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Coordination Compounds of Chelating Ligands Containing Imidazole Groups. Synthesis and Characterization of Copper(I) and Copper(II) Complexes of *N,N,N′,N′*-Tetrakis[(2-benzimidazolyl)methyl]-1,2-ethanediamine and the X-ray Structure of an [*N,N,N′,N′*-Tetrakis[(2-benzimidazolyl)methyl]-1,2-ethanediamine]copper(II) Cation[†]

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Copper(II) and copper(I) coordination compounds have been prepared and characterized with *N,N,N′,N″*-tetrakis[(2-benzimidazolyl)methyl]-1,2-ethanediamine (EDTB), a chelating ligand containing four benzimidazole groups and two amine nitrogens. The compounds have as formulas Cu(EDTB)(anion)$_2$, Cu$_2$(EDTB)(anion)$_4$, and Cu$^I{}_2$(EDTB)(anion)$_2$. The electronic spectra of Cu^{II}(EDTB)X$_2$ compounds suggest either a cis-distorted octahedral or a square-pyramidal coordination geometry. ESR spectra are consistent with a square-pyramidal geometry. The crystal structure of Cu(EDTB)(BF$_4$)(BF$_3$OC$_2$H$_5$)·H$_2$O has been solved. The compound crystallizes in the space group $C2/c$, with a = 14.402 (2) Å, b = 14.955 (2) Å, c = 18,.846 (2) Å, β = 101.17 (1)°, V = 3982.3 Å^3, Z = 4, d_m = 1.42 (1) g cm^{-3}, and d_x = 1.44 g cm^{-3}. The intensities of 3645 independent reflections were measured on an automatic diffractometer. The structure was solved by heavy-atom methods and refined by using least-squares techniques to a residual R value of 0.065 for 1727 reflections with $I > 2\sigma(I)$. The geometry of the coordination polyhedron around the copper atom in this compound can be described as derived from a cis-distorted octahedron having C_2 symmetry with four short Cu–N (imidazole) bonds (1.986 (7) and 2.039 (8) Å) and two very long Cu–N (amine) bonds (2.499 (8) Å). The presence of the BF$_3$(OC$_2$H$_5$)$^-$ anion in this compound is ascribed to partial decomposition of the BF$_4^-$ ion during the preparation of the crystals. This compound is the first example in which the boron-containing decomposition product of BF$_4^-$ is found to be present in the crystalline solid. The Cu^I EDTB compounds contain two copper ions coordinated to the same EDTB ligand. ESR and electronic spectra of the compounds Cu$^{II}{}_2$(EDTB)(anion)$_4$ indicate different coordination geometries in the presence of different anions. Within one compound the two copper ions most probably have different coordination numbers and geometries, as deduced from ESR.

Introduction

Copper-containing proteins occur widely in nature, displaying different properties[1] and functioning as an electron carrier,[2] oxidase,[3] oxygen carrier[4] or superoxide dismutase.[5]

Although the crystal structure is known for only a few of these proteins,[6] imidazole is believed to play an important role in the coordination chemistry of the copper ion in most of them.[3b,4c,7] An irregular metal environment has been suggested[8] as being responsible for the unusual redox properties[9] of some copper enzymes. The study of low molecular weight copper(I) and copper(VI) complexes mimicking the chemical and physical properties of these proteins will lead to a better understanding of the active site structures and the reaction mechanisms of these copper-containing enzymes[1c,10] (some of which may never be crystallized[11]).

In order to simulate a strained low-symmetry metal environment, as can be imposed by the protein backbone structure,[12] we are investigating the coordination chemistry of copper with synthetic chelating ligands, containing rigidly incorporated imidazole groups.[13]

In this paper we report the synthesis and properties of copper(I) and copper(II) complexes of *N,N,N′,N′*-tetrakis[(2-benzimidazolyl)methyl]-1,2-ethanediamine (abbreviated EDTB) as well as the crystal structure of one of the copper(II) compounds. Some preliminary results have been communicated earlier.[14]

Experimental Section

Preparations. The free ligand *N,N,N′,N′*-tetrakis[(2-benzimidazolyl)methyl]-1,2-ethanediamine (EDTB) was synthesized as described before.[14a] All other chemicals were commercially available and used without further purification.

Cu(EDTB)X$_2$, (X = Br, NO$_3$, BF$_4$, ClO$_4$) and Cu(EDTB)Cl$_2$·C$_2$H$_5$OH·H$_2$O. EDTB (1 mmol) was dissolved in 25 mL of warm absolute ethanol and filtered into a solution of 1 mmol of the appropriate copper salt in 10 mL of absolute ethanol containing 5 mL of triethyl orthoformate (for dehydration). The complexes crystallized

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[†] Dedicated to the memory of Dr. W. L. Groeneveld, who died on November 6, 1980.

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Table I. Colors and Analytical Data for the Copper Coordination Compounds with the Ligand EDTB

		anal.,[a] %			
compd	color	Cu	C	H	N
$Cu(EDTB)Cl_2 \cdot EtOH \cdot H_2O$	light green	7.9 (8.15)	54.80 (55.49)	5.13 (5.12)	17.91 (17.98)
$Cu(EDTB)Br_2$	light green	7.5 (7.90)	50.39 (50.79)	4.07 (3.98)	17.39 (17.42)
$Cu(EDTB)(NO_3)_2$	light green	8.1 (8.27)	52.30 (53.15)	3.90 (4.17)	22.10 (21.88)
$Cu(EDTB)(ClO_4)_2$	light blue	7.5 (7.53)	48.43 (48.43)	3.81 (3.83)	16.61 (16.61)
$Cu(EDTB)(BF_4)_2$	light blue	7.6 (7.77)	50.00 (49.93)	3.80 (3.94)	16.80 (17.13)
$Cu(EDTB)(BF_4)(BF_3OC_2H_5) \cdot H_2O$[b]	light blue	[c]	49.73 (50.16)	4.40 (4.56)	15.88 (16.25)
$Cu_2(EDTB)Cl_4 \cdot 3H_2O$	yellow	13.7 (13.49)	45.85 (45.19)	4.31 (4.24)	15.21 (15.50)
$Cu_2(EDTB)Br_4 \cdot 2H_2O$	dark green	11.9 (11.95)	38.10 (38.40)	3.40 (3.41)	13.10 (13.17)
$Cu_2(EDTB)(NO_3)_4$	green	12.5 (13.30)	42.93 (42.72)	3.41 (3.35)	20.25 (20.52)
$Cu_2(EDTB)(ClO_4)_4 \cdot 4H_2O$	dark green	10.6 (10.79)	34.11 (34.63)	3.58 (3.42)	11.60 (11.90)
$Cu_2(EDTB)(BF_4)_2$	white	14.3 (14.41)	46.45 (46.33)	3.75 (3.66)	15.93 (15.89)
$Cu_2(EDTB)(ClO_4)_2$	white	13.9 (14.02)	45.25 (45.04)	3.71 (3.56)	15.73 (15.45)

[a] Calculated values are in parentheses. [b] %B, 2.55 (2.51); %F, 15.7 (15.42). [c] No copper analysis was carried out for these crystals.

when the mixture was allowed to stand overnight; they were filtered off, washed with cold absolute ethanol and diethyl ether, and dried in vacuo at 60 °C.

