Thermal decomposition of a cyclohexane solution of **3** (0.024 M) and tricyclohexylphosphine (0.028 M) at 116 °C as described above yielded $k^{\mathrm{obsd}} = 5.93 \times 10^{-5}\ \mathrm{s}^{-1}$, compared to $k^{\mathrm{obsd}} = 105 \times 10^{-5}\ \mathrm{s}^{-1}$ in the absence of added phosphine.

Phosphine Exchange of 2 with 2-$(\mathbf{L}^{\mathbf{D}})_2$. A degassed cyclohexane solution of **2** (86 mM), **2**-$(\mathrm{L}^{\mathrm{D}})_2$ (86 mM), and triethyl phosphate (16 mM) was heated for 8 h at 50 °C in a 5-mm NMR tube. Examination of the resulting solution by $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (C_6H_{12}, 101.28 MHz) revealed the presence of the following compounds: **2**, δ 33.45 (t, 1:4:1, $J_{\mathrm{Pt-P}} = 1816$ Hz); **2**-$(\mathrm{L}^{\mathrm{D}})_2$, δ 32.16 (t, 1:4:1, $J_{\mathrm{Pt-P}} = 1820$ Hz); **2**-$\mathrm{L}^{\mathrm{H}}\mathrm{L}^{\mathrm{D}}$, δ 33.54 (d of t, $J_{\mathrm{Pt-P}} = 1818$ Hz, $J_{\mathrm{P-P}} = 4$ Hz). The doublet of triplets for L^{D} of **2**-$\mathrm{L}^{\mathrm{H}}\mathrm{L}^{\mathrm{D}}$ could not be resolved from the signal for **2**-$(\mathrm{L}^{\mathrm{D}})_2$ due to the broadness of the peak. No bis(triisopropylphosphine)platinum(0) was observed, and heating the solution for an additional 16 h at 50 °C produced no change in the distribution of products.

Registry No. 1, 70620-74-5; **2**, 81602-78-0; **2**-$(\mathrm{L}^{\mathrm{D}})_2$, 81602-79-1; **3**, 81602-80-4; tris(isopropyl)phosphine, 6476-36-4; 1,1-dimethylcyclopropane, 1630-94-0; neopentane, 463-83-1; 2,2,5,5-tetramethylhexane, 1071-81-4; 1,3,5-cyclooctatriene, 1871-52-9; tris(isopropyl-d_{21})phosphine, 81583-58-6; isopropyl-d_7 bromide, 39091-63-9; 1,5-COD, 111-78-4; $[(i\text{-Pr})_3P]_2Pt$, 60648-71-7; $(1,5\text{-COD})Pt[CH_2C(CH_3)_3]_2$, 75101-19-8; $(CH_3)_2C(CH_2D)_2$, 72110-09-9; $(CH_3)_3C(CH_2D)$, 4741-94-0; Cy_3P, 2622-14-2; $(Cy_3P)_2Pt$, 55664-33-0.

Synthesis and Characterization of Coordination Compounds of Chelating Ligands Containing Imidazole Groups. The Crystal and Molecular Structures of the Dinuclear Cu^{I} and Cu^{II} Compounds [*N*,*N*,*N'*,*N'*-Tetrakis(2-benzimidazolylmethyl)-1,2-ethanediamine]dicopper(I) Bis(perchlorate) and of μ-(Nitrato-*O*,*O'*)-bis(nitrato-*O*)-{*N*,*N*,*N'*,*N'*-tetrakis[(1-methyl-2-benzimidazolyl)methyl]-1,2-ethanediamine}dicopper(II) Nitrate Tetrahydrate

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Abstract: Copper(I) and copper(II) coordination compounds with general formulas $Cu^{\mathrm{II}}(L)(\mathrm{anion})_2$, $Cu^{\mathrm{II}}_2(L)(\mathrm{anion})_4$, and $Cu^{\mathrm{I}}_2(L)(\mathrm{anion})_2$ have been prepared and characterized, where L stands for one of the sexadentate benzimidazole-containing ligands *N*,*N*,*N'*,*N'*-tetrakis(2-benzimidazolylmethyl)-1,2-ethanediamine (abbreviated EDTB), *N*,*N*,*N'*,*N'*-tetrakis[(1-methyl-2-benzimidazolyl)methyl]-1,2-ethanediamine (NMEDTB), *N*,*N*,*N'*,*N'*-tetrakis[(1-benzyl-2-benzimidazolyl)methyl]-1,2-ethanediamine (NBEDTB), *N*,*N*,*N'*,*N'*-tetrakis[(5-methyl-2-benzimidazolyl)methyl]-1,2-ethanediamine (5-MEDTB), or *N*,*N*,*N'*,*N'*-tetrakis[(5,6-dimethyl-2-benzimidazolyl)methyl]-1,2-ethanediamine (5,6-DMEDTB). The electronic and ESR spectra of all compounds of composition $Cu^{\mathrm{II}}(L)(\mathrm{anion})_2$ are identical with those for $Cu(EDTB)(\mathrm{anion})_2$ and suggest a structure similar to the one found for $Cu(EDTB)(BF_4)(BF_3OC_2H_5)$, which has been described as highly distorted square pyramid. ESR and electronic spectra of the compounds $Cu_2(L)(\mathrm{anion})_4$ indicate different coordination geometries in the presence of different anions. In compounds with Cl^- or Br^- the Cu^{II} atom appears to have trigonal-bipyramidal coordination geometry. Square-pyramidal geometry seems more likely for compounds $Cu_2(L)X_4$, where $X = NO_3^-$, BF_4^-, or ClO_4^-. The crystal and molecular structures of $[Cu^{\mathrm{II}}_2(\mathrm{NMEDTB})(NO_3)_3]NO_3{\cdot}4H_2O$ (**1**) and of $Cu^{\mathrm{I}}_2(\mathrm{EDTB})(ClO_4)_2$ (**2**) have been determined by single-crystal X-ray analysis. Both compounds crystallize in space group $C2/c$. For compound **1**, $a = 19.159$ (4) Å, $b = 15.907$ (2) Å, $c = 16.816$ (3) Å, $\beta = 109.57$ (2)°, $V = 4829.0$ Å^3, $Z = 4$, $d_{\mathrm{measd}} = 1.51$ (1) g cm^{-3}, and $d_{\mathrm{calcd}} = 1.49$ g cm^{-3}. The intensities of 4241 independent reflections were measured on an automatic diffractometer, 2670 of which were considered as observed ($I > 2\sigma(I)$). For compound **2**, $a = 13.849$ (2) Å, $b = 18.913$ (2) Å, $c = 14.062$ (2) Å, $\beta = 102.10$ (1)°, $V = 3592.2$ Å^3, $Z = 4$, $d_{\mathrm{measd}} = 1.65$ (1) g cm^{-3}, and $d_{\mathrm{calcd}} = 1.68$ g cm^{-3}. A total of 3522 independent reflections were measured, 2627 of which were considered as observed. Both structures were solved by heavy-atom methods and refined by using least-squares techniques to a residual R value of 0.046 for **1** and 0.039 for **2**. Structure **1** consists of dinuclear $Cu_2(\mathrm{NMEDTB})(NO_3)_3^+$ cations having C_2 symmetry, a disordered nitrate ion, and disordered water molecules. The coordination geometry around each copper ion can be described as square pyramidal with two equatorial benzimidazole nitrogen atoms, one equatorial amine nitrogen atom, one equatorial oxygen atom of a monodentate coordinating nitrate ion, and one axial oxygen atom of a nitrate ion which is bridging to the axial position of the other copper ion in the cation. Structure **2** consists of dinuclear $Cu^{\mathrm{I}}_2(\mathrm{EDTB})^{2+}$ cations having C_2 symmetry and perchlorate ions. Each copper is linearly coordinated by two benzimidazole nitrogen atoms, with short Cu–N bonds of 1.869 (4) and 1.876 (4) Å, respectively. The Cu–Cu distance within one unit is 3.043 (1) Å. The structure of the $Cu^{\mathrm{I}}_2(\mathrm{EDTB})^{2+}$ ion shows a strong resemblance with a recently proposed model for the reduced state of hemocyanin. The compounds $Cu^{\mathrm{I}}_2(L)^{2+}$ do react with O_2 in a 1:1 molar ratio although no O_2 adducts could be isolated.

The oxygen-transporting copper protein hemocyanin has attracted much attention.[1] In a recently proposed[2] model for the active site in hemocyanin, two Cu(I) ions separated by ~3.4 Å are coordinated by two (or three) imidazoles of histidine residues.[3]

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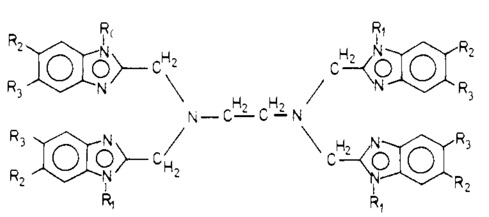

Figure 1. The EDTB ligand and its alkyl-substituted derivatives: EDTB, $R_1 = R_2 = R_3 = H$; NBEDTB, $R_1 = CH_2C_6H_5$, $R_2 = R_3 = H$; 5-MEDTB, $R_1 = R_3 = H$, $R_2 = CH_3$; NMEDTB, $R_1 = CH_3$, $R_2 = R_3 = H$; 5,6-DMEDTB, $R_1 = H$, $R_2 = R_3 = CH_3$.

In oxyhemocyanin the bound oxygen is in the form of peroxide (O_2^{2-}) bridging between two Cu(II) ions, while another atom of the protein (possibly a tyrosine oxygen atom) is also bridging.[2]

It has been generally accepted[4] that imidazole groups play an important role in the coordination chemistry of the copper ion in many other copper-containing proteins as well. Although several Cu(I) and Cu(II) coordination compounds with chelating ligands have been described in the literature as model compounds for hemocyanin[5] and other copper proteins,[6] only a few model systems have been reported in which copper ions are coordinated by chelating ligands containing imidazole groups.[7]

We are investigating the coordination chemistry of copper with imidazole groups rigidly incorporated as synthetic chelating ligands.[8] As part of this research project we recently reported the synthesis and complex formation with Cu(I) and Cu(II) of *N*,*N*,*N'*,*N'*-tetrakis(2-benzimidazolylmethyl)-1,2-ethanediamine (abbreviated EDTB, see Figure 1). With this ligand three classes of compounds have been described[9] with general formulas $[Cu^{II}(EDTB)]X_2$, $Cu^{II}_2(EDTB)X_4$, and $[Cu^{I}_2(EDTB)]X_2$, in which X is a monovalent anion, together with the crystal structure of one of the $Cu^{II}(EDTB)X_2$ compounds. In this paper a number of N- and C-alkylated EDTB derivatives (see Figure 1) and their reactivities toward Cu^I and Cu^{II} are reported. The X-ray structures of the novel dinuclear Cu^I_2 and Cu^{II}_2 compounds $[Cu^I_2(EDTB)](ClO_4)_2$ and $[Cu^{II}_2(NMEDTB)(NO_3)_3]NO_3{\cdot}4H_2O$ are presented (for abbreviations of ligands see Figure 1). Some preliminary results have been communicated earlier.[10]

The importance of the $[Cu^I_2(EDTB)]^{2+}$ ion as a potential model for hemocyanin is discussed.

Experimental Section

Preparations. General Information. All chemicals were of commercially available reagent grade quality. Satisfactory elemental analyses [Cu (if present), C, H, N] were obtained for all new compounds. The abbreviations are explained in Figure 1.

EDTB. This ligand was prepared as described before;[11] alternatively the ligand was obtained in good yield (83%) by refluxing stoichiometric quantities of ethylenediaminetetraacetic acid (EDTA) and 1,2-diaminobenzene in glycol for 20 h followed by precipitation of the crude product with water and purification by recrystallization from hot absolute ethanol. The NMR spectrum and infrared spectra of this preparation were identical with those of the product reported earlier.[11]

NMEDTB·$^1/_2$H$_2$O. This N-methylated EDTB derivative was prepared according to the N-methylation procedure with KOH and methyl iodide in acetone described by Kikugawa.[12] After the reaction with methyl iodide the product precipitated. It was filtered off, thoroughly washed with water, ethanol and diethyl ether, and dried in vacuo at 50 °C (yield 77%): ^{1}H NMR (trifluoroacetic acid; δ values in vs. $(CH_3)_4Si$) 7.77 (s, 16), 4.74 (s, 8), 4.00 (s, 12), 3.50 (s, 4) (relative intensities in parentheses; m and s indicate multiplet and singlet signals, respectively). Anal. ($C_{38}H_{41}N_{10}O_{1/2}$) C, H, N.

NBEDTB·H$_2$O. A procedure was used analogous to the preparation of NMEDTB (yield 79%). For removal of all traces of acetone, the product had to be dried for a prolonged period of time at 100 °C in vacuo: ^{1}H NMR (trifluoroacetic acid vs. $(CH_3)_4Si$) δ 7.75 (s, 16), 7.30 (m, 12), 7.10 (m, 8), 5.60 (s, 8), 4.25 (s, 8), 3.25 (s, 4). Anal. ($C_{62}H_{58}N_{10}O$) C, H, N.

5-MEDTB·2H$_2$O. A procedure was used analogous to the preparation of EDTB (glycol method) with 4-methyl-1,2-diaminobenzene instead of 1,2-diaminobenzene (yield 62%): ^{1}H NMR ($(CD_3)_2SO$ vs. $(CH_3)_4Si$) δ 7.40 (m, 8), 1.00 (m, 4), 4.03 (s, 8), 2.88 (s, 4), 240 (s, 12). Anal. ($C_{28}H_{44}N_{10}O_2$) C, H, N.

5,6-DMEDTB·2H$_2$O. The method described for the preparation of EDTB was adapted with 4,5-dimethyl-1,2-diaminobenzene and EDTB: ^{1}H NMR ($(CD_3)_2SO$ vs. $(CH_3)_4Si$) δ 7.25 (s, 8), 3.79 (s, 8), 2.85 (s, 4), 2.25 (s, 24). Anal. ($C_{39}H_{46}N_{10}O_2$) O, H, N.

