high-purity dinitrogen and carbon monoxide were used without further purification. The gases were dried by passing them through a cylinder filled with Sicapent (Merck). The ligand (1 mmol) was suspended in methanol (50 cm^3) or dissolved in a mixture of methanol (40 cm^3) and dichloromethane (10 cm^3). The suspension or solution was refluxed under a stream of nitrogen gas for at least 1 h in a 100-cm^3 three-necked round-bottomed flask equipped with a gas inlet, a condenser with a gas outlet, and an empty pressure-equalizing dropping funnel with another gas inlet. A glass-frit filter was placed between the funnel and the flask. In a few experiments the solution became turbid because of removal of some of the dichloromethane by the gas flow. The copper(I) salts were prepared in solution as their tetrakis(acetonitrile)copper(I) co-ordination compounds. The appropriate Cu^{II} salt (1 mmol scale) was dissolved in a mixture of acetonitrile (20—30 cm^3) and methanol (20—30 cm^3) and reduced with an excess of copper powder (4 mmol, Merck, electrochemically prepared). The suspension was stirred for 30 min and then transferred to the dropping funnel. Nitrogen was bubbled through the reaction mixture for at least 45 min. The Cu^{I} solution was added to the ligand solution or suspension through the filter. The funnel and filter were removed when all Cu^{I} had been added. The product precipitated either spontaneously, or after cooling to room temperature and partial evaporation of the solvent. The product was filtered with the help of a turnover filter. Oxygen-free diethyl ether was added as a transfer medium when the volume of the solvent was too small. The product was washed with diethyl ether and dried *in vacuo* (0.1 mmHg) at room temperature. Most products, if dry, can be manipulated in air. However, they must be stored in a nitrogen atmosphere, as they are slightly oxidized by (moist) air. Their solutions are all very sensitive to oxygen from the atmosphere. The compounds and their elemental analyses are listed in Table 1.

Cu(L)Y [Y = ClO_4 (**12**), BF_4 (**13**), *or* CF_3SO_3 (**14**)]. A solution of $[Cu(CH_3CN)_4]Y$ in acetonitrile (15 cm^3) and methanol (25 mmol) (starting with 0.5 mmol of the appropriate Cu^{II} salt) was added to a refluxing solution of the ligand in dichloromethane (10 cm^3) and methanol (40 cm^3). Even when the ligand had not completely dissolved by leaving out dichloromethane, a clear solution of Cu(L)Y was obtained. The solubility depends on the anion used; the perchlorate compound precipitated after concentration to *ca.* 50 cm^3, that containing tetrafluoroborate only after concentration to *ca.* 30 cm^3, and that with trifluoromethanesulphonate after concentration to 15 cm^3 and addition of oxygen-free diethyl ether (25 cm^3). The products were filtered off, washed, and dried in the usual way.

$Cu_2(L)X_2$ [X = Cl (**15**) *or* Br (**16**)]. A solution of $[Cu(CH_3CN)_4]X$ in acetonitrile (Cl, 10 cm^3; Br, 15 cm^3) and methanol (Cl, 40 cm^3; Br, 35 cm^3), obtained from 1 mmol of the appropriate Cu^{II} salt, was added to a refluxing solution of the ligand in dichloromethane (10 cm^3) and methanol (40 cm^3). A clear solution was obtained after addition of about half of the Cu^I compound, even if dichloromethane was not used. The product started to precipitate when almost all the Cu^I had been added. The mixture was cooled to room temperature and the product isolated in the usual way.

$Cu_2(L)I_2 \cdot CH_2Cl_2$ (**17**). A solution of $[Cu(CH_3CN)_4]I$ was prepared by reduction of I_2 (1 mmol), dissolved in acetonitrile (40 cm^3) and methanol (25 cm^3), using an excess of copper powder. This solution was added to a solution of the ligand in dichloromethane (10 cm^3) and methanol (40 cm^3). If no dichloromethane was used, a clear solution was obtained when about half of the Cu^I compound had been added. The product precipitated before all the Cu^I had been added. The mixture was refluxed for 15 min and cooled to room temperature. The product was isolated in the usual way. The same product, although contaminated with potassium salt, could be prepared by adding 2 mmol of crystalline KI to a solution of $Cu_2(L)Y_2$ ($Y = NO_3$, ClO_4, or CF_3SO_3), which was prepared in the usual way.

$Cu_2(L)(CO)_2(ClO_4)_2$ (**18**). A solution of $[Cu(CH_3CN)_4]ClO_4$ in acetonitrile (20 cm^3) and methanol (20 cm^3) (starting with 1:1.1 mmol of the appropriate Cu^{II} salt) was added to a refluxing solution of the ligand in a mixture of methanol (35 cm^3) and dichloromethane (15 cm^3). A clear solution was obtained, especially when using a slight excess of Cu^I salt. Carbon monoxide was passed over the solution for 30—60 min. The solution was concentrated to *ca.* 30 cm^3 (in an atmosphere of CO) to increase the yield. The product was isolated in the usual way in a nitrogen atmosphere.

Spectroscopic and other Techniques.—Infrared spectra were recorded on a Perkin-Elmer 580 spectrometer. Samples were prepared as alkali-metal halide pellets (KBr, CsCl, or CsI) and as Nujol mulls. Far-i.r. spectra (450—50 cm^{-1}) were recorded on a Nicolet 7000 Fourier-transform i.r. spectrometer at the University of Amsterdam.

Ligand-field spectra were recorded on a Beckman DK-2A spectrophotometer (diffuse reflectance) or on a Perkin-Elmer 330 spectrophotometer (diffuse reflectance and in solution). MgO was used as a reference in the reflectance mode.

E.s.r. spectra were recorded on a Varian E-3 (*X*-band) spectrometer at room temperature and 77 K for powdered solids and (frozen) solutions. *Q*-Band spectra were recorded on a Varian E-112 spectrometer at the Delft University of Technology.

N.m.r. spectra (^1H and ^{13}C) were recorded on JEOL PS-100 (100 MHz), JEOL FX-200 (200 MHz), or Bruker WM-300 (300 MHz) spectrometers. Tetramethylsilane or the solvent (in oxygen-free samples) was used as an internal reference. Chemical shift values are reported *vs.* $SiMe_4$.

Magnetic susceptibilities were measured at various temperatures with a PAR vibrating sample 150A magnetometer (2—80 K) and a standard low-temperature Faraday balance (77—320 K). The data were corrected for the diamagnetism of the compound constituents and for the temperature-independent paramagnetism of copper(II).

Conductivity measurements were carried out with a Seibold conductometer at 25 °C. Solvents ($MeNO_2$, dimethylformamide) were dried and distilled before use.[18]

Elemental Analyses.—Metal contents were determined complexometrically by back titration with ethylene diaminetetra-acetate (edta) and zinc acetate after destruction of the sample in a boiling mixture of sulphuric acid and hydrogen peroxide (2:1 v/v). Halogen contents (Cl, Br, or I) were determined by potentiometric titration (for chlorine and bromine) or by titration with thiosulphate (for iodine) after combustion of the sample according to Schoeniger.[19] In the case of iodine, edta was added to prevent oxidation of iodide by copper(II). Other elements (C, H, N, S, B, or F) were analysed at Pascher's Microanalytical Laboratory (Bonn), the Microanalytical Laboratory at Eindhoven University of Technology, Canadian Microanalytical Service (Vancouver), or the Microanalytical Laboratory of University College (Dublin).

X-Ray Diffraction and Structure Determination.—A suitable crystal in a glass capillary was mounted on the Nonius CAD-4 computer-controlled diffractometer used in Leiden [(**1**) and (**2**)] or the Syntex $P2_1$ four-circle diffractometer used in Münster [(**3**)]. Intensity data were collected as described in refs. 20 and 21 using graphite-monochromated Mo-K_α radiation ($\lambda = 71.073$ pm). Lattice constants were determined by a least-squares refinement of the angular settings of 24 selected reflections. Three standard reflections were measured every 5 400 s of radiation time to check for instrumental instability and crystal decomposition. The data were corrected for Lorentz and polarization effects in the usual way and also for absorption by de Graaff's method[22] if the variation in intensity of suitable reflections in different azimuthal positions was considered to be too large.

The structures were solved in general by means of a three-dimensional Patterson synthesis to locate the copper atoms, followed by the application of Patterson and direct methods to find the positions of the other non-hydrogen atoms. Subsequent Fourier syntheses and least-squares refinements, using local programs on local computers, gave the positions and thermal parameters of these atoms. Scattering factors for the non-hydrogen atoms were used with correction for anomalous dispersion according to ref. 23, whereas the scattering factors for the hydrogen atoms were taken from ref. 24. The metal ions in the asymmetric unit were usually located by means of a three-dimensional Patterson synthesis. Subsequent application of the direct methods programs AUTOFOUR[25] or DIRDIF[26] gave the positions of all the non-hydrogen atoms of L. The remaining parts of the ligands, counter ions, solvents *etc.* were found by difference Fourier methods, and will be described below for each of the three compounds. An absorption correction was applied only for compound (**1**), as the values of the variation in I(azimuth) were rather small for the others [0.86—1.06 for (**1**); much smaller for (**2**) and (**3**)]. The final R values, based on observed and calculated structure factors, were calculated from $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$, where w is a weight factor proportional to $[\sigma(I)]^{-2}$ [(**1**) or (**2**)] or $[\sigma^2(F_o) + (0.01|F_o|)^2]^{-1}$ [(**3**)].

$[Cu_2(L)F_2][BF_4]_2 \cdot 2H_2O \cdot H_2OBF_3$ (**1**). The *X*-ray intensity data were collected as described above at room temperature in the ω—θ scan mode.

Crystal data. $C_{42}H_{54}B_3Cu_2F_{13}N_{10}O_5$, $M = 1\,185.46$, orthorhombic, $a = 1.215\,9(2)$, $b = 1.690\,9(2)$, $c = 2.565\,4(5)$ nm, $U = 5.274(1)$ nm^3, space group *Pccn*, $D_m = 1.54$ g cm^{-3} (flotation in $CHCl_3$–CH_2Br_2), $Z = 4$, $D_c = 1.493$ g cm^{-3}, $F(000) = 2\,291$, green-blue rhomb-shaped plates, 0.66 × 0.50 × 0.10 mm, $\mu = 9.0$ cm^{-1}, scan range $2 < \theta < 22°$, $-12 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 17$, $0 \leqslant l \leqslant 27$, 6 264 reflections measured, 2 900 (3 227) independent, 1 685 (1 969) significant $[I > 2\,\sigma(I)]$ (the values in parentheses include the low-order reflections, see later), merging $R = 0.019$.

