c, which could be due to anhydrous lead(II) acetate since this sample is the only one that has been heated and is the only one in which this peak occurs. Other possible chemical products that could arise by air oxidation, dehydration, as well as reaction with carbon dioxide include various hydrates, solvates, basic acetates, and basic carbonates. The NMR spectrum of lead subacetate (V) indicates that V is not one of the major products of room-temperature or thermal decomposition of II, although IR spectra clearly show that V is the major product formed by exposure of II to infrared radiation. Chemical identification of the products that yield peaks a, b, and g is still uncertain, and the analysis is complicated by the presence of mixed solid-state phases in these samples.

The fact that solids undergo reactions and phase transformations, which are either unique or occur unexpectedly in the solid state, presents a general problem for solid-state NMR analysis. For example, ^{13}C CP/MAS NMR spectrum of calcium acetate has four lines in the carboxyl region, which have been attributed to the presence of four nonequivalent acetate groups in the asymmetric unit of the crystal.[3] Since the crystal structure has not yet been reported, this may be a reasonable assumption. However, we have found that a spectrum run in our lab of commercial calcium acetate hydrate matches the published spectrum of supposedly anhydrous calcium acetate, leading us to question the actual composition and stability of calcium acetate solids. We have not analyzed the solid-state chemistry of calcium acetate in detail but note that the ^{13}C CP/MAS spectrum in both the carboxyl and methyl regions is a sensitive function of sample history.

In summary, we have shown that ^{13}C CP/MAS NMR is an efficient means for characterizing solid-state reactions. When used in conjunction with X-ray crystallographic studies, correlations are possible between structural details and the chemical shift. The crystal structure of lead(II) acetate shows that at most one could expect two methyl carbon lines and two carbonyl carbon lines in the NMR spectrum. The presence of more lines in old samples indicates the presence of other phases; the presence of only one line for each group shows that the structural differences in the solid state are not sufficient to allow resolution of the crystallographically inequivalent sites. Changes that take place in the ^{13}C CP/MAS NMR spectrum of II as solid-state dehydration and subsequent phase transformations take place are readily monitored by following the changes in intensity of lead(II) acetate trihydrate lines relative to new product lines that appear.[20]

Acknowledgment. This work was supported by the National Institutes of Health (Grant GM29428) and the University of Minnesota. Helpful discussions with Prof. Doyle Britton and Dr. S. Ganapathy and assistance with ORTEP drawings by Russ Morrison, all of the University of Minnesota, are gratefully acknowledged.

Registry No. $Pb(O_2C_2H_3)_2 \cdot 3H_2O$, 92011-13-7.

Supplementary Material Available: Listings of thermal parameters for all atoms and observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(20) Upon completion of this manuscript, it was brought to our attention that the crystal structure of II had been recently published.[21] The structural features presented are essentially the same as described in the present paper, but the use of an automatic diffractometer and a crystal mounting technique which prevented crystal decomposition made the precision of the crystallographic results presented here significantly greater than those reported in ref 21.

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Synthesis, Spectroscopic Properties, and X-ray Structure of [1,7-Bis(5-methylimidazol-4-yl)-2,6-dithiaheptane]dichlorocopper(II): A Compound with Unusually Long Copper(II)–Thioether Bonds

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Received November 8, 1983

The synthesis, X-ray structure determination, and spectroscopic properties of (1,7-bis(5-methylimidazol-4-yl)-2,6-dithiaheptane)dichlorocopper(II) are described. The compound $CuC_{13}H_{20}N_4S_2Cl_2$ crystallizes in the orthorhombic space group *Pbca* with $a = 12.927$ (3) Å, $b = 18.933$ (5) Å, $c = 14.469$ (2) Å, $V = 3541$ (2) Å^3, $d_{obsd} = 1.62$ g/cm^3, and $d_{calcd} = 1.616$ (1) g/cm^3 for $Z = 8$. The structure was solved by heavy-atom and direct methods. Least-squares refinements and Fourier methods resulted in a $R_w = 0.022$ for 1641 reflections with $I > 2\sigma(I)$. The copper(II) ion has a compressed octahedral coordination geometry, with the two imidazole nitrogen atoms along the main axis at 1.949 (2) and 1.955 (2) Å and both chloride ions and the two thioether sulfur atoms at longer distances in the equatorial plane, [Cu–Cl = 2.395 (1), 2.457 (1) Å, Cu–S = 2.886 (1), 2.970 (1) Å]. This structure shows that long equatorial Cu(II)–S(thioether) bonding, like in type I copper proteins, is also possible in more simple coordination compounds. The ESR and electronic spectra are discussed on the basis of this geometry and agree with a d_{z^2} ground state.

