

Synthesis, Structure, and Spectroscopic Properties of Copper(II) Compounds containing Nitrogen–Sulphur Donor Ligands; the Crystal and Molecular Structure of Aqua[1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(II) Perchlorate †

Anthony W. Addison* and T. Nageswara Rao

Department of Chemistry, Drexel University, Philadelphia, PA 19104, U.S.A.

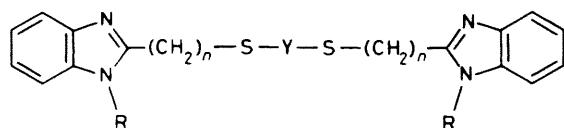
Jan Reedijk,* Jacobus van Rijn, and Gerrit C. Verschoor

Department of Chemistry, State University of Leiden, 2300 RA Leiden, The Netherlands

The linear quadridentate N_2S_2 donor ligand 1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane (bmdhp) forms mono- and di-hydrate 1 : 1 copper(II) complexes which are significantly more stable toward autoreduction than those of the non-methylated analogue. The deep green monohydrate of the perchlorate salt crystallises as the mononuclear aqua-complex, $[Cu(bmdhp)(OH_2)](ClO_4)_2$, in the monoclinic space group $P2_1/n$, with $Z = 4$, $a = 18.459(3)$, $b = 10.362(2)$, $c = 16.365(3)$ Å, and $\beta = 117.14(1)^\circ$. The structure was solved and refined by standard Patterson, Fourier, and least-squares techniques to $R = 0.047$ and $R' = 0.075$ for 3 343 independent reflections with $I > 2\sigma(I)$. The compound consists of $[Cu(bmdhp)(OH_2)]^{2+}$ ions and ClO_4^- counter ions. The co-ordination around copper is intermediate between trigonal bipyramidal and square pyramidal, with Cu–N distances of 1.950(4) and 1.997(4) Å, Cu–O(water) 2.225(4) Å, and Cu–S 2.328(1) and 2.337(1) Å. In the solid state, the perchlorate dihydrate's co-ordination sphere may be a topoisomer of the monohydrate's. A new angular structural parameter, τ , is defined and proposed as an index of trigonality, as a general descriptor of five-co-ordinate centric molecules. By this criterion, the irregular co-ordination geometry of $[Cu(bmdhp)(OH_2)]^{2+}$ in the solid state is described as being 48% along the pathway of distortion from square pyramidal toward trigonal bipyramidal. In the electronic spectrum of the complex, assignment is made of the S(thioether) \rightarrow Cu charge-transfer bands by comparison with those of the colourless complex $Zn(bmdhp)(OH)(ClO_4)$. E.s.r. and ligand-field spectra show that the copper(II) compounds adopt a tetragonal structure in donor solvents.

Continuing interest¹ in the chemistry of copper–thioether complexes has been promoted by the occurrence of the methionine side-chain as a structurally essential active-site component in a plastocyanin² and two azurins.^{3–5} The additional presence of strongly bound imidazole nitrogen has stimulated the synthesis of various types of copper compounds with biomimetic donors,^{6–11} which are intended to probe the consequences of the nitrogen/sulphur co-ordination and irregular geometry which are the hallmarks of the protein type-I copper centres.

We have prepared a series of chelating ligands with biomimetic donor atoms of the general structure shown below.^{12–15} These quadridentate ligands contain two imidazole nitrogen-donor atoms, sterically hindered because they form part of the bulky benzimidazole groups, and two thioether sulphur atoms, with a varying number of carbon atoms in the ligand



R	n	Y	Ligand abbreviation	Ref.
H	1	(CH ₂) ₂	bbdh	12
H	1	<i>o</i> -C ₆ H ₄	bbtb	14
H	1	(CH ₂) ₃	bbdhp	13
CH ₃	1	(CH ₂) ₃	bmdhp	This work
H	2	(CH ₂) ₂	bbdo	Unpublished

† Supplementary data available (No. SUP 23904, 14 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii–xix.

backbone. This paper describes the synthesis and spectral properties of copper(II) compounds with the ligand 1,7-bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane (abbreviated bmdhp) and the determination of the crystal and molecular structure of $[Cu(bmdhp)(OH_2)](ClO_4)_2$ by *X*-ray methods. The results are compared with the structures of previously described^{12,13} complexes, such as $[Cu(bbdh)Cl]^+$ and $[Cu^I(bbdhp)]^+$ and related compounds.^{14–16} It is shown that the effect of an added methylene group between the thioether sulphurs has a significant effect on the structures and the properties of the compounds formed.

Experimental

Syntheses.—1,7-Bis(*N*-methylbenzimidazol-2'-yl)-2,6-dithiaheptane (bmdhp). This compound was synthesised by the Phillips condensation^{17–19} of *N*-methyl-*o*-phenylenediamine dihydrochloride (4.10 g, 21 mmol) with 2,6-dithiaheptane-1,7-dicarboxylic acid¹⁹ (2.24 g, 10 mmol) in 4 mol dm⁻³ HCl (100 cm³, 17 h reflux). The hydrochloride which crystallised from the cooled solution as pale green prisms was filtered off, dissolved in water, and treated with excess of 5 mol dm⁻³ sodium hydroxide. The grey gum which precipitated was recrystallised from tetrahydrofuran (after charcoal treatment) by addition of cold water to the ice-cold solution, and the product was dried *in vacuo* over potassium hydroxide to give hygroscopic white crystals (1.2 g, 3 mmol, 50%) (Found: C, 63.9; H, 6.10; N, 14.1; remainder, 15.9. C₂₁H₂₄N₄S₂ requires C, 63.6; H, 6.10; N, 14.1, S, 16.2%). Mass spectrum: m/z 396 (6%, M^+) and more intense peaks at 251 (25), 146 (59), 145 (100), 131 (9), 92 (7), 76 (24), and 50 (7%). N.m.r. (in CDCl₃): δ 1.81 (2, q, $J = 7.2$, CH₂), 2.55 (4, t, $J = 7.2$ Hz, CH₂S), 3.67 (6, s, CH₃), 3.82 [4, s, SCH₂(benzimidazole)], 7.25 (4, m, H^{5,6}, benzo), and 7.72 (4, m, H^{4,7}, benzo).

[Cu(bmdhp)(OH₂)](ClO₄)₂. The ligand bmdhp (0.79 g, 2 mmol) dissolved in methanol (40 cm³) was added dropwise to a stirred solution of Cu(ClO₄)₂·6H₂O (3.7 g, 10 mmol) in methanol (20 cm³). The deep green precipitate which formed was filtered off, washed with methanol, and dried over P₄O₁₀ *in vacuo* (Found: C, 37.7; H, 3.85; N, 8.25. C₂₁H₂₆Cl₂CuN₄O₉S₂ requires C, 37.5; H, 3.85; N, 8.30%).

Cu(bmdhp)(ClO₄)₂·2H₂O. A solution of Cu(ClO₄)₂·6H₂O (190 mg, 0.51 mmol) in warm absolute ethanol (5 cm³) was added to a warm solution of bmdhp (203 mg, 0.50 mmol) in 20 cm³ of the same solvent. A green precipitate formed immediately. After refluxing for 30 min, the product was filtered off and dried. The green product is unchanged when recrystallised from absolute ethanol, or if triethyl orthoformate (1 cm³) is added during synthesis (Found: C, 36.4; H, 3.90; Cu, 8.9; N, 8.6. C₂₁H₂₈Cl₂CuN₄O₁₀S₂ requires C, 36.3; H, 4.05; Cu, 9.1; N, 8.1%).