The space group *Pccn* was indicated by the systematic

Table 2. Fractional positional parameters and B values (nm^2) of the non-hydrogen atoms in $[Cu_2(L)F_2][BF_4]_2 \cdot 2H_2O \cdot H_2OBF_3$ (**1**), with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c	Occupancy	B_{iso}
Cu(1)	0.873 04(9)	0.101 92(7)	0.474 20(5)	1.0	0.033 2(3)
F(2)	0.993 7(5)	0.167 4(4)	0.485 8(3)	1.0	0.058(2)
C(3A)	0.689 4(21)	0.217 1(15)	0.542 3(8)	0.5	0.044(4)
C(3B)	0.724 6(19)	0.227 4(13)	0.552 9(9)	0.5	0.044(4)
O(4A)	0.714 2(13)	0.173 8(10)	0.495 9(6)	0.5	0.035(2)
O(4B)	0.717 0(13)	0.168 9(9)	0.511 6(6)	0.5	0.035(2)
C(5A)	0.625 5(20)	0.119 7(13)	0.496 9(10)	0.5	0.055(4)
C(5B)	0.642 8(19)	0.105 3(13)	0.520 8(9)	0.5	0.055(4)
C(6A)	0.639 7(15)	0.063 1(13)	0.459 3(9)	0.5	0.039(3)
C(6B)	0.645 2(15)	0.048 7(13)	0.479 0(9)	0.5	0.039(3)
N(7)	0.750 3(6)	0.017 7(5)	0.457 4(4)	1.0	0.034(2)
C(8)	0.752 4(11)	−0.000 9(6)	0.403 3(5)	1.0	0.043(3)
C(9)	0.770 5(11)	−0.051 1(7)	0.492 6(5)	1.0	0.051(4)
C(10)	0.798 6(9)	0.069 4(7)	0.373 9(6)	1.0	0.041(3)
N(11)	0.855 6(7)	0.124 0(5)	0.400 3(3)	1.0	0.037(2)
C(12)	0.888 3(9)	0.179 2(7)	0.362 9(5)	1.0	0.039(3)
C(13)	0.947 7(10)	0.249 3(8)	0.369 4(6)	1.0	0.057(4)
C(14)	0.964 5(13)	0.291 5(12)	0.323 1(11)	1.0	0.086(7)
C(15)	0.926 9(16)	0.294 6(16)	0.274 7(10)	1.0	0.079(7)
C(16)	0.874 8(15)	0.199 1(13)	0.270 3(6)	1.0	0.073(5)
C(17)	0.851 2(9)	0.157 1(8)	0.315 7(6)	1.0	0.047(4)
N(18)	0.790 5(7)	0.085 1(6)	0.322 9(3)	1.0	0.042(3)
C(19)	0.736 8(14)	0.039 4(10)	0.283 3(5)	1.0	0.070(5)
C(20)	0.828 5(8)	−0.026 6(7)	0.538 8(5)	1.0	0.038(3)
N(21)	0.881 9(7)	0.041 2(5)	0.538 9(3)	1.0	0.039(3)
C(22)	0.928 0(8)	0.050 1(7)	0.588 5(5)	1.0	0.034(3)
C(23)	0.988 5(9)	0.109 7(8)	0.610 6(5)	1.0	0.047(4)
C(24)	1.019 2(10)	0.098 3(12)	0.661 7(6)	1.0	0.056(4)
C(25)	0.989 8(13)	0.033 5(12)	0.689 3(6)	1.0	0.065(5)
C(26)	0.928 5(12)	−0.024 7(11)	0.668 2(6)	1.0	0.054(4)
C(27)	0.898 7(8)	−0.015 7(8)	0.617 9(5)	1.0	0.044(4)
N(28)	0.833 3(8)	−0.063 9(6)	0.584 5(4)	1.0	0.042(3)
C(29)	0.785 5(12)	−0.140 1(8)	0.597 6(5)	1.0	0.060(4)
B(30A)	0.408 9(12)	−0.012 5(9)	0.349 9(6)	0.41(3)	0.060(4)
F(31A)	0.346 9(22)	0.032 0(12)	0.317 5(8)	0.41(3)	0.081(3)
F(32A)	0.364 6(23)	−0.085 7(10)	0.352 3(8)	0.41(3)	0.093(3)
F(33A)	0.410 2(24)	0.021 9(13)	0.397 4(7)	0.41(3)	0.095(4)
F(34A)	0.512 5(12)	−0.017 0(23)	0.331 2(9)	0.41(3)	0.114(4)
B(30B)	0.417 8(9)	−0.018 9(7)	0.346 3(5)	0.59(3)	0.060(4)
F(31B)	0.390 7(17)	0.038 8(7)	0.312 3(5)	0.59(3)	0.081(3)
F(32B)	0.328 9(13)	−0.064 9(11)	0.354 9(7)	0.59(3)	0.093(3)
F(33B)	0.450 6(17)	0.014 4(10)	0.391 5(5)	0.59(3)	0.095(4)
F(34B)	0.500 7(14)	−0.062 0(15)	0.325 8(6)	0.59(3)	0.114(4)
O(40)	1.138 4(7)	0.273 4(5)	0.514 6(4)	1.0	0.073(3)
O(41)	1.102 6(15)	0.318 1(11)	0.616 0(7)	0.5	0.072(4)

absences of the reflections for $0kl$ (l odd), $h0l$ (l odd), and $kh0$ ($h + k$ odd). An absorption correction was applied in a later stage[22] of the refinement and led to significantly better results. Fourier syntheses and least-squares refinements in a block-diagonal matrix yielded the position of a water molecule and some extra peaks, close to a two-fold axis, which could not be interpreted as positions of atoms in a discrete molecule. All hydrogen atoms of the ligand L were placed in calculated positions with an isotropic B factor of 0.05 nm^2, because only a few hydrogen atoms could be located. They were kept at a fixed distance (100 pm) from the parent carbon atom. The hydrogen atoms in the methyl groups were placed with the help of the direction of one hydrogen atom found in a difference Fourier map.

The elemental analysis elucidated some uncertainties concerning the cell contents. The unidentate ligand was assigned to be a fluoride anion (see Results and Discussion section). The other counter ion (tetrafluoroborate) had already been positioned and so the remaining part of the cell contents had to be neutral. Further refinement indicated some imperfections in the calculated model. First, a small part of the cell contents, formulated as $0.5(H_2OBF_3)$ in the asymmetric unit, could not be located unambiguously. Space-group symmetry requires that these atoms are either on a symmetry element or in partially occupied positions. A large hole in the calculated model was present around a point on a two-fold axis (0.25, 0.25, 0.22), which is in the area where the most intense remaining peaks had been found. Secondly, the atoms in the tetrafluoroborate anion and in the carbon chain between the amino nitrogen atoms had large anisotropic thermal parameters.

As disorder might be responsible for these problems, the low-order reflections (10% of the total number) were omitted from subsequent refinements. The tetrafluoroborate anion was divided into two independent ions (A and B) with a total occupancy equal to unity. The B–F bond lengths and F–B–F angles were constrained according to the method of Waser and co-workers[27] at 135 pm and 109.5° respectively and the isotropic thermal parameters were kept the same for each of the A and B atoms. The relative occupancy was refined. Because of the strong anisotropy in, especially, C(3), C(5), and C(6), these atoms and the interjacent oxygen atom [O(4)] in the 1,8-diamino-3,6-dioxaoctane bridge were also divided over two positions. The positions of the A and B atoms were refined independently. The occupancy of each one was kept at 0.5, as it was found that the most realistic C(3)–C(3′) bond lengths were found between A and B atoms. The thermal parameters were kept the same within each pair of A and B atoms and refined isotropically. The hydrogen atoms attached to these carbon atoms were recalculated for each individual A and B atom.

The remaining problem, *viz.* to fit the rest of the cell contents into the hole (diameter 350 pm) could not be solved. Various Fourier syntheses showed one predominant peak at hydrogen-bonding distance from the water molecule, which was assigned to a molecule of water. In a final difference Fourier map, only two peaks as high as 2×10^3 e nm^{-3} (three times the mean noise level) were found in that hole.

The refinement converged to final residuals R and R' of 0.071 and 0.068 respectively for the reduced data set and 0.075 and 0.157 if the low-order reflections were used too. The atomic positions, occupancies, and (calculated) isotropic thermal parameters of the non-hydrogen atoms are listed in Table 2.

$[Cu_2(L)Cl_2]Cl_2 \cdot 6H_2O$ (**2**). A crystal was taken from the mother-liquor and covered with paraffin oil to prevent decomposition by loss of solvent. Thereafter, it was mounted in a sealed capillary. The X-ray intensity data were collected as described above at room temperature in the ω scan mode.

Crystal data. $C_{42}H_{60}Cl_4Cu_2N_{10}O_8$, $M = 1\,101.90$, triclinic, $a = 1.406\,6(3)$, $b = 1.520\,4(6)$, $c = 1.575\,6(3)$ nm, $\alpha = 105.97(3)$, $\beta = 110.89(2)$, $\gamma = 96.72(3)°$, $U = 2.939(2)$ nm^3, space group $P\bar{1}$, $D_m = 1.34$ g cm^{-3} (flotation in C_6H_5Br–C_6H_5Cl), $Z = 2$, $D_c = 1.25$ g cm^{-3}, $F(000) = 1\,107$, green rectangular blocks, 0.55 × 0.30 × 0.25 mm, $\mu = 9.7$ cm^{-1}, scan range $2 < \theta < 22°$, $-14 \leqslant h \leqslant 14$, $-16 \leqslant k \leqslant 16$, $-16 \leqslant l \leqslant 0$, 7 522 measured reflections, 7 169 independent, 3 411 significant [$I > 2\sigma(I)$], merging $R = 0.025$, variation I(azimuth) = 0.97—1.03. Wilson statistics indicated the centrosymmetric space group $P\bar{1}$.

