Synthesis, Spectroscopic and Structural Properties of 2,2-Dimethylpropane-1,3-diaminecopper(II) Complexes. Temperature-dependent Tetragonal Distortion in Some Thermochromic Complexes. Crystal and Molecular Structure of Bis(2,2-dimethylpropane-1,3-diamine)diperchloratocopper(II)

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Some compounds of the type $[Cu(dmpd)_2X_2]$ (dmpd = 2,2-dimethylpropane-1,3-diamine and X = Cl, Br, or ClO_4) have been prepared and characterized by means of magnetic moments, e.s.r., electronic, and i.r. spectra. For one of them, bis(2,2-dimethylpropane-1,3-diamine)diperchloratocopper(II), the crystal structure has been determined by three-dimensional *X*-ray diffraction. Crystals are monoclinic, space group $P2_1/c$, with unit-cell dimensions: $a = 9.724(2)$, $b = 6.287(1)$, $c = 16.191(3)$ Å, $\beta = 97.66(1)°$, and $Z = 2$. The structure has been refined to $R = 0.036\,8$. Co-ordination around the copper is distorted tetragonal bipyramidal; two centrosymmetric chelate ligands form the base [Cu–N(1) 2.028(3), Cu–N(2) 2.021(3) Å], and the two centrosymmetric unidentate perchlorate ions form the apices [Cu–O(1) 2.602(3) Å]. The electronic and i.r. spectra of the $[Cu(dmpd)_2X_2]$ complexes are temperature-dependent suggesting reversible continuous thermochromism arising through a temperature-dependent axial interaction between the anion and the CuN_4 plane, with a more square form being favoured at higher temperature. Other complexes of the types $[Cu(dmpd)X_2]$ and $[Cu(H_2dmpd)X_4]$ (X = Cl or Br) were also prepared and investigated and their possible stereochemistries discussed.

A COMPARISON of the stability of metal–amine complexes as a function of chelate-ring size has only been reported for complexes in solution. It was found that the complexes of propane-1,3-diamine are less stable than those of ethylenediamine,[1-4] since there is a less favourable entropy change in the formation of the six-membered ring.[3,4] On the other hand, it is well known that the copper(II) complexes of *N*-substituted ethylenediamines in the solid state show interesting properties, on which considerable physical studies have been made.[5-11]

To investigate the effect of ring size on these properties we have studied the copper(II) complexes of 2,2-dimethylpropane-1,3-diamine (hereafter abbreviated as dmpd) in the solid state. The prepared compounds were investigated by means of magnetic and spectroscopic measurements, and the crystal structure was also reported for one of them, bis(2,2-dimethylpropane-1,3-diamine)diperchloratocopper(II), which shows the most interesting properties and may be compared with the corresponding ethylenediamine complexes.

EXPERIMENTAL

All chemicals were reagent grade and used as received. The 2,2-dimethylpropane-1,3-diamine was kindly supplied by BASF.

Preparation of the Complexes.—The compounds of the type $[Cu(dmpd)_2X_2]$ (X = Cl, Br, or ClO_4) were prepared by mixing the amine and the corresponding copper salt in a 2 : 1 stoicheiometric ratio in methanol and by cooling at 4—5 °C for some hours. The chloride and bromide complexes are light blue and the perchlorate is blue-violet (Found: C, 35.45; H, 8.40; N, 16.55. Calc. for $C_{10}H_{28}Cl_2CuN_4$: C, 35.45; H, 8.35; N, 16.55%. Found: C, 28.25; H, 6.70; N, 13.15. Calc. for $C_{10}H_{28}Br_2CuN_4$: C, 28.05; H, 6.60; N, 13.1%. Found: C, 25.7; H, 6.10; N, 12.0. Calc. for $C_{10}H_{28}Cl_2CuN_4O_8$: C, 25.7; H, 6.05; N, 12.0%).