$Cu_2(EDTB)X_4 \cdot nH_2O$ ($X = Cl$, $n = 3$; $X = Br$, $n = 2$; $X = NO_3$, $n = 0$; $X = ClO_4$, $n = 4$). EDTB (1 mmol) 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 triethyl orthoformate. The complexes crystallized when the mixture was allowed to stand overnight; they were filtered off, washed with cold absolute ethanol and diethyl ether, and dried in vacuo at 60 °C. **Caution**: $Cu_2(EDTB)(ClO_4)_4 \cdot 4H_2O$ is both shock and heat sensitive.

$Cu_2(EDTB)X_2$ ($X = ClO_4$, BF_4). $Cu(H_2O)_6X_2$ (1.1 mmol) was dissolved in 10 mL of acetonitrile under nitrogen; 2 mmol of copper powder was added to the solution, which was stirred and slightly warmed for about 10 min until the blue color had completely disappeared. The resulting Cu(I) solution was filtered into a solution of EDTB in hot absolute ethanol (1 mmol in 100 mL), which was kept under nitrogen. This yielded a white precipitate immediately. The mixture was slowly cooled to room temperature, and the product was filtered off under nitrogen and washed with cold absolute ethanol and diethyl ether. Drying in vacuo at 60 °C resulted in white powders which were not air sensitive.

Crystals of $Cu(EDTB)(BF_4)(BF_3OC_2H_5) \cdot H_2O$. EDTB (0.25 mmol) was dissolved in 20 mL of absolute ethanol and filtered; 0.25 mmol of $Cu(H_2O)_6(BF_4)_2$ was dissolved in 3 mL of absolute ethanol and filtered. The two filtrates were mixed, and after the mixture was allowed to stand for 2 weeks, blue, single crystals were isolated. Part of the BF_4^- ions appear to have decomposed (see Discussion).

Physical Measurements. Infrared spectra in the range 600–4000 cm^{-1} were recorded on a Perkin-Elmer 297 spectrophotometer; samples were either mulled in Nujol (between KBr pellets) or pelleted in KBr. Electron spin resonance spectra at X-band and Q-band frequencies were obtained with Varian E-9 and E-112 spectrometers, either as powered solids at room temperature or as frozen methanol to dimethyl sulfoxide solutions at −196 °C. Electronic spectra (30000–4000 cm^{-1}) were recorded in methanol or dimethyl sulfoxide on a Beckman DK-2A ratio recording spectrophotometer and as solids on a similar instrument fitted with a reflectance attachment. Low-temperature magnetic susceptibility measurements were performed on a PAR vibrating-sample magnetometer in the 4.2–15.0 K range. Copper analyses were carried out by using standard EDTA titrations;[15] all other elemental analyses were performed by the Organisch Chemisch Instituut TNO Utrecht, The Netherlands, or by Dr. Pascher, Bonn, Germany. Analytical data of the compounds are summarized in Table I.

X-ray Methods. A crystal of $Cu(EDTB)(BF_4)(BF_3OC_2H_5) \cdot H_2O$ of approximate dimensions 0.30 × 0.15 × 0.12 mm was sealed in a 0.3-mm, thin-walled, glass capillary. Preliminary Weissenberg photographs indicated the Laue symmetry $2/m$, and the systematic absences $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$ are consistent with Cc or $C2/c$ as a possible space group. The calculated density of 1.44 g cm^{-3} for $C_{36}H_{39}B_2CuF_7N_{10}O_2$ agrees with the experimental value of 1.42 (1) g cm^{-3} (flotation in $CHCl_3$ and hexane) for $Z = 4$. Precise lattice constants were determined by least-squares refinement of the angular settings of 24 reflections with $10° < \theta < 13°$. The resulting constants are $a = 14.402$ (2) Å, $b = 14.955$ (2) Å, $c = 18.846$ (2) Å, $\beta = 101.17$ (1)°, and $V = 3982.3$ Å^3. Intensity data were collected on a Nonius CAD-4 diffractometer (ω–θ scans) for all reflections with $2° < \theta < 25°$ and with $k > 0$ and $l \geq 0$ by using graphite-monochromated Mo Kα radiation. The scanning rate was adjusted to the required precision of $I/\sigma(I) > 50$, with a maximum scan time of 150 s/reflection. Each reflection was measured in 96 steps. Sixteen steps at each end of the scan were considered as background. Intensities, I, and their estimated 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 intensity of a suitable reflection at different azimuthal positions suggested that no absorption correction was necessary (maximal variation was 6%; $\mu = 6.6$ cm^{-1}). The intensities of 3763 reflections were measured, 3645 of which were symmetry independent, and 1727 were considered as observed ($I > 2\sigma(I)$). The measured intensities were corrected for Lorentz and polarization effects.