The 58 non-hydrogen atoms of the $[Cu_2(L)Cl_2]^{2+}$ entity were refined with anisotropic thermal parameters. As only a few hydrogen atoms could be located, all 48 hydrogen atoms in the

Table 3. Fractional positional parameters and *B* values (nm^2) of the non-hydrogen atoms in $[Cu_2(L)Cl_2]Cl_2{\cdot}6H_2O$ (**2**), with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Occupancy	B_{iso}
Cu(1)	0.361 6(2)	0.433 1(2)	0.400 5(2)	1.0	0.043(1)
Cu(2)	0.112 9(2)	0.149 0(2)	0.028 4(2)	1.0	0.044(1)
Cl(3)	0.495 6(5)	0.450 3(4)	0.357 3(5)	1.0	0.055(3)
Cl(4)	−0.015 8(5)	0.191 0(4)	0.067 9(5)	1.0	0.053(3)
C(13)	0.175(2)	0.406(2)	0.172(2)	1.0	0.059(14)
C(14)	0.256(2)	0.386(2)	0.135(2)	1.0	0.060(13)
O(15)	0.202(1)	0.384(1)	0.257(1)	1.0	0.048(8)
O(16)	0.261(1)	0.289(1)	0.113(1)	1.0	0.047(7)
C(17)	0.126(2)	0.401(2)	0.291(2)	1.0	0.053(12)
C(18)	0.333(2)	0.262(2)	0.072(2)	1.0	0.055(12)
C(19)	0.150(2)	0.374(2)	0.378(2)	1.0	0.055(14)
C(20)	0.330(2)	0.157(2)	0.052(2)	1.0	0.056(14)
N(21)	0.252(2)	0.425(1)	0.461(1)	1.0	0.040(9)
N(22)	0.228(1)	0.096(1)	−0.017(2)	1.0	0.039(9)
C(23)	0.246(2)	0.522(1)	0.511(2)	1.0	0.046(11)
C(24)	0.204(2)	0.095(2)	−0.114(2)	1.0	0.049(12)
C(25)	0.281(2)	0.368(1)	0.522(2)	1.0	0.045(11)
C(26)	0.227(2)	0.004(1)	−0.004(2)	1.0	0.049(11)
C(30)	0.285(2)	0.581(1)	0.469(1)	1.0	0.041(11)
N(31)	0.335(1)	0.558(1)	0.414(1)	1.0	0.037(8)
C(32)	0.361(2)	0.639(1)	0.393(2)	1.0	0.041(11)
C(33)	0.408(2)	0.648(2)	0.330(2)	1.0	0.051(12)
C(34)	0.416(2)	0.735(2)	0.316(2)	1.0	0.064(14)
C(35)	0.378(2)	0.805(2)	0.361(2)	1.0	0.072(15)
C(36)	0.331(2)	0.798(2)	0.421(2)	1.0	0.071(16)
C(37)	0.323(2)	0.711(1)	0.433(2)	1.0	0.047(12)
N(38)	0.279(1)	0.671(1)	0.483(1)	1.0	0.051(10)
C(39)	0.234(2)	0.723(1)	0.541(2)	1.0	0.076(14)
C(40)	0.135(2)	0.162(1)	−0.135(1)	1.0	0.050(12)
N(41)	0.087(1)	0.193(1)	−0.079(1)	1.0	0.043(9)
C(42)	0.029(2)	0.250(2)	−0.123(2)	1.0	0.050(13)
C(43)	−0.040(2)	0.301(2)	−0.099(2)	1.0	0.065(13)
C(44)	−0.082(2)	0.351(2)	−0.158(2)	1.0	0.078(17)
C(45)	−0.074(2)	0.346(2)	−0.244(2)	1.0	0.088(19)
C(46)	−0.001(2)	0.301(2)	−0.259(2)	1.0	0.078(16)
C(47)	0.048(2)	0.251(2)	−0.203(2)	1.0	0.052(13)
N(48)	0.116(1)	0.193(1)	−0.210(1)	1.0	0.050(10)
C(49)	0.158(2)	0.172(1)	−0.282(1)	1.0	0.074(15)
C(50)	0.325(2)	0.296(1)	0.475(1)	1.0	0.039(11)
N(51)	0.368(1)	0.314(1)	0.418(1)	1.0	0.039(9)
C(52)	0.405(2)	0.233(1)	0.391(1)	1.0	0.041(11)
C(53)	0.458(2)	0.210(2)	0.330(1)	1.0	0.049(12)
C(54)	0.483(2)	0.123(2)	0.313(2)	1.0	0.051(12)
C(55)	0.463(2)	0.062(2)	0.359(2)	1.0	0.069(15)
C(56)	0.413(2)	0.085(1)	0.419(2)	1.0	0.059(13)
C(57)	0.384(2)	0.171(1)	0.435(1)	1.0	0.042(11)
N(58)	0.334(1)	0.214(1)	0.490(1)	1.0	0.045(9)
C(59)	0.296(2)	0.176(2)	0.549(2)	1.0	0.073(14)
C(60)	0.198(2)	0.006(1)	0.079(1)	1.0	0.037(10)
N(61)	0.145(1)	0.066(1)	0.105(1)	1.0	0.044(9)
C(62)	0.129(2)	0.044(2)	0.181(1)	1.0	0.038(11)
C(63)	0.080(2)	0.086(1)	0.238(2)	1.0	0.046(11)
C(64)	0.076(2)	0.047(2)	0.306(2)	1.0	0.062(14)
C(65)	0.123(2)	−0.025(2)	0.320(2)	1.0	0.059(13)
C(66)	0.170(2)	−0.069(2)	0.264(2)	1.0	0.052(13)
C(67)	0.174(2)	−0.029(2)	0.196(1)	1.0	0.043(12)
N(68)	0.219(1)	−0.051(1)	0.132(1)	1.0	0.047(10)
C(69)	0.275(2)	−0.122(1)	0.124(2)	1.0	0.063(13)
Cl(70)	1.028(1)	0.451(1)	0.577(1)	0.5	0.119(4)
O(70)	1.028(1)	0.451(1)	0.577(1)	0.5	0.119(4)
Cl(71)	1.033(1)	0.245(1)	0.493(1)	0.5	0.120(4)
O(71)	1.033(1)	0.245(1)	0.493(1)	0.5	0.120(4)
O(72)	0.931(1)	0.063(1)	0.482(1)	1.0	0.094(5)
O(73)	0.566(1)	−0.127(1)	0.204(1)	1.0	0.101(6)
O(74)	0.511(3)	−0.020(3)	0.062(3)	0.5	0.103(11)
O(75)	0.724(2)	0.018(2)	0.356(2)	0.82(2)	0.100
O(76)	0.874(2)	0.186(2)	0.274(2)	0.69(2)	0.100
O(77)	0.728(5)	0.096(4)	0.215(4)	0.31(2)	0.100
O(78)	0.640(5)	0.310(5)	0.225(5)	0.27(2)	0.100
O(79)	0.599(3)	−0.410(3)	0.195(3)	0.46(2)	0.100
O(80)	0.824(3)	0.376(3)	0.274(3)	0.49(2)	0.100
O(81)	0.805(2)	0.434(2)	0.057(2)	0.64(2)	0.100

ligand L were placed in calculated positions and kept at a fixed distance (95 pm to an sp^2 carbon atom, 100 pm to an sp^3 atom) from the parent atom. The methyl groups were orientated with the C–H bond pointing to the methylene group in the aromatic plane. The C–C and C–N distances in the benzimidazole rings were constrained to values found for other benzimidazole containing copper chelates [in ref. 8 and compound (**1**)] and benzimidazole itself,[28] as some of the distances became very short (less than 130 pm). This is probably due to some disorder or thermal movement, which is reflected by the large anisotropic thermal parameters for these atoms.

The exact cell contents, including solvent molecules, could not be determined experimentally, because of decomposition of the crystals, which occurred due to loss of solvent. The elemental analysis given is that of a sample which was dried. The density was also affected by decomposition; it increased during the experiment (from 1.34 to 1.40 g cm^{-3}). The analysis indicated at least six molecules of water in the asymmetric unit, but further molecules of water or perhaps ethanol cannot be excluded; for instance the *X*-ray experiments indicated *ca.* seven water molecules.

A larger cluster of atoms at hydrogen-bonding distances to each other was found, which should contain two chloride anions and a number of water and perhaps ethanol molecules. The positions were assigned to water molecules and chloride ions with variable occupancies. The occupancy of each individual position was either refined (with a fixed isotropic thermal parameter of 0.1 nm^2) or varied by trial and error to a fixed number (0.5 or 1.0) with an isotropic thermal parameter of *ca.* 0.1 nm^2, that was refined. Two positions (atoms 70 and 71) were both occupied with half a chloride anion and half a water molecule. The fourth Cl^- ion could not be located.

The refinement converged to final residuals *R* and *R′* of 0.092 and 0.126 respectively. The atomic positions, occupancies, and (calculated) isotropic thermal parameters of the non-hydrogen atoms are listed in Table 3.

$[Cu_2(L)Br_2][CF_3SO_3]_2{\cdot}EtOH$ (**3**). The *X*-ray intensity data were collected as described above at 140 K in the θ–2θ scan mode.

Crystal data. $C_{46}H_{54}Br_2Cu_2F_6N_{10}O_9S_2$, M = 1 356.03, triclinic, a = 1.395 4(5), b = 1.442 0(5), c = 1.553 9(6) nm, α = 78.16(3), β = 75.90(3), γ = 61.85(3)°, U = 2.659(1) nm^3, space group $P\bar{1}$, Z = 2, D_c = 1.69 g cm^{-3}, blue needles, 0.10 × 0.08 × 0.25 mm, μ = 25.9 cm^{-1}, scan range $2 < \theta < 24°$, $0 \leqslant h \leqslant 14$, $-14 \leqslant k \leqslant 15$, $-17 \leqslant l \leqslant 17$, 8 309 measured reflections, 8 230 independent, 5 605 significant [$I > 1.96\,\sigma(I)$]. Wilson statistics indicated the centrosymmetric space group $P\bar{1}$, which was confirmed by the successful structure refinement.

During the refinement one triflate group was found to be disordered over two positions in a way that S(2), O(6), and O(7) coincide approximately for both of them, and the remaining atoms C(44), O(8), F(4), F(5), and F(6) were split into two partially occupied positions (Table 4). The occupancy of the split positions was refined to approximately 0.5 in several refinement cycles. In the next refinement cycles the Cu, Br, O, and N atoms were refined anisotropically, the remaining atoms were kept isotropic. In the final cycles the occupancy factors of the disordered triflate group were fixed at 0.5. Hydrogen atoms were placed at calculated positions (the orientations of the

Table 4. Fractional positional parameters and B values (nm^2) of the non-hydrogen atoms in $[Cu_2(L)Br_2][CF_3SO_3]_2{\cdot}EtOH$ (**3**) with estimated standard deviations in parentheses[a]