Cu^{II}(5-MEDTB)$X_2{\cdot}n$H$_2$O [X = NO$_3$ (n = 2), BF$_4$ (n = 2), ClO$_4$ (n = 1)]. A 1-mmol sample of the ligand was dissolved in 25 mL of absolute ethanol containing 5 mL of triethyl orthoformate (EOF) for dehydration. The compounds crystallized upon standing overnight; they were filtered off and washed with cold absolute ethanol and diethyl ether.

Cu^{II}(NMEDTB)$X_2{\cdot}n$H$_2$O (X = Cl (n = 7), Br (n = 3), NO$_3$ (n = 2)), Cu^{II}(NBEDTB)$X_2{\cdot}n$H$_2$O (X = Cl (n = 0), Br (n = 2), NO$_3$ (n = 1), BF$_4$ (n = 2), ClO$_4$ (n = 1), CF$_3$SO$_3$ (n = 1)), and Cu^{II}(5,6-DMEDTB)$X_2{\cdot}n$H$_2$O (X = BF$_4$ (n = 1), ClO$_4$ (n = 0)). A 1-mmol sample of the ligand NMEDTB NBEDTB, or 5,6-DMEDTB was suspended in about 200 mL of refluxing absolute ethanol. The appropriate copper salt (1 mmol in 10 mL of absolute ethanol) was added. The mixture was refluxed, and after several minutes the solution was clear. The volume was reduced

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[1] (a) Fager, L. Y.; Alben, J. O. *Biochemistry* **1972**, *11*, 4786–4792. (b) Moss, T. H.; Gould, D. C.; Ehrenberg, A.; Loehr, J. S.; Mason, H. S. *Ibid.* **1973**, *12*, 2444–2449. (c) Schoot Uiterkamp, A. J. M.; van der Deen, H.; Berendsen, H. C. J.; Boas, J. F. *Biochim. Biophys. Acta* **1974**, *372*, 407–425. (d) van Driel, R.; van Bruggen, Ed. F. J. *Biochemistry* **1974**, *13*, 4079–4083. (e) Loehr, J. S.; Freedman, T. B.; Loehr, T. M. *Biochem. Biophys. Res. Commun.* **1974**, *56*, 510–515. (f) Salvato, B.; Ghiretti-Magaldi, A.; Ghiretti, F. *Biochemistry* **1974**, *13*, 4778–4783. (g) Solomon, E. I.; Dooley, D. M.; Wang, R.-H.; Gray, H. B.; Cerdonio, M.; Mogno, F.; Romani, G. L. *J. Am. Chem. Soc.* **1976**, *98*, 1029–1031. (h) Larrabee, J. A.; Spiro, T. G.; Ferris, N. S.; Woodruff, W. H.; Maltese, W. A.; Kerr, M. S. *Ibid.* **1977**, *99*, 1979–1980. (i) van der Deen, H.; Hoving, H. *Biochemistry* **1977**, *16*, 3519–3525. (j) Himmelwright, R. S.; Eickman, N. C.; Solomon, E. I. *Biochem. Biophys. Res. Commun.* **1978**, *81*, 237–242. (k) Dooley, D. M.; Scott, R. A.; Ellinghaus, J.; Solomon, E. I.; Gray, H. B. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 3019–3022. (l) Himmelwright, R. S.; Eickman, N. C.; LuBien, C. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 5378–5388.

[2] (a) Brown, J. M.; Powers, L.; Kincaid, B.; Larrabee, J. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 4210–4216. (b) Larrabee, J. A.; Spiro, T. G. *Ibid.* **1980**, *102*, 4217–4223. (c) Co, M. S.; Hodgson, K. O.; Eccles, T. K.; Lontie, R. *Ibid.* **1981**, *103*, 984–986.

[3] EXAFS data[2a,2c] reveal only two imidazoles, while spectroscopic data suggest a higher coordination number.[2b]

[4] (a) Brändén, R.; Reinhammar, B. *Biochim. Biophys. Acta* **1975**, *405*, 236–242. (b) Richardson, J. S.; Thomas, K. A.; Rubin, B. H.; Richardson, D. C. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 1349–1353. (c) Camerman, N.; Camerman, A.; Sarkar, B. *Can. J. Chem.* **1976**, *54*, 1309–1316. (d) Bereman, R. D.; Kosman, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 7322–7325. (e) Colman, P. M.; Freeman, H. C.; Guss, J. M.; Murata, M.; Norris, V. A.; Ramshaw, J. A. M.; Venkatappa, M. P. *Nature (London)* **1978**, *272*, 319–324. (f) Adman, E. T.; Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H. *J. Mol. Biol.* **1978**, *123*, 35–47. (g) Tweedle, M. F.; Wilson, L. J.; García-Iñiguez, L.; Babcock, G. T.; Palmer, G. *J. Biol. Chem.* **1978**, *253*, 8065–8071.

[5] (a) Bulkowski, J. E.; Burk, P. L.; Ludmann, M.-F.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1977**, 498–499. (b) Gagné, R. R.; Allison, J. L.; Gall, R. S.; Koval, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7170–7178. (c) Simmons, M. G.; Merrill, C. L.; Wilson, L. J.; Bottomley, L. A.; Kadish, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 1827–1837. (d) Burnett, M. G.; McKee, V.; Nelson, S. M.; Drew, M. G. B. *J. Chem. Soc., Chem. Commun.* **1980**, 829–831. (e) Burk, P. L.; Osborn, J. A.; Youinou, M.-T.; Agnus, Y. A.; Louis, R.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1273–1274.

[6] (a) Yokoi, H.; Addison, A. W. *Inorg. Chem.* **1977**, *16*, 1341–1349. (b) Amundsen, A. R.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6730–6739. (c) Sakaguchi, U.; Addison, A. W. *J. Chem. Soc., Dalton Trans.* **1979**, 600–608. (d) Bereman, R. D.; Churchill, M. R.; Shields, G. *Inorg. Chem.* **1979**, *18*, 3117–3125. (e) Thompson, J. S.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4180–4192. (f) Karlin, K. D.; Dahlstrom, P. L.; Hyde, J. R.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1980**, 906–0908. (g) Downer, J. M.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1981**, *20*, 1081–1086.

[7] (a) Dagdigian, J. V.; Reed, C. A. *Inorg. Chem.* **1979**, *18*, 2623–2626. (b) Averill, B. A.; Chaudhuri, A. P.; Hendrix, D. C.; Silvis, H. C. *Cienc. Biol. (Coimbra)* **1980**, *5*, 167–168. (c) Pasquali, M.; Marini, G.; Floriani, C.; Gaetani-Manfredotti, A.; Guastini, C. *Inorg. Chem.* **1980**, *19*, 2525–2531. (d) Prochaska, H. J.; Schwindinger, W. F.; Schwartz, M.; Burk, M. J.; Bernarducci, E.; Lalancette, R. A.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 3446–3455.

[8] (a) Addison, A. W.; Hendriks, H. M. J.; Reedijk, J.; Thompson, L. K. *Inorg. Chem.* **1981**, *20*, 103–110. (b) Birker, P. J. M. W. L.; Helder, J.; Henkel, G.; Krebs, B.; Reedijk, J. *Ibid.* **1982**, *21*, 357–363. (c) Schilstra, M. J.; Birker, P. J. M. W. L.; Verschoor, G. C.; Reedijk, J. *Ibid.*, submitted for publication. (d) Hendriks, H. M. J.; Birker, P. J. M. W. L.; Verschoor, G. C.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1982**, 623–629.

[9] Birker, P. J. M. W. L.; Hendriks, H. M. J.; Reedijk, J.; Verschoor, G. C. *Inorg. Chem.* **1981**, *20*, 2408.

[10] Birker, P. J. M. W. L.; Hendriks, H. M. J.; Reedijk, J. *Inorg. Chim. Acta* **1981**, *55*, L17–L18.

[11] Hendriks, H. M. J.; ten Bokkel Huinink, W. O.; Reedijk, J. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 499–500.

[12] Kikugawa, Y. *Synth. Commun.* **1981**, 124–125.

to about 20 mL by evaporation, and, after the solution was cooled, the precipitate of the product formed. This was filtered off and washed with absolute ethanol and diethyl ether.

Cu(NMEDTB)$X_2\cdot nH_2O$ (X = BF_4 (n = 1), ClO_4 (n = 2)) and Cu(5,6-DMEDTB)$(NO_3)_2\cdot 2H_2O$. A 1-mmol sample of the ligand NMEDTB or 5,6-DMEDTB was suspended in 200 mL of refluxing methanol. The appropriate copper salt (1 mmol in 10 mL of methanol) was added. The mixture was refluxed for about 1 h. After the solution was cooled to room temperature, the solid compound was collected by filtration and washed with methanol and diethyl ether.

Cu^{II}_2(5-MEDTB)$X_4\cdot nH_2O$ (X = Cl (n = 3), Br (n = 3), NO_3 (n = 0)). A 1-mmol sample of 5-MEDTB was dissolved in 25 mL of warm absolute ethanol and filtered into a solution of 2 mmol of the appropriate copper salt in 10 mL of absolute ethanol, containing 5 mL of EOF. The complexes crystallized upon standing overnight. They were filtered off and washed with cold absolute ethanol and diethyl ether.

Cu^{II}_2(5-MEDTB)$X_4\cdot nH_2O$ (X = BF_4 (n = 4), ClO_4 (n = 5)). A 1-mmol sample of 5-MEDTB was dissolved in 50 mL of warm absolute ethanol and filtered into a solution of 3 mmol of the appropriate copper salt in 15 mL of absolute ethanol, containing 5 mL of EOF. The volume was reduced by evaporation to about 20 mL and, after the solution was cooled, a precipitate formed. This precipitate was filtered off and washed with absolute ethanol and diethyl ether.

Cu^{II}_2(NMEDTB)$X_4\cdot nH_2O$ (X = Cl (n = 1), Br (n = 1)) and Cu^{II}_2(5,6-DMEDTB)$X_4\cdot nH_2O$ (X = Cl (n = 3), NO_3 (n = 1)). A 1-mmol sample of the ligand NMEDTB of 5,6-DMEDTB was suspended in 200 mL of refluxing methanol. The appropriate copper salt (2 mmol) in 10 mL of methanol was added, and the mixture was refluxed until the solution was clear. The volume was reduced to about 50 mL by evaporation, and, after the solution was cooled, a precipitate formed. This was filtered off and washed with methanol and diethyl ether.

Cu^{II}_2(5,6-DMEDTB)$(BF_4)_4\cdot 6H_2O$. A 1-mmol sample of 5,6-DMEDTB was suspended in 300 mL of refluxing absolute ethanol. $Cu(BF_4)_2\cdot 6H_2O$ (6 mmol) in 25 mL of absolute ethanol was added. After being refluxed for 1 h, the solution was filtered. The volume of the filtrate was reduced to about 40 mL by evaporation. The green precipitate was filtered off and washed with absolute ethanol and diethyl ether.

Cu^{II}_2(5,6-DMEDTB)$Br_4\cdot 4H_2O$. A 1-mmol sample of 5,6-DMEDTB was suspended in 300 mL of refluxing methanol. $CuBr_2$ (2 mmol) in 10 mL of methanol was added. The mixture was refluxed for 1 h and cooled to room temperature. A green precipitate could be filtered off and washed with methanol and diethyl ether.

Cu^{II}_2(5,6-DMEDTB)$(ClO_4)_4\cdot 3H_2O$. A 1-mmol sample of 5,6-DMEDTB was suspended in 200 mL of refluxing absolute ethanol. $Cu(ClO_4)_2\cdot 6H_2O$ (4 mmol) in 20 mL of absolute ethanol was added. The volume of the clear solution was reduced to about 20 mL. After the solution was cooled to room temperature, a precipitate had formed. This was filtered off and washed with absolute ethanol and diethyl ether.

Cu^{I}_2(L)X_2 (L = EDTB, NMEDTB, 5-MEDTB, or 5,6-DMEDTB; X = ClO_4 or BF_4). A solution of 2.1 mmol of $CuClO_4$ or $CuBF_4$ was prepared in situ by reduction of 1.05 mmol of $Cu(ClO_4)_2\cdot 6H_2O$ or $Cu(BF_4)_2\cdot 6H_2O$ with copper powder in about 5 mL of slightly warmed (~50 °C) acetonitrile under nitrogen. The solution was filtered into a nitrogen-purged solution of the ligand (1.0 mmol) in hot absolute ethanol. For EDTB about 50 mL of solvent was used and the product immediately precipitated when the two solutions were mixed. For 5-MEDTB about 35 mL of ethanol was used and the product precipitated upon reduction of the volume to about 20 mL in a stream of nitrogen. 5,6-DMEDTB was dissolved in about 250 mL of absolute ethanol, and also in this case the volume had to be reduced to induce precipitation of the product. For 0.5 mmol of NMEDTB as much as 1 L of hot absolute ethanol was required; the Cu compound precipitated after the solution was cooled to room temperature. All products were filtered off under nitrogen and washed with cold absolute ethanol and diethyl ether. Drying in vacuo at about 50 °C resulted in white powders, which were not air sensitive.

Crystals of Cu^{II}_2(NMEDTB)$(NO_3)_4\cdot 4H_2O$ (1). NMEDTB (0.25 mmol) was refluxed in 50 mL of methanol. $Cu(NO_3)_2\cdot 3H_2O$ (2 mmol) in 10 mL of methanol was added, and the mixture was refluxed for several minutes. The resulting clear solution was cooled to room temperature, and after 2 weeks, blue single crystals of **1** were isolated.