[Cu(bmdhp)Br]ClO₄. A mixture of Cu(ClO₄)₂·6H₂O (0.17 g, 0.5 mmol) and CuBr₂ (0.11 g, 0.5 mmol) in methanol (30 cm³) was added to bmdhp (0.39 g, 1.0 mmol) in the same solvent (40 cm³). The resulting yellowish green precipitate was filtered off, washed with methanol and then with dry diethyl ether. The complex was dried over P₄O₁₀ *in vacuo* (Found: C, 39.2; H, 3.35; N, 8.60. C₂₁H₂₄BrClCuN₄O₄S₂ requires C, 39.5; H, 3.75; N, 8.75%).

Zn(bmdhp)(OH)(ClO₄). The ligand bmdhp (0.79 g, 2 mmol) dissolved in methanol (40 cm³) was added to Zn(ClO₄)₂·6H₂O (3.7 g, 10 mmol) also in methanol (20 cm³). The precipitated complex was filtered off, washed with methanol, and dried over P₄O₁₀ (Found: C, 43.8; H, 4.45; N, 9.65. C₂₁H₂₅ClN₄O₅S₂Zn requires C, 43.6; H, 4.30; N, 9.70%).

Crystal Growth.—Single crystals of [Cu(bmdhp)(OH₂)](ClO₄)₂ were obtained by the liquid-diffusion method²⁰ using acetone as solvent and light petroleum (b.p. 35–60 °C) as precipitant. An acetone solution (5 cm³) of the complex was placed in a test tube and light petroleum (25 cm³) was layered onto it. The sealed tube was allowed to stand and single crystals of the complex formed after 24 h.

Physical Measurements.—U.v.–visible spectra were recorded on Cary 14, Beckman DK-2A, and Perkin-Elmer 320 spectrophotometers. E.s.r. spectra were recorded on Varian E-4 and E-12, X-band spectrometers using diphenylpicrylhydrazyl as standard. The e.s.r. spectral simulations were performed using the SIM-14 program.²¹ Proton n.m.r. spectra were obtained at ambient temperature using a JEOL FX-90Q instrument, chemical shifts being quoted with respect to tetramethylsilane as internal standard. Mass spectra were recorded on a Finnigan 4000 GC-MS. Carbon, H, and N microanalyses were performed by the Canadian Microanalytical Service Ltd. (Vancouver) and the Eindhoven University of Technology Microanalytical Laboratory.

X-Ray Methods and Structure Determination.—Intensity data were collected at room temperature on a Nonius CAD-4 computer-controlled diffractometer (ω – θ scans) by using graphite-monochromated Mo-K_α radiation. Lattice constants were determined by a least-squares refinement of the angular setting of 24 reflections with 13 < θ < 15°. The space group *P*₂₁/*n* followed from the absent reflections for $k = 0, l + h = 2n$ and $h = l = 0, k = 2n$. Each reflection in the range 2 < θ < 24°, $h > 0, k > 0$ was measured in 96 steps. The intensity measurement in 16 steps at each end of a scan was used 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. The intensity *I* and its estimated standard deviation $\sigma(I)$ 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 which accounts for the variable scan speed, *P* is the peak scan count, and *B*₁ and *B*₂ are the low- and high-angle background counts. Three standard reflections were measured every 5 400 s of radiation time to check for instrumental instability and crystal decomposition. No absorption correction was applied. The measured intensities were corrected for Lorentz and polarisation effects in the usual way.

Crystal data. C₂₁H₂₆Cl₂CuN₄O₉S₂, *M* = 677.04, monoclinic, space group *P*₂₁/*n*, *a* = 18.459(3), *b* = 10.362(2), *c* = 16.365(3), β = 117.14(1)°, *U* = 2 785.6(9) Å³, *D*_m = 1.61(1) (floatation in CHCl₃–C₂H₅Br₂), *Z* = 4, *D*_c = 1.61 g cm⁻³, *F*(000) = 1 391, λ (Mo-K_α) = 0.710 73 Å, μ (Mo-K_α) = 11.7 cm⁻¹, crystal size 0.48 × 0.38 × 0.20 mm.

4 505 Reflections were measured, of which 4 353 were independent. The position of the copper atom was located by means of the Harker peaks in a three-dimensional Patterson synthesis. Shifted Patterson maps over the four copper positions gave the positions of 18 other atoms, which included the sulphur and oxygen atoms in the co-ordination sphere and two imidazole rings. Fourier syntheses and full-matrix least-squares refinements gave the positions of all other non-hydrogen atoms with individual isotropic *B* values. In subsequent block-diagonal least-squares refinement, all non-hydrogen atoms were given anisotropic thermal parameters. A Fourier difference map gave the position of 14 hydrogen atoms on the methylene and aromatic carbon atoms. The positions of the four remaining atoms of these kinds were calculated.

The eight hydrogen atoms of the methyl groups and water were found in a later Fourier difference map. All hydrogen atoms were placed on fixed positions and were given an isotropic *B* value of 5.0 Å². The final *R* values, using 1/ σ^2 weighting factors, are *R* = 0.047 ($\sum ||F_o| - s|F_c|| / \sum |F_o|$) and *R'* = 0.075 ($\{[\sigma^{-2}(F)(|F_o| - s|F_c|)^2 / \sigma^{-2}(F)|F_o|^2]\}^{1/2}$) for the significant reflections [3 343 with $I > 2\sigma(I)$]. In a final Fourier difference synthesis some peaks higher than three times the mean noise level were found near the perchlorate anions. Together with the large anisotropic thermal parameters for the oxygen atoms, these point to disorder. Scattering factors for all non-hydrogen neutral atoms²² were used with correction for the anomalous scattering, while the scattering factors for the hydrogen atoms were from ref. 23. The atomic positions are listed in Table 1.

Results and Discussion

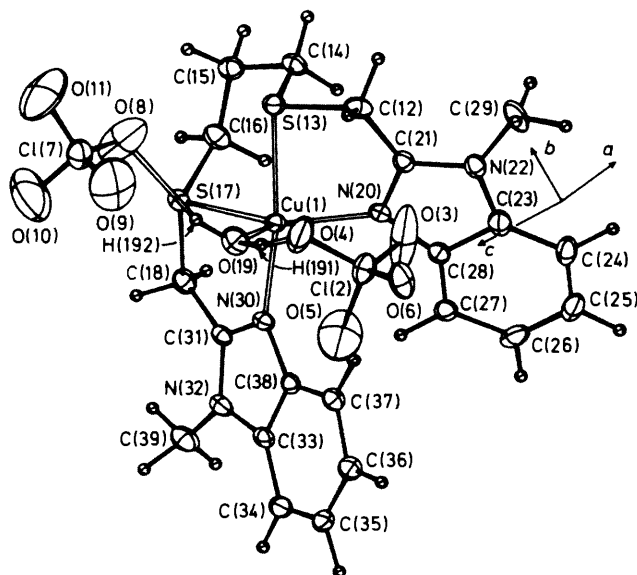
Description of the Structure of [Cu(bmdhp)(OH₂)](ClO₄)₂, and Comparison with Related Structures.—An ORTEP representation of the structure, including the atomic numbering scheme, is given in Figure 1. Intramolecular distances and selected interbond and torsion angles are listed in Table 2. The complex consists of a molecular [Cu(bmdhp)(OH₂)]²⁺ cation and two perchlorate anions. In the solid state, the individual cations lack all symmetry elements (but *E*) and are thus chiral. However, the unit cell (with *Z* = 4) is racemic in this space group.