The compounds of formula $[Cu(dmpd)X_2]$ (X = Cl or Br) instantaneously precipitated by adding the amine to a copper salt solution in methanol. The metal : amine molar ratio was 1 : 1 or 2 : 1. The chloride is pale blue and the bromide is green (Found: C, 25.2; H, 6.00; N, 11.8. Calc. for $C_5H_{14}Cl_2CuN_2$: C, 25.35; H, 5.95; N, 11.85%. Found: C, 18.35; H, 4.40; N, 8.60. Calc. for $C_5H_{14}Br_2CuN_2$: C, 18.45; H, 4.35; N, 8.60%).

The compounds of formula $[Cu(H_2dmpd)X_4]$ (X = Cl or Br) were prepared by mixing equimolar amounts of the copper salt and the dihydrohalide salts of the amine in methanol. The resulting solutions were slowly evaporated until precipitation of the compounds was effected. The tetrachlorocuprate complex is yellow and the tetrabromocuprate is dark violet (Found: C, 19.8; H, 5.25; Cl, 45.35; N, 8.90. Calc. for $C_5H_{16}Cl_4CuN_2$: C, 19.4; H, 5.20; Cl, 45.8%; N, 9.05. Found: C, 12.25; H, 3.35; Br, 66.05; N, 5.70. Calc. for $C_5H_{16}Br_4CuN_2$: C, 12.3; H, 3.30; Br, 65.6; N, 5.75%).

Physical Measurements.—The electronic spectra of the solid compounds were recorded as mull transmission spectra with a Beckman DK 2A spectrophotometer in the 293—393 K temperature range. Infrared spectra were recorded on a Perkin-Elmer 180 spectrophotometer as Nujol mulls or KBr discs in the 250—4 000 cm^{-1} range and in Nujol mull on Polythene, as support, in the 60—500 cm^{-1} range. The i.r. spectra of the $[Cu(dmpd)_2(ClO_4)_2]$ compound in the range 293—393 K were recorded between 500 and 1 300 cm^{-1} as powder on KBr discs with a Perkin-Elmer 457 spectrophotometer. The room-temperature magnetic moments were measured by the Gouy method using $[Ni(en)_3][S_2O_3]$ as calibrant and correcting for diamagnetism with the appropriate Pascal constants. The room-temperature e.s.r. spectra were recorded on a JEOL PE-3X spectrometer. Quartz sample tubes were employed for polycrystalline samples. Spectra were calibrated with diphenylpicrylhydrazyl ($g = 2.003\ 6$) as a field marker. Differential scanning calorimetric analysis was performed with a Perkin-Elmer DSC-1 instrument.

Crystallographic Data Collection.—Crystal data. $C_{10}H_{28}Cl_2CuN_4O_8$, $M = 466.8$, Monoclinic, $a = 9.724(2)$, $b = 6.287(1)$, $c = 16.191(3)$ Å, $\beta = 97.66(1)°$, $U = 981.0(3)$ Å^3, $D_m = 1.57$ g cm^{-3} (by flotation), $Z = 2$, $D_c = 1.58$, $F(000) = 486$, $\mu(\text{Cu-}K_\alpha) = 45.2$ cm^{-1}, space group $P2_1/c$ (from systematic absences).

Cell dimensions were obtained from rotation and Weissenberg photographs and refined by least squares using the 2θ values of 15 reflections accurately measured. For intensity data collection the crystal of dimensions $0.09 \times 0.12 \times 0.25$ mm was mounted with the [001] axis along the ϕ axis of an automated Siemens AED ' on line ' single-crystal diffractometer, using nickel-filtered Cu-K_α radiation ($\lambda = 1.541\ 78$ Å) and the ω—2θ scan technique within the range $0 < 2\theta < 140°$. 1 862 Independent reflections were measured; of these 1 580, having $I > 2\sigma(I)$, were considered observed and used in the analysis. The structure amplitudes were obtained after Lorentz and polarization corrections; the absolute scale was established by Wilson's method and refined by least squares. No absorption correction was applied because of the low μR value.