Crystals of Cu^{I}_2(EDTB)$(ClO_4)_2$ (2). Single crystals were prepared by slow diffusion of a solution of $CuClO_4$ in acetonitrile into a solution of EDTB in acetone/Me_2SO (20:1) in a nitrogen atmosphere. This was achieved by completely filling a small beaker with the ligand solution (0.5 mmol in 25 mL). The beaker was placed in a sealed nitrogen-filled vessel containing the $CuClO_4$ solution (prepared by reduction of about 5 mmol of $Cu(ClO_4)_2\cdot 6H_2O$ in about 100 mL of acetonitrile with an excess of copper powder). Enough acetonitrile was added so that it reached just over the rim of the beaker with the ligand solution. After 3 days colorless needles of $Cu_2(EDTB)(ClO_4)_2$ were obtained together with differently shaped colorless crystals of the free ligand; the crystals were washed with acetone and diethyl ether and dried in a stream of nitrogen. Separation of the crystals of **2** was carried out manually under a microscope.

Table I. Crystal Data and Number of Measured Reflections for $[Cu_2(NMEDTB)(NO_3)_3]NO_3\cdot 4H_2O$ (1) and for $Cu_2(EDTB)(ClO_4)_2$ (2)

	1	2
compositn	$C_{38}H_{48}Cu_2N_{14}O_{16}$	$C_{34}H_{32}Cl_2Cu_2N_{10}O_8$
cryst size	0.38 × 0.30 × 0.27 mm^3	0.50 × 0.15 × 0.13 mm^3
space group	$C2/c$	$C2/c$
D_{calcd}, g cm^{-3}	1.49	1.68
D_{exptl}(flotation), g cm^{-3}	1.51 (1)	1.65 (1)
Z	4	4
a, Å	19.159 (4)	13.849 (2)
b, Å	15.907 (2)	18.913 (2)
c, Å	16.816 (3)	14.026 (2)
β, deg	109.57 (2)	102.10 (1)
V, $Å^3$	4829.0	3592.2
μ(Mo Kα), cm^{-1}	7.3	14.5
no. of reflctns		
total	4379	7222
symmetry independent	4241	3522
obsd ($I > 2\sigma(I)$)	2670	2672

Physical Measurements. Infrared spectra of the solid compounds were recorded either on a Perkin-Elmer 297 spectrophotometer in the range 600–4000 cm^{-1} or on a Perkin-Elmer 580 spectrophotometer in the range 200–4000 cm^{-1}. Samples were either mulled in Nujol (and measured between KBr pellets) or pelleted in KBr. No indications for decomposition in the KBr pellets were observed. Electronic spectra (35 000–4000 cm^{-1}) were obtained on solids by using a Beckman DK-2A ratio-recording spectrophotometer fitted with a reflectance attachment. Electron spin resonance spectra at X-band and Q-band frequencies were obtained with Varian E-3, E-9, and E-112 spectrometers either as powdered solids at room temperature or as frozen methanol or dimethyl sulfoxide solutions at −196 °C. The field was calibrated by using an AEG proton NMR apparatus. Low-temperature magnetic susceptibility measurements were performed on a PAR vibrating sample magnetometer in the 4.2–15-K range. Proton NMR spectra were measured on a Varian T-60 instrument or on a JEOL PS-100 spectrometer. Copper analyses were carried out by using standard EDTA titrations;[13] all other elemental analyses were performed by the Organisch Chemisch Instituut, TNO Utrecht, the Netherlands, or by Dr. Pascher, Bonn, Germany.

X-ray Methods. The crystal data of $[Cu_2(NMEDTB)]NO_3\cdot 4H_2O$ (**1**) and of $Cu_2(EDTB)(ClO_4)_2$ (**2**) are listed in Table I. Preliminary Weissenberg photographs indicated Laue symmetry $2/m$ for both compounds, and the systematic absences $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$ are consistent with either Cc or $C2/c$ as possible space groups. Precise lattice constants were determined by least-squares refinement of the angular settings of 24 reflections with $10° < \theta < 14°$ for **1** and with $8° < \theta < 15°$ for **2**. Intensity data were collected on a Nonius CAD-4 diffractometer (ω–θ scans) for all reflections with $2° < \theta < 25°$ and $h > 0$ and $k > 0$ for **1** and with $2° < \theta < 26°$ and $h > 0$ for **2**. Graphite-monochromated Mo Kα radiation was used. The scanning rate was adjusted to the required precision of $\sigma(I)/I < 0.01$ and with a maximum scan time of 120 s/reflection for **1** and 90 s/reflection for **2**. For both compounds each reflection was measured in 96 steps. Sixteen steps at each end of the scan were considered as background. Intensities I and their standard deviations $\sigma(I)$ were calculated from $I = s[P - 2(B_1 + B_2)]$ and $\sigma(I) = s[P + 4(B_1 + B_2)]^{1/2}$, where s is a factor to account for the variable scan speed, P is the scan count, and B_1 and B_2 are the low and high angle background counts. Three standard reflections were measured after every 5400 s of radiation time to check for instrumental instability and crystal decomposition; there was no significant change in their intensities.

Measurement of the intensities of suitable reflections at different azimuthal positions suggested that no absorption correction was necessary (for compound **1**, the maximal variation was ±7%, for compound **2**, the variation was less than ±4%. The intensities were corrected for Lorentz and polarization effects. The numbers of measured and observable reflections are also given in Table I.

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(13) Vogel, A. I. "Quantitative Inorganic Analysis"; Longmans, Green and Co.: London, 1959.

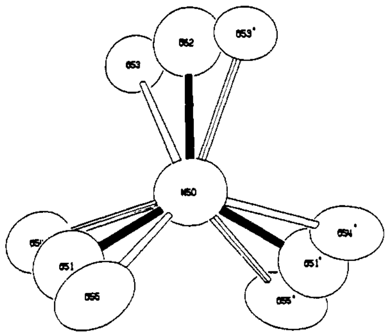

Figure 2. The disordered bridging nitrate group in $[Cu_2(NMEDTB)(NO_3)_3]NO_3 \cdot 4H_2O$. N(50)–O(52)–O(51)–O(51′) has a population of 60%; N(50)–O(53)–O(54′)–O(55) and N(50)–O(53′)–O(54)–O(55′) have a population of 20% each.

Structure Determination of $[Cu^{II}_2(NMEDTB)(NO_3)_3]NO_3 \cdot 4H_2O$ (1). Harker peaks found in the three-dimensional Patterson synthesis on positions *x*, 0, *z* suggested the centrosymmetric space group *C*2/*c* as the correct choice. This was confirmed by the successful solution of the crystal structure. From a Patterson map the position of the copper atom was located. Fourier maps and full-matrix least-squares refinements showed the positions of all other nonhydrogen atoms of the ligand and of two nitrate molecules (one on a general position, coordinating to a single copper atom, and another on a twofold axis, bridging two symmetry-related copper atoms). In subsequent block-diagonal least-squares refinement cycles using unit weights the copper and the ligand atoms as well as the atoms of the nonbridging nitrate molecule were given anisotropic thermal parameters. Difference Fourier maps revealed the positions of all hydrogen atoms of the ligand except the methyl hydrogen atoms. The nitrate ion on the twofold axis turned out to be disordered. A model was refined consisting of one nitrate ion on the twofold axis in three different orientations centered around the same nitrogen atom. One orientation has twofold symmetry with onn N–O bond along the twofold axis and the other two are mutually related by the twofold axis (see Figure 2). Comparison of the thermal parameters suggested values of 0.6, 0.2, and 0.2, respectively, for their occupancies. They were refined with these fixed values for their occupancies with anisotropic thermal parameters. As a result of the disorder the atomic parameters of the bridging nitrate group have large standard deviations. In the difference Fourier maps 20 peaks were found, whose heights were similar to those of hydrogen atoms. Since the fourth nitrate molecule and four water molecules (whose presence was clear from C, H, and N analyses and densities) could not be located, these peaks were considered as parts of disordered water and nitrate molecules. They were refined as oxygen atoms with isotropic thermal parameters and with occupancies of 0.10–0.25 (see supplementary material). No nitrate ions could be recognized in their geometry.

During the refinement many hydrogen atoms shifted to unrealistic positions. They were therefore kept fixed at the positions originally determined from the difference Fourier maps and were given isotropic thermal parameters of $B = 4.0$ Å^2. No hydrogen atoms were included for the methyl groups of the ligands. In the final difference Fourier map some residual electron density was found (peaks < 0.38 e/Å^3), which is ascribed to parts of distorted water molecules and nitrate ions with very low occupancies. They were not included in the refinement. Full-matrix least-squares refinement was continued until the parameter shifts for the ordered atoms were less than 0.2 times their standard deviations and the parameter shifts for the atoms positions with partial occupancies were less than their standard deviations. The refinement (384 parameters) resulted in a final *R* value[14] of 0.046 for the 2670 reflections with $I > 2\sigma(I)$.

Scattering factors for neutral atoms were taken for all nonhydrogen atoms from ref 15 and used with a correction for the real part of the anomalous dispersion $\Delta f'$ and those for copper were corrected for the imaginary part of the anomalous dispersion $\Delta f''$. The scattering factors for the hydrogen atooms were taken from Stewart et al.[16] Final atomic parameters for the nonhydrogen atoms of the cation are given in Table II and those for the hydrogen atoms are given in Table III. The 20 partially occupied nitrate or water atom positions are separately listed and available as supplementary material, together with a list of observed and calculated structure factors.

Table II. Positional Parameters ($\times 10^4$) and Anisotropic Thermal Parameters (Å^2, $\times 10^3$) of the Nonhydrogen Atoms[b] of $Cu_2(NMEDTB)(NO_3)_4 \cdot 4H_2O$ with Their Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{13}$	$2U_{23}$
Cu	3644(1)	3046(1)	1487(1)	58(1)	40(1)	49(1)	13(1)	16(1)	52(1)
N(10)	4003(3)	3543(3)	650(3)	64(4)	49(3)	45(3)	6(5)	9(5)	56(6)
N(20)	3235(3)	2206(3)	2041(3)	59(3)	40(3)	64(3)	5(5)	14(5)	62(6)
N(30)	4312(3)	2023(3)	1376(3)	49(3)	41(3)	45(3)	8(5)	5(5)	34(5)
N(11)	4449(3)	3361(3)	-389(3)	69(4)	65(4)	45(3)	5(6)	5(5)	63(6)
C(11)	4313(3)	3014(4)	278(4)	53(4)	56(4)	41(3)	9(7)	1(7)	36(6)
C(12)	3923(4)	4302(4)	211(4)	68(5)	51(4)	45(3)	5(7)	17(7)	55(7)
C(13)	4204(4)	4193(4)	-442(4)	69(5)	59(4)	51(4)	0(7)	13(7)	37(8)
C(14)	4448(4)	2119(4)	548(4)	60(4)	60(5)	45(4)	18(7)	2(7)	44(7)
C(15)	4216(4)	4838(5)	-996(5)	90(6)	75(5)	60(5)	2(9)	31(8)	84(9)
C(16)	3937(5)	5587(5)	-852(5)	94(6)	67(5)	72(5)	-4(9)	52(8)	79(10)
C(17)	3651(5)	5706(5)	-204(5)	93(6)	56(5)	75(6)	19(9)	37(8)	80(10)
C(18)	3641(4)	5066(5)	334(5)	89(6)	59(5)	61(5)	12(9)	16(8)	87(9)
C(19)	4770(5)	2936(6)	-969(5)	111(7)	89(6)	72(5)	31(11)	-4(10)	125(10)
N(21)	2974(3)	862(4)	2126(4)	68(4)	39(3)	72(4)	-12(6)	5(6)	58(7)
C(21)	3368(4)	1427(4)	1864(4)	51(4)	40(3)	55(4)	1(6)	11(6)	31(7)
C(22)	2704(4)	215(4)	2436(5)	66(5)	45(4)	73(5)	9(7)	27(7)	73(8)
C(23)	2533(4)	1301(4)	2494(5)	68(5)	51(4)	75(5)	4(8)	22(8)	70(8)
C(24)	3886(4)	1239(4)	1387(4)	57(4)	37(4)	59(4)	-3(6)	-3(7)	35(7)
C(25)	2016(5)	1039(5)	2849(6)	98(7)	62(5)	110(7)	9(10)	43(10)	126(12)
C(26)	1681(5)	1657(6)	3148(6)	111(8)	84(7)	135(9)	3(12)	47(12)	180(14)
C(27)	1841(6)	2507(6)	3104(7)	127(8)	71(6)	141(9)	42(12)	39(12)	203(16)
C(28)	2352(5)	2762(5)	2746(6)	105(7)	51(5)	118(8)	16(9)	32(9)	148(13)
C(29)	3010(5)	-65(4)	2048(6)	109(7)	28(4)	132(8)	-23(9)	-7(9)	128(13)
C(31)	5037(4)	2026(4)	2065(4)	53(4)	43(4)	51(4)	11(7)	-3(6)	39(6)
N(40)	2334(3)	3828(4)	907(4)	58(4)	71(4)	75(5)	46(7)	11(7)	33(7)
O(41)	2926(4)	3948(3)	1517(3)	54(3)	47(3)	55(3)	14(5)	4(5)	38(5)
O(42)	2292(3)	3235(4)	425(3)	86(4)	88(5)	82(4)	40(7)	-67(7)	13(7)
O(43)	1818(3)	4312(4)	818(4)	89(5)	116(6)	127(6)	93(9)	-54(9)	16(8)
N(50)	5000	4303(5)	2500	73(6)	52(5)	43(3)	0	0	57(9)
O(51)[c]	4476(3)	3913(4)	2569(4)	34(4)	43(4)	34(4)	36(6)	29(6)	-1(6)
O(52)[c]	5000	5065(6)	2500	69(8)	45(6)	63(7)	0	0	36(13)
O(53)[d]	4732(11)	5062(13)	2248(13)	61(17)	52(13)	53(17)	34(22)	43(22)	43(24)
O(54)[d]	4279(8)	4081(11)	2401(10)	12(9)	31(10)	29(9)	60(15)	41(16)	-13(15)
O(55)[d]	4619(12)	3725(12)	2723(12)	71(15)	30(11)	59(14)	49(21)	58(20)	75(24)

[a] The thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] The atom numbering scheme is given in Figures 2 and 3. [c] These atoms have a population of 0.6. [d] These atoms have a population of 0.2.