Introduction

The copper sites in some type I proteins are now fairly well-known, both by spectral and crystallographical studies.[2-4] The copper ion appears to be unusually coordinated in a distorted-tetrahedral geometry, with the sulfur- and nitrogen-containing residues of the amino acids cysteine, methionine, and histidine forming the CuN_2S_2 chromophore.[3,5]

The use of chelating ligands with built-in thioether and imidazole groups as model compounds for type I copper proteins may shed more light on their interesting structural, spectral, and electrochemical properties and their mutual dependencies. Several closely related compounds containing

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the CuN_2S_2 chromophore have been reported by our group and other groups.[5-13] The Cu(II)–N distances were invariably found to be 1.97 ± 0.05 Å. The Cu(II)–S distances vary from 2.33 to 2.82 Å. Although we have reported a Cu(I)–S contact of 2.87 Å in one case,[8] the long Cu(II)–S(thioether) distance of 2.90 Å, as found in plastocyanin, has not yet been reported in such biomimetic chelates.

In the present paper we report the synthesis and spectral and structural properties of a copper(II)-containing chelate with the ligand 1,7-bis[5(4)-methylimidazol-4(5)-yl]-2,6-dithiaheptane (abbreviated as bidhp), which has unusually long copper(II)–thioether bond distances. These equatorial Cu–S distances in fact compare well with those in azurine and plastocyanine and have been very rarely encountered in simple coordination compounds.

Experimental Section

Preparation of Cu(bidhp)Cl_2. The ligand, as its dihydrochloride salt, was prepared from 4(5)-hydroxymethyl-5(4)-methylimidazole hydrochloride[14] and commercially available propane-1,3-dithiol in refluxing acetic acid. The yield was 52% after recrystallization from 2-propanol (mp 216–220 °C). A solution of this salt (0.25 mmol) in 10 mL of absolute ethanol was neutralized with 1 mL of 0.5 M sodium hydroxide solution, whereafter a solution of copper(II) chloride dihydrate (0.25 mmol) in 5 mL of ethanol was added. After the mixture was allowed to stand at room temperature, a yellow-brown crystalline precipitate was formed, which contained suitable crystals for X-ray diffraction. Addition of a total of 50 mL of diethyl ether yielded a microcrystalline material, which appeared to be the same product, as deduced from IR, ESR, and ligand field spectra. Anal. (Pascher's Microanalytical Laboratory, Bonn, FRG) Found (calcd for $CuC_{13}H_{20}N_4S_2Cl_2$: Cu, 14.7 (14.8); C, 36.01 (36.24); H, 4.79 (4.68); N, 13.0 (13.0); S, 14.7 (14.9); Cl, 16.1 (16.4).

Spectral Measurements. The IR spectra were recorded on a Perkin-Elmer 580 IR spectrometer as KBr pellets and as Nujol mulls. The ESR spectra were recorded on a Varian E-3 (X-band) spectrometer and the ligand field spectra on Beckmann DK-2A (diffuse reflectance) and Perkin-Elmer 330 (solution spectra) spectrophotometers. A chloride-free solution of the ligand was prepared by adding a slight excess of silver perchlorate and removing the precipitated silver chloride by filtration.

X-ray Diffraction and Structure Determination. A plate-shaped crystal of Cu(bidhp)Cl_2 was selected and mounted on a Nonius CAD-4 computer-controlled diffractometer. Intensity data were collected at room temperature in the ω–θ scan mode, using graphite-monochromated Mo Kα radiation. This scan mode was selected as it gives the smallest contribution of the beam divergence to the optimum counter slit width. Precise lattice constants were determined from the angular settings of 24 reflections with $12 < \theta < 14$ by a least-squares refinement. The absent reflections for $0kl$ (k odd), $h0l$ (l odd), and $hk0$ (h odd) indicated the orthorhombic space group *Pbca*, which confirmed the results of preliminary Weissenberg photographs. Each reflection in the range $2 \leq \theta \leq 23$ with $h \geq 0$, $k \geq 0$, and $-15 \leq l \leq 15$ was measured in 96 steps.