Structure Determination and Refinement.—The crystal structure was solved by the conventional heavy-atom method. One cycle of structure-factor calculation with the contribution from the copper atom fixed at the origin and the successive Fourier synthesis revealed the positions of all non-hydrogen atoms. Refinement with isotropic thermal parameters converged at $R = 0.107$ and with anisotropic thermal parameters at $R = 0.057$. A subsequent difference-Fourier map revealed all hydrogen atoms, which were included in the refinement with isotropic thermal parameters. The final R index was 0.0368. The effects of the anomalous dispersion for Cu and Cl were included in all structure-factor calculations. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$ and the reflections were weighted according to the scheme $w^{-1} = [\sigma^2(F_o) + 0.004\ (F_o^2)]$. The atomic scattering factors were those of Cromer and Mann [12] for Cu, Cl, O, N, and C and those of Stewart *et al.*[13] for H. Final observed and calculated structure amplitudes and thermal parameters are available in Supplementary Publication No. SUP 22857 (13 pp.).* The final atomic co-ordinates are listed in Table 1. All the calculations were performed on the Cyber 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord Orientale.

Nitrogen, carbon, and hydrogen were analyzed by Mr. G. Pistoni using a Carlo Erba elemental analyzer. Halides were directly determined in an aqueous solution of the complexes using the Volhard method.

TABLE 1

Fractional atomic co-ordinates ($\times 10^4$ for Cu, Cl, O, N, C; $\times 10^3$ for H atoms) with estimated standard deviations in parentheses

	x	*y*	*z*
Cu	0	0	0
Cl	1 677(1)	3 690(1)	−1 248(1)
O(1)	957(3)	3 542(5)	−528(2)
O(2)	1 678(4)	1 662(5)	−1 646(2)
O(3)	996(6)	5 249(6)	−1 788(3)
O(4)	3 052(4)	4 337(8)	−1 011(3)
N(1)	763(3)	1 026(6)	1 158(2)
N(2)	1 780(3)	−1 553(5)	−125(2)
C(1)	2 274(3)	1 433(6)	1 369(2)
C(2)	3 183(4)	−479(6)	1 227(2)
C(3)	3 157(4)	−878(8)	298(2)
C(4)	2 741(6)	−2 484(8)	1 675(3)
C(5)	4 684(5)	112(11)	1 582(4)
H(1)	44(5)	10(6)	147(3)
H(2)	35(4)	211(7)	129(3)
H(3)	253(4)	272(7)	103(3)
H(4)	249(4)	191(7)	197(3)
H(5)	340(5)	30(7)	−4(3)
H(6)	373(4)	−192(7)	17(3)
H(7)	332(5)	−373(9)	162(3)
H(8)	270(5)	−232(9)	222(4)
H(9)	179(6)	−314(8)	147(3)
H(10)	494(6)	151(10)	137(4)
H(11)	459(6)	45(9)	219(4)
H(12)	547(6)	−116(9)	149(3)
H(13)	162(4)	−283(7)	1(2)
H(14)	187(4)	−155(6)	−61(3)

RESULTS AND DISCUSSION

All the compounds are stable in air and soluble in polar organic solvents, except the [Cu(dmpd)X_2] complexes which are insoluble. Their physical properties are such as to divide them into three types: (i) [Cu(dmpd)$_2X_2$] (X = Cl, Br, or ClO_4); (ii) [Cu(dmpd)X_2] (X = Cl or Br); and (iii) [Cu(H_2dmpd)X_4] (X = Cl or Br), which are examined separately.