Table III. Positional Parameters ($\times 10^3$) for the Hydrogen Atoms[a] in $Cu_2(NMEDTB)(NO_3)_4 \cdot 4H_2O$

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
H(15)	48	24	138	H(28)	251	334	286
H(16)	399	389	380	H(141)	401	190	10
H(17)	337	373	483	H(142)	492	186	62
H(18)	153	14	426	H(241)	345	113	76
H(25)	197	41	295	H(242)	429	76	170
H(26)	120	147	326	H(311)	529	159	198
H(27)	160	296	341	H(312)	525	256	205

[a] The first two digits ofthe atom number correspond with the number of the parent atom.

Structure Determination of $Cu^{I}_2(EDTB)(ClO_4)_2$ (2). Also for this structure the space group *C*2/*c* was the correct choice as indicated by the presence of many Harker peaks in the *x*, 0, *z* plane in the three-dimensional Patterson synthesis. The structure was solved from Patterson and Cu–Cu-shifted Patterson maps. Subsequent Fourier syntheses and full-matrix least-squares refinement cycles showed the positions of all atoms. When the *R* value[14] was 0.10, all ligand hydrogen atoms could be located in a difference Fourier map.

The ClO_4^- ion turned out to be disordered and is present in two different orientations centered around the same chlorine atom. The anion is refined with one oxygen atom at two differential positions (O(2) and O(21)) while the positional disorder of the other three oxygen atoms is reflected by their large thermal parameters and anisotropies (see Figure 6). Comparison of the isotropic thermal parameters of O(2) and O(21) suggested occupancies of $^2/_3$ and $^1/_3$, respectively. All nonhydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms with isotropic thermal parameters. In the final full-matrix least-squares refinement cycle all parameter shifts were less than 0.10

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(14) $R = \sum||F_o| - |F_c||/\sum|F_o|$.
(15) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. IV.
(16) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

Table IV. Positional Parameters (×10^4) and Anisotropic Thermal Parameters[a] (Å^2, ×10^3) of the Nonhydrogen Atoms[b] of $Cu_2(EDTB)(ClO_4)_2$ with Their Estimated Standard Deviations in Parentheses

atom	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Cu	4714(1)	4303(1)	3490(1)	33(1)	48(1)	51(1)	-1(1)	7(1)	18(1)
N(10)	6077(2)	4449(2)	3628(2)	36(2)	40(2)	39(2)	0(2)	-4(3)	14(2)
C(10)	6736(2)	3926(2)	3642(2)	37(2)	40(2)	35(2)	0(3)	-2(3)	7(3)
N(11)	7654(2)	4188(1)	3779(2)	33(1)	38(2)	46(2)	12(3)	-11(3)	11(3)
C(11)	6604(2)	5039(2)	3785(2)	40(2)	37(2)	33(2)	1(3)	-2(3)	18(3)
C(12)	7603(2)	4910(2)	3882(2)	40(2)	37(2)	36(2)	1(3)	-8(3)	19(3)
C(13)	8315(3)	5433(2)	4048(3)	44(2)	52(2)	52(2)	-9(4)	-6(3)	28(4)
C(14)	7993(3)	6112(2)	4102(3)	66(2)	46(2)	58(2)	-36(4)	-7(4)	33(4)
C(15)	7003(3)	6268(2)	3994(3)	73(3)	35(2)	71(3)	1(4)	-2(4)	51(5)
C(16)	6293(3)	5754(2)	3838(3)	49(2)	45(2)	59(2)	20(4)	0(4)	32(4)
C(17)	6491(2)	3167(2)	3412(3)	49(2)	37(2)	46(2)	2(3)	4(3)	9(3)
N(20)	3365(2)	4303(2)	3515(2)	36(1)	40(2)	40(2)	2(3)	-3(3)	20(2)
C(20)	2845(2)	3725(2)	3377(3)	40(2)	44(2)	39(2)	-2(3)	7(3)	26(3)
N(21)	1877(2)	3853(2)	3380(2)	40(2)	50(2)	51(2)	-13(3)	3(3)	29(3)
C(21)	2716(2)	4850(2)	3613(2)	41(2)	43(2)	34(2)	8(3)	4(3)	20(3)
C(22)	1774(3)	4567(2)	3345(3)	43(2)	54(2)	37(2)	6(3)	9(3)	25(3)
C(23)	965(3)	4983(2)	3576(3)	43(2)	71(3)	60(3)	16(4)	19(5)	30(4)
C(24)	1138(3)	3691(3)	3731(3)	56(3)	68(3)	69(3)	48(5)	27(5)	44(4)
C(25)	2071(3)	5977(2)	3843(3)	74(3)	45(2)	54(3)	27(4)	11(4)	31(4)
C(26)	2878(3)	5565(2)	3764(3)	48(2)	48(2)	46(2)	4(4)	1(4)	18(3)
C(27)	3431(3)	3013(2)	3231(3)	31(2)	41(2)	55(2)	-13(3)	6(4)	37(4)
N(30)	3976(2)	3053(1)	2626(2)	41(2)	31(1)	40(2)	2(3)	4(3)	17(3)
C(30)	4571(3)	2402(2)	2752(3)	51(2)	28(2)	45(2)	-6(3)	5(3)	13(3)
Cl	400(1)	2754(1)	966(1)	51(1)	71(1)	62(2)	-24(1)	6(1)	16(1)
O(1)	-584(3)	2670(3)	778(5)	63(3)	146(5)	272(7)	-63(6)	131(10)	-32(7)
O(2)[c]	483(3)	3441(4)	1411(5)	124(6)	109(5)	180(7)	-57(9)	-158(10)	77(10)
O(3)	968(4)	2388(4)	1693(5)	132(5)	352(11)	170(6)	159(14)	229(13)	-13(8)
O(4)	841(5)	2944(4)	248(4)	222(7)	352(11)	116(4)	-221(14)	27(11)	160(9)
O(21)[d]	327(12)	2091(8)	401(11)	179(6)	122(14)	121(12)	-69(22)	-113(20)	146(23)

[a] The thermal parameters are of the same form as in Table II. [b] The atom numbering scheme is given in Figures 6 and 7. [c] This atom has a population of 0.67. [d] This atom has a population of 0.33.

times their standard deviations. The final R value for 2627 reflections with $I > 2\sigma(I)$ is 0.039. The same scattering factors and corrections were used as for structure **1**. Final atomic parameters for the nonhydrogen atoms are given in Table IV and those for the hydrogen atoms are listed in Table V. A list of observed and calculated structure factors is available.[17]

Reactions with Gases. Reactions with gases were carried out in a closed thermostated system, containing the appropriate gaseous reagent. In the closed system Me_2SO (10–25 mL) was magnetically stirred and saturated with the gas. Subsequently the solid metal compound (0.05–0.2 mmol) was added to this solvent, and the pressure change was followed as a function of time. The stoichiometry of the reaction could be determined from the pressure at the end of the reaction. The gas uptake was in general found to be complete after 2–10 h.

Results and Discussion

General Data. The newly prepared ligands NMEDTB, NBEDTB, 5-MEDTB, and 5,6-DMEDTB (see Figure 1) were characterized by elemental analyses and IR and NMR spectroscopy (see Experimental Section). In the NMR spectra of EDTB,[11] 5-MEDTB, and 5,6-DMEDTB the methylene protons of the ethylenediamine group are found at δ 2.90 ± 0.05, whereas the methylene protons of the CH_2 groups bonded to imidazole appear at 4.00 ± 0.05 ppm. The aromatic EDTB protons appear as two equally intense multiplets with high symmetry similar to the spectra observed for ortho-disubstituted benzene rings.[18] As expected, in 5-MEDTB these multiplets have lost their symmetry and their intensities are no longer equal, whereas in 5,6-DMEDTB the remaining eight aromatic protons appear as a singlet. These observations indicate that the imidazole N–H proton is in fast exchange. Because of this fast exchange, it is not found in the spectra of EDTB and 5-MEDTB, whereas in 5,6-DMEDTB only a very broad, faint resonance is observed at ~12 ppm downfield from Me_4Si. The solubility of NMEDTB and NBEDTB in dimethyl sulfoxide is not sufficient for NMR spectroscopy, and therefore their NMR spectra were recorded in trifluoroacetic acid. The use of this solvent can be the reason for higher δ values (~0.6 ppm) for the protons in these ligands, compared to the protons in EDTB, 5-MEDTB, and 5,6-DMEDTB. No explanation is put forward for the fact that the benzimidazole protons in free NMEDTB and NBEDTB occur as single sharp peaks at 7.75 ppm. The structures of NMEDTB and EDTB are confirmed by the X-ray determination of three copper coordination compounds (this paper and ref 9).

Table V. Positional Parameters (×10^3) and Isotropic Thermal Parameters for Hydrogen Atoms[a] of $Cu_2(EDTB)(ClO_4)_2$ with Their Estimated Standard Deviations in Parantheses

atom	x/a	y/b	z/c	B_{iso}, Å^2
H(11)	814 (2)	395 (2)	383 (2)	3.3 (7)
H(13)	896 (2)	531 (2)	414 (3)	3.7 (8)
H(14)	846 (3)	647 (2)	423 (3)	4.8 (9)
H(15)	683 (3)	670 (2)	403 (3)	5.3 (1.0)
H(16)	562 (2)	585 (2)	374 (3)	3.9 (8)
H(171)	703 (2)	290 (2)	361 (2)	3.6 (8)
H(172)	606 (2)	304 (2)	377 (3)	3.2 (8)
H(21)	148 (2)	359 (2)	331 (3)	3.9 (8)
H(23)	35 (3)	477 (2)	349 (3)	4.0 (8)
H(25)	218 (3)	644 (2)	392 (3)	4.4 (9)
H(26)	348 (2)	575 (2)	384 (2)	3.1 (7)
H(271)	270 (3)	273 (2)	294 (3)	3.9 (8)
H(272)	353 (3)	285 (2)	382 (3)	4.2 (9)
H(301)	415 (2)	199 (2)	255 (2)	3.1 (7)
H(302)	480 (2)	234 (2)	336 (2)	3.2 (8)

[a] The first two digits of the atom number correspond with the number of the parent atom.

Three classes of compounds were prepared with these ligands with general formulas $Cu^{II}(L)X_2$, $Cu^{II}_2(L)X_4$, and $Cu^{I}_2(L)X_2$, where L = NMEDTB, 5-MEDTB, or 5,6-DMEDTB and X = Cl, Br, NO_3, BF_4, or ClO_4. When L = NBEDTB, only compounds $Cu^{II}(L)X_2$ were obtained for the same anions and also for X = $CF_3SO_3^-$. Satisfactory Cu, C, H, and N analyses were obtained for all copper compounds. In most cases the synthesis of compounds $Cu_2(L)X_4$, where X = ClO_4^- or BF_4^-, had to be carried out with an excess of the copper salt. Despite several attempts (e.g., with large excesses of copper salts) no pure compounds with formulas $Cu_2(NMEDTB)(ClO_4)_4$, $Cu_2(NMEDTB)(BF_4)_4$, or $Cu_2(NBEDTB)X_4$ could be obtained. On the other hand, attempts to prepare $Cu(4\text{-}MEDTB)Cl_2$, $Cu(4\text{-}MEDTB)Br_2$, $Cu(5,6\text{-}DMeDTB)Cl_2$, or $Cu(4,5\text{-}DMEDTB)Br_2$ persistently yielded the corresponding 2:1 compound. Apparently when anions are used which are relatively strongly bonded by Cu(II), like Cl^- or Br^-, it is difficult for the ligand to coordinate to a metal ion with all six of its nitrogen donor atoms and a second metal ion is chelated by the ligand. On the other hand, when weakly coordinating anions are used, such as ClO_4^- or BF_4^-, it is apparently difficult for the ligand to bind more than one metal ion.

As in the case of $Cu^{I}_2(EDTB)X_2$,[11] Cu(I) compounds could only be prepared with ClO_4^- and BF_4^- as anions. With Cl^-, Br^-, and NO_3^- anions, gelatinous air-sensitive white precipitates were isolated for which no reproducible analyses were obtained. Reaction of Cu(I) with one of the ligands in a 1:1 ratio resulted in the precipitation of the free ligand. No pure Cu(I) compounds could be isolated with the ligand NBEDTB.

In the following section the structures of $[Cu_2(NMEDTB)(NO_3)_3]NO_3\cdot 4H_2O$ (**1**) and $[Cu_2(EDTB)](ClO_4)_2$ (**2**) will be described in detail. Subsequently, the spectral properties of the copper compounds will be discussed in view of the crystal structures.

Description of the Structure of $[Cu_2(NMEDTB)(NO_3)_3]NO_3\cdot 4H_2O$ (1). This compound consists of a binuclear $Cu_2(NMEDTB)(NO_3)_3^+$ cation and a separate NO_3^- anion. A perspective view of the binuclear cation including the atom numbering scheme is shown in Figure 3. Bond distances and angles are listed in Tables VI and VII, respectively.

The $Cu_2(NMEDTB)(NO_3)_3^+$ cation has C_2 symmetry. Each copper atom is coordinated by two imidazole nitrogen atoms and one amine nitrogen atom of the ligand, two oxygen atoms of an

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(17) Supplementary material.

(18) Thompson, L. K.; Ramaswamy, B. S.; Seymour, E. A. *Can. J. Chem.* **1977**, *55*, 878–888.