The intensity measurements at each end of a scan were considered as background. The scanning rate was adjusted to the required precision of $\sigma(I)/I < 0.01$ with a maximum scan time of 90 s.[15] Every 5400 s of radiation time, three standard reflections were measured for instrumental instability and crystal decomposition. The data were corrected for Lorentz and polarization effects in the usual way and for absorption by using De Graaff's method.[16] This last correction was necessary as the variation in the transmission of two suitable reflections at different azimuthal positions is 22%. The factor R_{int}, based on the intensities of equivalent reflections, is 0.029.[17] Crystal and unit cell data are summarized in Table I. Scattering factors with correction for anomalous dispersion were taken from ref 18a,b.

Table I. Crystal and Unit Cell Data of Cu(bidhp)Cl_2

mol compn	$CuC_{13}H_{20}N_4S_2Cl_2$
mol wt	430.91
space group	*Pbca*
lattice constants	
a, Å	12.927 (3)
b, Å	18.933 (5)
c, Å	14.469 (5)
V, Å^3	3541 (2)
$\alpha = \beta = \gamma$, deg	90
Z	8
d_{calcd}, g/cm^3	1.616 (1)
d_{obsd}(flotation in $CHCl_3/1,2-C_2H_4Br_2$), g/cm^3	1.62
no. of reflcns measd	4793
no. of indep reflcns	2455
no. of significant ($I/\sigma(I) > 2$) reflcns	1641
abs coeff (μ), cm^{-1}	17.70
cryst size, mm	0.45 × 0.33 × 0.05
transmissn range	0.58–0.91

Table II. Positional Parameters (×10^5 for Cu1–Cl3 and ×10^4 for S4–C26) and B Values (in Å^2, ×10^2) for the Non-Hydrogen Atoms in Cu(bidhp)Cl_2[a]

atom	x/a	y/b	z/c	B(iso)
Cu1	13006 (3)	−18362 (2)	12566 (3)	249 (1)
Cl2	28255 (6)	−25339 (5)	10324 (6)	322 (3)
Cl3	−2405 (6)	−25700 (5)	15123 (6)	297 (3)
S4	2560 (1)	−596 (1)	695 (1)	385 (3)
C5	1571 (4)	9 (2)	300 (3)	375 (13)
C6	1161 (4)	459 (2)	1072 (3)	424 (14)
C7	867 (4)	58 (2)	1933 (3)	399 (14)
S8	−28 (1)	−655 (1)	1680 (1)	430 (3)
C10	2713 (3)	−1076 (3)	−375 (3)	363 (14)
C11	1741 (3)	−1416 (2)	−689 (2)	245 (10)
N12	1094 (2)	−1773 (2)	−75 (2)	220 (8)
C13	345 (3)	−2032 (2)	−584 (3)	240 (11)
N14	468 (2)	−1861 (2)	−1465 (2)	268 (9)
C15	1349 (3)	−1461 (2)	−1545 (2)	274 (10)
C16	1698 (5)	−1152 (3)	−2440 (3)	467 (18)
C20	−137 (3)	−1029 (3)	2820 (3)	343 (13)
C21	846 (3)	−1334 (2)	3172 (2)	242 (10)
N22	1511 (2)	−1695 (2)	2582 (2)	230 (8)
C23	2266 (3)	−1932 (2)	3104 (2)	263 (11)
N24	2115 (2)	−1737 (2)	3981 (2)	304 (10)
C25	1215 (3)	−1352 (2)	4038 (2)	258 (10)
C26	821 (5)	−1066 (3)	4923 (3)	432 (16)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

The position of the copper atom was found by means of a three-dimensional Patterson synthesis. All other non-hydrogen atoms were located by use of the direct-methods program DIRDIF.[19] Full-matrix

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Table III. Bonding and Interatomic Distances (Å) in Cu(bidhp)Cl_2 with Their Estimated Standard Deviations in Parentheses[a]