TABLE 2

Bond distances (Å) and angles (°) in the complex

	x	*y*	*z*
Cu–O(1)	2.602(3)	N(1)–C(1)	1.486(4)
Cu–N(1)	2.028(3)	N(2)–C(3)	1.482(5)
Cu–N(2)	2.021(3)	C(1)–C(2)	1.528(5)
Cl–O(1)	1.441(4)	C(2)–C(3)	1.522(5)
Cl–O(2)	1.429(3)	C(2)–C(4)	1.544(6)
Cl–O(3)	1.418(5)	C(2)–C(5)	1.541(6)
Cl–O(4)	1.401(4)		
N(1)–H(1)	0.86(4)	C(3)–H(6)	0.91(5)
N(1)–H(2)	0.83(5)	C(4)–H(7)	0.98(5)
N(2)–H(13)	0.85(4)	C(4)–H(8)	0.89(6)
N(2)–H(14)	0.80(4)	C(4)–H(9)	1.03(5)
C(1)–H(3)	1.03(4)	C(5)–H(10)	0.99(6)
C(1)–H(4)	1.01(4)	C(5)–H(11)	1.03(6)
C(3)–H(5)	0.97(4)	C(5)–H(12)	1.13(6)
N(1)–Cu–N(2)	91.9(1)	Cu–N(2)–C(3)	123.3(2)
O(1)–Cu–N(1$^{\mathrm{I}}$)	85.9(1)	N(1)–C(1)–C(2)	113.8(3)
N(1$^{\mathrm{I}}$)–Cu–N(2)	88.1(1)	C(1)–C(2)–C(3)	110.2(3)
O(1)–Cu–N(2)	91.8(1)	C(1)–C(2)–C(4)	111.7(3)
O(3)–Cl–O(4)	108.6(3)	C(1)–C(2)–C(5)	107.0(4)
O(2)–Cl–O(4)	108.9(2)	C(5)–C(2)–C(3)	107.4(3)
O(1)–Cl–O(4)	110.3(3)	C(4)–C(2)–C(5)	109.3(4)
O(1)–Cl–O(3)	107.8(3)	C(3)–C(2)–C(4)	111.2(3)
O(1)–Cl–O(2)	109.7(2)	N(2)–C(3)–C(2)	113.5(3)
O(2)–Cl–O(3)	111.6(2)		
Cu–N(1)–C(1)	119.8(2)		

I = $\bar{x}, \bar{y}, \bar{z}$.

Type (i) *Complexes.—Description of the structure of bis*(2,2-*dimethylpropane*-1,3-*diamine*)*diperchlorato-copper*(II). As shown in Figure 1, the copper atom lying on the inversion centre co-ordinates four nitrogen atoms of two centrosymmetric ligand molecules in a square-planar arrangement. Two oxygen atoms from two perchlorate ions complete the co-ordination to form an elongated tetragonal bipyramid. The equatorial