The copper atom is co-ordinated by two thioether sulphur atoms, two benzimidazole nitrogen atoms, and a molecule of water. The almost linear S(13)–Cu–N(30) moiety has the appearance of the axis in a rough trigonal bipyramid, in which the equatorial positions are occupied by a sulphur atom S(17), a nitrogen atom N(20), and an oxygen atom O(19), and the axial positions by the other sulphur S(13) and nitrogen N(30) atoms. The Cu–O bond distance of 2.225(4) Å would thus seem rather long for a co-ordinated water molecule.¹⁴ The Cu–N bond distances are in the range found in similar compounds,^{9,12–15} while the Cu–S distances are quite short, although not exceptionally so. The 0.01–0.05 Å axial compression of the structure, if it is regarded as a trigonal bipyra-

Table 1. Fractional positional parameters ($\times 10^5$ for Cu, $\times 10^4$ all others) for $[\text{Cu}(\text{bmdhp})(\text{OH}_2)][\text{ClO}_4]_2$ with estimated standard deviations in parentheses

Atom *	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Cu(1)	4 899(2)	22 235(3)	31 655(2)	C(21)	1 313(3)	1 880(5)	2 077(3)
Cl(2)	3 217(1)	244(2)	4 463(1)	N(22)	1 501(3)	1 128(5)	1 517(2)
O(3)	2 771(6)	407(10)	3 575(4)	C(23)	1 001(3)	64(5)	1 278(3)
O(4)	3 342(4)	1 359(5)	4 982(4)	C(24)	911(5)	-981(7)	712(4)
O(5)	280(1)	-53(1)	483(1)	C(25)	324(5)	-1 855(7)	586(4)
O(6)	3 935(3)	-411(5)	4 662(3)	C(26)	-195(4)	-1 698(6)	995(4)
Cl(7)	2 418(1)	4 833(2)	6 043(1)	C(27)	-113(4)	-659(5)	1 577(3)
O(8)	1 922(8)	4 736(6)	5 174(4)	C(28)	501(3)	223(5)	1 722(3)
O(9)	299(1)	394(1)	630(1)	C(29)	2 130(4)	1 441(7)	1 241(4)
O(10)	204(1)	468(1)	653(1)	N(30)	-49(2)	860(4)	3 506(2)
O(11)	275(1)	606(1)	627(1)	C(31)	-758(3)	1 118(5)	3 522(3)
C(12)	1 709(3)	3 114(5)	2 483(4)	N(32)	-1 042(2)	69(4)	3 770(2)
S(13)	1 093(1)	4 024(1)	2 876(1)	C(33)	-484(3)	-927	3 930(3)
C(14)	249(3)	4 609(5)	1 830(3)	C(34)	-478(4)	-2 203(6)	4 200(4)
C(15)	-387(3)	5 242(6)	2 041(4)	C(35)	181(5)	-2 914(5)	4 314(4)
C(16)	-928(3)	4 352(6)	2 227(4)	C(36)	816(4)	-2 438(5)	4 171(4)
S(17)	-417(1)	3 605(1)	3 367(1)	C(37)	795(3)	-1 177(5)	3 884(3)
C(18)	-1 148(3)	2 390(5)	3 298(4)	C(38)	129(3)	-420(5)	3 765(3)
O(19)	1 633(2)	2 134(4)	4 481(2)	C(39)	-1 809(3)	-27(7)	3 807(4)
N(20)	732(2)	1 366(4)	2 225(2)				

* The atomic numbering is according to Figure 1.

**Figure 1.** ORTEP representation of the complex cation in $[\text{Cu}(\text{bmdhp})(\text{OH}_2)][\text{ClO}_4]_2$, showing anisotropic vibration ellipsoids (probability 50%). The hydrogen atoms have an arbitrarily isotropic B value (1.0 \AA^2) for clarity

mid, is similar to those observed previously for trigonal-bipyramidal systems such as $[\text{Cu}(\text{tren})(\text{NH}_3)][\text{ClO}_4]_2$ (0.04 – 0.06 \AA)²⁴ and $[\text{Cu}(\text{tren})(\text{NCS})]\text{NCS}$ (0.022 \AA)²⁵ [$\text{tren} = \text{tris}(2\text{-aminoethyl})\text{amine}$].

However, as we shall show below, the co-ordination geometry is probably better described as a trigonally distorted rectangular pyramid with the sulphur and nitrogen atoms in the equatorial positions and the oxygen atom in the apical position. The sterically demanding benzimidazole groups prevent the sulphur and nitrogen atoms from lying in the same plane, and thus introduce a tetrahedral distortion²⁶ of 35.6° into the N_2S_2 equator. The now 'apical' Cu–O bond is then nearly perpendicular (84.1°) to this N_2S_2 mean plane.

The central six-membered CuS_2C_3 chelate ring formed by Cu(1), S(13), S(17), and the intermediate carbon atoms

C(14)–C(16) has the unstrained chair conformation, as can easily be seen in Figure 1, and is confirmed by the torsion angles in Table 2. The C(12) and C(18) methylenes attached to S(13) and S(17) are thus equivalent to 1,3-substituents on a cyclohexane ring, in the low-strain, mutually equatorial disposition.

The bond distances and angles within the ligand have normal values. The mean planes of the two benzimidazoles intersect at $129.2(1)^\circ$. The two perchlorate anions are each hydrogen-bonded to the water molecule. There is some disorder or libration of the perchlorate anions, which is reflected in some rather short apparent Cl–O distances. All other intermolecular contact distances are equal to or slightly larger than the sums of the van der Waals radii.

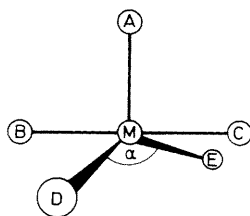
The three compounds with two carbon atoms between the sulphur atoms, $[\text{Cu}(\text{bbdh})\text{Cl}]^+$, $[\text{Cu}(\text{bbidh})\text{Br}]^+$ [$\text{bbidh} = 1,6\text{-bis}(N\text{-benzylimidazol-2'-yl})\text{-2,5-dithiahexane}$], and $[\text{Cu}(\text{bbtb})(\text{OH}_2)]^{2+}$, all have similar donor-atom arrays. Viewed as trigonal bipyramids, they have the two sulphur atoms and the unidentate ligand X in the equatorial plane and the two nitrogen atoms in the axial positions.^{12,14,15} This is not the case in the present structure; these 'trigonal-axial' atoms are not of the same type. The ligand bbdh is very closely related to bbdp and its methyl-substituted analogue, bmdhp ; it only contains one methylene group less in the bridge Y between the two sulphur atoms. We have little reason to expect that methylation of the pyrrole-like nitrogen in benzimidazole will change the intrinsic donor properties of the ligand to such an extent that a totally different geometry will be achieved. The bridging group Y therefore seems to be the main cause for the structural differences, so that the insertion of the extra methylene group thus has marked consequences. The conformational preferences of the chelate ring formed by the copper, sulphur, and intermediate carbon atoms may also be a contributing factor. However, it should probably not be presumed from the detailed structural results that alternative ground-state stereochemistries are excluded for ligands such as bmdhp (see below).