Atom	X/a	Y/b	Z/c	B_{iso}	Atom	X/a	Y/b	Z/c	B_{iso}
Cu(1)	0.037 28(10)	0.620 84(10)	0.458 65(8)	0.014 3(4)	C(26)	0.243 0(9)	0.528 7(8)	0.091 0(7)	0.016(2)
Cu(2)	0.389 55(11)	0.612 68(10)	0.080 14(8)	0.015 3(4)	C(27)	0.284 2(8)	0.372 6(8)	0.168 4(6)	0.014(2)
Br(1)	0.108 74(9)	0.487 71(8)	0.361 28(7)	0.019 8(4)	C(28)	0.284 4(9)	0.276 1(8)	0.210 6(7)	0.018(2)
Br(2)	0.567 62(9)	0.511 89(9)	0.121 55(8)	0.023 1(4)	C(29)	0.369 9(9)	0.216 6(8)	0.260 8(7)	0.018(2)
O(1)	0.145 2(6)	0.732 0(5)	0.400 2(4)	0.019 4(2)	C(30)	0.446 5(9)	0.250 2(8)	0.269 0(7)	0.018(2)
O(2)	0.276 3(6)	0.696 5(5)	0.213 3(4)	0.016 7(2)	C(31)	0.443 4(8)	0.347 6(8)	0.225 6(6)	0.014(2)
N(1)	−0.100 3(7)	0.707 9(6)	0.412 6(5)	0.014 0(3)	C(32)	0.358 1(8)	0.407 6(7)	0.173 6(6)	0.012(2)
N(2)	−0.035 5(7)	0.736 5(6)	0.547 8(5)	0.014 4(3)	C(33)	0.485 2(8)	0.778 8(8)	−0.006 5(6)	0.014(2)
N(3)	0.148 4(7)	0.553 3(6)	0.536 0(5)	0.013 7(3)	C(34)	0.579 7(9)	0.750 7(8)	0.029 0(7)	0.019(2)
N(4)	−0.279 6(7)	0.816 6(6)	0.446 9(5)	0.016 1(3)	C(35)	0.635 0(9)	0.815 7(8)	−0.001 1(7)	0.019(2)
N(5)	0.200 4(7)	0.555 0(7)	0.659 5(5)	0.022 9(3)	C(36)	0.593 5(9)	0.905 5(9)	−0.063 9(7)	0.023(2)
N(6)	0.234 3(7)	0.700 3(6)	0.039 5(5)	0.016 6(3)	C(37)	0.498 6(9)	0.934 4(8)	−0.099 2(7)	0.017(2)
N(7)	0.415 3(7)	0.731 4(6)	0.007 0(5)	0.015 6(3)	C(38)	0.447 0(9)	0.868 6(8)	−0.069 0(7)	0.016(2)
N(8)	0.332 2(7)	0.506 9(6)	0.123 1(5)	0.014 1(3)	C(39)	0.338 9(8)	0.789 2(8)	−0.046 2(7)	0.015(2)
N(9)	0.355 1(7)	0.872 8(6)	−0.091 3(5)	0.015 7(3)	C(40)	0.251 9(9)	0.759 9(8)	−0.051 1(7)	0.020(2)
N(10)	0.209 9(7)	0.451 8(6)	0.115 2(5)	0.012 7(3)	C(41)	0.289 1(9)	0.954 9(9)	−0.156 6(7)	0.023(2)
C(1)	−0.152 5(9)	0.719 8(8)	0.342 2(7)	0.016(2)	C(42)	0.115 7(9)	0.448 0(9)	0.092 0(7)	0.024(2)
C(2)	−0.110 1(9)	0.677 9(8)	0.259 6(7)	0.021(2)	S(1)	0.045 3(2)	0.214 6(2)	0.097 3(2)	0.018 8(5)
C(3)	−0.183 3(10)	0.705 9(9)	0.201 4(8)	0.026(2)	S(2)	0.262 5(3)	0.909 4(3)	0.592 5(3)	0.047 1(9)
C(4)	−0.298 3(10)	0.774 7(9)	0.225 6(7)	0.024(2)	O(3)	0.096 1(6)	0.213 6(6)	0.167 2(5)	0.026(2)
C(5)	−0.342 0(9)	0.817 9(9)	0.308 0(7)	0.024(2)	O(4)	−0.072 1(6)	0.245 0(6)	0.121 3(5)	0.026(2)
C(6)	−0.265 2(8)	0.788 2(8)	0.363 4(7)	0.015(2)	O(5)	0.076 9(7)	0.261 8(6)	0.012 2(5)	0.035(2)
C(7)	−0.182 2(8)	0.768 6(8)	0.472 4(6)	0.014(2)	O(6)	0.232 8(7)	0.943 9(6)	0.509 4(5)	0.036(2)
C(8)	−0.158 0(8)	0.775 2(8)	0.560 3(6)	0.014(2)	O(7)	0.360 0(7)	0.899 8(7)	0.610 4(6)	0.043(2)
C(9)	0.006 9(9)	0.688 7(8)	0.633 9(7)	0.021(2)	O(8)	0.188 8(13)	1.010 8(12)	0.645 1(10)	0.033(4)^{b}
C(10)	0.119 7(9)	0.597 5(8)	0.610 8(7)	0.016(2)	O(8a)	0.287 9(16)	0.781 5(15)	0.585 4(12)	0.051(5)^{b}
C(11)	0.289 5(9)	0.477 1(8)	0.612 4(7)	0.021(2)	O(9)	0.363 8(7)	0.973 8(6)	0.349 9(5)	0.034(2)
C(12)	0.396 8(10)	0.411 9(9)	0.633 2(8)	0.030(3)	F(1)	0.056 1(6)	0.061 5(6)	0.023 0(5)	0.047(2)
C(13)	0.471 2(11)	0.344 8(10)	0.569 4(8)	0.035(3)	F(2)	0.207 5(6)	0.030 8(6)	0.056 8(5)	0.049(2)
C(14)	0.438 3(9)	0.343 1(9)	0.490 2(7)	0.022(2)	F(3)	0.079 4(7)	0.021 1(6)	0.158 4(5)	0.053(2)
C(15)	0.331 7(9)	0.408 4(8)	0.471 6(7)	0.019(2)	F(4)	0.297 2(11)	0.729 7(10)	0.619 0(8)	0.032(3)^{b}
C(16)	0.257 9(8)	0.476 5(8)	0.536 3(7)	0.015(2)	F(4a)	0.060 0(13)	0.939 2(12)	0.644 6(10)	0.047(3)^{b}
C(17)	−0.385 3(9)	0.889 0(8)	0.495 5(7)	0.019(2)	F(5)	0.132 5(11)	0.833 1(10)	0.669 2(8)	0.029(3)^{b}
C(18)	0.196 2(11)	0.581 3(11)	0.748 3(9)	0.042(3)	F(5a)	0.121 1(12)	1.035 2(11)	0.682 5(9)	0.039(3)^{b}
C(19)	−0.010 0(9)	0.827 8(8)	0.504 5(7)	0.022(2)	F(6)	0.264 5(11)	0.793 5(10)	0.740 1(8)	0.031(3)^{b}
C(20)	0.111 1(10)	0.795 8(9)	0.473 2(7)	0.026(2)	F(6a)	0.158 3(13)	0.877 4(12)	0.749 0(10)	0.046(3)^{b}
C(21)	0.264 2(9)	0.688 8(8)	0.376 1(7)	0.019(2)	C(43)	0.099 2(11)	0.075 5(10)	0.085 2(8)	0.034(3)
C(22)	0.301 9(9)	0.627 0(8)	0.295 1(7)	0.019(2)	C(44)	0.236(2)	0.814(2)	0.661(1)	0.022(5)^{b}
C(23)	0.164 8(9)	0.731 3(8)	0.201 0(7)	0.020(2)	C(44a)	0.144(2)	0.943(2)	0.672(2)	0.030(5)^{b}
C(24)	0.161 9(9)	0.781 0(8)	0.105 4(7)	0.018(2)	C(45)	0.382 0(11)	0.878 2(11)	0.230 7(9)	0.041(3)
C(25)	0.186 4(9)	0.628 1(8)	0.033 9(7)	0.015(2)	C(46)	0.300 7(11)	0.966 1(10)	0.285 6(9)	0.040(3)

[a] B_{eq} values for Cu, Br, N, and O atoms; B_{eq} values are calculated from the anisotropic thermal coefficients as one third of the orthogonalized B_{ij} tensor: $B_{eq} = \frac{1}{3} \Sigma_i \Sigma_j B_{ij} a_i^* a_j^* a_i a_j$. [b] Occupancy factor 0.5.

methyl groups were determined from one or two hydrogen atoms located from a difference Fourier map), and their contributions were included in the structure factor calculations with fixed distances from the neighbouring carbon atoms and fixed B values ($= 1.2\ B_{iso}$ of neighbouring carbon). The refinement converged to final residuals R and R' of 0.072 and 0.066 respectively. The atomic positions, occupancies, and (calculated) isotropic thermal parameters of the non-hydrogen atoms are listed in Table 4.

Results and Discussion

Description of the Structures of $[Cu_2(L)F_2][BF_4]_2{\cdot}2H_2O{\cdot}H_2OBF_3$ (**1**), $[Cu_2(L)Cl_2]Cl_2{\cdot}6H_2O$ (**2**), *and* $[Cu_2(L)Br_2][CF_3SO_3]_2{\cdot}EtOH$ (**3**).—The structures of the cationic species $[Cu_2(L)X_2]^{2+}$ are depicted in Figures 2, 3, or 4 respectively for X = F, Cl, or Br. These figures clearly show similarities between the structures. The main difference between the fluoro and chloro compounds on the one hand and the bromo compound on the other is the orientation of both ligand halves (see later). The main bond lengths and interbond angles are listed in Tables 5, 6, and 7, respectively. The compounds are not isomorphous; space groups, unit-cell dimensions, and/or the asymmetric units are different. The parts of the i.r. spectra attributed to the ligand are not identical but resemble each other quite well.

In the fluoro complex (**1**), the asymmetric unit contains one copper ion and half a ligand molecule as there is a two-fold crystallographic axis (0.75, 0.25, z) within the molecule. The 1,8-diamino-3,6-dioxaoctane bridge appears to be misaligned relative to this axis. As described above, the conformation of this bridge is either not symmetrical, or two different conformations are possible with half of the molecules in the unit cell in one conformation, the other half in the other.

The asymmetric unit of the chloro complex (**2**) contains two copper ions and a whole ligand molecule as there are no intramolecular symmetry elements possible in this space group. However, a pseudo-two-fold axis is present, similar to the crystallographic one in the fluoro derivative, as can be seen in Figure 3.

The asymmetric unit of the bromo complex (**3**) also contains two copper ions and a complete ligand molecule, but has no simple pseudo-symmetry element.