Table VI. Bond Distances (Å) for $Cu_2(NMEDTB)(NO_3)_4 \cdot 4H_2O$ with Their Estimated Standard Deviations in Parentheses[a]

Cu-N(10)	1.931 (5)	N(40)-O(43)	1.222 (8)	N(50)-O(53)	1.32 (7)
Cu-N(20)	1.940 (6)	N(40)-O(41)	1.262 (8)	N(50)-O(54)	1.40 (5)
Cu-N(30)	2.118 (5)	N(40)-O(42)	1.229 (8)	N(50)-O(55)	1.31 (5)
Cu-O(41)	2.000 (4)	N(50)-O(50)	1.22 (5)	Cu-O(54)	2.29 (6)
Cu-O(51)	2.41 (4)	N(50)-O(52)	1.21 (5)	Cu-O(55)	2.53 (15)
Cu···O(42)	2.626 (5)	Cu···Cu	5.171 (2)		

N(10)-C(11)	1.305 (8)	N(20)-C(21)	1.320 (8)	C(16)-C(17)	1.388 (11)	C(26)-C(27)	1.393 (13)
C(11)-N(11)	1.351 (8)	C(21)-N(21)	1.337 (8)	C(17)-C(18)	1.367 (10)	C(27)-C(28)	1.369 (12)
N(11)-C(19)	1.480 (9)	N(21)-C(29)	1.389 (10)	C(18)-C(12)	1.372 (10)	C(28)-C(22)	1.383 (11)
N(10)-C(12)	1.394 (8)	N(20)-C(22)	1.390 (9)	C(11)-C(14)	1.492 (10)	C(21)-C(24)	1.500 (10)
C(12)-C(13)	1.386 (9)	C(22)-C(23)	1.403 (10)	C(14)-N(30)	1.510 (8)	C(24)-N(30)	1.494 (8)
C(13)-C(15)	1.391 (10)	C(23)-C(25)	1.388 (11)	N(30)-C(31)	1.480 (9)	C(31)-C(31′)	1.519 (13)
C(15)-C(16)	1.359 (12)	C(25)-C(26)	1.371 (12)				

[a] The atom numbering scheme is given in Figures 2 and 3; the superscript in the atom labels indicates the symmetry operation $1-x, y, {}^1\!/_2-z$.

Table VII. Interbond Angles (Deg) for $Cu_2(NMEDTB)(NO_3)_4 \cdot 4H_2O$ with Their Estimated Standard Deviations in Parentheses[a]

N(10)-Cu-N(20)	158.9 (2)	O(41)-Cu-O(51)	82 (1)	Cu-N(30)-C(24)	107.0 (4)
N(10)-Cu-N(30)	83.0 (2)	O(42)-Cu-N(10)	88.1 (2)	Cu-N(10)-C(11)	114.5 (5)
N(10)-Cu-O(41)	98.0 (2)	O(42)-Cu-N(20)	88.6 (2)	Cu-N(10)-C(12)	137.6 (5)
N(10)-Cu-O(51)	90 (1)	O(42)-Cu-N(30)	121.1 (2)	Cu-N(20)-C(21)	113.5 (5)
N(20)-Cu-N(30)	82.3 (2)	O(42)-Cu-O(41)	53.5 (2)	Cu-N(20)-C(22)	138.6 (5)
N(20)-Cu-O(41)	95.2 (2)	O(42)-Cu-O(51)	134 (2)	Cu-O(41)-N(40)	108.0 (4)
N(20)-Cu-O(51)	108 (1)	Cu-N(30)-C(31)	111.4 (4)	Cu-O(42)-N(40)	78.8 (4)
N(30)-Cu-O(41)	174.2 (2)	Cu-N(30)-C(14)	107.4 (4)	Cu-O(51)-N(50)	125 (2)
N(30)-Cu-O(51)	104 (1)				

C(11)-N(10)-C(12)	106.9 (6)	C(21)-N(20)-C(22)	106.1 (6)	C(12)-C(13)-C(15)	122.5 (7)	C(22)-C(23)-C(25)	123.8 (8)
N(10)-C(11)-N(11)	112.4 (7)	N(20)-C(21)-N(21)	112.5 (6)	C(11)-C(14)-N(30)	108.2 (5)	C(21)-C(24)-N(30)	107.6 (5)
N(10)-C(11)-C(14)	122.1 (6)	N(20)-C(21)-C(24)	121.4 (6)	C(13)-C(15)-C(16)	115.6 (7)	C(23)-C(25)-C(26)	114.7 (8)
C(14)-C(11)-N(11)	125.4 (6)	C(24)-C(21)-N(21)	126.1 (6)	C(15)-C(16)-C(17)	122.7 (7)	C(25)-C(26)-C(27)	123.6 (8)
C(11)-N(11)-C(13)	106.5 (6)	C(21)-N(21)-C(23)	107.7 (6)	C(16)-C(17)-C(18)	121.1 (7)	C(26)-C(27)-C(28)	120.7 (9)
C(11)-N(11)-C(19)	126.9 (7)	C(21)-N(21)-C(29)	126.1 (7)	C(17)-C(18)-C(12)	117.8 (7)	C(27)-C(28)-C(22)	118.0 (8)
C(19)-N(11)-C(13)	126.7 (7)	C(29)-N(21)-C(23)	126.2 (7)	C(14)-N(30)-C(31)	108.3 (5)	C(24)-N(30)-C(31)	111.5 (5)
N(10)-C(12)-C(13)	108.0 (6)	N(20)-C(22)-C(23)	108.5 (6)	C(14)-N(30)-C(24)	111.2 (5)	N(30)-C(31)-C(31′)	112.9 (7)
N(10)--C(12)-C(18)	131.5 (6)	N(20)-C(22)-C(28)	131.7 (7)	O(41)-N(40)-O(42)	119.7 (7)	O(51)-N(50)-O(51′)	119 (6)
C(13)-C(12)-C(18)	120.5 (7)	N(23)-C(22)-C(28)	119.8 (7)	O(41)-N(40)-O(43)	118.4 (7)	O(51)-N(50)-O(52)	121 (3)
N(11)-C(13)-C(12)	106.2 (6)	N(21)-C(23)-C(22)	105.2 (7)	O(42)-N(40)-O(43)	121.9 (8)	O(53)-N(50)-O(54′)	123 (9)
N(11)-C(13)-C(15)	131.3 (7)	N(21)-C(23)-C(25)	131.6 (7)	O(53)-N(50)-O(55)	123 (15)	O(55)-N(50)-O(54′)	115 (11)

[a] The atom numbering scheme is given in Figures 2 and 3; the superscript in the atom labels indicates the symmetry operation $1-x, y, {}^1\!/_2-z$.

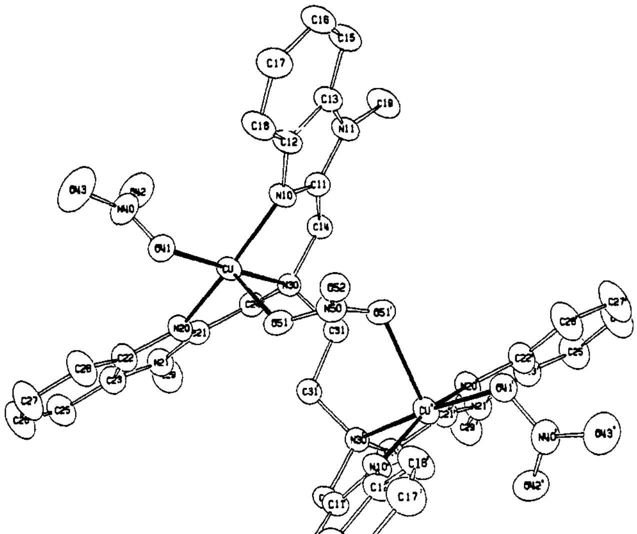

Figure 3. ORTEP drawing of the $[Cu_2(NMEDTB)(NO_3)_3]^+$ cation in $[Cu_2(NMEDTB)(NO_3)_3]NO_3 \cdot 4H_2O$, showing the anisotropic vibration ellipsoids (probability 30%). Hydrogen atoms have been omitted for clarity. Bond distances and angles are given in Tables VI and VII, respectively.

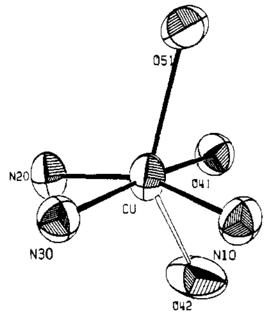

Figure 4. Coordination geometry of the copper atom in $[Cu_2(NMEDTB)(NO_3)_3]NO_3 \cdot 4H_2O$.

asymmetric, bidentate nitrate, and one oxygen atom of a second bidentate nitrate, which lies on the twofold axis forming a bridge between the two symmetry-related copper atoms. For clarity only one position of the disordered nitrate bridge (the one with largest population) will be considered in this discussion. Figure 4 shows the detailed coordination geometry around Cu(II). This geometry can be described as distorted octahedral with four short copper–ligand contacts in the equatorial plane (1.931–2.118 Å) and two longer axial Cu–O distances (2.41 (4) and 2.626 (5) Å). The ligand atoms in the equatorial plane are displaced +0.09 to −0.09 Å from the least-squares plane through these atoms, and the copper atom is displaced 0.18 Å from it toward the axial oxygen atom with the shortest Cu–O distance (0(51). This, together with the Cu–O(42)–N(40) angle of 78.8 (4)°, the rather long Cu–O distance of 2.626 (5) Å, and the bond angles O(51)–Cu–O(42) and O(41)–Cu–O(42) of 134 (2) and 53.5 (2)°, respectively, suggests that O(42) should be considered as weakly coordinating and that the coordination geometry can also be described as square

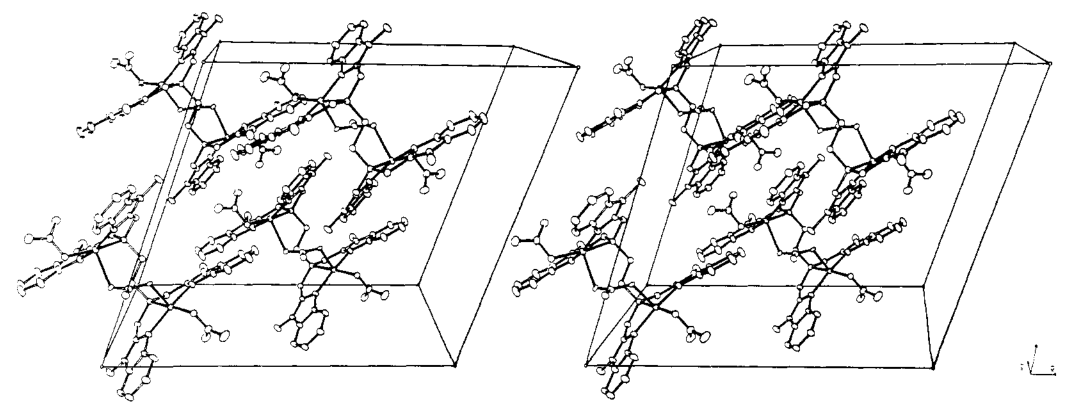

Figure 5. Stereodrawing of the unit cell of $[Cu_2(NMEDTB)(NO_3)_3]NO_3 \cdot 4H_2O$. The disordered anionic nitrate and water molecules are not shown.

Table VIII. Interatomic Distances (Å) for $Cu_2(EDTB)(ClO_4)_2$ with Their Estimated Standard Deviations in Parentheses[a]

Cu···Cu	3.043 (1)	N(10)-C(10)	1.320 (6)	N(20)-C(20)	1.316 (6)
Cu-N(10)	1.869 (4)	N(10)-C(11)	1.392 (6)	N(20)-C(21)	1.395 (6)
Cu-N(20)	1.876 (4)	C(10)-N(11)	1.340 (6)	C(20)-N(21)	1.336 (6)
Cu···N(30)	2.774 (4)	N(11)-C(12)	1.378 (6)	N(21)-C(22)	1.392 (7)
Cl-O(1)[b]	1.342 (5)	C(11)-C(12)	1.389 (6)	C(21)-C(22)	1.392 (7)
Cl-O(2)	1.436 (7)	C(11)-C(16)	1.390 (7)	C(21)-C(26)	1.380 (7)
Cl-O(3)[b]	1.343 (7)	C(12)-C(13)	1.381 (7)	C(22)-C(23)	1.383 (7)
Cl-O(4)[b]	1.332 (7)	C(13)-C(14)	1.367 (8)	C(23)-C(24)	1.370 (9)
Cl-O(21)	1.475 (16)	C(14)-C(15)	1.383 (8)	C(24)-C(25)	1.381 (9)
		C(15)-C(16)	1.367 (8)	C(25)-C(26)	1.379 (8)
		C(10)-C(17)	1.490 (7)	C(20)-C(27)	1.489 (7)
		N(30′)-C(17)	1.479 (6)	N(30)-C(27)	1.470 (6)
		N(30)-C(30)	1.471 (6)	C(30)-C(30′)	1.503 (10)
		N(11)-H(11)	0.81 (5)	N(21)-H(21)	0.75 (5)
		C(13)-H(13)	0.90 (5)	C(23)-H(23)	0.93 (5)
		C(14)-H(14)	0.93 (6)	C(24)-H(24)	0.88 (5)
		C(15)-H(15)	0.86 (6)	C(25)-H(25)	0.89 (5)
		C(16)-H(16)	0.94 (5)	C(26)-H(26)	0.90 (5)
		C(17)-H(171)	0.90 (5)	C(27)-H(271)	0.94 (5)
		C(30)-H(301)	0.98 (5)	C(30)-H(302)	0.85 (5)

[a] The atom numbering scheme is given in Figures 6 and 7. The superscript in the atom labels indicate the symmetry operation $1 - x$, y, $^1/_2 - z$. [b] These distances should not be considered as real bond lengths because of the disorder of the ClO_4^- ion.

pyramidal. In this respect the present structure is similar to the structure of several other copper(II) compounds,[19] for which it is not clear whether the geometry has been described as five- or six-coordinated. Especially since the coordination geometry of copper in α-$Cu(NO_3)_2$[19b] shows a great similarity to the present one: four relatively short in-plane coordinating atoms (average Cu–O distance = 1.98 Å), one axial oxygen atom at 2.43 Å, and one "off the z axis" oxygen atom at 2.68 Å. In the following discussion the geometry of the present compound is considered as square pyramidal and the nitrate group N(40)–O(41)–O(42)–O(43) is considered as a monodentate ligand.