As the title complex is one of a series, which contains a range of structural types intermediate between the idealised square-pyramidal and trigonal-bipyramidal extremes, it seems

Table 2. Intramolecular bond distances (in Å) and angles (°) for [Cu(bmdhp)(OH₂)] [ClO₄]₂ with estimated standard deviations in parentheses; all C-H bond distances are between 0.93 and 1.09 Å

Cu(1)-S(13)	2.328(1)	O(4)-H(191)	2.030(7)	N(20)-C(21)	1.316(6)	N(30)-C(31)	1.348(6)
Cu(1)-S(17)	2.337(1)	O(8)-H(192)	2.040(6)	N(20)-C(28)	1.392(6)	N(30)-C(38)	1.385(6)
Cu(1)-O(19)	2.225(4)	O(19)-H(191)	0.968(4)	C(21)-N(22)	1.363(6)	C(31)-N(32)	1.346(6)
Cu(1)-N(20)	1.997(4)	O(19)-H(192)	0.882(4)	N(22)-C(23)	1.375(7)	N(32)-C(33)	1.396(6)
Cu(1)-N(30)	1.950(4)	C(12)-S(13)	1.806(5)	N(22)-C(29)	1.460(7)	N(32)-C(39)	1.448(6)
Cl(2)-O(3)	1.314(5)	C(12)-C(21)	1.472(7)	C(23)-C(24)	1.385(8)	C(33)-C(34)	1.393(7)
Cl(2)-O(4)	1.390(5)	S(13)-C(14)	1.814(5)	C(23)-C(28)	1.423(7)	C(33)-C(38)	1.380(6)
Cl(2)-O(5)	1.419(9)	C(14)-C(15)	1.516(8)	C(24)-C(25)	1.354(10)	C(34)-C(35)	1.361(9)
Cl(2)-O(6)	1.389(4)	C(15)-C(16)	1.490(8)	C(25)-C(26)	1.405(10)	C(35)-C(36)	1.386(9)
Cl(7)-O(8)	1.297(6)	C(16)-S(17)	1.833(5)	C(26)-C(27)	1.400(8)	C(36)-C(37)	1.383(7)
Cl(7)-O(9)	1.317(8)	S(17)-C(18)	1.813(5)	C(27)-C(28)	1.390(7)	C(37)-C(38)	1.397(7)
Cl(7)-O(10)	1.292(8)	C(18)-C(31)	1.466(7)				
Cl(7)-O(11)	1.384(8)						
S(13)-Cu(1)-S(17)	88.69(5)	S(13)-C(12)-C(21)	110.6(3)	C(21)-N(20)-C(28)	107.0(4)	C(31)-N(30)-C(38)	106.3(4)
S(13)-Cu(1)-O(19)	84.2(1)	C(12)-S(13)-C(14)	104.3(2)	C(12)-C(21)-N(20)	123.2(4)	C(18)-C(31)-N(30)	123.0(4)
S(13)-Cu(1)-N(20)	84.5(1)	S(13)-C(14)-C(15)	110.5(3)	C(12)-C(21)-N(22)	125.0(4)	C(18)-C(31)-N(32)	125.9(4)
S(13)-Cu(1)-N(30)	172.7(1)	C(14)-C(15)-C(16)	116.1(5)	N(20)-C(21)-N(22)	111.8(4)	N(30)-C(31)-N(32)	111.1(4)
S(17)-Cu(1)-O(19)	108.2(1)	C(15)-C(6)-S(17)	112.8(4)	C(21)-N(22)-C(23)	107.8(4)	C(31)-N(32)-C(33)	107.4(4)
S(17)-Cu(1)-N(20)	143.9(1)	C(16)-S(17)-C(18)	102.0(3)	C(21)-N(22)-C(29)	124.3(5)	C(31)-N(32)-C(39)	126.1(5)
S(17)-Cu(1)-N(30)	85.0(1)	S(17)-C(18)-C(31)	110.0(3)	C(23)-N(22)-C(29)	127.9(5)	C(33)-N(32)-C(39)	126.4(4)
O(19)-Cu(1)-N(20)	106.3(1)	H(191)-O(19)-H(192)	103.4(3)	N(22)-C(23)-C(28)	105.6(4)	N(32)-C(33)-C(38)	106.3(4)
O(19)-Cu(1)-N(30)	94.4(1)	O(4)-H(191)-O(19)	168.1(3)	C(24)-C(23)-C(28)	121.6(6)	C(34)-C(33)-C(38)	122.4(5)
N(20)-Cu(1)-N(30)	102.7(2)	O(8)-H(192)-O(19)	158.4(3)	C(23)-C(24)-C(25)	117.9(6)	C(33)-C(34)-C(35)	115.8(5)
O(3)-Cl(2)-O(4)	114.5(4)	O(8)-Cl(7)-O(9)	111.1(7)	C(24)-C(25)-C(26)	121.5(6)	C(34)-C(35)-C(36)	123.8(5)
O(3)-Cl(2)-O(5)	110.4(7)	O(8)-Cl(7)-O(10)	111.0(8)	C(25)-C(26)-C(27)	121.9(6)	C(35)-C(36)-C(37)	119.9(6)
O(3)-Cl(2)-O(6)	111.8(4)	O(8)-Cl(7)-O(11)	111.7(6)	C(26)-C(27)-C(28)	116.6(6)	C(36)-C(37)-C(38)	117.7(5)
O(4)-Cl(2)-O(5)	100.8(5)	O(9)-Cl(7)-O(10)	107.0(8)	N(20)-C(28)-C(23)	107.8(5)	N(30)-C(38)-C(33)	108.9(4)
O(4)-Cl(2)-O(6)	112.9(4)	O(9)-Cl(7)-O(11)	111.7(8)	C(23)-C(28)-C(27)	120.4(5)	C(33)-C(38)-C(37)	120.5(4)
O(5)-Cl(2)-O(6)	105.5(5)	O(10)-Cl(7)-O(11)	104.0(7)				
Torsion angles							
Cu(1)-S(13)-C(14)-C(15)	74.1(4)	C(15)-C(16)-S(17)-Cu(1)	-69.9(4)	C(12)-S(13)-C(14)-C(15)	172.2(4)		
S(13)-C(14)-C(15)-C(16)	-77.1(5)	C(16)-S(17)-Cu(1)-S(13)	61.5(2)	C(18)-S(17)-C(16)-C(15)	-169.8(4)		
C(14)-C(15)-C(16)-S(17)	75.0(5)	S(17)-Cu(1)-S(13)-C(14)	-64.1(2)				

desirable to systematise these geometries by using a structural index parameter. In a five-co-ordinate system such as that represented below, ideally square-pyramidal geometry is associated with $\alpha = \beta = 180^\circ$, for A as the axial ligand (β is the greater of the basal angles, BMC). For perfectly trigonal-



bipyramidal geometry, α becomes 120° and BMC the principal axis. In the great majority of real square-pyramidal systems M is displaced out of the BCDE plane²⁷ toward A, so that these C_{4v} geometries usually have $\alpha = \beta < 180^\circ$, and can be characterised by the value of $(\beta - \alpha)$, which is 0° for a C_{4v} , and 60° for a D_{3h} co-ordination polyhedron. We thus define the geometric parameter $\tau = (\beta - \alpha)/60$ which is applicable to five-co-ordinate structures as an index of the degree of trigonality, within the structural continuum between trigonal bipyramidal and rectangular pyramidal. For a perfectly tetragonal geometry τ is equal to zero, while it becomes unity for a perfectly trigonal-bipyramidal geometry. The approach here is conceptually similar to that used by Muetterties and Guggenberger²⁸ in developing a C_{2v} reaction pathway model for the Berry pseudorotation. Other workers²⁹⁻³¹ have recently limited the 'distortion' index to a single bond angle, but

the τ index also takes into account the remaining two donors. The donor A is simply chosen by the criterion that it should not be any of the four which define the two largest angles, α and β .