Cu1–Cl2	2.395 (1)	C10–S4	1.807 (4)
Cu1–Cl3	2.457 (1)	S4–C5	1.810 (4)
Cu1–S4	2.970 (1)	C5–C6	1.500 (6)
Cu1–S8	2.886 (1)	C6–C7	1.508 (6)
Cu1–N12	1.949 (2)	C7–S8	1.816 (4)
Cu1–N22	1.955 (2)	S8–C20	1.801 (4)
C10–C11	1.483 (5)	C20–C21	1.486 (5)
C11–N12	1.395 (4)	C21–N22	1.390 (4)
N12–C13	1.311 (4)	N22–C23	1.313 (4)
C13–N14	1.326 (5)	C23–N24	1.336 (5)
N14–C15	1.372 (4)	N24–C25	1.375 (4)
C15–C11	1.341 (4)	C25–C21	1.342 (4)
C15–C16	1.491 (5)	C25–C26	1.480 (5)
N14–H141	0.82 (3)	N24–H241	0.76 (3)
Cl3–H141′	2.46 (3)	Cl2′–H241	2.69 (3)
Cl3–N14′	3.250 (3)	Cl2′–N24	3.400 (3)

[a] Primed atoms at $x, -\frac{1}{2} - y, \frac{1}{2} + z$.

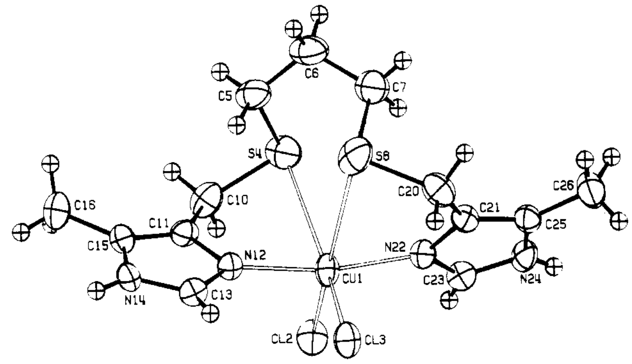

Figure 1. ORTEP drawing of Cu(bidhp)Cl_2, with thermal ellipsoids at 50% probability, showing the atomic numbering scheme. The hydrogen atoms, whose numbering is related to that of the attached atom, have been drawn with a B value of 1.0 Å^2 for clarity.

Table IV. Interbond and Torsion Angles (deg) in Cu(bidhp)Cl_2 with Their Estimated Standard Deviations in Parentheses[a]

Cl2–Cu1–S8	161.11 (4)	C11–C10–S4	112.8 (3)
Cl3–Cu1–S4	158.86 (3)	C10–S4–C5	97.2 (2)
N12–Cu1–N22	168.6 (1)	S4–C5–C6	112.0 (3)
Cl2–Cu1–Cl3	112.08 (3)	C5–C6–C7	114.7 (4)
Cl2–Cu1–S4	87.00 (3)	C6–C7–S8	111.6 (3)
Cl3–Cu1–S8	85.62 (3)	C7–S8–C20	99.1 (2)
S4–Cu1–S8	76.81 (3)	S8–C20–C21	113.6 (3)
Cl2–Cu1–N12	90.7 (1)	Cl2–Cu1–N22	95.4 (1)
Cl3–Cu1–N12	94.2 (1)	Cl3–Cu1–N22	92.4 (1)
S4–Cu1–N12	75.9 (1)	S4–Cu1–N22	94.8 (1)
S8–Cu1–N12	94.6 (1)	S8–Cu1–N22	76.6 (1)
C10–C11–N12	121.6 (3)	C20–C21–N22	120.6 (3)
N12–C11–C15	109.3 (3)	N22–C21–C25	110.0 (3)
C11–N12–C13	105.5 (3)	C21–N22–C23	105.9 (3)
N12–C13–N14	111.0 (3)	N22–C23–N24	110.1 (3)
C13–N14–C15	108.4 (3)	C23–N24–C25	109.1 (3)
C11–C15–N14	105.7 (3)	C21–C25–N24	104.9 (3)
N14–C15–C16	122.8 (4)	N24–C25–C26	122.5 (4)
C13–N14–H141	129 (3)	C23–N24–H241	125 (3)
Cl3–H141′–N14′	161 (3)	Cl2′–H241–N24	157 (3)
Cu1–Cl3–H141′	99 (1)	Cu1′–Cl2′–H241	102 (1)
Cu1–S4–C5	101.5 (2)	Cu1–S8–C7	103.9 (2)
Cu1–S4–C10	84.1 (2)	Cu1–S8–C20	86.3 (2)
Cu1–N12–C11	125.3 (2)	Cu1–N22–C21	125.7 (2)
S4–C5–C6–C7	−48.5 (5)	C5–C6–C7–S8	−53.6 (5)
Cu1–S4–C5–C6	88.5 (3)	C6–C7–S8–Cu1	88.5 (3)
C10–S4–C5–C6	174.0 (3)	C6–C7–S8–C20	176.9 (3)
S8–Cu1–S4–C5	−33.1 (2)	C7–S8–Cu1–S4	−28.9 (2)
Cu1–S4–C10–C11	41.8 (3)	Cu1–S8–C20–C21	38.8 (3)
S4–C10–C11–N12	−43.4 (5)	S8–C20–C21–N22	−38.0 (5)
C10–C11–N12–Cu1	3.8 (5)	C20–C21–N22–Cu1	1.5 (5)
C11–N12–Cu1–S4	19.8 (3)	C21–N22–Cu1–S8	19.7 (3)
N12–Cu1–S4–C10	−31.0 (2)	N22–Cu1–S8–C20	−29.1 (2)