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

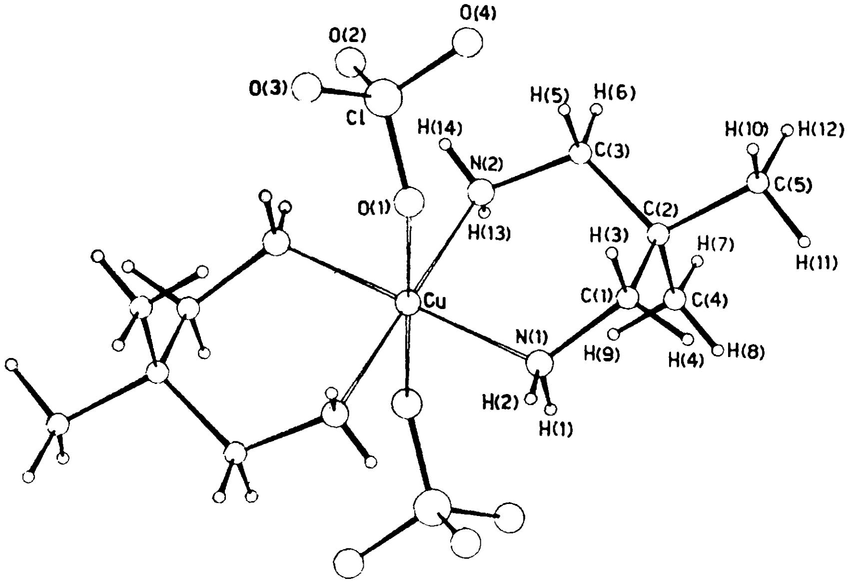

FIGURE 1 Perspective view of the structure

plane is constrained to planarity by the inversion centre at Cu, and the line through O(1)CuO(1^{I}) (I = $\bar{x}$, $\bar{y}$, $\bar{z}$) forms an angle of 4.4° with the normal to the N(1)-N(2)N(1^{I})N(2^{I}) plane. The Cu-N distances (Table 2) [Cu-N(1) = 2.028(3), Cu-N(2) = 2.021(3) Å] are in agreement with those found in other copper amine complexes; *e.g.* 2.031(6) Å in [Cu(NH$_3$)$_4$(OH$_2$)][SO$_4$],[14] 2.03(1) Å in μ_3-hydroxo(oxo)-tri-μ-(3-methyl-3-propylaminobutan-2-one oximato-*NN'O*)-tris[aquocopper(II)],[15] 2.01(1) in sperminecopper(II) perchlorate,[16] † 2.02(3) Å in [Cu(NH$_2$CH$_2$CHMeNH$_2$)$_2$(ClO$_4$)$_2$],[17] and 2.027(5), 2.029(5) Å in the two crystalline forms of [Cu(NH$_2$CH$_2$CH$_2$CHMe-NH$_2$)$_2$(ClO$_4$)$_2$].[18] The Cu-O distance is in the range of values (2.52—2.68 Å) found in other copper(II) complexes with unidentate perchlorate groups.[17-23]

On co-ordinating, the ligand forms a six-membered chelate ring, which shows the ' chair ' conformation, as revealed by puckering parameters:[24] q_2 = 0.219 Å, q_3 = −0.502 Å, ϕ_2 = 349.6°, Q = 0.55 Å. The ' chair ' conformation is also found in chelate rings involving the propane-1,3-diamine ligand.[25,26] Bond distances and angles in the present ligand are comparable with those found in propane-1,3-diamine complexes and the angles around C(2) range from 107.0 to 111.7°.

The geometry of the perchlorate group is slightly distorted tetrahedral with the Cl-O distances in the range 1.401(4)—1.441(4) Å and the O-Cl-O angle ranging from 107.8(3) to 110.3(3)°. The Cu-O(1)-Cl bond angle, 123.7(2)°, is in reasonable agreement with the corresponding values found in perchlorate complexes in which the Cu-O distance is similar.[21-23] In bis[2-(2-aminoethyl)pyridine]diperchloratocopper(II),[27] in which the perchlorate ion is more weakly co-ordinated [Cu-O 2.833(2) Å], the Cu-O-Cl angle is much larger [148.8(1)°] than that found in the present compound.

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† (4, 9-Diazadodecane-1,12-diamine-*NN'N''N'''*) copper(II) perchlorate.

TABLE 3

Hydrogen bonds and contacts less than 3.6 Å

(*a*) Hydrogen bonds (Å) and associated angles (°)

* N(1) ··· O(3^{II})	3.39(6)				
N(1)–H(1)	0.86(4)	N(1) ... O(3^{II})	2.81(4)	N(1)–H(1) ··· O(3^{II})	128(3)
* N(1) ··· O(2^{I})	3.101(5)				
		H(1) ··· O(2^{I})	2.39(4)	N(1)–H(1) ··· O(2^{I})	140(4)
N(1) ··· O(3^{III})	3.149(6)				
N(1)–H(2)	0.83(4)	H(2) ··· O(3^{III})	2.32(4)	N(1)–H(2) ··· O(3^{III})	171(4)
* N(2) ··· O(3^{IV})	3.365(6)				
N(2)–H(14)	0.80(4)	H(14) ··· O(3^{IV})	2.82(4)	N(2)–H(14) ··· O(3^{IV})	127(3)
* N(2) ··· O(4^{IV})	3.277(6)				
		H(14) ··· O(4^{IV})	2.94(4)	N(2)–H(14) ··· O(4^{IV})	108(3)
N(2) ··· O(1^{IV})	3.231(5)				
N(2)–H(13)	0.85(4)	H(13) ··· O(1^{IV})	2.49(4)	N(2)–H(13) ··· O(1^{IV})	146(3)