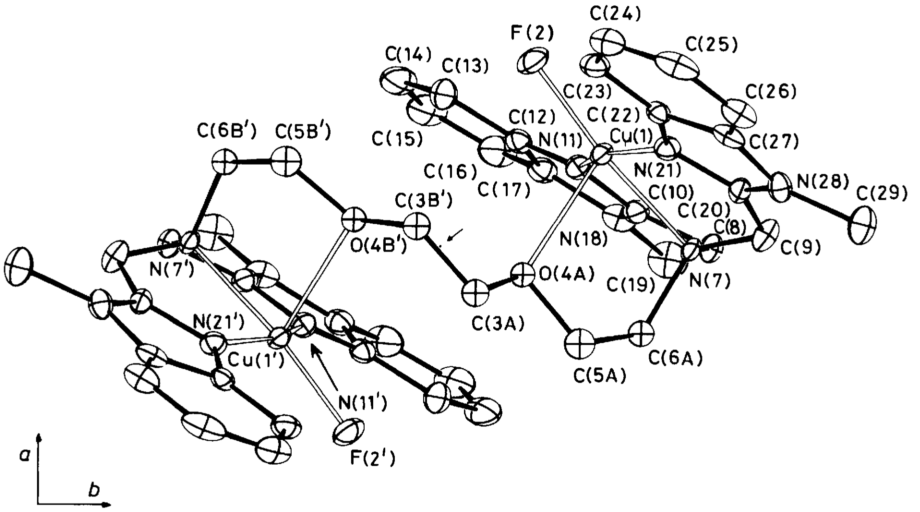

Figure 2. ORTEP representation of $[Cu_2(L)F_2]^{2+}$ with thermal ellipsoids of 50% probability, showing the atomic numbering scheme. Hydrogen atoms have been omitted for clarity. The arrow points towards the two-fold axis perpendicular to the plane of the drawing

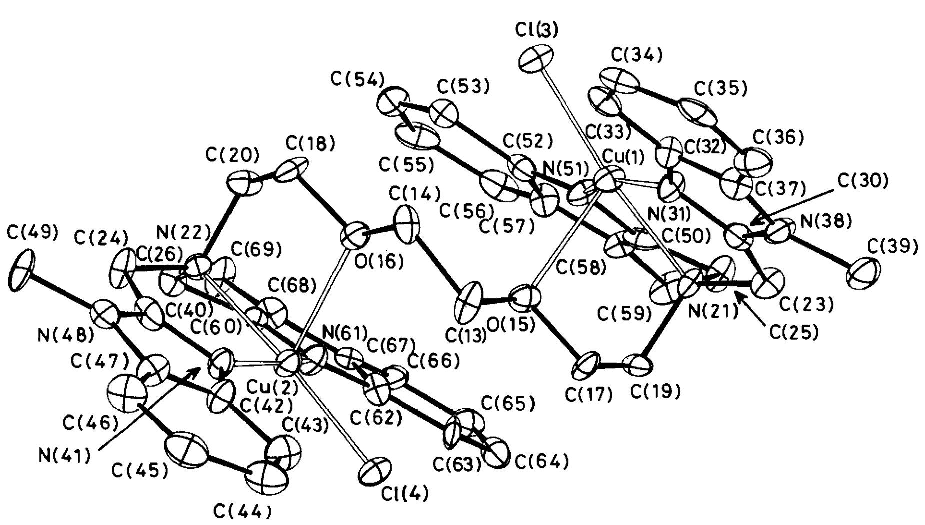

Figure 3. ORTEP representation of $[Cu_2(L)Cl_2]^{2+}$ with thermal ellipsoids of 50% probability, showing the atomic numbering scheme. Hydrogen atoms have been omitted for clarity

In (1) and (2) not all the atoms assumed to be present have been located *i.e.* in (1) part of a decomposition product of tetrafluoroborate, and in (2) solvent molecules and solvated chloride ions. These problems did not occur for compound (3).

The co-ordination geometry of each copper ion is close to a square pyramid in all compounds. The three nitrogen atoms of the ligand and the halide ion (X) are then in the equatorial plane, with X *trans* to the amino group. The ether group occupies the apical position. The distance to the nearest halide in the neighbouring molecules (in all cases through a centre of inversion) is too long for a co-ordination bond: Cu–F′ 494(1), Cu–Cl′ 342(1) and 484(1), Cu–Br′ 359(1) and 371(1) pm. The deviations of the bond angles from the ideal values are mainly due to the restrictions imposed by the ligand. All angles between the co-ordination bonds in the five-membered chelate rings are *ca.* 80°.

The Cu–F distance is quite small [186.1(6) pm], which is in agreement with the occurrence of a very asymmetric Cu–F ··· Cu″ bridge [(″) at $-x + 2$, $-y$, $-z + 1$].[29] A non-bridging fluoride anion has been reported for a Cu^I compound (also five-co-ordinate) with a slightly longer distance of 193 pm.[30]

The assignment of this unidentate ligand to be a fluoride ion instead of a molecule of water (or hydroxide ion) is based on: (*i*) the small bond length, which is more likely for a bound anion than for a water molecule (the latter being at least 10 pm longer);[31] (*ii*) a peak in the i.r. spectrum at 478 cm^{-1}, which was also found in compounds synthesized with stoicheiometric amounts of CuF_2 and another Cu^{II} salt, but not in corresponding chloro and bromo compounds; and (*iii*) near an atom at hydrogen-bridging distance, *i.e.* the oxygen atom of the water molecule, both hydrogen atoms have been located.

The Cu–Cl distances are comparable to those of other non-bridging ions.[32,33] The same holds for the Cu–Br distances [237.0(2) and 238.5(2) pm].[34] The Cu–N(benzimidazole) and Cu–N(amino) distances are in the same range as those found for similar compounds.[8,9,12,13,35,36] The Cu–O(ether) distances are close to 240 pm, except for Cu(1) in (3) [258.4(8) pm]. Kida and co-workers[35] reported a number of structures with the ligand bis(benzimidazol-2-ylmethyl)(2-hydroxyethyl)amine

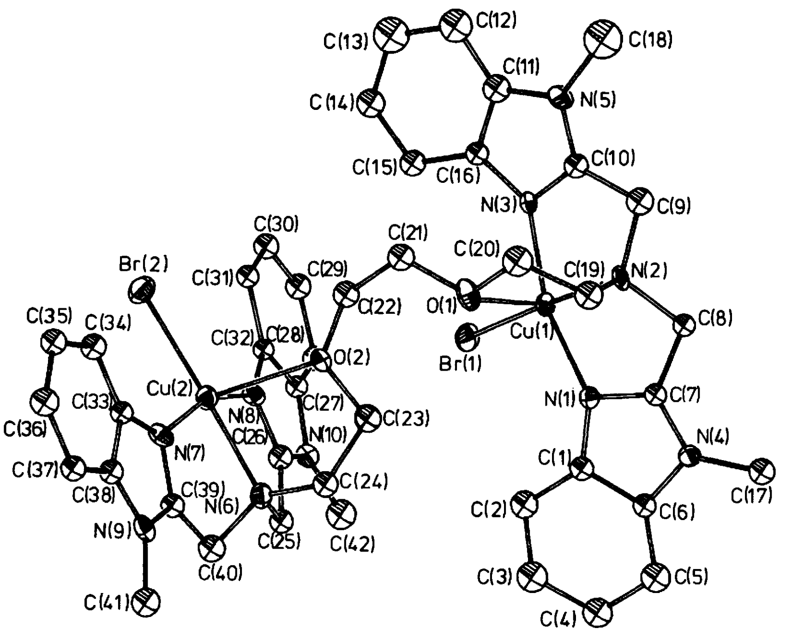

Figure 4. SHELXTL molecular plot of $[Cu_2(L)Br_2]^{2+}$, showing the atomic numbering scheme. Hydrogen atoms have been omitted for clarity

Table 5. Selected bond lengths (pm) and interbond angles (°) in $[Cu_2(L)F_2][BF_4]_2{\cdot}2H_2O{\cdot}H_2OBF_3$ (**1**), with estimated standard deviations in parentheses*

Cu(1)–F(2)	186.1(6)	Cu(1)–N(7)	210.7(8)
Cu(1)–O(4A)	235(2)	Cu(1)–O(4B)	241(2)
Cu(1)–N(11)	194.5(9)	Cu(1)–N(21)	195.5(9)
F(2)–O(40)	261.8(9)	O(40)–H(402)	85
O(40)–O(40′)	283(2)		

F(2)–Cu(1)–N(7)	173.0(3)	O(4A)–Cu(1)–O(4B)	9.8(6)
F(2)–Cu(1)–O(4A)	107.6(4)	F(2)–Cu(1)–O(4B)	106.1(4)
F(2)–Cu(1)–N(11)	97.3(4)	F(2)–Cu(1)–N(21)	97.7(3)
O(4A)–Cu(1)–N(7)	79.4(4)	O(4B)–Cu(1)–N(7)	80.9(4)
O(4A)–Cu(1)–N(11)	92.4(4)	O(4B)–Cu(1)–N(11)	102.3(4)
O(4A)–Cu(1)–N(21)	96.6(5)	O(4B)–Cu(1)–N(21)	87.3(4)
N(7)–Cu(1)–N(11)	81.6(4)	N(7)–Cu(1)–N(21)	81.8(4)
N(11)–Cu(1)–N(21)	159.3(4)		

* (′) at $-x + \frac{5}{2}, -y + \frac{1}{2}, z$.

Table 6. Selected bond lengths (pm) and interbond angles (°) in $[Cu_2(L)Cl_2]Cl_2{\cdot}6H_2O$ (**2**), with estimated standard deviations in parentheses

Cu(1)–Cl(3)	223.2(6)	Cu(2)–Cl(4)	222.0(6)
Cu(1)–O(15)	241(2)	Cu(2)–O(16)	246(1)
Cu(1)–N(21)	209(2)	Cu(2)–N(22)	214(2)
Cu(1)–N(31)	194(2)	Cu(2)–N(41)	191(2)
Cu(1)–N(51)	192(2)	Cu(2)–N(61)	195(2)

Cl(3)–Cu(1)–O(15)	108.0(5)	Cl(4)–Cu(2)–O(16)	105.7(4)
Cl(3)–Cu(1)–N(21)	172.1(6)	Cl(4)–Cu(2)–N(22)	174.9(6)
Cl(3)–Cu(1)–N(31)	98.4(6)	Cl(4)–Cu(2)–N(41)	98.2(6)
Cl(3)–Cu(1)–N(51)	98.3(6)	Cl(4)–Cu(2)–N(61)	96.5(6)
O(15)–Cu(1)–N(21)	79.9(7)	O(16)–Cu(2)–N(22)	79.3(6)
O(15)–Cu(1)–N(31)	83.8(6)	O(16)–Cu(2)–N(41)	83.8(6)
O(15)–Cu(1)–N(51)	99.2(6)	O(16)–Cu(2)–N(61)	106.6(6)
N(21)–Cu(1)–N(31)	81.3(8)	N(22)–Cu(2)–N(41)	82.4(8)
N(21)–Cu(1)–N(51)	81.0(8)	N(22)–Cu(2)–N(61)	81.7(8)
N(31)–Cu(1)–N(51)	161.2(9)	N(41)–Cu(2)–N(61)	159.6(9)

(L″), which contains the same array of donor atoms as in one half of L. With Cu^{II} a quite similar structure has been found in the case of $[Cu(L'')Cl]^+$, with a Cu–O distance of 241 pm.

The Cu^{II} ion is displaced slightly [F, 17(1); Cl, 14(1) and 16(1); Br, 9(1) and 10(1) pm] out of the least-squares plane through the four equatorial atoms towards the apical atom. The Cu–O bond is not fully perpendicular [F, 75—76(1); Cl, 73—74(1); Br, 73—76(1) °] to the equatorial plane because of the restriction of the N–C–C–O bite.

