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Copper complexes with di-pyridylmethane. The synthesis and X-ray structures of bis(di-pyridylmethane)copper(I) perchlorate, bis(di-pyridylmethane)copper(II) perchlorate and dichloro-μ-dichloro-bis(di-pyridylmethane)dicopper(II)

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Abstract

Three di-(2-pyridyl)methane copper(II) complexes have been prepared, $[Cu(DPM)_2]ClO_4$, $[Cu(DPM)_2](ClO_4)_2$ and $[Cu(DPM)Cl_2]_2$. These are monoclinic ($C2/c$), triclinic ($P\bar{1}$) and monoclinic ($P2_1/c$) crystalline species. The corresponding lattice constants are $a=8.4281(49)$, $b=21.2619(84)$, $c=13.0444(36)$ Å, $\beta=97.412(36)°$ for $[Cu(DPM)_2]ClO_4$; $a=8.6455(11)$, $b=8.9158(12)$, $c=9.0675(12)$ Å, $\alpha=96.414(11)$, $\beta=115.752(10)$, $\gamma=105.161(10)°$ for $[Cu(DPM)_2](ClO_4)_2$; $a=8.7444(25)$, $b=12.1243(36)$, $c=11.6478(22)$ Å, $\beta=104.425(19)°$ for $[Cu(DPM)Cl_2]_2$. The structure of $[Cu(DPM)_2]ClO_4$ (**1**) consists of a distorted tetrahedral arrangement around the copper(I) atom with Cu–N bond lengths of 2.010(6), 2.060(7) Å and N–Cu–N angle of the chelating ligand at 94.4(3)°. The structure of $[Cu(DPM)_2](ClO_4)_2$ (**2**) puts the copper(II) atom in a tetragonal environment with a long perchlorate interaction at the axial positions. $[Cu(DPM)Cl_2]_2$ (**3**) is a dimeric five-coordinate copper complex with asymmetrically bridging Cl atoms approximating a distorted trigonal bipyramid. The dimeric complex displays a ferromagnetic behavior. Spectral and cyclic voltammetric data are presented for the three complexes.

Introduction

Copper di-(2-pyridyl)methane complexes show interesting redox chemistry. Not only can the copper(I) complex be oxidized by molecular oxygen to the copper(II) species, but the $-CH_2-$ group of the ligand can suffer oxidation or oxygenation in the presence of copper(II) ions. In aqueous solution the compound obtained is the corresponding ketone [1], and in methanolic solution, $[Cu(DPM)(DPMA)Cl]ClO_4$, has been isolated [2], where DPMA is the oxygenated ligand di-(2-pyridyl)methanol.

In order to study in detail the redox system, the bis(di-(2-pyridyl)methane)copper(II) and copper(I) perchlorate complexes were prepared, together with the dichloro[di-(2-pyridyl)methane]copper(II) complex.

This paper describes the electronic spectra and voltammetric properties of these complexes, together with the structure determination by single crystal X-ray diffraction of $[Cu(DPM)_2]ClO_4$, $[Cu(DPM)_2](ClO_4)_2$ and $[Cu(DPM)Cl_2]_2$. The magnetic properties of the dimeric dichloro complex are described.

Experimental

The ligand H-DPM was prepared according to the method of Leetle and Marion [3].

Syntheses

Bis(di-pyridylmethane)copper(I) perchlorate, $[Cu(DPM)_2]ClO_4$ (1)

One mmol of copper sulfate hydrate in an ammoniacal aqueous solution was reduced with $NH_2OH–HCl$. The solution was heated and purged with prepurified nitrogen. The ligand, dissolved in EtOH (2 mmol), was added to this solution. A deaerated saturated aqueous solution of sodium perchlorate was added and a yellow microcrystalline solid precipitated immediately. The complex was recrystallized under N_2 from a hot $MeOH–H_2O$ mixture.

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Bis(di-pyridylmethane)copper(II) perchlorate, $[Cu(DPM)_2](ClO_4)_2$ (2)

The ligand (3 mmol) was added to a hot solution of metal perchlorate (1 mmol) in MeOH and the mixture was boiled under reflux for 15 min. (Contact with air was avoided since oxidation of the ligand may occur.) The crystalline red–violet complex was filtered and recrystallized from hot MeOH–H_2O (20:1 ratio).