(*b*) Contacts less than 3.6 Å

O(2) ··· O(3^{V})	3.496(6)	O(1) ··· N(1)	3.182(5)
O(3) ··· C(4^{VI})	3.489(7)	O(1) ··· N(2)	3.345(5)
N(2) ··· Cl^{IV}	3.495(7)	O(1) ··· C(1)	3.433(5)
O(1) ··· N(1^{I})	3.410(5)		

I	$\bar{x}, \bar{y}, \bar{z}$	IV	$x, y - 1, z$
II	$x, \frac{1}{2} - y, \frac{1}{2} + z$	V	$\bar{x}, y - \frac{1}{2}, \bar{z} - \frac{1}{2}$
III	$\bar{x}, 1 - y, \bar{z}$	VI	$x, \frac{1}{2} - y, z - \frac{1}{2}$

* Considered as a bifurcated hydrogen bond.

TABLE 4

Spectroscopic and magnetic properties of the solid complexes

	θ_c/°C	d–d bands/cm^{-1}	Charge-transfer bands/cm^{-1}			$\mu_{eff.}$/B.M.[a]	$g_{\parallel}$	$g_{\perp}$	g_0	ν(Cu–N)/cm^{-1}	ν(Cu–X)/cm^{-1}
(*a*) Type (i) complexes											
[Cu(dmpd)$_2$Cl$_2$]	20	17 390	35 710 (sh)	42 550		1.84	2.234	2.050	2.124	418vs	
	120	16 840									
[Cu(dmpd)$_2$Br$_2$] [b]	20	17 100	35 100	41 670		1.84			2.123	415s	
	120	16 800									
[Cu(dmpd)$_2$(ClO$_4$)$_2$] [c]	20	19 120	35 710 (sh)	42 550		1.85	2.242	2.053	2.145	420s	
	120	18 350									
(*b*) Type (ii) complexes											
[Cu(dmpd)Cl$_2$]	20	15 630	28 990 (sh)	33 330	40 490	1.82	2.190	2.034	2.086	401s	204vs
[Cu(dmpd)Br$_2$]	20	15 630	24 100	29 410 (sh)	33 900	1.95			2.161	399s	142vs
			37 740 (sh)	44 440							
(*c*) Type (iii) complexes											
[Cu(H$_2$dmpd)Cl$_4$]	20	7 410, 9 850	25 640			1.88	2.363	2.053	2.156		300vs 274vs
[Cu(H$_2$dmpd)Br$_4$]	20	8 000, 11 110	16 390 (sh)	19 230	27 670	1.87			2.126		235vs

[a] 1 B.M. = 9.274×10^{-24} A m^2. [b] This complex shows three g values: $g_1 = 2.047$, $g_2 = 2.089$, $g_3 = 2.234$. [c] $A = 196 \times 10^{-4}$ cm^{-1}.

Packing (Table 3) is mainly determined by N $\cdots$ O interactions, some of which can be regarded as hydrogen bonds, and by van der Waals contacts.

Magnetic and Spectroscopic Results.—As reported in Table 4, the [Cu(dmpd)$_2$X$_2$] complexes show a gradual red shift (toward lower energy) in the visible absorption with increasing temperature, which may be explained as reversible continuous thermochromism, as demonstrated by the absence of endothermic transitions in the differential scanning calorimetric analysis.