Table 3 shows [Cu(bmdhp)(OH₂)]²⁺ to have a τ value of 0.48, and compares it with structural results for complexes with related geometries or donor atoms. The limiting values of the angles α and β define ideal geometries for which there are known relationships between the axial and equatorial bond lengths in copper(II) complexes. The data in Table 3 suggest that the implied relationships amongst the lengths and angles of the consequently defined bonds indeed hold for a wide range of structural types. The model predicts that the Cu-A bond should be elongated relative to the Cu-D/E bonds. Table 3 shows this to be the case. For example, in the Cu₂S₂X chelates [Cu(bbidh)Br]⁺, [Cu(bbdh)Cl]⁺ and [Cu(bbtb)(OH₂)]²⁺, site A is occupied by one sulphur while the other S occupies a D/E-type position. In each case, the A-axial Cu-S bond is indeed longer than this other Cu-S bond. In the case of [Cu(bmdhp)(OH₂)]²⁺, neither sulphur is bound at position A (occupied by water) and the two Cu-S bonds are thus very similar in length, as they also are in [Cu(pdto)(ClO₄)]⁺ [pdto = 1,8-bis(2-pyridyl)-3,6-dithiaoctane]. When the complex becomes trigonal bipyramidal, the sites A, D, and E become equivalent, and the tetragonal-component elongation of the Cu-A bond should become zero. This is indeed the case for $\tau = 1.0$, as illustrated by [Cu(tren)(NH₃)]²⁺, [CuCl₃]³⁻, and [Cu(Me₆tren)Br]⁺ [Me₆tren = tris(2-dimethylaminoethyl)amine]. Amongst the four benzimidazole-thioether complexes, the elongation is also least for [Cu(bbtb)(OH₂)]²⁺, the most trigonal complex.

Table 3. Structural indices for selected copper(II) complexes

Complex ^a	Donor set			τ	% Tetragonal elongation ^b	% Trigonal compression ^c	Ref.
	A	B/C	D/E				
[Cu(cyclops)(CN)]	C	N,N	N,N	0.06	<i>d</i>	0.3	33
[Cu(pdto)(ClO ₄) ⁺	O	N,S	N,S	0.12	<i>d</i>	0	16
[CuL] ²⁺	S	N,N	N,S	0.15	3.9	-6 ^e	<i>f</i>
[Cu(tpea)Cl] ⁺	N	N,N	N,Cl	0.19	ca. 6	2.4	<i>g</i>
[Cu(bbes)(MeOH)(OH ₂) ²⁺	O	N,N	S,O	0.27	13	<i>d</i>	41
[Cu(bdmes)(OH ₂)(ClO ₄) ⁺	O	N,N	S,O	0.34	<i>d</i>	<i>d</i>	9
[Cu(bbidh)Br] ⁺	S	N,N	S,Br	0.37	3.8	<i>d</i>	15
[Cu(bbdh)Cl]	S	N,N	S,Cl	0.38	5.2	<i>d</i>	12
[Cu(bmdhp)(OH ₂) ²⁺	O	N,S	N,S	0.48	<i>d</i>	1.4 ^h	This work
[Cu(bipy) ₂ (O ₂ CR)] ⁺	N	N,N	N,O	0.50	4.7	3.5	43
[Cu(dmim) ₃ Cl ₂]	N	N,N	Cl,Cl	0.64 ^j	<i>d</i>	<i>d</i>	32
[Cu(tmbpc)(tu)] ²⁺	N	N,N	N,S	0.64	4.7	2.7	<i>k</i>
[Cu(bbtb)(OH ₂) ²⁺	S	N,N	S,O	0.65	1.1	<i>d</i>	14
[Cu(tren)(NCS)] ⁺	N	N,N	N,N	0.81	4.3	1.1	25
[Cu(bipy) ₂ (tu)] ²⁺	N	N,S	N,N	0.83	0.1	5.6	<i>k</i>
[Cu(Me ₆ tren)Br] ⁺	N	N,Br	N,N	1.00	0	1.4	<i>l</i>
[Cu(tren)(NH ₃) ²⁺	N	N,N	N,N	1.00	0	2.4 ^m	25
[CuCl ₃] ³⁻	Cl	Cl,Cl	Cl,Cl	1.00	0	4.5	<i>n</i>

^a cyclops = N₄ macrocycle (1,2,8,9-tetramethyl-3,7-diazanona-2,7-dien-1,9-dione dioximato)difluoroborate(1-); L = N₃S₂ macrocycle, 2,15-dimethyl-7,10-dithia-3,14,20-triazabicyclo[14.3.1]icosa-1(20),2,14,16,18-pentaene; tpea = tris[2-(2-pyridyl)ethyl]amine; bbes = bis(2-benzimidazolethyl) sulphide; bdmes = 5,5',6,6'-tetramethylated bbes; tmbpc = NN'-tetramethylenebis(pyridine-2-carbaldimine); tu = thiourea. ^b A bond vs. D (or E) bond, as 100(A - D)/D. ^c B (or C) bond vs. D (or E) bond, as 100(B - D)/B. ^d Not definable; the donor atoms involved are not of the same type. ^e Ligand structure constrains r(Cu-D) to be unusually short. ^f M. G. B. Drew, C. Cairns, S. M. Nelson, and J. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 942. ^g K. D. Karlin, J. C. Hayes, S. Juen, J. P. Hutchinson, and J. Zubieta, *Inorg. Chem.*, 1982, 21, 4106. ^h Mean of the values for the S and N pairs. ⁱ Only the nearer carboxylate O is considered. ^j Mean of values for two inequivalent molecules in unit cell. ^k M. B. Ferreri, A. B. Corradi, G. G. Fava, C. G. Palmieri, M. Nardelli, and C. Pelizzi, *Acta Crystallogr., Sect. B.*, 1973, 29, 1808. ^l M. DiVaira and P. L. Orioli, *Acta Crystallogr., Sect. B.*, 1968, 24, 595. ^m Averaged over different types of amino N-donors. ⁿ K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, 1968, 7, 1111.

The trigonal-component axial compression (defined in Table 3) observed for the above $\tau = 1.0$ structures is quite variable, but averages about 3%. It is also observed for the structures with $\tau < 1$. In [Cu(bmdhp)(OH₂)²⁺ it is manifested less in the Cu-S than in the Cu-N bonds, the average being comparable to that for [Cu(Me₆tren)Br]⁺. This trigonal compression should become zero as the structure approaches square pyramidal* (e.g. first two entries in Table 3). For [Cu(dmim)₃Cl₂] (dmim = 1,2-dimethylimidazole) the trigonal compression of the Cu-N bonds is exaggerated because the 'equatorial' ³² donor against which the compression is usually reckoned actually occupies an A-type site, which causes bond elongation. A similar correlation, amongst bond lengths and bond angles, has been demonstrated for [Cu(bipy)₂Cl]⁺ cations (bipy = 2,2'-bipyridyl).³³

A number of the increasing distortions away from the tetragonal (as revealed by the τ values in Table 3) are the consequence of inter- or intra-ligand steric interferences in the equatorial plane. The nearly planar N₂S₂ in [Cu(pdto)(ClO₄)⁺ must presumably be disrupted when the pyridyl units are replaced by sterically more demanding benzimidazoles; coplanarity of two 2,2'-bipyridyl ligands (as in the [Cu(bipy)₂X]⁺ species) is likewise avoided when alternative geometry is accessible. We thus take the view that the increasing τ values of Table 3 reflect increasing net constraint at the metal.