[a] Primed atoms at $x, -\frac{1}{2} - y, \frac{1}{2} + z$.

refinement of these positions, first with isotropic and later with anisotropic temperature parameters, rendered a difference Fourier map with the positions of the hydrogen atoms bound to the imidazole ring and the methylene carbon atoms and some of those in the methyl groups. The other hydrogen atoms were placed at calculated positions. All hydrogen atoms were refined isotropically, with Waser constraints for the C–H distances and H–C–H angles in the methyl groups.[20] At this stage a weight scheme with factors inversely proportional to $\sigma(I)^2$ was used. The refinement rapidly converged to final R values of $R = 0.024$ and $R_w = 0.022$ for the significant reflections.[21] The remaining peaks in a final difference Fourier map were less than twice the noise level of 0.15 e/Å^3.

The atomic positions and calculated isotropic thermal parameters of the non-hydrogen atoms are listed in Table II. The anisotropic thermal parameters of these atoms, the positional and thermal parameters of the hydrogen atoms, and a table of observed and calculated structure factors are available as supplementary material.[22]

Results and Discussion

Description of the Structure. An ORTEP representation of Cu(bidhp)Cl_2, also showing the atomic numbering, is depicted in Figure 1. Table III gives the most relevant bond lengths and atomic distances; the main interbond and torsion angles are given in Table IV. The asymmetric unit consists of one molecule of [1,7-bis(5-methylimidazol-4-yl)-2,6-dithiaheptane]dichlorocopper(II). As may be seen from the drawing and the geometrical tables, there appears to be a (pseudo) twofold rotation axis within the molecule through the atoms Cu(1) and C(6), which is nearly parallel (4.2° deviation) to the crystallographic b axis. The copper ion is coordinated by two imidazole nitrogen atoms, two chloride ions, and two thioether sulfur atoms in a compressed octahedral geometry, with the nitrogen atoms along the main axis and the chloride ions and sulfur atoms on mutual cis positions in the equatorial plane. The Cu–N distances are comparable to related compounds with (benz)imidazole groups.[6–13] The Cu–Cl distances are relatively long, although not exceptionally, and the equatorial Cu–S distances are so long that the question may arise whether they can still be regarded as coordination bonds. In fact, the distances are comparable with the Cu(II)–S(methionine) distances in azurin and plastocyanin[3,4] and on the very far end of the range found in thioether-containing copper(II) compounds.[6–13,23,24] The Cu–S–C angles nevertheless indicate that the lone pair orbitals on the sulfur atoms are directed toward the copper ion, as they are close to the expected value of 90–100°; so, the sulfur atoms are coordinating, although weakly. Apart from being compressed, the coordination octahedron has other distortions apparently originating from the steric constraints imposed by the ligand.

Most striking is the twist in the equatorial plane, where the angle between the S–Cu–S and Cl–Cu–Cl planes amounts to 13.2°. The Cl–Cu–Cl plane is nearly perpendidcular (87.7°) to the axis through both nitrogen atoms.