The bond distances in the ligand molecules are in the expected range, although some (see above) had been constrained to a range of *ca.* 2 pm around a fixed value. Bond angles were not constrained. The torsion angles of the 1,8-diamino-3,6-dioxaoctane bridge clearly show the staggered conformation of this chain. The crucial difference between the ligand conformation of the bromo compound compared to the others is reflected in the C(21)–C(22)–O(2)–C(23) torsion angle, which is 84° instead of the expected 170–180°. The other torsion angles are fully comparable to those in the corresponding compounds, except for a sign change in one N–C–C–O bite. The C–C bonds are all in the *gauche* conformation, which is required within the N–C–C–O bite. The benzimidazole rings are all planar, the largest distances of the aromatic atoms to the least-squares plane being in the same range (2—4 pm) as the standard deviations in these distances. The intramolecular planes of benzimidazole groups bound to the same copper ion are nearly parallel to each other (F, 9; Cl, 6 and 13; Br, 8°; errors less than 1°). Drawings of the unit cell of the fluoro and chloro compounds show that two of the four aromatic rings in a molecule of L are close together and almost parallel. The shortest C–C distance is 349 pm in both compounds, and the angles amount to 16 (F) and 17° (Cl). The other aromatic rings are much further (at least 955 pm) removed from each other and the angle is larger (35 and 37°), which gives the molecule its calix shape. In the case of the bromo compound both halves of

Table 7. Selected bond lengths (pm) and interbond angles (°) in $[Cu_2(L)Br_2][CF_3SO_3]_2 \cdot EtOH$ with estimated standard deviations in parentheses

Cu(1)–Br(1)	237.0(2)	Cu(2)–Br(2)	238.5(2)
Cu(1)–O(1)	258.4(8)	Cu(2)–O(2)	242.3(7)
Cu(1)–N(1)	195.0(9)	Cu(2)–N(6)	210.9(10)
Cu(1)–N(2)	209.7(8)	Cu(2)–N(7)	198.3(9)
Cu(1)–N(3)	195.0(9)	Cu(2)–N(8)	197.1(9)
Br(1)–Cu(1)–O(1)	106.4(2)	Br(2)–Cu(2)–O(2)	103.0(2)
Br(1)–Cu(1)–N(1)	96.1(3)	Br(2)–Cu(2)–N(6)	178.2(3)
Br(1)–Cu(1)–N(2)	176.0(3)	Br(2)–Cu(2)–N(7)	97.7(3)
Br(1)–Cu(1)–N(3)	98.9(3)	Br(2)–Cu(2)–N(8)	98.6(3)
O(1)–Cu(1)–N(1)	102.6(3)	O(2)–Cu(2)–N(6)	78.8(3)
O(1)–Cu(1)–N(2)	77.4(3)	O(2)–Cu(2)–N(7)	100.3(3)
O(1)–Cu(1)–N(3)	80.4(3)	O(2)–Cu(2)–N(8)	85.9(3)
N(1)–Cu(1)–N(2)	81.8(4)	N(6)–Cu(2)–N(7)	81.8(4)
N(1)–Cu(1)–N(3)	163.2(4)	N(6)–Cu(2)–N(8)	81.6(4)
N(2)–Cu(1)–N(3)	82.8(4)	N(7)–Cu(2)–N(8)	160.7(4)

the molecule are almost perpendicular to each other (106° between the equatorial planes). Stacking also occurs between the benzimidazole rings in symmetry-related molecules (through a centre of inversion). The overlap is not complete. The intermolecular angles between the planes of benzimidazole groups are small (F, 9; Cl, 6 and 13; Br, 8°; errors less than 1°).

The various Cu–Cu distances and other structural information of the Cu–Cu sites are listed in Table 8. The intramolecular distance through the glycol ether bridge of the ligand is quite long and depends on the conformation of the ligand. In fact, shorter Cu–Cu distances occur between two molecules through the halide ions which results in an alternating chain of copper ions. In compound (**1**) the fluoride ion is bound by a hydrogen bridge to a water molecule, which itself is bound similarly to a symmetry-related water molecule. This furnishes a third Cu–Cu distance of 1 044.6(2) pm. In compound (**2**) there are no distances shorter than 400 pm between the co-ordinated chloride anions and the water molecules. In the bromo compound (**3**) the same applies to the bromide anions and the molecule of ethanol.

In the fluoro compound, the connected copper ions lie in parallel chains below or above a plane parallel to the a and b axes at $z = 0.5$. In the chloro compound, the connected copper ions lie along a main-body diagonal of the unit cell. In the bromo compound the connected copper ions lie below or above a plane parallel to the a and c axes at $y = 0.5$.

Copper(II) *Compounds with* L; *Spectroscopic and Magnetic Properties.*—Both 1,8-bis[bis(benzimidazol-2'-ylmethyl)-amino]-3,6-dioxaoctane and L appear to have a large preference to bind two bivalent metal ions (Co, Ni, Cu, or Zn)[36] (and unpublished results). The four anions may be either the same or two pairs. Compounds with completely different properties were obtained in the case of combination of one azolate and three non-co-ordinating anions, which will be treated later. A few mononuclear compounds could be isolated, but not without concentrating the solution or adding diethyl ether. The metal content was mostly greater than expected in these cases and sometimes a mixture containing the free ligand and copper-containing species were obtained. On the other hand, most dinuclear compounds crystallized readily under the same conditions. Sufficient elemental analyses were obtained for these co-ordination compounds. Water molecules are present in all compounds and may be bound to the metal ion, to the ligand, to the anions, and/or to other water molecules in the crystal lattice. The i.r. spectra mainly contain peaks due to ligand and anion vibrations. The spectra of related compounds were often similar, but not identical in each detail. In fact, no isomorphous dinuclear compounds were found by comparing their i.r. spectra and *X*-ray powder diffractograms. This may be due to differences in the conformation of the ligand, imposed by the crystal lattice. This is illustrated by the crystal structure determinations.

Table 8. Comparison of the Cu–Cu sites in $[Cu_2(L)X_2]^{2+}$ with estimated standard deviations in parentheses*

	X		
	F	Cl	Br
Cu–X/pm	186.1(6)	223.2(6)	237.0(2)
		222.0(6)	238.5(2)
Cu···X'/pm	494.1(7)	342.3(7)	358.7(2)
		484.2(7)	371.4(2)
Cu···Cu'/pm	481.3(2)	388.1(6)	397.6(2)
		487.6(6)	404.9(2)
Cu···Cu''/pm	583.4(2)	576.0(4)	666.5(2)
Cu–X–Cu'/°	75.2(2)	83.9(2)	81.0(1)
		77.7(2)	80.0(1)

* (') Intermolecular through a centre of inversion, ('') intramolecular.

The spectroscopic data of the Cu^{II} co-ordination compounds are listed in Table 9. The reflectance spectra of the dinuclear Cu^{II}–L compounds all show one maximum between 14 and 15×10^3 cm^{-1}. This agrees with the square-pyramidal co-ordination geometries found for compounds (**1**), (**2**), and (**3**).[37] The metal–halogen stretching vibrations occurred at 478 (F) and 310 cm^{-1} (Cl) respectively.[38] The ligand-field spectra also showed an intense absorption below 400 nm, which is ascribed to a Cu^{II}–N(benzimidazole) charge transfer. The spectra of zinc-containing compounds show no absorptions above 300 nm, except for some weak overtones in the near-i.r. region.[36] The e.s.r. spectra in the solid state of the dinuclear Cu^{II}–L compounds all show a broad isotropic signal around $g = 2.08$, with broadening or in a few cases a shoulder at higher g values (2.17—2.24). This spectrum is not inconsistent with the square-pyramidal co-ordination geometry, which has a $d_{x^2-y^2}$ ground state.[39] Some spectra also contain signals near $g = 4.2$ and below $g = 2$, which are characteristic for Cu^{II} dimeric systems. The absence of these signals, however, does not exclude Cu–Cu interactions.[39]

The close similarity of the spectroscopic properties of the compounds $Cu_2(L)X_4 \cdot nH_2O$ and $Cu_2(L)X_2Y_2 \cdot nH_2O$ suggests that they all have the same co-ordination geometry, *viz.* a five-co-ordinated copper ion in a square-pyramidal geometry. Each half of the ligand L is equivalent and contains two benzimidazole, one amino, and one ether group. The three nitrogen atoms and an external unidentate ligand are in the equatorial plane, the ether oxygen atom is in the apical position. The ligand L appears to have a large preference for a halide ion as the external ligand. In $[Cu_2(L)Cl_2]Cl_2 \cdot 6H_2O$ (**2**), only two of the four chloride ions are co-ordinating, the other two are within the crystal lattice together with the water molecules. Compound $[Cu_2(L)F_2][BF_4]_2 \cdot 2H_2O \cdot H_2OBF_3$ (**1**) was formed after decomposition of part of the tetrafluoroborate anions. This is known to facilitate the synthesis of copper fluoride compounds.[40] The tetrafluoroborate ions are not co-ordinating either. Similar compounds have been synthesized starting from a mixture of copper salts with equal amounts of halide (F, Cl, or Br) and non-co-ordinating ions (BF_4, ClO_4, or CF_3SO_3).[36] Even when the halide ion is present in a sub-stoicheiometric amount, the product (**3**) contained them in a 1:1 ratio to the

Table 9. Spectroscopic data of the Cu^{II} co-ordination compounds with L

Complex	State[a]	Λ[b]	$10^{-3}\ \nu_{max.}$[c]/cm^{-1}			*g* values[d]			
(1)	r.t.			14.5		4.26		2.11	
	77 K					4.25		2.11	
	77 K (*Q*)							2.11	2.07 (sh)
	EtOH–H_2O			14.1 (75)			2.34 (180)	2.06	
	$MeNO_2$	211		14.5 (85)					
(2)	r.t.			14.6		4.25		2.08	1.96 (sh)
	77 K					4.30	2.18 (sh)	2.09	1.93 (sh)
	77 K (*Q*)						2.17	2.08	2.02
	EtOH–H_2O			14.4 (80)		4.09	2.24 (190)	2.05	1.92
	$MeNO_2$	104	9.9 (sh)	13.2 (95)					
(3)	r.t.			14.6				2.11	
	77 K							2.11	
(4)	r.t.			14.2				2.09	
	77 K							2.09	
	EtOH–H_2O			14.8 (60)			2.40 (200)	2.08	1.83
	$MeNO_2$	126	9.9 (sh)	12.9 (125)	14.8 (sh)				
(5)	r.t.			14.8				2.08	
	77 K					4.18		2.08	
	EtOH–H_2O			14.8 (55)			2.33 (185)	2.06	
	$MeNO_2$	148		14.9 (80)					
(6)	r.t.			14.6				2.08	
	77 K					4.18		2.07	
	EtOH–H_2O			14.4 (75)			2.33 (185)	2.06	
	$MeNO_2$	228		15.9 (100)			2.32 (190)	2.05	
(7)	r.t.			14.5				2.07	
	77 K						2.24 (sh)	2.07	
	EtOH–H_2O			14.1 (55)			2.35 (180)	2.04	
	$MeNO_2$	192		15.8 (90)			2.32 (190)	2.03	
(8)	r.t.			14.5		4.15	2.18	2.07	1.93
	77 K					4.20	2.18	2.07	1.93

				S = 1				*S* = ½	
				$\Delta m = 2$	$g_{\parallel}$	$g_{\perp}$	*D*	$g_{\parallel}$ $A_{\parallel}$	$g_{\perp}$
(9)	r.t.		15.2	4.35	2.19	2.09	0.079		
	77 K			4.33 (140)	2.19	2.08	0.078		2.07
	77 K (*Q*)				2.20	2.08	0.083		
	Dmso–EtOH			4.26	2.28		0.083	2.25 (170)	2.08
	$MeNO_2$	205	15.5 (115)						
(10)	r.t.		15.5	4.38	2.29	2.07	0.084		
	77 K			4.36	2.29	2.07	0.079		
	$MeNO_2$	201	14.9 (115)						
(11)	r.t.		15.6	4.35 (125)	2.25	2.07	0.071		2.09
	77 K			4.31	2.25	2.08	0.068		2.08

[a] In the solid state or in solution (solvent stated) at stated temperature; r.t. = room temperature; *Q* represents *Q*-band. [b] In ohm^{-1} cm^2 mol^{-1}, 25 °C, *ca.* 1 mmol dm^{-3}. [c] ε/dm^3 mol^{-1} cm^{-1} in parentheses. [d] 10^4 *A*/cm^{-1} in parentheses.

other anion. If there are no halide ions present, the external ligand is likely to be a water molecule, especially if the anion has very weakly co-ordinating properties, *e.g.* perchlorate or trifluoromethanesulphonate. In the case of nitrate or sulphate, however, the anion may co-ordinate as well.