Structure Determination. The positions of many Harker peaks in the three-dimensional Patterson synthesis suggested that the centrosymmetric space group $C2/c$ was the correct choice. From the Patterson map the position of the unique copper atom was determined to be 0.0, 0.03, 0.25. This position was refined together with a scale factor in a least-square procedure to give a residual R value of 0.39 where $R = \sum||F_c| - |F_o||/\sum|F_o|$. A subsequent Fourier synthesis showed the positions of the nitrogen atoms coordinated to the copper. Two more cycles of full-matrix least-squares refinement and difference Fourier maps gave the positions of all other nonhydrogen atoms of the cation and of the tetrafluoroborate anion. No separate ethanol molecule, the presence of which was expected from initial C, H, and N analyses (see Table I), could be found; however, the difference Fourier map did show two significant peaks (not three) near the tetrafluoroborate anion. Inspection of angles and distances suggested that $C_2H_5OBF_3^-$ and BF_4^- were superimposed in the maps. Additional analyses for boron and fluorine did indeed indicate that decomposition of BF_4^- had occurred (boron/fluorine ratio of 2:7) and suggested the molecular composition $Cu(EDTB)(BF_4)(BF_3OC_2H_5) \cdot H_2O$ (see Table I). Subsequent block-diagonal least-squares refinement was carried out with use of unit weights; all the atoms were refined with anisotropic thermal motion parameters. The C_2H_5O part of $C_2H_5OBF_3^-$ and the F atom of BF_4, which is at nearly the same position as the oxygen atom in $C_2H_5OBF_3^-$, were given an occupancy of 0.5. Hydrogen atoms were placed at calculated positions (C–H = 0.95 Å and N–H = 0.87 Å[16]) and were given isotropic thermal parameters of 4.0 Å^2; no hydrogen atoms were included for the ethoxy part of the anion. This resulted in a final R value of 0.065 (276 parameters). In the final difference Fourier map some electron density was found near the anion

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Table II. Positional Parameters ($\times 10^4$) and Anisotropic Thermal Parameters[a] ($\times 10^3$) of Nonhydrogen Atoms[b] of $Cu(EDTB)(BF_4)(BF_3OC_2H_5)\cdot H_2O$ with their Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
Cu	0	332 (1)	2500	34 (1)	48 (1)	29 (1)	0	0	7 (1)
N(10)	259 (4)	496 (4)	1511 (4)	42 (4)	49 (5)	30 (3)	1 (7)	4 (7)	16 (6)
N(11)	209 (5)	1266 (5)	506 (4)	57 (5)	49 (5)	25 (3)	−1 (8)	18 (7)	5 (7)
N(30)	−933 (5)	1700 (5)	2062 (4)	44 (4)	50 (5)	41 (1)	2 (8)	−11 (8)	16 (7)
C(11)	−142 (5)	1165 (5)	1108 (5)	45 (5)	38 (5)	37 (5)	−9 (9)	4 (8)	3 (8)
C(12)	898 (6)	622 (6)	502 (5)	47 (5)	39 (5)	30 (4)	−14 (8)	−5 (8)	11 (7)
C(13)	918 (5)	126 (6)	1135 (4)	36 (5)	51 (6)	35 (5)	−11 (8)	−8 (8)	−1 (7)
C(14)	−909 (6)	1740 (6)	1288 (5)	53 (6)	55 (6)	46 (6)	6 (10)	17 (10)	25 (9)
C(15)	1508 (7)	−591 (6)	1278 (1)	66 (6)	58 (7)	39 (5)	24 (10)	−3 (9)	31 (9)
C(16)	2093 (7)	−775 (7)	796 (5)	70 (7)	65 (7)	59 (7)	29 (11)	−13 (11)	42 (11)
C(17)	2092 (7)	−251 (8)	191 (5)	69 (7)	80 (8)	53 (6)	−7 (13)	−27 (12)	62 (10)
C(18)	1486 (7)	452 (7)	34 (4)	70 (6)	68 (7)	36 (5)	−14 (12)	−1 (11)	34 (9)
C(31)	−532 (7)	2485 (6)	2455 (5)	69 (6)	42 (6)	66 (7)	9 (10)	2 (10)	38 (11)
C(24)	−1868 (6)	1441 (7)	2188 (5)	49 (6)	64 (7)	47 (6)	31 (10)	−2 (10)	19 (9)
N(20)	−1338 (4)	−102 (4)	2092 (3)	37 (4)	51 (5)	37 (4)	1 (7)	−7 (7)	3 (6)
N(21)	−2854 (4)	132 (5)	1630 (4)	28 (4)	81 (6)	53 (5)	13 (8)	9 (9)	9 (7)
C(21)	−2092 (5)	482 (6)	1978 (4)	35 (4)	61 (7)	38 (5)	15 (9)	11 (9)	17 (7)
C(22)	−2673 (6)	−740 (6)	1491 (4)	38 (5)	66 (6)	37 (5)	−21 (9)	−2 (9)	8 (8)
C(23)	−1727 (6)	−896 (6)	1785 (4)	43 (5)	52 (6)	28 (4)	−15 (9)	3 (8)	22 (8)
C(25)	−3232 (7)	−1406 (8)	1097 (5)	53 (6)	98 (9)	64 (7)	−52 (13)	15 (13)	0 (11)
C(26)	−2795 (8)	−2210 (8)	1031 (6)	91 (9)	82 (9)	72 (8)	−96 (15)	−12 (14)	8 (13)
C(27)	−1854 (8)	−2362 (7)	1337 (6)	95 (9)	52 (7)	87 (9)	−28 (13)	−26 (13)	46 (14)
C(28)	−1307 (7)	−1716 (7)	1719 (5)	59 (6)	63 (7)	56 (6)	−26 (11)	2 (11)	3 (10)
B	4255 (10)	1740 (11)	4427 (9)	55 (9)	111 (13)	108 (13)	−43 (18)	−59 (21)	−33 (17)
F(1)	3342 (5)	1930 (6)	4357 (5)	88 (6)	126 (7)	199 (9)	23 (11)	−71 (14)	−13 (12)
F(2)	4827 (7)	2434 (6)	4426 (5)	169 (9)	126 (8)	221 (11)	−151 (14)	−197 (15)	192 (16)
F(3)	4482 (8)	1596 (9)	5207 (6)	175 (11)	228 (13)	163 (10)	50 (19)	−76 (19)	−8 (16)
F(4)[c]	4453 (19)	1119 (20)	4086 (16)	232 (27)	350 (35)	349 (37)	−329 (51)	−613 (64)	219 (51)
C(40)[c]	5403 (20)	57 (25)	3384 (17)	97 (21)	203 (37)	150 (28)	−152 (47)	−152 (53)	64 (39)
C(41)[c]	5354 (15)	588 (21)	4078 (19)	26 (11)	132 (27)	222 (35)	22 (29)	22 (49)	18 (32)
O[c]	4415 (9)	947 (8)	4073 (8)	30 (6)	25 (7)	115 (12)	6 (11)	−41 (15)	−7 (14)

[a] The thermal parameters (Å^2) 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 Figure 1. [c] These atoms have a population of 0.5.