The positions of the atoms in the monodentate nitrate group are in agreement with the commonly found geometry.[20] This nitrate group is planar, the largest deviation from the least-squares plane through N(40), O(41), O(42), and O(43) being 0.004 Å. The copper atom lies 0.017 Å out of this plane. The oxygen atom bonded to copper (O(41)) has the largest N–O bond distance (1.262 (8) Å), and the O–N–O interbond angle opposite to this oxygen atom (121.9 (8)°) is slightly larger than the other two O–N–O angles (average value 119.0°).[20a] The fact that the other two angles and distances are almost equal confirms that this nitrate group has to be considered as monodentate.

The positions of the atoms of the bridging nitrate group have been determined with low accuracy (see above), but even here the oxygen atoms bonded to copper have the longest N–O distance and the smallest O–N–O angle is opposite to the noncoordinating oxygen atom. The ionic nitrate counterion and the water molecules are disordered. They are represented by 20 atom positions which were refined as partially occupied oxygen atoms (10–25%), forming clusters between the cations. There are no contacts between these oxygen atoms and nonhydrogen atoms of the cation with distances smaller than 3.0 Å.

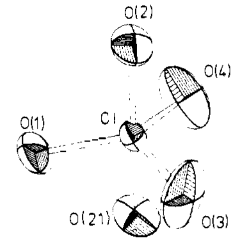

Figure 6. The disordered ClO_4^- ion in $Cu_2(EDTB)(ClO_4)_2$. O(2) and O(21) have an occupancy of $^2/_3$ and $^1/_3$, respectively.

All distances (Table VI) and angles (Table VII) in the benzimidazole groups of the ligand are normal[9,21] (see also Tables VIII and IX). The phenyl and imidazole rings are planar, the largest deviation from their least-squares planes (i.e., the planes through six phenyl atoms or five imidazole atoms) being 0.006 Å. The copper atom is lying close to the planes of the imidazole rings, the distances being 0.293 and 0.356 Å. Each imidazole ring is

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(19) (a) Hathaway, B. J. *Struct. Bonding (Berlin)* **1973**, *14*, 49–67. (b) Wallwork, S. C.; Addison, W. E. *J. Chem. Soc.* **1965**, 2925–2933.

(20) (a) Addison, C. C.; Logan, N.; Wallwork, S. C.; Garner, C. D. *Q. Rev., Chem. Soc.* **1971**, *25*, 289–322. Cameron, A. F.; Taylor, D. W.; Nuttall, R. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1603–1608. (c) McFadden, D. L.; McPhail, A. T. *Ibid.* **1975**, 1993–1998. (d) Sletten, E. S.; Erevik, G. *Acta Crystallogr. Sect. B* **1977**, *B33*, 1633–1635. (e) Thompson, L. K.; Ball, R. G.; Trotter, J. *Can. J. Chem.* **1980**, *58*, 1566–1576. (f) Nakai, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1321–1326.

(21) (a) Dik-Edixhoven, C. J.; Schenk, H.; van der Meer, H. *Cryst. Struct. Commun.* **1973**, *2*, 23–24. (b) Battaglia, L. P.; Ferrari, M. B.; Corradi, A. B.; Fava, G. G.; Pelizzi, C.; Tani, M. E. V. *J. Chem. Soc., Dalton Trans.* **1976**, 2197–2202. (c) Hamilton, G. J.; Ferraro, J. R.; Sinn, E. *Ibid.* **1979**, 515–519. (d) Udapa, M. R.; Krebs, B. *Inorg. Chim. Acta* **1979**, *32*, 1–5.

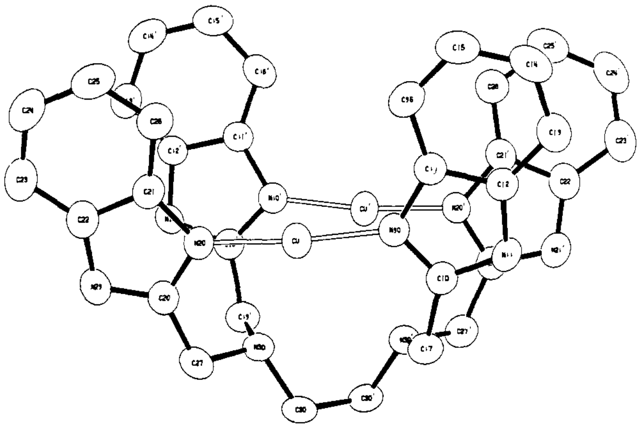

Figure 7. ORTEP drawing of the $Cu_2(EDTB)^{2+}$ cation, showing the anisotropic vibration ellipsoids (probability 50%). Hydrogen atoms have been omitted for clarity. Bond distances and angles are given in Tables VIII and IX, respectively.

coplanar with its corresponding phenyl ring (the dihedral angles are 0.89 and 0.65°, respectively). The C–H distances range from 0.86 to 1.11 Å (average C–H = 1.00 Å). The interbond angles involving C–H bonds are as expected for sp^2 and sp^3 carbon atoms. A stereodrawing of the unit cell, showing the packing of the molecules, is presented in Figure 5.

Description of the Structure of $Cu_2(EDTB)(ClO_4)_2$ (2). The $Cu_2(EDTB)^{2+}$ cation has C_2 symmetry. An ORTEP drawing of its structure is given in Figure 7. Bond distances are listed in Table VIII and interbond angles in Table IX. The coordination geometry around each Cu(I) atom is nearly linear with short[5b,22] Cu–N distances, Cu–N(10) = 1.869 (4) Å and Cu–N(20) = 1.876 (4) Å. The other contacts are Cu···N(amine) and Cu···Cu with distances of 2.774 (4) and 3.043 (1) Å, respectively, which can hardly be considered as bonds.[23] The angles between the Cu–N(amine) vector and the bonds around this nitrogen atom indicate that the lone pair on nitrogen atom N(30) does not point toward the Cu(I) atom (see Table IX). If the N–Cu–N geometry would be perfectly linear, the Cu–Cu distance would be somewhat larger than the presently found 3.043 Å. There is, however, no reason to consider this an indication of Cu–Cu interaction, since the nonlinearity can be a consequence of the ligand geometry.

Several years ago, two structures were published, which also contain Cu(I) linearly coordinated by N-donor ligands, i.e., ((diazoamino)benzene)copper(I)[24] and (dimethyltriazene)copper(I).[25] They have shorter Cu···Cu contacts of 2.45 and 2.66 Å, respectively, which might be considered as bonding contacts. In these compounds the average Cu(I)–N distances are also rather short, i.e., 1.92 and 1.87 Å, respectively. Recently the crystal structure of a complicated Cu(I)–Cu(II) cluster was reported,[26] in which Cu(I) is linearly coordinated by two imidazole groups with Cu–N distances of 1.87 and 1.88 Å (in addition, an acetonitrile nitrogen atom is present at a distance of 2.92 Å). As part of a related research project we recently solved the X-ray structure of a Cu^I compund of 1,7-bis(2-benzimidazolyl)-2,6-dithiaheptane, BBDHp. In $Cu^I(BBDHp)^+$ the Cu atom is linearly coordinated by two benzimidazole N atoms at distances of 1.918 (4) Å.[8c] The short Cu–N distances in these compounds are probably caused by the low coordination number. Cu(I)–N distances in compounds with more than two ligands normally are in the range 1.9–2.2 Å.[5b,22]

Table IX. Interbond Angles (Deg) for $Cu_2(EDTB)(ClO_4)_2$ with Their Estimated Standard Deviations in Parentheses[a]

N(10)–Cu–N(20)	170.9 (1)		
Cu–N(10)–C(11)	126.9 (3)	Cu–N(20)–C(21)	131.1 (3)
Cu–N(10)–C(10)	126.9 (3)	Cu–N(20)–C(20)	123.0 (3)
C(10)–N(10)–C(11)	106.1 (3)	C(20)–N(20)–C(21)	105.9 (4)
N(10)–C(10)–N(11)	111.5 (4)	N(20)–C(20)–N(21)	112.2 (4)
N(10)–C(10)–C(17)	124.5 (4)	N(20)–C(29)–C(27)	123.6 (4)
N(11)–C(10)–C(17)	123.9 (4)	N(21)–C(20)–C(27)	124.3 (4)
C(10)–N(11)–C(12)	108.4 (4)	C(20)–N(21)–C(22)	108.1 (4)
N(10)–C(11)–C(12)	108.7 (4)	N(20)–C(21)–C(22)	108.5 (4)
N(10)–C(11)–C(16)	131.3 (4)	N(20)–C(21)–C(26)	130.9 (4)
C(12)–C(11)–C(16)	120.0 (4)	C(22)–C(21)–C(26)	120.6 (4)
N(11)–C(12)–C(11)	105.3 (4)	N(21)–C(22)–C(21)	105.4 (4)
N(11)–C(12)–C(13)	132.6 (4)	N(21)–C(22)–C(23)	132.5 (4)
C(11)–C(12)–C(13)	122.2 (4)	C(21)–C(22)–C(23)	122.1 (5)
C(12)–C(13)–C(14)	117.0 (5)	C(22)–C(23)–C(24)	116.6 (5)
C(13)–C(14)–C(15)	121.4 (5)	C(23)–C(24)–C(25)	121.8 (5)
C(14)–C(15)–C(16)	122.0 (5)	C(24)–C(25)–C(26)	121.8 (5)
C(11)–C(16)–C(15)	117.4 (5)	C(21)–C(26)–C(25)	117.1 (5)
C(10)–C(17)–N(30′)	111.7 (4)	C(20)–C(27)–N(30)	111.3 (4)
C(17′)–N(30)–C(30)	111.0 (4)	C(27)–N(30)–C(30)	109.3 (4)
C(17′)–N(30)–C(27)	111.2 (4)	N(30)–C(30)–C(30′)	114.9 (3)
C(30)–N(30)···Cu	121.4 (3)		
C(27)–N(30)···Cu	91.8 (3)		
C(17′)–N(30)···Cu	110.4 (3)		

[a] The atom numbering scheme is given in Figure 7. The angles within the ClO_4^- anion are not listed, since the positions of O(1), O(3), and O(4) do not represent real bond lengths because of the disorder of the ClO_4^- ion.

In the present compound each copper(I) atom atom is coordinated by two imidazole groups, which are bonded via methylene groups to different amine nitrogen atoms. In this aspect this compound differs from $Cu_2(NMEDTB)(NO_3)_4{\cdot}4H_2O$, in which the copper(II) is coordinated by two imidazole groups, connected to the same amine nitrogen atom (cf. Figures 3 and 7). This explains why $Cu^I_2(L)X_2$ cannot be prepared by reduction of the corresponding $Cu^{II}_2(L)X_4$. Moreover, the two Cu(I) atoms are held close together at a short distance of 3.043 (1) Å by the molecular structure, whereas the Cu–Cu distance in $Cu_2(NMEDTB)(NO_3)_4{\cdot}4H_2O$ is as long as 5.171 (2) Å.

In the benzimidazole groups of the ligand the angles and distances are all quite normal[9,21] (see also Tables VI and VII). The phenyl and imidazole rings are planar. The largest deviation from the least-squares planes through the nonhydrogen atoms of each imidazole or phenyl ring is 0.006 Å. The dihedral angles between a phenyl ring and its corresponding imidazole ring are not significant (0.50 and 0.86°, respectively). The copper atom is lying close to the planes of the imidazole rings, the distances being as small as 0.062 and 0.089 Å, respectively.

The C–H and N–H distances are normal (see Table VIII), and the interbond angles involving N–H or C–H bonds are as expected for sp^2 or sp^3 nitrogen or carbon atoms.

The ClO_4^- ion is disordered and is present in two orientations, which are related by a pseudomirror plane, containing the Cl atom, followed by a slight rotation so that the two orientations are close to each other. They were refined on there average positions (in the mirror plane) which resulted in high thermal parameters and large anisotropies. O(2) and its analogue O(21) were refined separately with occupancies $^2/_3$ and $^1/_3$, respectively. Because averaged positions for O(1), O(3), and O(4) are so obtained, no O–Cl–O angles are given in Table IX.

A stereodrawing of the unit cell, showing the packing of the molecules, is presented in Figure 8. Both O(1) and O(2) are involved in hydrogen bonding with the cation. The distances O(2)–N(21) and O(2)–N(11′) are 3.117 (8) and 3.000 (8) Å, respectively, whereas the distance between O(1) and the N(21′) atom of a symmetry-related cation translated along the *a* axis is 3.237 (8) Å. These hydrogen bonds constitute infinite anion–cation chains in the *a* direction.

Spectroscopic Results. The electronic absorption and ESR spectral parameters of the Cu(II) compounds are listed in Tables X and XI, respectively. The compounds with general formula

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(22) (a) Lewin, A. H.; Michl, R. J.; Ganis, P.; Lepore, U. *J. Chem. Soc., Chem. Commun.* **1972**, 661–662. (b) Balt, S.; Renkema, W. E.; van Cappelveen, C.; Stam, C. H. *J. Inorg. Nucl. Chem.* **1976**, *38*, 459–462. (c) Mealli, C.; Arcus, C. S.; Wilkinson, J. C.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 711–718.

(23) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187–2189.

(24) Brown, I. D.; Dunitz, J. D. *Acta Crystallogr.* **1961**, *14*, 480–485.

(25) O'Connor, J. E.; Janusonis, G. E.; Corey, E. R. *J. Chem. Soc., Chem. Commun.* **1968**, 445–446.

(26) Agnus, Y.; Louis, R.; Weiss, R. *J. Chem. Soc., Chem. Commun.* **1980**, 876–869.