The magnetic susceptibility of some compounds, among those whose crystal structures are known, has been determined as a function of temperature in order to obtain more information about the Cu–Cu interactions. $[Cu_2(L)Cl_2]Cl_2\cdot 6H_2O$ (**2**) was found to be almost paramagnetic. The Curie–Weiss plot (3—80 K) is not fully linear and indicates a weak ferromagnetic exchange ($0 < \theta < 8$ K, a small decrease of μ at higher temperatures). $[Cu_2(L)F_2][BF_4]_2\cdot 2H_2O\cdot H_2OBF_3$ (**1**) shows antiferromagnetic behaviour; a Curie–Weiss plot, which is nearly linear, yields a value for θ of $-31(\pm 1)$ K. A shoulder in χ occurs at 6 K. The data could not be fitted to the Bleaney–Bowers equation for Cu^{II} dimers.[41] The magnetic interaction does not only depend on the distance between the copper nuclei, but also on the relative orientations of the magnetic orbitals and of connecting orbitals in the bridging ligands.[42] Presumably a combination of different magnetic interactions in these compounds determines the overall result. Therefore, detailed interpretation is not possible.

The specific conductivities of the compounds (listed in Table 9) cannot be interpreted as characteristic for *e.g.* 1:2 or 1:4 electrolytes. The cation is large and contains two metal ions. Nevertheless, these data show that the degree of dissociation in the case of the chloride, bromide, and thiocyanate anions is less than in the case of the perchlorate, tetrafluoroborate, and trifluoromethanesulphonate ions, with nitrate in between these two groups. This trend corresponds with the co-ordinating properties of the anions. The ligand-field maxima in aqueous ethanol are only slightly shifted compared to the solid state, which indicates that the co-ordination geometry has not essentially changed. In nitromethane the changes are large for the compounds containing two potential anionic ligands [(**2**) and (4)] for each copper ion and for compounds (6) and (7), which contain only weakly co-ordinating anions, whereas they are small for the compounds which contain just one anionic ligand per copper ion. Presumably, more than one halide ion, if available, co-ordinates in an aprotic solvent, and an ion that is usually non-co-ordinating may co-ordinate if there are no other anions available. This agrees with the observation that the specific conductivities of these compounds [(6) and (7)] are comparable to those of compounds that contain one halide and one non-co-ordinating ion [(1)]. [Compound (3) not determined.]

For most compounds the e.s.r. spectra recorded of frozen solutions agree with a similar geometry in solution as in the solid state. The values of $g_{\parallel}$ and $A_{\parallel}$ are in the expected range for three nitrogen donors and one oxygen donor (water or nitrate) or halide anion. No ligand–superhyperfine splitting has been observed. The interpretation of the spectra of compounds (2) and (4) was complicated by the presence of several mono- and dinuclear species. The reported g values are those corresponding to the most intense signals.

In summary it appears that the spectroscopic properties of most copper(II) co-ordination compounds described in this section are in agreement with the co-ordination geometry found by the crystal-structure determinations of compounds (1), (2), and (3).

In the structures of $[Cu_2(L)X_2]^{2+}$ halide ions connect the copper ions in two adjacent molecules, but the spectroscopic and magnetic properties are predominantly determined by mononuclear fragments of the dimeric species. Dinuclear Cu^{II} compounds of a different stoicheiometry and with very different spectroscopic and magnetic properties were obtained if one equivalent of sodium azolate was added to a solution of $Cu_2(L)Y_4$, where Y is a non-co-ordinating anion such as perchlorate. Tetrafluoroborate was not used because of the possibility of decomposition (see above). The stoicheiometry of the product was found to be $Cu_2(L)(az)Y_3 \cdot nH_2O$, with az = imidazolate or benzotriazolate, Y = nitrate, perchlorate, or trifluoromethanesulphonate, and $n = 1$ or 6. This composition suggests that the azolate group acts as a bridge.[8]

In the case of perchlorate the product precipitated immediately. Only the imidazolate- and benzotriazolate-containing compounds gave e.s.r. spectra, which are typical for an $S = 1$ system, consisting of two Cu^{II} ions.[43,44] Compounds with trifluoromethanesulphonate were far more soluble in ethanol; only sodium benzotriazolate yielded a compound with an $S = 1$ e.s.r. signal. The product obtained with imidazolate exhibited i.r. and e.s.r. spectra that were very similar to those of a compound synthesized with sodium hydroxide (the base used to deprotonate the azole). The different results obtained with related azolates may be due to: (*i*) the differences in acidity (benzotriazole is much more acidic), (*ii*) the steric hindrance by the substituent on C(2), and (*iii*) different solubilities of the products. The amount of sodium hydroxide used was found to be quite critical; an excess yielded a product with a much larger monomeric impurity according to the e.s.r. spectrum. In the case of nitrate, the product was very soluble in ethanol. Single crystals of (10), which were very fragile, yielded an *X*-ray single-crystal diffraction pattern at room temperature that was too poor in relation to the large size of the unit cell.

The ligand-field spectra of these compounds are not very informative. They show one broad maximum near 15×10^3 cm^{-1}, both in the solid state and in solution. This is consistent with a tetragonal geometry as in other dinuclear Cu^{II}–L compounds, albeit with a stronger external ligand (*i.e.* azolate).[37]

The e.s.r. spectra of $S = 1$ systems have been interpreted using the formulae derived by Wasserman *et al.*[43] for organic triplets. For co-ordination compounds, the bands are generally broad and may overlap, precluding the determination of the expected eight resonances.[44] The rhombic zero-field splitting parameter (E) is very small in these compounds as the H(X) and H(Y) resonances are hardly split.[43,44] The small anisotropy corresponds to an E value of *ca.* 0.004 cm^{-1}, which is negligibly small compared to the axial zero-field splitting parameter D (0.080 cm^{-1}). The approximate values obtained for D and g fit in reasonably well with the observed spectra. These values, the g values corresponding to the $\Delta m = 2$ transition, as well as the $S = \frac{1}{2}$ impurity signals, are listed in Table 9. The D values are in the range found for the azolate-bridged Cu^{II}–tris(1-methylbenzimidazol-2-ylmethyl)amine dimers.[8] The seven-line hyperfine splitting pattern on the $\Delta m = 2$ signal is characteristic for a Cu^{II} dimer. The solution spectrum of compound (9) was obscured by an $S = \frac{1}{2}$ signal, obviously because of partial dissociation of the Cu^{II} dimer. Nevertheless, the $S = 1$ signals were still present, which suggests that an intramolecularly bridging azolate as drawn in Figure 1 is quite likely.

The temperature dependence of the magnetic susceptibility showed a maximum at 56 K for $Cu_2(L)(im)(ClO_4)_3 \cdot H_2O$ (9) and at 38 K for $Cu_2(L)(btz)(CF_3SO_3)_3 \cdot H_2O$ (10). The magnetic behaviour has been interpreted on the basis of the Bleaney–Bowers equation.[41] A least-squares fit for (9) converged to a magnetic exchange parameter J of $-31.9(4)$ cm^{-1}, with a g value of 2.16(1) and 5.0(1)% of a paramagnetic impurity. The amount of paramagnetic species is quite high and is probably related to the rapid precipitation of the product. Compound (10) crystallized slowly and, according to the least-squares fit, contains a paramagnetic impurity of only 0.7(1)%. The J value was $-21.7(1)$ cm^{-1} and the g value 1.84(1). The apparent low g value may be due to a too low value for the molecular weight. These values are comparable to other azolate-bridged Cu^{II} dimeric systems[8] and to the enzyme superoxide dismutase after substitution of the Zn^{II} ion by a second Cu^{II} ion ($J = -27$ cm^{-1}).[45]

Copper(I) *Compounds; Spectroscopic Properties.*—The elemental analyses of the Cu^{I} compounds (12)—(18) (Table 1) show the occurrence of three types of compound, *viz.* Cu(L)Y [(12)—(14)], $Cu_2(L)X_2$ [(15)—(17)], and $Cu_2(L)(CO)_2Y_2$ (18). Stable mononuclear compounds Cu(L)X could only be isolated in the case of the so-called non-co-ordinating anions perchlorate, tetrafluoroborate, and trifluoromethanesulphonate. The ligand regions of the i.r. spectra were identical for these compounds. The anion peaks showed no broadening, which excludes co-ordination of these ions. The conductivity of compound (12) in dimethylformamide (dmf) is typical for a 1:1 electrolyte.[46] A tetrahedral geometry with four benzimidazole groups, as found for $[Cu(edtp)]ClO_4$ [edtp = *N,N,N′,N′*-tetrakis(pyrazol-1′-ylmethyl)-1,2-diaminoethane], is likely.[47] The long and flexible 1,8-diamine-3,6-dioxaoctane bridge allows the four benzimidazole groups to be part of the same molecule, but another conformation, *viz.* two halves of different L molecules, is equally possible. A crystal-structure determination should give definite insight into the co-ordination geometry and the structure of the ligand.