(peaks <0.98 eÅ^{-3}). This is probably caused by disordered water molecules which occupy the holes near BF_4^- when no ethoxy group is present. In the final stage of the refinement all parameter shifts of the cation were less than 20% of their standard deviations; shifts in the parameters of the anions were less than their standard deviations. Examination of the values of $|F_o|$ and $|F_c|$ suggested that no secondary extinction correction was necessary, and none was applied. Atomic scattering factors for neutral atoms were taken for all nonhydrogen atoms from ref 17 and used with correction for the real part of the anomalous dispersion, $\Delta f'$; those for hydrogen were taken from Stewart et al.[18] Final atomic parameters for the non-hydrogen atoms are given in Table II; those for the hydrogen atoms are listed in Table III.[19] A list of observed and calculated structure factors is given in Table IV.[19]

Results and Discussion

General Methods. Three classes of compounds were prepared with the ligand EDTB and with the general formulas $Cu^{II}(EDTB)X_2$, $Cu^{II}_2(EDTB)X_4$, and $Cu^{I}_2(EDTB)X_2$. These compounds are listed in Table I together with their colors and analytical data. Despite several attempts (e.g., with excess copper), no compound with formula $Cu^{II}_2(EDTB)(BF_4)_4$ could be synthesized. With Cu(I) only the two compounds mentioned in the table were prepared. With Cl^-, Br^-, or NO_3^- as anions, gelationous air-sensitive white precipitates were isolated; no reproducible analyses were obtained. Reaction of Cu(I) with EDTB in a ratio of 1:1 resulted in the precipitation of the free ligand. $Cu^{I}_2(EDTB)(ClO_4)_2$ and $Cu^{I}_2(EDTB)(BF_4)_2$ can only be prepared by reaction of the ligand with the copper(I) salt in solution and not by chemical reduction of $Cu^{II}_2(EDTB)^{4+}$; this might indicate different structures for $Cu^{II}_2(EDTB)^{4+}$ and $Cu^{I}_2(EDTB)^{2+}$. The IR spectra of the Cu(I) compounds are practically identical (except for the anion frequencies). The spectra resemble the spectrum of the free ligand, but many bands are shifted or split. The crystal structure determination of one of these Cu(I) compounds is in progress.[20] In the following section the structure of one

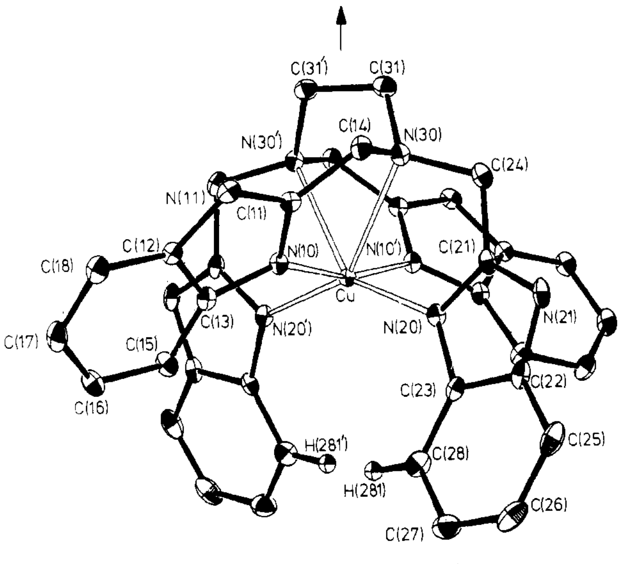

Figure 1. ORTEP drawing of the $Cu(EDTB)^{2+}$ cation in $Cu(EDTB)(BF_4)(BF_3OC_2H_5)\cdot H_2O$ showing the anisotropic vibration ellipsoids (probability 11%). Hydrogen atoms have been omitted for clarity, except the two H atoms in close contact, H(281) and H(281'). Bond distances and angles are given in Table V.

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Table V. Interatomic Distances (Å) and Angles (Deg) for Cu(EDTB)(BF$_4$)(BF$_3$OC$_2$H$_5$)·H$_2$O with their Estimated Standard Deviations in Parentheses[a]