The bond distances and the angles within the ligand are in the expected range. The imidazole rings are planar with deviations less than 0.007 Å. The angle between the imidazole planes amounts to 66°.

The unit cell contains 8 molecules of Cu(bidhp)Cl_2, one in each octant. Each molecule is bound by four hydrogen bridges between all available chloride ions and the N(1) atoms of the imidazole groups to the ones below and above it along the c

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(20) $R = \sum||F_o| - s|F_c||/\sum|F_o|$; $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2)^{1/2}$.

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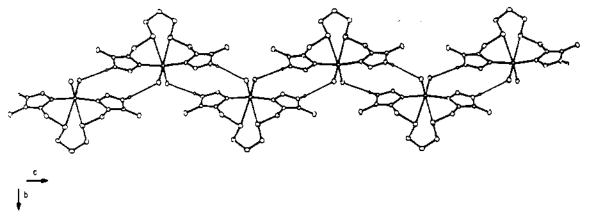

Figure 2. ORTEP drawing of a chain of symmetry-related molecules of Cu(bidhp)Cl$_2$ showing intermolecular bonding by hydrogen bridges and stacking of the imidazole rings. The carbon-bound hydrogen atoms have been omitted for clarity.

axis. An ORTEP drawing of such a chain is shown in Figure 2. There is also considerale stacking between the aromatic planes in these molecules; the best planes through the ring atoms are nearly parallel (1.6°) at a distance of 3.45 Å. The other intermolecular distances are larger than, or close to, the sum of the van der Waals radii.

Spectral Properties. In view of the wealth of spectral information available for Cu(II) in several geometries,[25] it seemed worthwhile to study the electronic and ESR spectra of the title compound.

The solid-state ESR spectrum of Cu(bidhp)Cl$_2$ is typical for a so-called compressed geometry with a d_{z^2} ground state. Both at room temperature and at 77 K the spectrum is axial ($g_{\parallel} = 2.01$, $g_{\perp} = 2.19$) with a weak rhombic distortion (shoulder near $g = 2.10$). The ESR powder spectrum does not show the expected copper hyperfine splitting, which is likely to be the result of small coupling between the copper ions.[25] Such a coupling causes exchange narrowing and must be of the order of magnitude of the hyperfine splitting (0.01 cm^{-1}). Figure 2 in fact shows that such exchange mechanism is easily realized via the N–H···Cl hydrogen bonds. The diffuse reflectance spectrum shows ligand field maxima at 9.2 and 13.2 × 10^3 cm^{-1} (of about equal intensity) and a charge-transfer band at 27.0 × 10^{-3} cm^{-1}. The two low-energy transitions are assigned to the d_{xz}, $d_{yz} \rightarrow d_{z^2}$ and d_{xy}, $d_{x^2-y^2} \rightarrow d_{z^2}$ transitions, respectively, on the basis of a C_2 (distorted octahedral) symmetry. The charge-transfer band is ascribed to a π(imidazole) → Cu(II) charge-transfer transition.[11] Although a S → Cu(II) charge-transfer band has been found in many compounds with short Cu–S distances, such a transitions is not likely to occur in the title compound. Both ESR and LF spectra are in agreement with the d_{z^2} ground state, expected for this geometry and the crystal packing in the solid state. Infrared spectra obtained in the solid state show the presence of ligand bands, in some cases shifted or split as a result of coordination. Metal–Ligand vibrations were difficult to assign unambiguously in the far-IR region, due to overlap with ligand vibrations.

To see whether the same structure exists in solution and to obtain (super) hyperfine splitting information, ligand field and ESR spectra were also obtained in ethanol solution under varying conditions. It appears however that the spectral behavior is quite different from that of the solid state in this solvent. The ligand field spectra now show only one broad absorption at 13.6 × 10^3 cm^{-1}, which is shifted to 14.9 × 10^3 cm^{-1} when the chloride concentration has been decreased. The ESR spectra of the frozen solutions with Cu(bidhp)X$_2$ (X is Cl$^-$ or ClO$_4^-$) indicate the presence of several species, including even dimeric ones. The relative amounts appear to be dependent on the chloride concentration. Therefore, this was not investigated further.

In contrast to the compounds with benzimidazole-containing ligands,[8,10] the present copper(II) compounds appear to be difficult to reduce to the Cu(I) state in solution.