Spectroscopic Properties.—N.m.r. and i.r. spectra. In (CD₃)₂SO and CDCl₃ the free ligand's aromatic protons

* For a sample of 30 complexes the tetragonal elongation is in fact inversely correlated ($n = 29$, $r = -0.82$) with τ , and also with the trigonal compression ($n = 20$, $r = -0.88$); [Cu(Me₆tren)Br]⁺ and possibly [Cu(tren)(NH₃)²⁺, with small trigonal compressions, are possible exceptions to the latter.

occur as multiplets at δ 7.25 and 7.72, in the expected 4:4 ratio, and this is also true for the zinc(II) complex, so that the two halves of the ligands are equivalent. This fortifies the assignment of a stereochemistry in solution which is more symmetric than that of the copper(II) complex in the solid state. The zinc(II) complex is noteworthy as we have not been able to isolate the expected aqua-complex. Syntheses have yielded only Zn(bmdhp)(OH)(ClO₄) and never Zn(bmdhp)(OH₂)(ClO₄).

The i.r. spectra of Cu(bmdhp)(ClO₄)₂·H₂O and Cu(bmdhp)(ClO₄)₂·2H₂O are very similar. There is little evidence of any perchlorate co-ordination, and only slight differences are seen in the Nujol mull spectra: ν_3 (ClO₄⁻), 1104 (monohydrate) and 1102 cm⁻¹ (dihydrate); δ (out-of-plane) (C-H), 765 and 757 cm⁻¹; ν_4 (ClO₄⁻), 628 cm⁻¹ in both.

Optical and e.s.r. spectra. In the electronic spectrum of the ligand there are two bands (Table 4) in the u.v. region, assigned to $\pi-\pi^*$ transitions.³⁴ These are only slightly affected by co-ordination of the ligand to either Cu^{II} or Zn^{II} and are the only absorptions detectable with the latter. The optical spectrum of the copper(II) complex is somewhat solvent-dependent (Table 4), as expected if solvent molecules replace co-ordinated H₂O, or if the geometry is slightly different in the solution state. In CH₃CN three absorption bands are apparent, which are absent from the zinc(II) chelate, of which the most intense, at 335 nm, is assigned to $\sigma(S) \rightarrow d$ (Cu) charge transfer.^{11,35} The possibility that $\pi(S) \rightarrow d$ (Cu) charge transfer enhances the absorptions at 860 and 640 nm cannot be discounted at this stage, but these bands are nonetheless clearly basically $d-d$ in nature. In solution, the presence of two well separated absorption envelopes is consistent with the presence of square-derived geometry, with considerable axial interaction, similar spectral shapes being displayed in the literature³⁶ for such co-ordination. A simple crystal-field approach yields the relative orbital energies of Figure 2. The right-hand half

Table 4. Electronic spectral data ^a

[Cu(bmdhp)Br]ClO ₄ (in CH ₃ CN)	910 [11.0] (440)	675 [14.8] (720)	480 ^b [20.8] (580)	337 [29.7] (3 600)	278 [36.0] (3 500)	250 [40.0] (12 000)
[Cu(bmdhp)(OH ₂)](ClO ₄) ₂ (in CH ₃ CN)	860 [11.6] (310)	640 [15.6] (290)	—	335 [29.9] (3 200)	278 [36.0] (3 800)	250 [40.0] (18 000)
(in dmf)	875 [11.4] (130)	650 [15.4] (160)	—	335 [29.9] (3 100)	<i>c</i>	<i>c</i>
(reflectance of solid)	840 [11.9]	675 ^d [14.8]	—	<i>c</i>	<i>c</i>	<i>c</i>
Cu(bmdhp)(ClO ₄) ₂ ·2H ₂ O (reflectance of solid)	—	755 [13.2]	—	<i>c</i>	<i>c</i>	<i>c</i>
Zn(bmdhp)(OH)(ClO ₄) (in CH ₃ CN)	—	—	—	—	278 [36.0] (3 600)	260 [38.5] (2 700)
bmdhp (in CH ₃ CN)	—	—	—	—	278 [36.0] (3 800)	254 [39.4] (3 600)

^a λ in nm, ν in 10^3 cm^{-1} (in square brackets), and ϵ in $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (in parentheses). ^b Shoulder. ^c Not observed; solvent or instrument limitation. ^d The two bands are of about equal intensity.

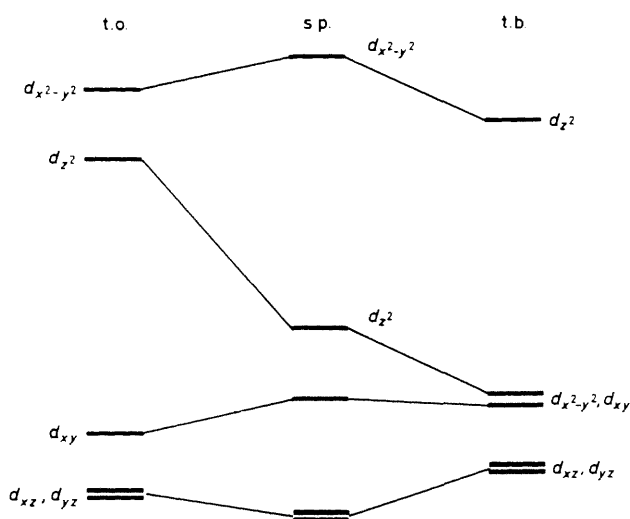


Figure 2. Effect on *d*-orbital energies of conversion of square-pyramidal (s.p.) structure to tetragonal six-co-ordinate (t.o.) (left) and effect of distortion of the tetragonal five-co-ordinate structure to a trigonal five-co-ordinate (t.b.) one (right)

of this is similar to more quantitative diagrams in the literature,^{29,37} which treat the five-co-ordinate systems in terms of a C_{2v} model.

The reflectance spectrum of [Cu(bmdhp)(OH₂)](ClO₄)₂ is slightly different from the solution spectrum, and is not inconsistent with roughly square-pyramidal geometry for the solid-state co-ordination. The frozen-solution e.s.r. spectra (Figure 3) are indicative of a $d_{x^2-y^2}$ ground state ($g_{\parallel} > g_{\perp}$, $g_{\text{min.}} > 2.03$)³⁸ and thus suggest a dominantly tetragonal component in the solution stereochemistries. Observation of identical values for g_0 at 300 K and $\langle g \rangle$ at 77 K indicates that the solution co-ordination is not significantly temperature-dependent. The solution $d_{x^2-y^2}$ ground state thus leads to a tentative assignment of the *d-d* bands as $d_{x^2-y^2} \rightarrow d_{z^2}$ for the lower-energy band, and $d_{x^2-y^2} \rightarrow d_{xy}, d_{xz}, d_{yz}$ within the higher-energy envelope.