		Distances			
Cu-N(10)	1.986 (7)	N(10)-C(11)	1.320 (12)	N(20)-C(21)	1.309 (12)
Cu-N(20)	2.039 (8)	N(10)-C(16)	1.402 (12)	N(20)-C(23)	1.390 (13)
Cu-N(30)	2.499 (8)	C(11)-C(14)	1.490 (14)	C(21)-C(24)	1.495 (16)
N(30)-C(31)	1.447 (13)	C(11)-N(11)	1.337 (12)	C(21)-N(21)	1.347 (13)
C(31)-C(31′)	1.508 (23)	N(11)-C(12)	1.383 (12)	N(21)-C(22)	1.365 (14)
B-F(1)	1.33 (2)	C(12)-C(13)	1.400 (13)	C(22)-C(23)	1.388 (14)
B-F(2)	1.33 (2)	C(13)-C(15)	1.363 (14)	C(23)-C(28)	1.384 (16)
B-F(3)	1.46 (2)	C(15)-C(16)	1.381 (14)	C(27)-C(28)	1.361 (17)
B-F(4)	1.19 (3)	C(16)-C(17)	1.384 (16)	C(26)-C(27)	1.384 (20)
B-O	1.40 (4)	C(17)-C(18)	1.363 (17)	C(25)-C(26)	1.374 (21)
O-C(41)[b]	1.45 (5)	C(18)-C(12)	1.361 (14)	C(22)-C(25)	1.401 (17)
C(41)-C(40)[b]	1.54 (5)	N(30)-C(14)	1.466 (12)	N(30)-C(24)	1.465 (13)
H(281)···H(281′)	2.59	Cu···H(281)	3.45		
		Angles			
N(20)-Cu-N(20′)	142.9 (5)	N(10)-Cu-N(10′)	165.9 (5)	N(10)-Cu-N(20′)	93.3 (3)
N(20)-Cu-N(30′)	142.6 (3)	N(10)-Cu-N(30′)	91.3 (3)	N(20)-Cu-N(10)	91.2 (3)
N(30)-Cu-N(30′)	70.1 (4)	N(10)-Cu-N(30)	77.1 (3)	N(20)-Cu-N(30)	74.2 (3)
Cu-N(10)-C(11)	119.5 (7)	N(10)-C(13)-C(15)	131.9 (9)	N(20)-C(21)-N(21)	113.0 (10)
Cu-N(10)-C(13)	134.0 (7)	C(12)-C(13)-C(15)	119.7 (9)	N(20)-C(21)-C(24)	121.5 (9)
C(11)-N(10)-C(13)	105.8 (8)	C(11)-C(14)-N(30)	111.4 (9)	N(21)-C(21)-C(24)	125.4 (10)
Cu-N(30)-C(14)	104.3 (6)	C(13)-C(15)-C(16)	117.6 (10)	C(21)-N(21)-C(22)	106.3 (9)
Cu-N(30)-C(31)	111.0 (6)	C(15)-C(16)-C(17)	121.8 (11)	N(21)-C(22)-C(23)	107.1 (10)
C(14)-N(30)-C(31)	113.1 (9)	C(16)-C(17)-C(18)	120.9 (10)	N(21)-C(22)-C(25)	132.0 (11)
N(10)-C(11)-N(11)	112.2 (9)	C(17)-C(18)-C(12)	117.1 (10)	C(23)-C(22)-C(25)	120.7 (13)
N(10)-C(11)-C(14)	124.6 (9)	N(30)-C(31)-C(31′)	110.7 (8)	N(20)-C(23)-C(22)	107.8 (10)
N(11)-C(11)-C(14)	123.1 (9)	Cu-N(20)-C(21)	118.9 (7)	N(20)-C(23)-C(28)	130.4 (10)
C(11)-N(11)-C(12)	108.4 (8)	Cu-N(20)-C(23)	134.7 (7)	C(22)-C(23)-C(28)	121.7 (11)
N(11)-C(12)-C(13)	105.1 (8)	C(21)-N(20)-C(23)	105.7 (8)	C(21)-C(24)-N(30)	108.1 (8)
N(11)-C(12)-C(18)	132.1 (10)	Cu-N(30)-C(24)	100.5 (6)	C(22)-C(25)-C(26)	116.4 (12)
C(13)-C(12)-C(18)	122.7 (10)	C(14)-N(30)-C(24)	111.8 (8)	C(25)-C(26)-C(27)	122.3 (13)
N(10)-C(13)-C(12)	108.5 (9)	C(24)-N(30)-C(31)	114.8 (9)	C(26)-C(27)-C(28)	121.6 (14)
				C(27)-C(28)-C(23)	117.3 (12)
F(1)-B-F(2)	115.9 (20)	F(2)-B-F(4)	113.3 (26)	F(3)-B-O	109.1 (21)
F(1)-B-F(3)	99.0 (19)	F(3)-B-F(4)	113.4 (29)	B-O-C(41)	123.2 (29)
F(1)-B-F(4)	116.6 (22)	F(1)-B-O	112.6 (19)	O-C(41)-C(40)	112.4 (28)
F(2)-B-F(3)	95.7 (15)	F(2)-B-O	120.2 (22)		

[a] The atom numbering scheme is given in Figure 1; the superscript in the atom labels indicate the symmetry operation $-x, y, \frac{1}{2} - z$.
[b] C(40) and C(41) are the carbon atoms of the ethoxytrifluoroborate ion.

of the Cu^{II}(EDTB)$^{2+}$ compounds will be described in detail. Subsequently, the spectral properties of the Cu^{II} compounds will be discussed in view of the crystal structure.

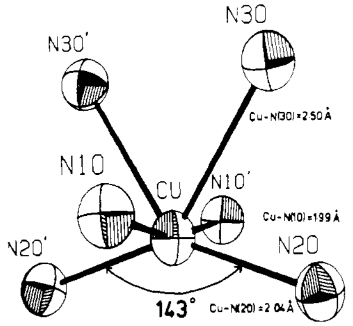

Figure 2. Coordination geometry of the copper atom in Cu(EDTB)(BF$_4$)(BF$_3$OC$_2$H$_5$)·H$_2$O. The atom numbering scheme is the same as in Figure 1.

Description of the Structure of Cu(EDTB)(BF$_4$)(BF$_3$OC$_2$H$_5$)·H$_2$O. The Cu(EDTB)$^{2+}$ cation is a monomeric Cu(II) complex in which the copper ion is bonded to four imidazole nitrogen atoms and two amine nitrogen atoms, forming five five-membered chelate rings. The copper atom lies on a crystallographic twofold axis. The structure of the cation is shown in Figure 1, together with the atom numbering scheme used. Figure 2 shows the detailed coordination geometry around Cu(II). Bond distances and angles are listed in Table V. The coordination geometry is very unusual: if the structure is described as being derived from a distorted octahedral configuration, the most surprising features are (i) the cis distortion with two very long Cu–N distances (Cu–N(30) = 2.50 Å) which is unusual for Cu–N$_6$ chromophores and (ii) the very large N(20)–Cu–N(20′) angle of 142.9° and the small N(30)–Cu–N(30′) angle of 70.1°; the usual value in copper ethylenediamine compounds is 80–85°.[21] This highly distorted geometry is probably forced by the steric interference between the hydrogen atoms on C(28) and C(28′) (Figure 1). The close contact between these hydrogen atoms (2.59 Å) does not allow a smaller N(20)–Cu–N(20′) angle than the presently found 142.9°. This steric hindrance is further illustrated by the dihedral angles in the benzimidazole groups of the ligand: whereas the angle between the planes of the phenyl ring C(12)–C(13)–C(15)–C(16)–C(17)–C(18) and the imidazole ring N(10)–C(11)–N(11)–C(13)–C(12) in the unhindered benzimidazole is 1.9°, the corresponding angle in the other benzimidazole amounts to 3.9°. Apparently, the phenyl rings carrying H(281) and H(281′) tend to twist away from each other: the dihedral angle between the imidazole ring N(20)–C(21)–N(21)–C(23)–C(22) and the symmetry-related imidazole group N(20′)–C(21′)–N(21′)–C(23′)–C(22′) is 30.1°, whereas the angle between the corresponding phenyl rings is 37.1°. Apart from this steric effect all angles and distances in the benzimidazole groups of the ligand are normal.[22] The phenyl and imidazole rings are planar, the de-

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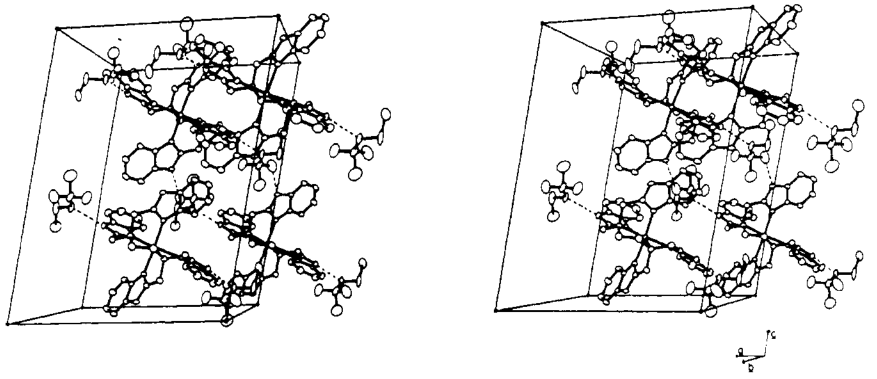

Figure 3. Stereodrawing of the unit cell of $Cu(EDTB)(BF_4)(BF_3OC_2H_5)\cdot H_2O$. Only $BF_3OC_2H_5$ ions are shown. Dashed lines represent hydrogen bonds.