Continuous and discontinuous thermochromism of copper(II) complexes with *N*-substituted ethylenediamines [11] has been attributed to a thermally sensitive tetragonal distortion in the copper-atom environment [7a] or to changes in the in-plane Cu–N co-ordination.[7b] The experimental results are consistent with an increase in axial interaction with the central atom brought about by increasing the temperature.[7a,11]

Differences are observed in the results of the effects of temperature on the mid-i.r. region between our complexes and those of *N*-substituted ethylenediamine. In fact in [Cu(dmpd)$_2$(ClO$_4$)$_2$] the splitting of the perchlorate bands at around 1 100, 920, and 620 cm^{-1} (ν_3, ν_1, and ν_4 respectively in C_{3v} symmetry) continuously decreases with increasing temperature (Figure 2), indicating a change in symmetry of the perchlorate ion from C_{3v} (room-temperature, see structural results) to T_d. This, contrary to those found for *N*-substituted ethylenediamines, provides unequivocal evidence for diminished ion perturbation of the perchlorate group at higher temperature, consistent with a decrease in axial interactions with the central atom. Therefore the electronic and i.r. data indicate that the thermochromism in our complexes may be associated with temperature-dependent changes in the stereochemistry of the chromophore, from distorted tetragonal bipyramidal to strongly distorted tetrahedral, with a change in the coordination number from six to four. This hypothesis is reasonable since by cooling the sample, the tetragonal complex is favoured due to the contraction of the metal–ligand bond distances, the higher vibrational states are depopulated,[7a] and hydrogen-bonding interactions increase due to the decrease in the disorder of hydrogen bonding.[28,29]

Differences in packing forces, basicity, and crystal-field stabilization energy of the ligands and the possibility of compression or expansion along the MN$_4$ plane, between dmpd and the *N*-substituted ethylenediamine, may explain their different behaviour.

The room-temperature e.s.r. parameters, as well as the d–d bands, are typical of distorted tetragonal-bipyramidal complexes with a $d_{x^2-y^2}$ ground state and are essentially the same as those found for other complexes with diamine ligands.[6-8,30,31]

Type (ii) and (iii) Complexes.—The [Cu(dmpd)X$_2$] (X = Cl or Br) complexes exhibited very broad weak

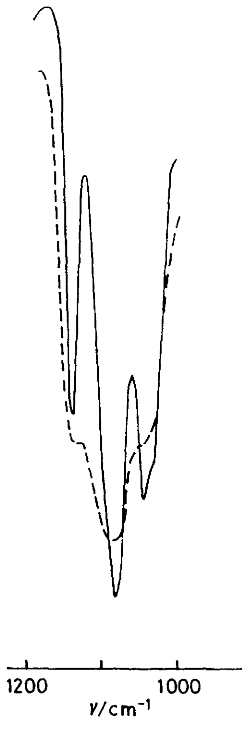

FIGURE 2 Infrared spectra of [Cu(dmpd)$_2$(ClO$_4$)$_2$] at 293 (—) and 393 K (- - -) in the 950—1 200 cm^{-1} region

symmetrical bands centred around 15 630 cm^{-1} and e.s.r spectra of the axial type which seem to indicate a tetragonal stereochemistry of the copper(II) ion, although a distorted tetragonal-pyramidal co-ordination, as found in some [(CuLX$_2$)$_2$] (L = tetramethylethylenediamine and X = Cl;[32] L = *NN*-dimethylethylenediamine and X = Cl or Br[33]) complexes can not be excluded. However, the dimeric or polymeric nature of these compounds is suggested by their insolubility and by the low energy of the far-i.r. bands assignable to the copper(II)–halide bond (Table 4).

The [Cu(H$_2$dmpd)X$_4$] (X = Cl or Br) complexes show two *d–d* bands in the near-i.r. region, which together with e.s.r. parameters and vibrational spectra strongly suggest the presence of copper(II) ions in a distorted tetrahedral configuration.[34] The *d–d* band positions are higher than those normally found for flattened tetrahedral [CuX$_4$]$^{2-}$ species[34-39] and may be explained by the greater degree of distortion towards planarity, which increases the overall splitting of the *d*-orbital energy levels.[40]

We thank Professor M. Nardelli for helpful discussion, the Centro Strumenti of the University of Modena for recording the i.r. spectra, and the Consiglio Nazionale delle Ricerche (C.N.R.) of Italy for financial support. We are also grateful to the BASF AG 6700 Ludwigshafen (West Germany) for supplying the amine.

[9/2024 *Received*, 31*st December*, 1979]

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