A striking difference in spectroscopic properties is observed when the monohydrate and the dihydrate of Cu(bmdhp)-

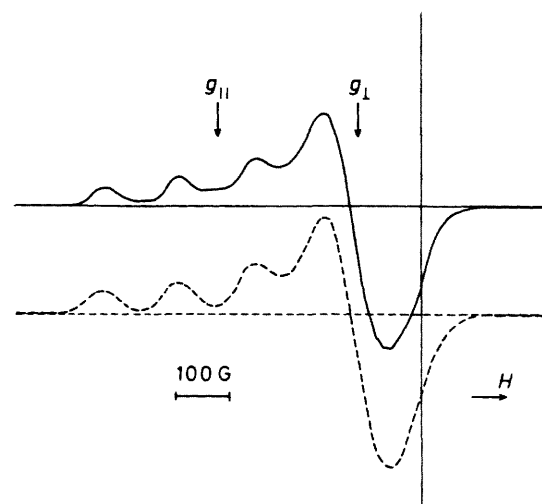


Figure 3. 77-K X-Band e.s.r. spectrum (solid line) of [Cu(bmdhp)(OH₂)](ClO₄)₂ in dmf and the simulation (broken line) using $g_z = 2.267$, $g_y = 2.088$, $g_x = 2.072$, $A_z = 0.0140$, $A_y = A_x = 0.0006 \text{ cm}^{-1}$, and parallel and perpendicular linewidths of 55 and 110 G ($G = 10^{-4} \text{ T}$) respectively. The vertical bar locates $g = 2$

(ClO₄)₂ are compared in their solid states. This is exemplified in Figure 4. The neat powder e.s.r. of [Cu(bmdhp)(OH₂)](ClO₄)₂ may not be as informative as it appears. Although one might expect an axial-tetragonal (or rhombic) spectrum with a shape like that in Figure 4, the apparent g values lead to a g anisotropy,³⁸ G , of 2.3. This low value, along with a temperature dependence of the spectrum, suggests the presence of a weak exchange interaction.³⁸ In fact, the misalignment of the molecular axes in this space group (Figure 1) does not allow firm conclusions to be drawn about the electronic structure. Thus the molecular electronic principal axis is not necessarily the one (A-Cu) on which the τ computation is based.

The e.s.r. spectrum of Cu(bmdhp)(ClO₄)₂·2H₂O is of the 'inverted' type (Figure 4) with $g_{\parallel} < g_{\perp}$ ($G = 4.0$). The implied d_{z^2} ground state is expected for a limited number of co-ordination geometries, but including the trigonal-bipyramidal type, which is observed for other benzimidazole-thioether

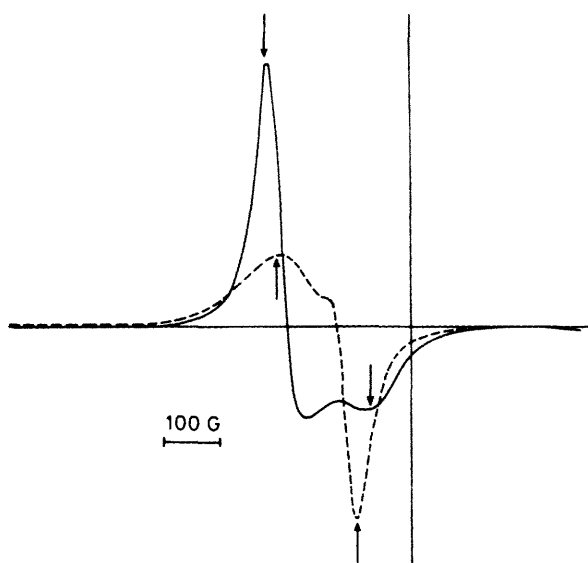


Figure 4. Ambient-temperature solid-state X-band e.s.r. spectra of $[\text{Cu}(\text{bmdhp})(\text{OH}_2)](\text{ClO}_4)_2$ (broken line) and of $\text{Cu}(\text{bmdhp})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (solid line). The vertical bar marks $g = 2$, while the arrows indicate apparent g values of 2.16, 2.14, 2.06, and 2.04

complexes.^{12,14,15,38} The reflectance spectra (Table 4) are also different, for the mono- and di-hydrate. For the latter, the two bands in the visible region have merged into one, consistent with the diminished band separations inherent in the right-hand side of Figure 2, for more trigonally distorted stereochemistries.

These observations suggest that in the dihydrate the coordination is such that its τ value is greater than that of the monohydrate. The more trigonal geometry, in conjunction with an oxygen donor as the fifth ligand, is probably associated with the two benzimidazoles being mutually *trans*-axial, as is observed¹⁴ for $[\text{Cu}(\text{bbtb})(\text{OH}_2)]^{2+}$.

In solution, the present complex and its non-methylated analogue have similar optical spectra,¹² and their e.s.r. spectra in dimethylformamide (dmf) are also very similar, the respective values of g_{\parallel} and A_{\parallel} being essentially identical (Figure 3). The position of the dmf-solution data on an A_{\parallel} vs. g_{\parallel} plot confirms that the equatorial planes in the two complexes contain at least one sulphur donor in this solvent.^{26,39,40} Because aromatic nitrogen donors frequently give pronounced nitrogen superhyperfine splitting in the g_{\perp} region,³¹ the low resolution of such splitting in the e.s.r. spectrum of $[\text{Cu}(\text{bmdhp})(\text{OH}_2)]^{2+}$ was unanticipated, but is likely related to the distorted structure.⁴¹

The solution e.s.r. spectra of the bromo-complex, $[\text{Cu}(\text{bmdhp})\text{Br}]\text{ClO}_4$, are quite complex, both at ambient temperatures and 77 K, where the presence of $\Delta M = 2$ transitions in dmf and propylene carbonate solutions strongly suggests that a dimerisation equilibrium is operating. Even the ambient-temperature spectra in dmf solution contain more fine structure than expected for a simple $\text{CuN}_2\text{S}_2\text{X}$ system.* In the solid state the rhombic e.s.r. spectrum (g_{app} 2.01, 2.11, and 2.168) of $[\text{Cu}(\text{bmdhp})\text{Br}]\text{ClO}_4$ strongly resembles those of the five-co-ordinate complexes $[\text{Cu}(\text{bipy})\text{X}]^+$ ($\text{X} = \text{carboxylate}$)

* This may also reflect the presence of superhyperfine structure due to the Br nucleus. Such structure has been observed previously in Cu-Br systems with a trigonal component to their symmetry.⁴²

† The quantitative redox aspects of the complexes will be discussed elsewhere.

(Table 3), which have a geometry intermediate between square pyramidal and trigonal bipyramidal.^{43,44} No $\Delta M = 2$ transition is observed.

The electronic spectrum (Table 4) of $[\text{Cu}(\text{bmdhp})\text{Br}]\text{ClO}_4$ resembles that of the corresponding aqua-complex, but with the $d-d$ transitions shifted slightly to lower energy, in accord with a slightly weaker donor set (including Br^- rather than H_2O or CH_3CN). The intense band at 337 nm is again assigned to $\sigma(\text{S}) \rightarrow \text{Cu}$ charge transfer, and the shoulder at 480 nm to $\text{Br} \rightarrow \text{Cu}$ charge transfer.³⁵

Chemical Properties—A critical difference between the chemistry of the methylated ligand and that of the non-methylated one is that the copper(II) compounds of the latter more readily undergo autoreduction in solution.^{13,45} For example, evaporation of a methanolic solution of bmdhp and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in 1 : 1 molar ratio, at or below room temperature, yields green crystals of $[\text{Cu}(\text{bmdhp})(\text{OH}_2)](\text{ClO}_4)_2$. On the other hand, with bbdhp under the same conditions, only colourless copper(I) complexes are obtained as solids. This tendency is less marked in more strongly co-ordinating solvents, from which separation of these Lewis-acidic complexes is usually very difficult.