Table VI. Electronic Absorption and ESR Parameters of Copper EDTB Compounds

			ESR							
	electronic absorption[a]		polycrystalline[g]				MeOH soln[h]			
compd	powder-reflectance	MeOH soln	g_1	g_2	g_3	A_3[b]	g_1	g_3	A_1[b]	A_3[b,f]
$Cu(EDTB)Cl_2\cdot EtOH\cdot H_2O$	14.1 (8.9)	14.3 (10.0)	2.03	2.14	2.28		2.03	2.28	70	135
$Cu(EDTB)Br_2$	14.5 (10.2)	14.5 (~10)	2.03	2.12	2.28		2.03	2.27	75	135
$Cu(EDTB)(NO_3)_2$	14.3 (10.0)	14.3 (~10)	2.03	2.12	2.26	133	2.03	2.28	70	135
$Cu(EDTB)(ClO_4)_2$	14.5 (10.5)	14.3 (10.0)	2.03	2.12	2.28	133	2.03	2.28	65	135
$Cu(EDTB)(BF_4)_2$	14.5 (10.3)	14.5 (~10)	2.03	2.12	2.28	138	2.03	2.28	65	135
$Cu_2(EDTB)Cl_4\cdot 3H_2O$	9.1 (11.8)	14.2 (~10)	*c*				*d*			
$Cu_2(EDTB)Br_4\cdot 2H_2O$	11.8 (13.4)	14.0 (11.4)[e]		2.12			*d*			
$Cu_2(EDTB)(NO_3)_4$	15.0	14.2 (~9)	2.06	2.10	2.28		*d*			
$Cu_2(EDTB)(ClO_4)_4\cdot 4H_2O$	14.5	14.2 (~10)	*c*				*d*			

[a] Frequencies are in 10^3 cm^{-1}; shoulders are given in parentheses. [b] A is given in 10^{-4} cm^{-1}. [c] See text. [d] Signals due to a mixture of compounds are observed; see text. [e] Dimethyl sulfoxide solution. [f] The values of g_2 and A_2 could not be determined accurately; $g_2 \approx 2.11$. [g] Q band, room temperature. [h] X band, 77 K.

viations from the least-squares planes being <0.02 Å. An alternative description of the geometry is as a distorted, bicapped square pyramid: N(10), N(20), N(10′), and N(20′) constitute the basal plane, while N(30) and N(30′) occupy the axial coordination sites. The basal plane, however, shows a marked tetrahedral twist, which suggests a distorted tetrahedron as still another way to describe the geometry; in that case N(30) and N(30′) have to be considered as noncoordinating. The tetrahedral distortion is illustrated by the dihedral angles between the N(10)–Cu–N(20′) and the N(10′)–Cu–N(20) planes and between the N(10)–Cu–N(20) and the N(10′)–Cu–N(20′) planes, 39.2° and 39.7°, respectively (90° for tetrahedral and 0° for square planar), and by the average of the six N–Cu–N angles: 112.9° (109.5° for tetrahedral and 120° for square-planar coordination). Recently the crystal structure was published[23] of a copper compound with a geometry resembling the present one, i.e., $[Cu(NO_3)(bpy)_2]NO_3\cdot H_2O$, in which bpy stands for bipyridine. Its geometry was also described as distorted square pyramidal; the axial position is occupied by two oxygen atoms, one at 2.30 Å and one at 2.82 Å (average Cu–O distance = 2.51 Å). The basal plane in this compound shows a similar tetrahedral distortion (dihedral angle = 42.8° compared to 39.3° in our case); this distortion was ascribed to interligand repulsion between the two bipyridine ligands. In our case, molecular model building shows that when N(10), N(20), N(10′), and N(20′) are forced into a plane, the hydrogen atoms on C(15), C(28), C(15′), and C(28′) come into close contact (<2.0 Å). Apparently the tetrahedral distortion is caused by the repulsion between these atoms.[24]

When the electronic properties are taken into account (vide infra), the most appropriate description for the geometry of this compound seems to be the square-pyramidal model.

Figure 1 might suggest that a small ligand such as F^- can be accomodated in the space below Cu; the distance between Cu and H(281), 3.45 Å, however, is too small for such a ligand.

During the synthesis of the crystals, part of the tetrafluoroborate ions have been solvolyzed, yielding $C_2H_5OBF_3^-$. Because of the resulting disorder, the angles and distances in the anions are not accurate. Decomposition of BF_4^- during the synthesis of transition-metal complexes in ethanol with imidazole- and pyrazole-containing ligands has been observed before.[25] In those cases the decomposition product F^- is invariably found in the resulting complexes, yielding dimers,[25a] chains,[25b] or cluster compounds,[25c] while BF_3 or its reaction products are assumed to remain in the solution, solvated by ethanol molecules. The present complex is the first example where the boron-containing decomposition product of BF_4^- is found in the solid product. The ethoxytrifluoroborate ion has been described before.[26]

A stereodrawing of the unit cell showing the packing of the molecules is presented in Figure 3. Both anions (BF_4^- and $C_2H_5OBF_3^-$) are involved in hydrogen bonding with the hy-

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drogen atoms of the imidazole groups of the complex cation. This hydrogen bonding involves two fluorine atoms of BF_4^- N–F distances 2.79 (1) and 2.84 (3) Å) or the corresponding fluorine and oxygen of $C_2H_5OBF_3^-$ (N–F and N–O distances are 2.79 (1) and 2.67 (4) Å, respectively). By means of these hydrogen bonds the cations and anions are joined in infinite chains along the [101] direction.