Stable dinuclear compounds without CO [*viz.* $Cu_2(L)X_2$] could only be isolated with the halide ions (Cl, Br, or I). The i.r. spectra of compounds (15) and (16) were very similar above 300 cm^{-1}, but the *X*-ray powder diffractograms, although closely related, gave no definite indications for isomorphism. The iodide compound (17) showed a different i.r. spectrum. The far-i.r. region (400—100 cm^{-1}) contained some relatively intense peaks, which can be tentatively assigned to Cu–ligand vibrations by comparing the spectra of these and other related compounds: (15) (Cl), 315 (Cu–N) and 275 (Cu–Cl) cm^{-1}; (16) (Br), 314 (Cu–N), 205 and 172 (Cu–Br) cm^{-1}; (17) (I), 335 (Cu–N) and 144 (Cu–I) cm^{-1}. Dinuclear compounds containing for instance perchlorate anions could be prepared in solution. They were very soluble in the acetonitrile–methanol mixture and could only be precipitated after addition of diethyl ether. The initial white product, dried in a nitrogen atmosphere, turned green when in contact with air. Obviously the Cu^I ion is co-ordinatively unsaturated in this state (two- or perhaps three-co-ordinated) and has to be stabilized, either by a halide ion, or another L molecule (see above), or an extra ligand (carbon monoxide).

The conductivities of the halide compounds in dmf are low for 1:2 electrolytes, which indicates that the halide ions are also co-ordinating in solution. Several co-ordination geometries are possible with this ligand, *e.g.* two benzimidazole groups and the halide ion, resulting in a trigonal or T-shaped geometry. Participation of a fourth group will result in a tetrahedral-like environment. This group may either be the nitrogen (amino) atom of L, its oxygen (ether) atom, or a (bridging) halide ion from a neighbouring molecule.

In the presence of carbon monoxide stable adducts could be isolated with the non-co-ordinating anions. Elemental analyses showed that they have the general stoicheiometric formula $Cu_2(L)(CO)_2Y_2$. The Cu:CO ratio of 1:1 was confirmed by measurements of the oxygen uptake of compound (**18**) and that of related compounds without CO. In the case of (**18**) the amount of gas initially increased, with a maximum of 0.39 mol gas for each mol Cu^I, and then decreased because of the simultaneous oxidation of copper(I) by dioxygen. With compound (**15**) under the same experimental conditions, the volume had decreased with 0.55 mol gas, which gives an approximate indication of the amount of dissociated CO, *viz.* 0.95 mol for each mol Cu^I.

Compound $Cu_2(L)(CO)_2(ClO_4)_2$ (**18**) is remarkably stable in the solid state in a nitrogen atmosphere. In moist air it slowly turned green. However, the i.r. spectrum did not change, which indicates that the bulk of the crystals are not affected by the oxidation. The e.s.r. spectrum of a slightly oxidized batch was comparable to those of the Cu^{II}–L compounds [$g_{\parallel}$ 2.24 ($A_{\parallel}$ = 200×10^{-4} cm^{-1}) and $g_{\perp}$ 2.06]. A similar co-ordination geometry for Cu^{II} as in these compounds is probable. Carbon monoxide could only be removed from the solid sample at 150 °C in high vacuum (0.05 mmHg). The copper ion was oxidized under these conditions and the ligand decomposed. Part of the decomposition products sublimed. Spectroscopic analyses of these products (i.r., ^1H and ^{13}C n.m.r., mass spectra) indicated the presence of 1-methylbenzimidazol-2-one and 2-formyl-1-methylbenzimidazole. The CO compounds could be recrystallized in a CO atmosphere.

The i.r. spectra of compound (**18**) and its tetrafluoroborate derivative were very similar. The anion peaks were sharp and not split, which agrees with a non-co-ordinating situation. A pair of CO bands with equal intensity occurs just below 2 100 cm^{-1} at 2 097 and 2 084 cm^{-1}. The ^{13}C satellites are at 2 047 and 2 036 cm^{-1}. The isotopic shifts agree well with values calculated for simple harmonic oscillation.[38] The splitting of the CO band may be due to two slightly different copper sites. For a dinuclear Cu^I–CO compound containing two crystallographically independent Cu^I ions in an effectively identical chemical environment, Gagné *et al.*[48] found a pair of CO bands at 2 097 and 2 107 cm^{-1}. The frequencies of the CO vibrations are typical for Cu^I–CO compounds containing a terminal CO molecule and nitrogen donor groups. Compounds containing similar N–N′–N moieties as in L (two azoles attached to an amino group) showed CO bands at 2 082 cm^{-1} (pyrazole, in solution) and 2 102 cm^{-1} (pyridine).[48] No similar imidazole- or benzimidazole-containing compounds have been found, which gave stable Cu^I–CO adducts. Haemocyanin, which binds only one CO molecule at each dinuclear site, has its CO band at 2 063

Table 10. Spectroscopic data of the Cu^I co-ordination compounds with L

		Chemical shift values[c]												
Complex[a]	Λ[b]	CH_2 (1,8) (t)	CH_2 (4,5) (s)	CH_2 (2,7) (t)	CH_3 (s)	CH_2–aryl (s)	$CH^{6\,d}$ (t of t)	$CH^{5\,d}$ (t of t)	CH^7 (d of t)	CH^4 (d of t)	C^{3a}	C^{7a}	C^2	CO
L		2.75	3.25	3.37	3.61	4.00	7.19	7.13	7.55	7.42				
		(5.5)		(5.5)			(7/1.5)		(7/1.5)					
		53.84	70.28	69.95	29.61	51.75	121.98	122.68	119.76	109.02	136.27	142.51	151.64	
(**12**)	58													
		2.67	3.04	3.27	3.71	4.05	7.17	7.28	7.54	7.58				
		(4.9)		(4.9)			(7.5/—)		(7.7/—)					
(**13**)		2.67	3.04	3.28	3.71	4.06	7.17	7.28	7.54	7.58				
		(5.2)		(5.2)			(7.6/1.0)		(7.7/—)					
		54.28	69.17	68.90	29.63	51.50	122.08	122.66	117.96	110.34	135.28	140.09	152.94	
(**14**)		2.67	3.04	3.27	3.71	4.06	7.17	7.28	7.54	7.58				
		(4.9)		(4.9)			(7.4/1.2)		(7.7/—)					
(**15**)	59													
		2.71	3.12	3.36	3.74	4.06	7.19	7.29	7.58	7.67				
		(5.2)		(5.2)			(7.6/1.5)		(7.7/—)					
(**16**)	31													
		2.79	3.29	3.55	3.78	4.08	7.22	7.29	7.58	8.03				
		(4.7)		(4.7)			(6.8/—)		(7.4/—)					
(**17**)	26													
		2.77	3.25	3.60	3.77	4.07	7.20	7.29	7.59	8.11				
		(4.6)		(4.6)			(7.6/—)		(7.6/—)					
		54.57	69.70	69.20	29.77	50.07	121.93	122.63	118.54	110.19	135.01	139.83	152.83	
(**18**)	93													
		3.23	3.04	3.56	3.76	4.31	7.33	7.36	7.68	7.85				
		(4)		(4)			(7.2/3.0)		(7.2/3.0)					
		57.75	69.08	68.96	29.86	53.17	122.90	123.07	117.29	110.63	135.25	138.61	154.23	173.10

[a] In solution in stated solvent at stated temperature (see footnotes *b* and *c*). [b] In ohm^{-1} cm^2 mol^{-1}, in dmf at 25 °C, *ca.* 1 mmol dm^{-3}. [c] In [$^2H_6$]dmso at 50 °C, 200 MHz, δ/p.p.m. *vs.* $SiMe_4$, ^1H at first line, *J*/Hz or multiplicity on second line, ^{13}C at third line, assignment according to systematic name. [d] Assignment may be interchanged.

cm^{-1}.[49] A tetrahedral geometry for each copper ion consisting of three nitrogen atoms of the ligand and one CO molecule is possible in $[Cu_2(L)(CO)_2]^{2+}$. The steric constraints because of the small N–C–C–N bite do not allow any angles to be larger than 90°. Participation of the oxygen (ether) atom instead of the nitrogen (amino) atom cannot be excluded as it is in a more favourable position for a tetrahedral geometry. Single crystals of compound (**18**) could be grown reproducibly, but were not suitable for a standard *X*-ray structure determination.

The Cu^I-containing co-ordination compounds with L were further characterized by n.m.r. spectroscopy. The data are listed in Table 10. The mononuclear compounds (**12**), (**13**), and (**14**) yielded identical proton spectra, which confirmed their close resemblance. The spectrum is symmetric and shows no signals of inequivalent benzimidazole groups. No indication has been found for exchange of Cu^I ions with azole ligands,[50–52] which suggests a symmetric overall structure. The signals of the methylene groups in the 1,8-diamino-3,6-dioxaoctane bridge are shifted upfield, compared to the free ligand, probably due to a different ligand conformation (see later).[52,53] The shifts of the methylene groups in the ^{13}C spectrum are not significant and only small changes are observed in the aromatic region (7–8 p.p.m.). The downfield shifts of the hydrogen atoms at C^5 and C^4 are most likely the result of the electron-withdrawing properties of the metal ion. The corresponding carbon atoms are shifted upfield, which parallels the effect of protonation of a benzimidazole ring.[54]

Each of the dinuclear Cu^I halide compounds (**15**), (**16**), and (**17**) yielded a different proton spectrum clearly dependent on the anion. The downfield signals of the methylene groups next to the oxygen atoms may indicate that the halogen is within the co-ordination sphere. The chemical shift of the $H(C^4)$ atom differs considerably from its value in the free ligand and depends heavily on the kind of halide ion.

The dinuclear carbonyl compound (**18**) shows large downfield shifts for the methylene groups next to the amino atoms, which suggests that the nitrogen atoms are co-ordinating.[52,53] The aromatic pattern is complicated and a first-order approximation is not valid anymore, because the frequency difference of the chemical shifts is of the same order of magnitude as the coupling constant. Simulation of the spectrum confirmed the reported values. The ^{13}C spectrum contains an extra signal at 173.1 p.p.m., which is very likely due to a co-ordinated CO molecule. The chemical shift of CO in various metal–carbonyl compounds ranges between 150 and 250 p.p.m.[55] The assignment was confirmed by the absence of a CO signal in a sample of dmso saturated with carbon monoxide. The chemical shifts in the co-ordination compounds are not only determined by the presence of the metal ions through their direct electronic effects, but also by the shielding and de-shielding effects of the ligand. Very likely the conformation of the ligand has changed by co-ordination to the Cu^I ion, which is also influenced by occasional external ligands.

Conclusions

The results described above indicate and confirm that benzimidazole-type chelating ligands are interesting model systems for the active sites of metalloproteins. The ligand L appears to be a flexible system, able to chelate two copper ions. The formed structures appear to add one external ligand (F, Cl, or Br) to form $Cu^{II}N_3XO$ chromophores. A tetrahedral chromophore Cu^IN_3CO is likely for the CO adduct of the Cu^I system. Only with typical bridging ligands such as azolato anions (imidazolato or benzotriazolato) clear dinuclear systems are formed (e.s.r. and magnetic susceptibility evidence only). Unfortunately, no single-crystal structure determinations of these systems could be performed.

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