Di-pyridylmethanecopper(II) chloride, $[Cu(DPM)Cl_2]_2$ (3)

The complex was prepared by addition of 1 mmol of anhydrous $CuCl_2$ to a degassed solution containing 1 mmol of ligand in freshly distilled methanol. The resultant solution was refluxed under N_2. Dark green crystals formed when the reaction mixture was cooled.

Structural determinations

The structures of complexes **1**, **2** and **3** have been determined using a Nicolet R3m/E automated diffractometer. X-ray data collection parameters are given in Table 1. Tables of atomic coordinates, bond lengths and angles are presented for each compound.

Physical measurements

Electronic spectra were recorded with a Carl Zeiss DMR 22 spectrophotometer equipped with a ZR 21 accessory for reflectance measurements at room temperature. Conductance measurements were made at 25 °C with a Wayne-Kerr Universal bridge. Voltammetric data were obtained by cyclic voltammetry using a PAR 370 electrochemistry system in a glass cell with a glassy carbon working electrode, a platinum auxiliary electrode and an aqueous saturated calomel reference electrode (SCE). All measurements were performed in an argon atmosphere. Tetraethylammonium perchlorate (TEAP) was used as background electrolyte (0.1 M). The magnetic susceptibility of compound **3** was measured between 5 and 289 K, using a SHE variable temperature magnetometer (model 906). A metallic sample holder with a known temperature independent paramagnetic signal was used. The samples were slowly cycled between two counterwound superconducting pickup coils carried out at 1 KG. The data were corrected to compensate for the diagmagnetism of the constituent atoms and for the temperature independent paramagnetism of copper(II) (60×10^{-6} emu/mol) [4].

TABLE 1. X-ray data collection parameters

Compound	$[Cu(DPM)_2]ClO_4$	$[Cu(DPM)_2](ClO_4)_2$	$[Cu(DPM)Cl_2]_2$
Diffractometer	Nicolet R3m/E	Nicolet R3m/E	Nicolet R3m/E
Crystal class	monoclinic	triclinic	monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$
Lattice constants			
a (Å)	8.428(49)	8.6455(11)	8.7444(25)
b (Å)	21.2619(84)	8.9158(12)	12.1243(36)
c (Å)	13.0444(36)	9.0675(12)	11.6478(22)
α (°)		96.414(11)	
β (°)	97.412(36)	115.752(10)	104.425(19)
γ (°)		105.161(10)	
V (Å^3)	2317.98(170)	586.84(14)	1195.96(53)
Z	4	2	2
μ Radiation (Mo Kα) (cm^{-1})	10.93	12.6	23.10
Crystal size (mm)	$0.040\times0.10\times0.45$	$0.30\times0.30\times0.075$	$0.30\times0.30\times0.30$
D_{calc} (g/cm^3)	1.44	1.79	1.69
Orientation reflections			
no., range 2θ (°)	25, 20–25	25, 20–30	25, 20–30
Scan method	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
Total reflections measured	2118	2058	2475
No. unique data, total with $F_o^2>3\sigma(F_o^2)$	1832, 868	1846, 1568	2113, 1853
Check reflections	3	3	3
No. parameters refined	145	166	145
Transmission factors: max., min.	0.785, 0.731	0.763, 0.668	0.876, 0.744
R^a	0.0565	0.486	0.0235
$R_w{}^b$	0.0593	0.0579	0.0269
Goodness-of-fit indicator	1.494	2.372	1.495
Largest shift/e.s.d. final cycle	0.006	0.001	0.005
Largest peak (e/Å^3)	0.430	1.105	0.456
g	0.00118	0.00057	0.00021

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $R_w=[\Sigma\sqrt{w}(|F_o|-|F_c|)]/\Sigma\sqrt{w}|F_o|$; $w^{-1}=[\sigma^2(|F_o|)+g|F_o|^2]$.