The presence of water is indicated by the elemental analyses (Table I); the final difference Fourier map did show some electron density in the region of the anions despite anisotropic refinement of the anion atoms. The water moelcules, however, could not be located and are assumed to be disordered in holes near BF_4^-.

Spectroscopic Results. The electronic absorption and ESR spectra of the compounds are listed in Table VI. The compounds with general formula $Cu_2(EDTB)X_4$ show different absorption maxima in the solid state, depending on the nature of the anion. Apparently the anion or water molecules of crystallization participate in the coordination of the copper. The low frequency of the absorption maximum of $Cu_2(EDTB)Cl_4{\cdot}3H_2O$ and to a lesser extent of $Cu_2(EDTB)Br_4{\cdot}2H_2O$ indicates that the geometry is not square planar, tetragonal, or square pyramidal.[27] The IR spectrum of $Cu^{II}_2(EDTB)(NO_3)_4$ indicates the presence of two different kinds of NO_3^-; two symmetric bending vibrations at 805 and 820 cm^{-1} are observed (only one vibration is found for $Cu^{II}(EDTB)(NO_3)_2$ at 820 cm^{-1}, and EDTB compounds with other anions have no absorptions in this region). One of the nitrates is assumed to be coordinated to copper. The frequency of the d–d absorption maximum of this compound (see Table VI) is too low for square-planar coordination; distorted tetrahedral or square-pyramidal geometries are possible.[27] The latter would implicate bidentate coordination by the nitrate. A similar kind of coordination geometry is proposed for $Cu^{II}_2(EDTB)(ClO_4)_4{\cdot}4H_2O$; one or two water molecules are probably bonded to each copper atom, since apparently the ClO_4^- ions are not coordinating: only a single asymmetric stretching vibration at 1100 cm^{-1} is found.[28] However, the chemical environments of the two copper ions in a single binuclear compound are not necessarily identical. The ESR spectra of the chloride and the perchlorate compound suggest the presence of two copper species in each case. For $Cu^{II}_2(EDTB)Cl_4{\cdot}3H_2O$ four signals between $g = 2.03$ and 2.13 are observed in the $g_\perp$ region (no hyperfine splitting). The relative intensities of these signals depend on the particular sample. For one sample a three g value spectrum is observed with $g_1 = 2.03$, $g_2 = 2.13$, and $g_3 = 2.28$. Although these parameters very much resemble that of $Cu(EDTB)Cl_2$, the geometries must be different according to the different electronic absorption spectra. For $Cu^{II}_2(EDTB)(ClO_4)_4{\cdot}4H_2O$ the $g_\parallel$ absorption is split in at least five components, also suggesting more than one species. The three g values for $Cu^{II}_2(EDTB)(NO_3)_4$ are compatible with the square-pyramidal geometry suggested above. Apparently due to exchange narrowing, no hyperfine structure in the $g_\parallel$ region is observed. Only the bromide compound shows a very broad absorption without fine structure, as often found in copper bromide compounds.[29] No isolated dimers occur, as in none of the ESR spectra is a triplet signal observed. Susceptibility measurements down to 4.2 K indicate only very small magnetic copper–copper interactions. The effective bohr magneton number, μ_{eff}, at 4.2 K varies between 1.53 and 1.66 μ_B for this class of compounds with the exception of $Cu^{II}_2(EDTB)Br_4{\cdot}2H_2O$ which shows a somewhat larger interaction: $\mu_{eff} = 1.23\ \mu_B$ at 4.2 K. Frozen-solution ESR spectra of $Cu^{II}_2(EDTB)X_4$ either in methanol or in dimethyl sulfoxide show the same signals as the spectra of the corresponding $Cu^{II}(EDTB)X_2$ solutions (vide infra). Apart from these, an ESR signal with $g_\parallel = 2.43$ and $A_\parallel = 112.10^4\ cm^{-1}$ is observed; such signals are also found for free $CuCl_2$ in methanol. Moreover, the electronic absorption spectra of these binuclear compounds in solution are identical with those of the mononuclear compounds. Apparently decomposition occurs with loss of one of the copper ions. So far no single-crystal studies of these compounds were possible.

As can be seen in Table VI, the electronic absorption spectra of all compounds of compositions $Cu^{II}(EDTB)X_2$ in the solid state and in methanolic solution are the same. These spectra are similar to those of the compounds with general formula $[Cu(L)_2(OXO)]Y$;[30] herein L stands for the bidentate ligands bipyridine or phenanthroline, OXO stands for nitrite or acetate, and Y is another anion. The stereochemistries of these compounds range from cis-distorted octahedral[30a] to five-coordinated square pyramidal[30b] (depending on the distance of the second oxygen atom to the copper atom). For the cis-distorted octahedral coordination geometry usually a d_{z^2} ground state is observed,[30a] while for square-pyramidal coordination a $d_{x^2-y^2}$ ground state is suggested.[30b] The EPR spectra of $Cu^{II}(EDTB)X_2$ compounds in frozen solutions are all very similar and show more resolution than the solid-state powder spectra. The solution spectra can be interpreted as three g value spectra, with parameters similar to those obtained from single-crystal measurements[30c] on $Cu(EDTB)(BF_4)(BF_3OC_2H_5){\cdot}H_2O$; i.e.: $g_1 = 2.03$, $g_2 = 2.11$, and $g_3 = 2.28$, $A_1 = 80 \times 10^{-4}$, $A_2 = 80 \times 10^{-4}$, and $A_3 = 135 \times 10^{-4}\ cm^{-1}$. Similar values were obtained from the powder spectra. This suggests that in solution the compounds have the same geometry as in the solid state. In our compounds, the low value of g_1 in the ESR spectrum (see Table VI) seems to suggest a d_{z^2} ground state;[27a,31] the value of g_2, however, is much closer to g_1 than to g_3; this is a strong indication for a $d_{x^2-y^2}$-based ground state[32] (which is usually connected with a distorted square pyramidal geometry). This $d_{x^2-y^2}$ ground state excludes a trigonal-bipyramidal geometry for our compounds. The electronic absorption spectrum is not compatible with a trigonal-bipyramidal geometry[27a,30b,33] either.