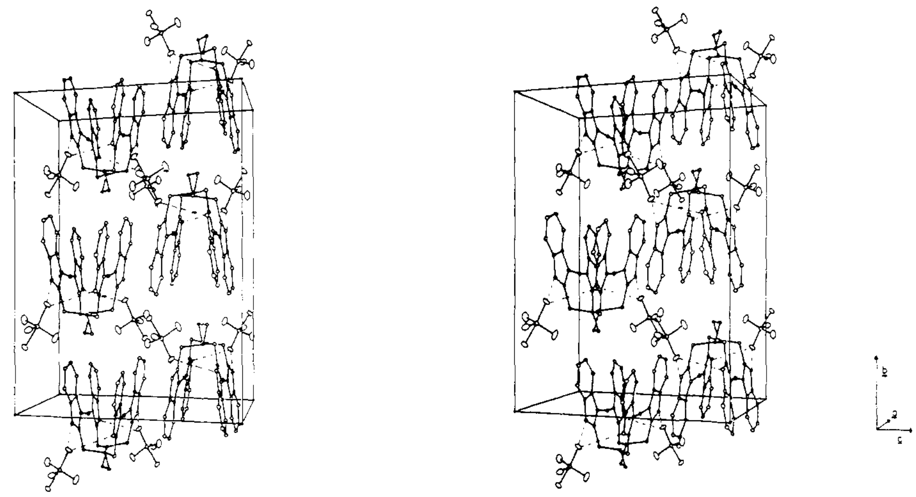

Figure 8. Stereodrawing of the unit cell of $Cu_2(EDTB)(ClO_4)_2$. Dashed lines represent hydrogen bonds.

$Cu_2(L)X_4$ show different absorption maxima in their solid-state reflectance spectra, depending on the nature of the anion. Apparently the anion or water molecules of crystallization participate in the coordination of copper, as was found earlier[9] for compounds $Cu_2(EDTB)X_4$. $Cu_2(NMEDTB)Cl_4{\cdot}H_2O$ has in its electronic spectrum a low absorption maximum with a distinct high-energy shoulder. This has frequently been considered as an indication of trigonal-bipyramidal coordination geometry for copper,[27] although examples are known of copper compounds with trigonal-bipyramidal coordination geometry and a low-energy shoulder in the electronic spectrum.[8a] The suggestion for a trigonal-bipyramidal Cu coordination in $Cu_2(NMEDTB)Cl_4{\cdot}H_2O$ is supported by the solid-state ESR spectrum. The value of g_2 is much closer to g_3 than to g_1, indicative of a d_{z^2} ground state.[28] The other $Cu_2(L)Cl_4$ and $Cu_2(L)Br_4$ compounds have a single low absorption maximum (10.500–11.800 cm^{-1}), excluding the possibility of square-planar or square-pyramidal geometry,[29] whereas pseudooctahedral coordination geometry is only compatible with these spectra, when the axial bond lengths are relatively short.[29b] The low frequencies of the maxima do not contradict a distorted trigonal-bipyramidal geometry for these compounds. The ESR spectra show only one signal. Apparently the solids are not magnetically dilute enough to yield resolved ESR spectra that allow conclusions to be drawn about the solid-state coordination geometry. In none of the ESR spectra are triplet signals characteristic of Cu dimers observed. Trigonal-bipyramidal coordination geometry can be obtained for the compounds $Cu_2(L)Cl_4$ and $Cu_2(L)Br_4$ when the ligand has a conformation similar to the one found for $[Cu_2(NMEDTB)(NO_3)_3]NO_3{\cdot}4H_2O$ (see Figure 3). The positions of O(41), O(51), O(51), and O(41) are occupied by Cl^- or Br^-, and the trigonal equatorial plane is then constituted by these halogen atoms and N(30), whereas N(10) and N(20) act as axial ligands.

Table X. Electronic Absorption Parameters[a] of $Cu(L)X_2$ and $Cu_2(L)X_4$

compd	powder reflectance	methanol soln
$Cu(NMEDTB)Cl_2{\cdot}7H_2O$	14.9 (11.0)	14.4 (~10)
$Cu(NMEDTB)Br_2{\cdot}3H_2O$	14.9 (11.0)	14.3 (9.5)
$Cu(NMEDTB)(NO_3)_2{\cdot}2H_2O$	14.3 (9.5)	14.4 (9.6)
$Cu(NMEDTB)(BF_4)_2{\cdot}H_2O$	14.3 (9.0)	14.5 (9.5)[b]
$Cu(NMEDTB)(ClO_4)_2{\cdot}2H_2O$	14.3 (9.1)	14.3 (~10)
$Cu(NBEDTB)Cl_2$	14.3 (9.9)	14.5 (9.9)[b]
$Cu(NBEDTB)Br_2{\cdot}2H_2O$	14.3 (9.8)	14.5 (9.9)[b]
$Cu(NBEDTB)(NO_3)_2{\cdot}H_2O$	15.5 (9.8)	14.4 (10.0)[c]
$Cu(NBEDTB)(BF_4)_2{\cdot}2H_2O$	14.4 (9.8)	14.5 (10.0)[b]
$Cu(NBEDTB)(ClO_4)_2{\cdot}H_2O$	14.5 (9.7)	14.6 (10.0)[b]
$Cu(NBEDTB)(CF_3SO_3)_2{\cdot}H_2O$	14.6 (9.9)	14.4 (10.0)[c]
$Cu(5\text{-}MEDTB)(NO_3)_2{\cdot}2H_2O$	14.3 (10.0)	14.4 (10.0)
$Cu(5\text{-}MEDTB)(BF_4)_2{\cdot}2H_2O$	14.3 (10.0)	14.6 (~10)
$Cu(5\text{-}MEDTB)(ClO_4)_2{\cdot}H_2O$	14.3 (10.0)	14.4 (10.0)
$Cu(5,6\text{-}DMEDTB)(NO_3)_2{\cdot}2H_2O$	14.1 (9.1)	14.4 (10.0)
$Cu(5,6\text{-}DMEDTB)(BF_4)_2{\cdot}H_2O$	14.0 (9.5)	14.3 (10.1)
$Cu(5,6\text{-}DMEDTB)(ClO_4)_2$	14.3 (9.1)	14.4 (10.0)
$Cu_2(NMEDTB)Cl_4{\cdot}H_2O$	(11.3) 8.8	14.1 (~10)
$Cu_2(NMEDTB)Br_4{\cdot}H_2O$	10.5	13.5 (11.5)
$Cu_2(NMEDTB)(NO_3)_4{\cdot}4H_2O$	14.5	14.1 (9.5)
$Cu_2(5\text{-}MEDTB)Cl_4{\cdot}3H_2O$	11.8	14.1 (10.5)[b]
$Cu_2(5\text{-}MEDTB)Br_4{\cdot}3H_2O$	11.5	14.1 (~11)[b]
$Cu_2(5\text{-}MEDTB)(NO_3)_4$	15.5	14.3 (10.0)
$Cu_2(5\text{-}MEDTB)(BF_4)_4{\cdot}9H_2O$	14.5	14.1 (10.5)
$Cu_2(5\text{-}MEDTB)(ClO_4)_4{\cdot}5H_2O$	15.0	14.1 (10.5)
$Cu_2(5,6\text{-}DMEDTB)Cl_4{\cdot}3H_2O$	11.0	14.1 (9.5)
$Cu_2(5,6\text{-}DMEDTB)Br_4{\cdot}4H_2O$	11.1	14.1 (~11)[b]
$Cu_2(5,6\text{-}DMEDTB)(NO_3)_4{\cdot}H_2O$	15.4	14.3 (~10)
$Cu_2(5,6\text{-}DMEDTB)(BF_4)_4{\cdot}6H_2O$	15.5	14.5 (9.5)
$Cu_2(5,6\text{-}DMEDTB)(ClO_4)_4{\cdot}EtOH{\cdot}H_2O$	15.4	14.5 (9.5)

[a] Frequencies in 10^3 cm^{-1}; shoulders are in parentheses. [b] Me_2SO solution. [c] Ethanol solution.

The IR spectra of the $Cu_2(L)(NO_3)_4$ compounds indicate the presence of different kinds of NO_3^- groups in all of the compounds. $Cu_2(NMEDTB)(NO_3)_4{\cdot}4H_2O$ (**1**) has three symmetric bending vibrations in the 810–835-cm^{-1} region, in accordance with the three different nitrate groups found in the crystal structure determination. Combination bands in the range 1720–1760 cm^{-1} confirm the presence of three different kinds of nitrate.[30] 5-MEDTB has a strong ligand absorption at 815 cm^{-1} which obscures the nitrate absorptions in this region for $Cu_2(5\text{-}MEDTB)(NO_3)_4$. The combination bands for this compound in the 1700–1800-cm^{-1} range are too weak to allow conclusions to be drawn about the coordination for NO_3^-. As was found[9] for $Cu_2(EDTB)(NO_3)_4$, $Cu_2(5,6\text{-}DMEDTB)(NO_3)_4{\cdot}H_2O$ has two absorptions in the range 800–850-cm^{-1}. For this compound, the presence of both uncoordinated and metal-bound nitrates is confirmed by three combination bands in the 1720–1760-cm^{-1} region. The electronic absorption and ESR spectra for the four $Cu_2(L)(NO_3)_4$ com-

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[27] (a) Ciampolini, M.; Nardi, N. *Inorg. Chem.* **1965**, *5*, 41–44. (b) Slade, R. C.; Tomlinson, A. A. G.; Hathaway, B. J.; Billing, D. E. *J. Chem. Soc. A* **1968**, 61–63. (c) Albertin, G.; Bordignon, E.; Orio, A. A. *Inorg. Chem.* **1975**, *14*, 1411–1413. (d) Thompson, L. K.; Ramaswamy, B. S.; Dawe, R. D. *Can. J. Chem.* **1978**, *56*, 1311–1318. (e) Barbucci, R.; Mastroianni, A.; Campbell, M. J. M. *Inorg. Chim. Acta* **1978**, *27*, 109–114. (f) Ray, N.; Hulett, L.; Sheahan, R.; Hathaway, B. J. *Inorg. Nucl. Chem. Lett.* **1978**, *13*, 305–308.

[28] (a) Hitchman, M. A. *J. Chem. Soc. A* **1970**, 4–9. (b) Billing, D. E.; Dudley, R. J.; Hathaway, B. J.; Tomlinson, A. A. G. *J. Chem. Soc. A* **1971**, 691–696. (c) Bew, M. J.; Dudley, R. J.; Fereday, R. J.; Hathaway, B. J.; Slade, R. C. *J. Chem. Soc. A* **1971**, 1437–1441.

[29] (a) Hathaway, B. J.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143–207. (b) Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1196–1199.

[30] Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds"; Wiley: New York, 1978.

Table **XI**. ESR Parameters of $Cu(L)X_2$ and $Cu_2(L)X_4$

	polycrystalline[a]				methanol soln[b]			
compd	g_1	g_2	g_3	A_3[c]	(g_1	g_3	A_1	A_3[c])[d]
$Cu(NMEDTB)Cl_2·7H_2O$	2.02	2.11	2.26		2.02	2.28	65	130
$Cu(NMEDTB)Br_2·3H_2O$	2.03	2.13	2.31		2.02	2.26	65	125
$Cu(NMEDTB)(NO_3)_2·2H_2O$	2.02	2.11	2.28		2.02	2.26	75	125
$Cu(NMEDTB)(BF_4)_2·H_2O$	2.04	2.09	2.27		2.03	2.28	65	125[g]
$Cu(NMEDTB)(ClO_4)_2·2H_2O$	2.03	2.12	2.30		2.02	2.26	75	125[g]
$Cu(NBEDTB)Cl_2$	2.01	2.12	2.27	125	2.03	2.27	60	125[f]
$Cu(NBEDTB)Br_2·2H_2O$	2.01	2.13	2.27	115	2.02	2.28	60	125[f]
$Cu(NBEDTB)(NO_3)_2·H_2O$	2.01	2.12	2.26	125	2.03	2.28	60	125[f]
$Cu(NBEDTB)(BF_4)_2·2H_2O$	2.01	2.11	2.27	130	2.02	2.28	60	125[f]
$Cu(NBEDTB)(ClO_4)_2·H_2O$	2.01	2.12	2.28	130	2.03	2.27	60	130[f]
$Cu(NBEDTB)(CF_3SO_3)_2·H_2O$	2.01	2.10	2.28	130	2.03	2.28	60	125[f]
$Cu(5\text{-}MEDTB)(NO_3)_2·2H_2O$	2.03	2.13	2.29	130	2.03	2.03	70	125
$Cu(5\text{-}MEDTB)(BF_4)_2·2H_2O$	2.03	2.12	2.28	130	2.04	2.28	75	125
$Cu(5\text{-}MEDTB)(ClO_4)_2·H_2O$	2.13	2.12	2.26		2.02	2.28	75	130
$Cu(5,6\text{-}DMEDTB)(NO_3)_2$	2.03	2.13	2.30	130	2.02	2.28	70	130
$Cu(5,6\text{-}DMEDTB)(BF_4)_2·H_2O$	2.04	2.13	2.29		2.01	2.28	70	130
$Cu(5,60DMEDTB)(ClO_4)_2$	2.04	2.13	2.29	135	2.02	2.28	70	130
$Cu_2(NMEDTB)Cl_4·H_2O$	2.04	2.19	2.23			*h*		
$Cu_2(NMEDTB)Br_4·H_2O$		2.16				*h*		
$Cu_2(NMEDTB)(NO_3)_4·4H_2O$	2.06	2.09	2.24			*h*		
$Cu_2(5\text{-}MEDTB)Cl_4·3H_2O$		2.13				*g, h*		
$Cu_2(5\text{-}MEDTB)Br_4·3H_2O$		2.12				*g, h*		
$Cu_2(5\text{-}MEDTB)(NO_3)_4$	2.06	2.07	2.24			*h*		
$Cu_2(5\text{-}MEDTB)(BF_4)_4·9H_2O$		*e*				*h*		
$Cu_2(5\text{-}MEDTB)(ClO_4)_4·5H_2O$		2.09	2.19			*h*		
$Cu_2(5,6\text{-}DMEDTB)Cl_4·3H_2O$		2.15				*h*		
$Cu_2(5,6\text{-}DMEDTB)Br_4·4H_2O$		2.13				*g, h*		
$Cu_2(5,6\text{-}DMEDTB)(NO_3)_4·H_2O$		2.07	2.24			*h*		
$Cu_2(5,6\text{-}DMEDTB)(BF_4)_4·6H_2O$		2.09	2.24			*h*		
$Cu_2(5,6\text{-}DMEDTB)(ClO_4)_4·EtOH·H_2O$		2.07	2.26			*h*		

[a] Room temperature. [b] Liquid-nitrogen temperature. [c] A is given in 10^{-4} cm^{-1}. [d] The values of g_2 and A_2 could not be determined accurately; $g_2 \approx 2.11$. [e] See text. [f] Ethanol solution. [g] Me_2SO solution. [h] A mixture of signals is observed.

pounds are all similar and suggest either square-pyramidal or tetragonal geometry. Square-pyramidal geometry has been confirmed for $[Cu_2(NMEDTB)(NO_3)_3]NO_3·4H_2O$ by the crystal structure determination. The other three $Cu_2(L)(NO_3)_4$ compounds, which have other nitrate bands in their IR spectra, might have a related structure with two bidentate coordinating and two ionic nitrates.