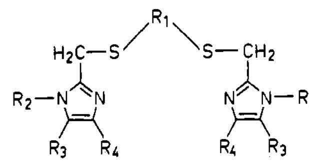

Figure 3. Schematic formula of tetradentate imidazole–thioether ligands: BBDH, R$_1$ = (CH$_2$)$_2$, R$_2$ = H, R$_3$ = R$_4$ = benzo;[6] BBIDH, R$_1$ = (CH$_2$)$_2$, R$_2$ = CH$_2$C$_6$H$_5$, R$_3$ = R$_4$ = H;[7] bbtb, R$_1$ = *o*-C$_6$H$_4$, R$_2$ = H, R$_3$ = R$_4$ = benzo;[9] BBDHp, R$_1$ = (CH$_2$)$_3$, R$_2$ = H, R$_3$ = R$_4$ = benzo;[8] Me$_2$BBDHp, R$_1$ = (CH$_2$)$_3$, R$_2$ = CH$_3$, R$_3$ = R$_4$ = benzo.[10]

Comparison with Related Structures. The molecular structure of the title compound appears to be of great interest in view of those published earlier by our group and other groups and also in view of the long Cu(II)–methionine distance in azurins and plastocyanin.[2,3]

The only known other example of a long Cu(II)–S(thioether) bond with an imidazole-containing ligand is a copper compound with the ligand 1,3-bis(5-phenylimidazol-2-yl)-2-thiapropane. In this compound the copper ion is six-coordinated by two ligand molecules: four nitrogen atoms in the equatorial plane and two sulfur atoms on the axial positions of a common elongated octahedron.[11]

An even longer bond, viz. 2.919 Å, has been found in a dinuclear Cu(II) cryptate.[23] Our compound not only has longer Cu···S contacts but also has these contacts in the equatorial ligands, rather than in the more common axial ones. The origin for this unique structure seems therefore to lie in the geometry of the ligand backbone, which apparently imposes this geometry. However, other contributions can also be responsible, as seen by comparing the present structure with those obtained for a group of N$_2$S$_2$ ligands, shown schematically in Figure 3.

The first three examples in this figure (all with a two-carbon atom bridge between the sulfur atoms) have a trigonal-bipyramidal geometry around Cu(II) with two nitrogen atoms on the axial positions and the two sulfur atoms and one additional ligand (an anion or a solvent molecule) in the equatorial plane.[6,7,9] The other two examples have the same chelating arrangement as in the present structure. The structure of [Cu^{I}BBDHp]$^+$ resembles the title compound very closely as far as the ligand, which has nearly the same geometry. The major difference, besides the valency state, is the absence of extra coordinating anions.[8] The Cu(II) compound with nearly the same ligand shows a striking difference in the coordination geometry: still five-coordinate, but more close to a square pyramid with a N$_2$S$_2$ plane and H$_2$O on the apex.[11]

Probably a delicate balance between bite, ligand size, and solid-state effects (H bonding, stacking, and crystal packing) determines the ultimate structure, just as the protein backbone does in the copper proteins. This is also reflected in the solution behavior of the title compound, which shows that other geometries are possible (vide supra).

This structure shows first of all that Cu(II)–S(thioether) bonds of the same lengths as in blue copper proteins may also occur in low molecular weight compounds with biomimetic ligands. It has further been shown that the observed structure is not stable in solution, although the title compound can be recrystallized from ethanol.

The actual Cu–S distances in coordination compounds appear to vary almost continuously within the range 2.3–3.0 Å and appear to be determined by ligand constraints such as in open-chain and cryptand-type species[23,26] and by solid-state effects.

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Further work in this area will concentrate on the incorporation of thiolato groups (the origin of the blue color) and on more rigid ligand constraints, as well as on the redox properties of the resulting compounds.

Acknowledgment. We thank Hoffmann-La Roche Inc. for a gift of 1,7-bis[5(4)-methylimidazol-4(5)-yl]-2,6-dithiaheptane dihydrochloride and S. Gorter and Dr. G. C. Verschoor for assistance with the data collection and for many helpful suggestions in the structure determination.