When only the nitrogen donor atoms are considered, the symmetry of the CuN_6 chromophore in $Cu(EDTB)(BF_4)(BF_3OC_2H_5){\cdot}H_2O$ is C_{2v}. Polarized single-crystal electronic spectra of distorted square-pyramidal copper compounds with C_{2v} symmetry have been assigned.[32a,34] The one electron orbital sequence is $d_{x^2-y^2} > d_{z^2} \approx d_{xy} > d_{xz} \approx d_{yz}$. The high-frequency transition is assigned to $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$, and $d_{z^2} \rightarrow d_{x^2-y^2}$ is the low-energy band. In unpolarized spectra of compounds with weak axial interactions these transitions are not resolved. The $d_{xy} \rightarrow d_{x^2-y^2}$ transition is usually observed as a weak absorption. The fact that both strong bands can be observed separately in the unpolarized powder reflectance

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spectra of our compounds suggests that the two amine nitrogen atoms at 2.50 Å from Cu have a much larger effect on the energy of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition than a single nitrogen atom on the axial position of a square pyramid does.[32a] In fact, the spectrum of our compound is comparable to that of square-pyramidal structures with one axial ligand at about 2.15 Å from the copper atom.[27b,35]

Concluding Remarks. The ligand EDTB is capable of forming copper coordination compounds with unusual geometries. When two Cu(II) ions per ligand are present, different coordination geometries are assumed, depending on the anion. In view of the crystal structure and of the electronic and ESR spectra, the copper coordination in the $Cu(EDTB)^{2+}$ cation has to be described as highly distorted square pyramidal.

Copper derivatives of EDTB ligands with methyl substituents on benzimidazole carbon or nitrogen atoms are under investigation, and related ligand systems in which sulfur donor atoms are present have been synthesized.[36]

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Registry No. $Cu(EDTB)(BF_4)(BF_3OC_2H_5)\cdot H_2O$, 77590-35-3; $Cu(EDTB)Cl_2$, 77590-36-4; $Cu(EDTB)Br_2$, 77590-37-5; $Cu(EDTB)(NO_3)_2$, 77590-38-6; $Cu(EDTB)(ClO_4)_2$, 77590-39-7; $Cu(EDTB)(BF_4)_2$, 72555-19-2; $Cu_2(EDTB)Cl_4\cdot 2H_2O$, 77630-27-4; $Cu_2(EDTB)Br_4\cdot 2H_2O$, 72555-16-9; Cu, 7440-50-8; $Cu_2(EDTB)(ClO_4)_4\cdot 2H_2O$, 77590-41-1; $Cu_2(EDTB)(BF_4)_2$, 77590-43-3; $Cu_2(EDTB)(ClO_4)_2$, 77590-44-4; EDTB, 72583-85-8.

Supplementary Material Available: Calculated positional parameters (Table III) for the hydrogen atoms and a listing of structure factor amplitudes (Table IV) (5 pages). Ordering information is given on any current masthead page.

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Coordination Chemistry of Methylmercury(II). Synthesis, ^1H NMR, and Crystallographic Studies of Cationic Complexes of $MeHg^{II}$ with Ambidentate and Polydentate Ligands Containing Pyridyl and N-Substituted Imidazolyl Donors and Involving Unusual Coordination Geometries[1]

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Complexes $[MeHgL]NO_3$ (L = 4,4′,4″-triethyl-2,2′:6′,2″-terpyridyl (Et_3terpy), terpy, bis(2-pyridyl)methanes ($(py)_2CH_2$'s), $(py)_2CMe_2$, $(py)_2CEt_2$, tris(2-pyridyl)methane, several *N*-alkylimidazoles, *N*-(2-pyridyl)imidazole, and *N*-methyl-2-(2-pyridyl)imidazoles) are obtained from addition reactions in acetone. Proton magnetic resonance spectroscopy is used to deduce coordination behavior of potential uni- or polydentate ligands in methanol, indicating that Et_3terpy, terpy, $(py)_2CH_2$'s, and *N*-methyl-2-(2-pyridyl)imidazoles act as bidentates to give three-coordinate mercury, but $(py)_2CR_2$ (R = Me, Et) are present as unidentates. A linear relation is obtained between $^2J(^1H-^{199}Hg)$ for $[MeHgL]^+$ and protonation constants for L, where L = *N*-alkylimidazoles, and the relation is similar to that obtained previously for L = pyridines. The ambidentate ligand *N*-(2-pyridyl)imidazole binds to mercury via the imidazole ring. Crystalline $[MeHg((py)_2CH_2)]NO_3$ has $(py)_2CH_2$ present as a bidentate ligand with "T-shape" coordination geometry based on a dominant C–Hg–N moiety [Hg–N = 2.16 (1) Å, C–Hg–N = 172 (1)°] and a weaker Hg–N′ bond [2.75 (2) Å]. [Crystal data: space group $P2_1/n$, $Z = 4$, a = 16.875 (2) Å, b = 8.540 (1) Å, c = 9.353 (1) Å, β = 96.544 (8)°, R = 0.054 for 1142 reflections having $I \geq 3\sigma(I)$.] Crystalline $[MeHg(Et_3terpy)]NO_3$ has Et_3terpy present as a tridentate ligand with $MeHg^{II}$ bonded strongly to the central nitrogen [2.26 (2) Å, C–Hg–N = 171 (1)°] and weakly to the terminal nitrogens [2.51 (2), 2.61 (2) Å]. [Crystal data: space group $P2_1/n$, $Z = 4$, a = 9.115 (2) Å, b = 15.725 (3) Å, c = 15.566 (3) Å, β = 94.465 (14)°, R = 0.063 for 1286 observed intensities having $I \geq 3\sigma(I)$.] Syntheses of new ligands containing pyridyl and *N*-methylimidazolyl donor groups are described.

The $MeHg^{II}$ cation is the fundamental organomercury species, and with a coordination geometry restricted almost entirely to linear geometry,[4,5] e.g., MeHgX (X = halide) and $[MeHg(py)]^+$, may be regarded as one of the simplest Lewis acids, and as such it has been studied extensively as a prototype soft acid,[6] as a model spectroscopic probe for binding of metal ions to complex molecules,[7] and finds application as a probe for the study of polynucleotides[5,8] and proteins.[5] However, 2,2′-bipyridyls act as bidentates toward $MeHg^{II}$ in $[MeHgL]NO_3$[9,10] to give irregular three-coordination for mercury based on a dominant C–Hg–N moiety [164 (1)°, Hg–N = 2.24 (3) Å] and a weaker Hg–N′ bond [2.43 (3) Å][10] with both bonds longer than the value for linear $[MeHg(py)]^+$

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