The structure of $[\text{Cu}(\text{bmdhp})(\text{OH}_2)](\text{ClO}_4)_2$ is also of interest, inasmuch as the structure of a corresponding copper(I) compound, viz. $[\text{Cu}(\text{bbdhp})][\text{PF}_6]_{0.66}[\text{BF}_4]_{0.34}$, has recently been resolved.¹³ In the latter compound the copper atom is linearly co-ordinated by the two benzimidazole nitrogen atoms, the sulphur atoms having moved out of range for strong bonding. The structure of the copper(II) compound with bmdhp does not bear any obvious resemblance to that of this copper(I) analogue.† A related ligand, of which the structures of both copper(I) and copper(II) compounds are known, is 1,8-bis-(2-pyridyl)-3,6-dithiaoctane (pdto, Table 3).¹⁶ The less bulky pyridine groups apparently make possible a square-pyramidal structure for the copper(II) form and a more closely related tetrahedral one for the reduced form. The complexation of the benzimidazole analogue of this ligand (bbdo) with copper(I) and copper(II) is under current investigation.

Acknowledgements

We thank N. Amin for assistance with n.m.r. spectra, and Drexel University for research support. The assistance of S. Gorter with the X-ray data collection is gratefully acknowledged.

References

- 1 'Copper Coordination Chemistry: Biochemical and Inorganic Perspectives,' eds. K. D. Karlin and J. A. Zubieta, Adenine Press, Guilderland, New York, 1983.
- 2 P. M. Colman, H. C. Freeman, J. M. Guss, M. Murata, V. A. Norris, J. A. M. Ramshaw, and M. P. Venkatappa, *Nature (London)*, 1978, **272**, 319.
- 3 E. T. Adman, R. E. Stenkamp, L. C. Sieker, and L. H. Jensen, *J. Mol. Biol.*, 1978, **123**, 35.
- 4 E. T. Adman and L. E. Jensen, *Isr. J. Chem.*, 1981, **21**, 8.
- 5 G. E. Norris, B. F. Anderson, and E. N. Baker, *J. Mol. Biol.*, 1983, **165**, 501.
- 6 R. Osterberg, *Coord. Chem. Rev.*, 1974, **12**, 309.
- 7 J. S. Thompson, T. J. Marks, and J. A. Ibers, *J. Am. Chem. Soc.*, 1979, **101**, 4180.
- 8 J. J. Prochaska, W. F. Schwindinger, M. Schwartz, M. H. Burk, E. Bernarducci, R. A. Lalancette, J. A. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, 1981, **103**, 3446.
- 9 J. V. Dargigian, V. McKee, and C. A. Reed, *Inorg. Chem.*, 1982, **21**, 1332.
- 10 A. W. Addison and E. Sinn, *Inorg. Chem.*, 1983, **22**, 1225.

- 11 D. E. Nikles, M. J. Powers, and F. L. Urbach, *Inorg. Chim. Acta*, 1979, **37**, L499.
- 12 P. J. M. W. L. Birker, J. Helder, G. Henkel, B. Krebs, and J. Reedijk, *Inorg. Chem.*, 1982, **21**, 357.
- 13 M. J. Schilstra, P. J. M. W. L. Birker, S. Gorter, G. C. Verschoor, and J. Reedijk, *Inorg. Chem.*, 1982, **21**, 2637.
- 14 F. J. Rietmeijer, P. J. M. W. L. Birker, S. Gorter, and J. Reedijk, *J. Chem. Soc., Dalton Trans.*, 1982, 1191.
- 15 P. J. M. W. L. Birker, E. F. Godefroi, J. Helder, and J. Reedijk, *J. Am. Chem. Soc.*, 1982, **104**, 7556.
- 16 G. R. Brubaker, J. N. Brown, M. K. Yoo, R. A. Kinsey, T. M. Kutchan, and E. A. Mottel, *Inorg. Chem.*, 1979, **18**, 299.
- 17 M. A. Phillips, *J. Chem. Soc.*, 1928, 2393.
- 18 J. V. Dagdigan and C. A. Reed, *Inorg. Chem.*, 1979, **18**, 2623.
- 19 A. W. Addison and P. J. Burke, *J. Heterocycl. Chem.*, 1981, **18**, 803.
- 20 P. G. Jones, *Chem. Br.*, 1981, **17**, 222.
- 21 G. P. Lozos, B. M. Hoffman, and C. G. Fronz, Quantum Chemistry Program Exchange, 1974, **11**, 265.
- 22 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
- 23 R. F. Steward, E. R. Davidson, and W. J. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.
- 24 M. Duggan, N. Ray, B. Hathaway, G. Tomlinson, P. Brint, and K. Pelin, *J. Chem. Soc., Dalton Trans.*, 1980, 1342.
- 25 P. C. Jain and E. C. Lingafelter, *J. Am. Chem. Soc.*, 1967, **89**, 6131.
- 26 (a) A. W. Addison, in ref. 1, p. 109; (b) B. J. Hathaway, *Coord. Chem. Rev.*, 1982, **41**, 423.
- 27 B. F. Hoskins and F. D. Whillans, *Coord. Chem. Rev.*, 1972, **9**, 365.
- 28 E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1974, **96**, 1748.
- 29 A. Bencini, I. Bertini, D. Gatteschi, and A. Scozzafava, *Inorg. Chem.*, 1978, **17**, 3194.
- 30 S. Tyagi and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 2029.
- 31 W. D. Harrison, D. M. Kennedy, M. Power, R. Sheahan, and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 1556.
- 32 F. Huq and A. C. Skapski, *J. Chem. Soc. A*, 1971, 1927.
- 33 O. P. Anderson and A. B. Packard, *Inorg. Chem.*, 1980, **19**, 2941.
- 34 S. F. Mason, 'Physical Methods in Heterocyclic Chemistry,' vol. II, ed. A. R. Katritzky, Academic Press, New York, 1963, ch. 7.
- 35 V. M. Miskowski, J. A. Thich, R. Solomon, and H. J. Schugar, *J. Am. Chem. Soc.*, 1976, **98**, 8344.
- 36 E. D. McKenzie, *J. Chem. Soc. A*, 1970, 3095.
- 37 N. J. Ray, L. Hulett, R. Sheahan, and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 1463.
- 38 B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 1970, **5**, 143.
- 39 A. Sakaguchi and A. W. Addison, *J. Chem. Soc., Dalton Trans.*, 1979, 600.
- 40 J. Peisach and W. E. Blumberg, *Arch. Biochem. Biophys.*, 1974, **165**, 691.
- 41 A. W. Addison, P. J. Burke, K. Henrick, T. N. Rao, and E. Sinn, *Inorg. Chem.*, 1983, **22**, 3645.
- 42 U. Nishida, N. Oishi, and S. Kida, *Inorg. Chim. Acta*, 1980, **44**, L257.
- 43 W. Fitzgerald and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 567.
- 44 R. J. Fereday, P. Hodgson, S. Tyagi, and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, 1981, 2070.
- 45 P. L. Verheijdt, J. G. Haasnoot, and J. Reedijk, *Inorg. Chim. Acta*, 1982, **76**, L43.

Received 2nd August 1983; Paper 3/1356