Registry No. Cu(bidhp)Cl_2, 91670-04-1; bidhp, 91631-43-5; 4-(5)-hydroxymethyl-5(4)-methylimidazole hydrochloride, 38585-62-5; propane-1,3-dithiol, 109-80-8.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen positional parameters, and calculated and observed structure factors (8 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
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Synthesis and Spectroscopic Characterization of Transition-Metal Chelates Containing a New Hexadentate Ligand. Crystal and Molecular Structure of the Heptacoordinated Compound (Perchlorato-*O*)[*N*,*N*,*N'*,*N'*-tetrakis(pyrazol-1-ylmethyl)-1,2-diaminoethane]manganese(II) Perchlorate

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Received December 9, 1983

Coordination compounds of the type M(edtp)(anion)$_2$(H_2O)$_x$ are described in which M is one of the divalent metals Mn, Fe, Co, Ni, Cu, Zn, and Cd, the anion is ClO_4^- or BF_4^-, edtp stands for $C_{18}H_{24}N_{10}$ or *N*,*N*,*N'*,*N'*-tetrakis(pyrazol-1-ylmethyl)-1,2-diaminoethane, and x = 0–1. The compounds have been characterized by several analytical techniques and spectroscopic methods. The ligand is hexadentate in all compounds. For Mn, Fe, Cd, and Zn (in this case only for the perchlorate compound) also one counterion is coordinated to the metal ion, resulting in seven-coordination. In the case of six-coordination (M = Co, Ni, and Cu and the zinc fluoroborate compound) the coordination geometry is close to octahedral, as deduced from ligand field spectra for Co(II) and Ni(II) and powder isomorphism within this group. For Cu(II), ligand field and ESR spectra indicate a distorted octahedral geometry with parameters not largely different from those of other CuN_6 species. The water molecules appear to be present in the crystal lattice. The compound Mn(edtp)(ClO_4)$_2$ crystallizes in the space group $P2_1/c$ (monoclinic) with a = 9.522 (2) Å, b = 12.190 (6) Å, c = 22.913 (5) Å, β = 94.201 (5)°, and Z = 4. The structure was solved by heavy-atom techniques and refined by least-squares methods to a residual R value of 0.046. The coordination geometry around the Mn(II) ion can be described as derived from octahedral, with one axial donor atom replaced by two less strongly bonded donor atoms (bicapped), resulting in a seven-coordinate geometry. Apart from the six nitrogen atoms of the ligand that bind to Mn(II) (four normal distances of about 2.25 Å and two long (bicapped) distances of about 2.50 Å), an oxygen atom of one of the perchlorate ions is tightly bonded to Mn(II) (Mn–O is about 2.26 Å). In dimethylformamide solution this perchlorate ion dissociates, as deduced from conductivity data.

Introduction

As part of a research program on the synthesis and structure of coordination compounds modelling the active site in metalloproteins we have been working on tetradentate and hexadentate ligands containing imidazole groups in a more or less flexible orientation.[1–4] In these studies imidazole groups and substituted imidazole groups were selected as ligands, because they are known to occur in copper, zinc, and iron proteins.[5] Similar studies by other workers on pyridine groups held together in chelating ligands have shown that dramatic differences may occur between imidazole-containing chelates and pyridine-containing chelates.[6–8] To investigate whether or not this difference is due to steric or electronic effects, we have set up a study on the coordination chemistry of similar ligands containing pyrazole groups. The synthesis of such ligands is possible by using a new ligand-condensation technique.[9] This paper describes the first results of this investigation. As a starting ligand *N*,*N*,*N'*,*N'*-tetrakis(pyrazol-1-ylmethyl)-1,2-diaminoethane, which is easily prepared from 1-(hydroxymethyl)pyrazole and ethylenediamine,[9] has been used.

To prove the chelating nature of edtp and to see to what extent all potential donor sites are involved in coordination, a crystal structure determination of a representative example has been included.

Experimental Section

The compound *N*,*N*,*N'*,*N'*-tetrakis(pyrazol-1-ylmethyl)-1,2-diaminoethane (edtp) was synthesized as described before.[9]

All other chemicals were commercially available, were of sufficient purity, and were used without further treatment.

The coordination compounds were prepared by dissolving the hydrated metal salts (5 mmol) in 25 mL of ethanol and adding the warm (ca. 60 °C) solutions to warm solutions of the ligand edtp (5 mmol) in 25 mL of ethanol. After the mixtures were allowed to stand at

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