Low-temperature susceptibility measurements indicate no Cu–Cu interaction for **1** despite the bridging nitrate ($\mu_{eff} = 1.99$ μ_B/copper at 4.2 K). No triplet signal is observed in the EPR spectrum. The reason for this may be the square-pyramidal coordination geometry of the copper ions; this geometry results in a $d_{x^2-y^2}$-based ground state, so that the unpaired electron will have very little or no density in orbitals pointing toward the bridging nitrate (*z* direction). Only weak coupling can then occur through this nitrate bridge.[32] The Q-band EPR spectrum of **1** shows a few additional low-intensity signals in the $g_\perp$ region. These signals could arise from slightly different coordinated Cu ions caused by the disorder of the nitrate bridge. Such differences in the geometry of the copper site occur for the different positions of this nitrate.

A geometry similar to the one found for **1** is proposed for the compounds $Cu_2(L)(ClO_4)_4·nH_2O$ and $Cu_2(L)(BF_4)_4·nH_2O$. One or two water molecules are probably bound to each copper, since apparently the ClO_4^- and BF_4^- ions are not coordinating, as only single asymmetric stretching vibrations are found near 1100 cm^{-1}.[31] In the EPR spectra of these compounds $g_\parallel$ is not resolved and only two *g* values are listed in Table XI. The chemical environment of each of the two copper ions in a single binuclear compound are not necessarily identical.

The ESR spectrum of $Cu_2(5\text{-}MEDTB)(BF_4)_4·3H_2O$, with g_3 split into at least five components, suggests the presence of two different copper species, similar to that for $Cu_2(EDTB)(ClO_4)_4·H_2O$.[9] No hyperfine structure is observed in the g_3 region for any of the other $Cu_2(L)X_4$ compounds, probably due to magnetic exchange narrowing.

In none of the ESR spectra is a triplet signal observed, and susceptibility measurements down to 4.2 K indicate only weak Cu–Cu interactions. μ_{eff} at 4.2 K varies between 1.53 and 1.72 μ_B/copper for this class of compounds with the exception of compounds $Cu_2(L)B_4$, which show a somewhat stronger interaction, as seen from values of $\mu_{eff} \approx 1.25$ μ_B at 4.2 K.

In methanol or Me_2SO solution, the compounds $Cu_2(L)X_4$ apparently decompose into $Cu(L)^{2+}$ ions with the loss of one of the copper ions, as is proved by the solution electronic absorption spectra and the frozen-solution ESR spectra (Tables X and XI).

The electronic absorption spectra and the ESR spectra in the solid state, as well as in solution, of all other compounds of composition $Cu(L)X_2$ are almost identical with the spectra found for $Cu(EDTB)X_2$.[9] These spectra are in agreement with the structure found for $Cu(EDTB)(BF_4)(BF_3OC_2H_5)$, which is best described as a distorted bicapped square pyramid.[9] Most probably, the copper coordination is the same for all the $Cu(L)X_2$ compounds.

The IR spectra of the Cu(I) compounds $Cu_2(L)(ClO_4)_2$ are practically identical with the spectra of the corresponding $Cu_2(L)(BF_4)_2$ compounds; only the anion peaks are different. For L = EDTB, 5-MEDTB, and 5,6-DMEDTB, weak symmetric vibrations ν_1 are found at 930 cm^{-1} in the perchlorate compounds and at 765 cm^{-1} in the tetrafluoroborate compounds (in $Cu_2(EDTB)(BF_4)_2$ this peak is hidden under a ligand band). Although this observation might suggest anion coordination to the copper atom,[30] hydrogen bonding of the ClO_4 and BF_4 to neighboring N–H groups is more likely. This is confirmed by the much lower intensity of these "forbidden" bonds in the corresponding NMEDTB compounds, where hydrogen bonding with N–H groups is not possible. Many differences are found between the IR spectra of $Cu^I_2(L)X_2$ and the corresponding $Cu^{II}_2(L)X_4$ compounds, in agreement with different ligand conformations for the two classes of compounds.

Reactivity of Cu^I Compounds and the Relation to the Proposed Hemocyanin Structures. It is tempting to compare the structure

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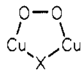
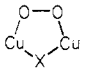
[31] Hathaway, B. J.; Underhill, A. E. *J. Chem. Soc.* **1961**, 3091–3096.

[32] Chauvel, J.; Girerd, J. J.; Jeannin, Y.; Kahn, O.; Lavigne, G. *Inorg. Chem.* **1979**, *18*, 3015–3020.

of the present copper compounds with those proposed for deoxyhemocyanin and oxyhemocyanin from spectroscopic and EXAFS data.[2] EXAFS studies on two different oxyhemocyanins suggested the presence of dimeric copper sites with Cu–Cu separations of 3.55[2c] or 3.67 Å[2a] with a possible bridging



unit, in which the bridging ligand X could be an oxygen donor. The coordination sphere is completed by two[2c] or three[2a] imidazole ligands. The very strong magnetic interaction suggests that the magnetic orbitals on each of the copper atoms must be in close contact or in the plane of the



unit. In deoxyhemocyanin either the bridging ligand X or one of the imidazole residues is removed from the coordination sphere around copper, and the resulting Cu(I) ions are two coordinated[2c] or three coordinated.[2a] The copper–copper distance in this case is reported to be 3.37 Å. This distance is only 10% larger than the Cu···Cu distance in $Cu^I_2(EDTB)^{2+}$, whereas the coordination geometry most likely is very similar (see Figure 7). The compound $[Cu^{II}_2(NMEDTB)(NO_3)_3]^+$ on the other hand has a much more open structure (Figure 3) which has no resemblance to the structure proposed for oxyhemocyanin. In order to obtain a better understanding of the reactivity of the Cu(I) compounds and to see whether or not Cu(II) compounds of a different structure could be obtained by oxidation of the $Cu^I_2(EDTB)$ species, a study of the reactivity of the several $[Cu^I_2(L)]^{2+}$ species was undertaken. The first results of this investigation are described in this paper. A future communication will deal with the details of this study.[33]

Oxygenation reactions of the Cu^I compounds were carried out in Me_2SO solution at 25 °C. The colorless solution of $Cu_2(EDTB)(ClO_4)_2$ in Me_2SO (0.05 mmol in 10 mL) showed an uptake of dioxygen of 0.96 ± 0.05 mmol/Cu^I_2. With $[Cu^I_2(NMEDTB)](ClO_4)_2$ the uptake was 0.97 ± 0.05 mmol/Cu^I_2. This suggests the formation of a CuO_2Cu species. The resulting solution is green with an electronic spectrum characteristic for Cu(II) (maximum at 14 500 cm^{-1} with a molar extinction coefficient of 80 L mol^{-1} cm^{-1}/Cu. Flushing the solution with dinitrogen, however, does not decolorize the solution (although a decrease in the intensity of color occurs), indicating that the reaction with oxygen is not completely(?) reversible. Addition of ascorbic acid or hydrazine results in a complete decolorization of the solution. When small amounts of the reducing agent are used, this cycle can be repeated three to five times. Methylation of the EDTB ligand has no effect on the reaction with oxygen, showing that acid hydrogens, which are present in nonmethylated EDTB only, are not responsible for the reaction with oxygen. In subsequent experiments it was shown that also variations in the counterion has no effect upon the reaction with oxygen. Attempts to isolate a solid oxygen adduct, however, have remained unsuccessful. In Raman spectra of Me_2SO solutions of the oxygenated product, no bands could be found that could be assigned to coordinated O_2 (neither in the 1125-cm^{-1} region nor in the 750-cm^{-1} region, where new bands should be expected). If present, these bands could be hidden by the strong solvent bands (near 1100 cm^{-1}) or ligand bands (725–775 cm^{-1}). Frozen-solution EPR spectra (in Me_2SO/MeOH) of an oxygenated solution of $Cu^I_2(NMEDTB)^{2+}$ are very similar to those of $[Cu(NMEDTB)](NO_3)_2$. Apparently the dimeric unit decomposes after the reaction with oxygen. No EPR signal due to the other copper ion could be detected. Reaction with the solvent might have resulted in an EPR-inactive species. Apart from Me_2SO, oxygenation reactions were carried out in other solvents such as MeOH, CH_3CN, and DMF. The best reproducible results were obtained with Me_2SO, however.

At the present no definite proof is available for the existence of an oxygenated reaction product having the copper ions close together. If such a species is formed at all, the resulting product rapidly decomposes, producing the species $[Cu(L)]^{2+}$, resulting from the removal of one copper ion from the reaction site. This might indicate that the present chelate system is still too flexible to be a good structural model for both the Cu(I) and the Cu(II) states in hemocyanin. On the other hand, the fact that a colorless solution can be regenerated after reduction in situ suggests that the initial product indeed has a dioxygen bridge between the two copper ions.

Concluding Remarks

The present study has shown that chelates containing imidazole groups held together in special orientations are good ligands for both copper(I) and copper(II) compounds. The dimeric compounds of formula $Cu^I_2(L)(anion)_2$ are good structural models for the active site in hemocyanin. The reactivity toward dioxygen is promising and suggests that derivatives of such chelating systems might possibly mimick the active site even better. Upon oxidation of the copper(I) compounds of formula $[Cu^I_2(L)]^{2+}$, apparently the species $Cu(L)^{2+}$ are formed, rather than $Cu_2(L)^{4+}$. The compounds $[Cu_2(L)^{4+}](anion^-)_4$ prepared from Cu(II) salts and the ligands do have a different, open structure not related to the oxygenated form of hemocyanin. Further work in this area will deal with new ligands containing different constraints in the chelate geometry and with a detailed investigation of the reactions with O_2, NO, CO, and O_2^- and possible catalytic oxidation reactions.

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Registry No. 1, 81643-45-0; **2**, 77009-43-9; $Cu(NMEDTB)Cl_2$, 81625-52-7; $Cu(NMEDTB)Br_2$, 81625-53-8; $Cu(NMEDTB)(NO_3)_2$, 81625-55-0; $Cu(NMEDTB)(BF_4)_2$, 81625-56-1; $Cu(NMEDTB)(ClO_4)_2$, 81625-57-2; $Cu(NBEDTB)Cl_2$, 81625-58-3; $Cu(NBEDTB)Br_2$, 81625-59-4; $Cu(NBEDTB)(NO_3)_2$, 81625-61-8; $Cu(NBEDTB)(BF_4)_2$, 81625-62-9; $Cu(NBEDTB)(ClO_4)_2$, 81625-63-0; $Cu(NBEDTB)(CF_3SO_3)_2$, 81625-64-1; $Cu(5\text{-}MEDTB)(NO_3)_2$, 81625-66-3; $Cu(5\text{-}MEDTB)(BF_4)_2$, 81625-67-4; $Cu(5\text{-}MEDTB)(ClO_4)_2$, 81643-46-1; $Cu(5,6\text{-}DMEDTB)(NO_3)_2$, 81625-69-6; $Cu(5,6\text{-}DMEDTB)(BF_4)_2$, 81625-70-9; $Cu(5,6\text{-}DMEDTB)(ClO_4)_2$, 81625-71-0; $Cu_2(5\text{-}MEDTB)(NO_3)_4$, 81643-48-3; $Cu_2(5,6\text{-}DMEDTB)(NO_3)_4$, 81656-27-1; $Cu_2(EDTB)(ClO_4)_2$, 77009-43-9; $Cu_2(NMEDTB)(BF_4)_2$, 81625-73-2; $Cu_2(NMEDTB)(ClO_4)_2$, 81625-74-3; $Cu_2(5\text{-}MEDTB)(BF_4)_2$, 81625-76-5; $Cu_2(5\text{-}MEDTB)(ClO_4)_2$, 81625-77-6; $Cu_2(5,6\text{-}DMEDTB)(BF_4)_2$, 81625-79-8; $Cu_2(5,6\text{-}DMEDTB)(ClO_4)_2$, 81625-80-1; NMEDTB, 81624-53-4; NBEDTB, 81624-54-6; 5-MEDTB, 81624-55-7; 5,6-DMEDTB, 81643-39-2.

Supplementary Material Available: Listings of observed and calculated structure amplitudes for $Cu_2(NMEDTB)(NO_3)_4(H_2O)_4$ (**1**) and $Cu_2(EDTB)(ClO_4)_2$ (**2**) (17 pages). Ordering information is given on any current masthead page.

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