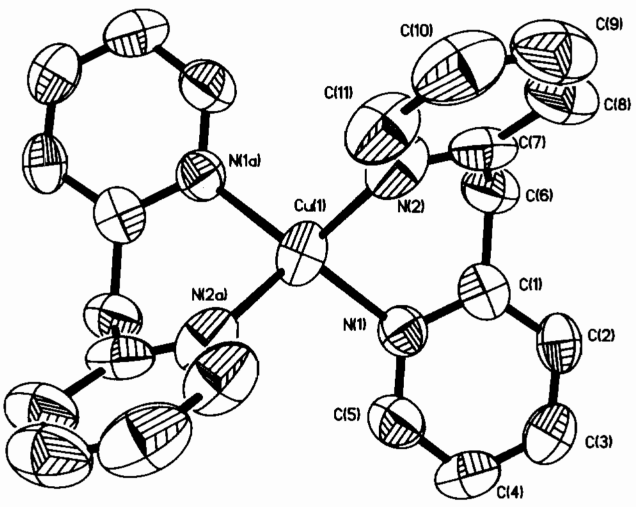

Fig. 1. A view of the molecule [Cu(DPM)$_2$]ClO$_4$ with atom numbering and hydrogen excluded for clarity.

TABLE 2. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$)[a] for [Cu(DPM)$_2$]ClO$_4$ (**1**)

	x	y	z	U_{iso}[b]
Cu(1)	0	1325(1)	2500	72(1)
N(1)	457(7)	950(3)	1155(5)	55(2)
N(2)	−1919(9)	1848(3)	1838(5)	69(3)
C(1)	−766(9)	871(3)	411(6)	52(3)
C(2)	−534(10)	732(3)	−604(6)	59(3)
C(3)	997(12)	677(4)	−839(7)	69(4)
C(4)	2255(11)	764(4)	−70(8)	73(4)
C(5)	1929(10)	902(4)	904(7)	71(4)
C(6)	−2421(9)	935(4)	715(7)	67(4)
C(7)	−2840(9)	1600(4)	1010(7)	61(3)
C(8)	−4074(11)	1920(4)	449(8)	81(4)
C(10)	−3487(15)	2775(5)	1630(9)	100(5)
C(11)	−2263(12)	2423(4)	2129(7)	85(4)
C(9)	−4413(13)	2525(6)	779(10)	98(5)
Cl	5000	9407(2)	2500	84(1)
O(1)	6516(16)	9690(11)	2515(16)	122(3)
O(2)	4816(25)	9742(9)	1559(10)	122(3)
O(3)	6413(18)	9052(10)	2494(16)	122(3)
O(4)	4745(25)	9011(9)	1626(12)	122(3)
O(5)	5727(96)	9981(19)	2286(72)	122(3)
O(6)	5491(110)	8819(17)	2151(69)	122(3)

[a] e.s.d.s in the least significant digits are given in parentheses. [b] The equivalent isotropic U is defined as 1/3 of the trace of the U_{ij} tensor.

Results and discussion

Structural descriptions

[Cu(DPM)]$_2$ClO$_4$ (1) (Fig. 1)

Atomic coordinates and isotropic thermal parameters are given in Table 2. Bond lengths and bond angles are given in Tables 3 and 4. The four nitrogen atoms define a distorted tetrahedral arrangement around the copper atom with bond lengths of 2.010(6) and 2.060(7) Å. The N1–Cu–N2 angle which is defined by the chelating unit is 94.4(3)°. The other N–Cu–N angles are 110.6(3), 114.6(4) and 133.3(3)° indicating a distortion from tetrahedral geometry. Indeed the angle between the two planes defined by N1–Cu1–N2A and N2–Cu1–N1A is 71.5° which corresponds to 18.5° deviation from tetrahedral geometry. Another angle of interest is the angle defined by the two pyridyl rings. Previous studies of similar complexes indicate that a tetrahedral geometry of the bridgehead atom corresponds to an angle of approximately 60° [5]. Here we observe a 59.1° angle.

TABLE 3. Bond lengths (Å) for [Cu(DPM)$_2$]ClO$_4$

Cu(1)–N(1)	2.018(6)	Cu(1)–N(2)	2.059(7)
Cu(1)–N(1a)	2.008(6)	Cu(1)–N(2a)	2.059(7)
N(1)–C(1)	1.333(9)	N(1)–C(5)	1.327(11)
N(2)–C(7)	1.353(10)	N(2)–C(11)	1.322(11)
C(1)–C(2)	1.396(11)	C(1)–C(6)	1.505(11)
C(2)–C(3)	1.369(13)	C(3)–C(4)	1.375(13)
C(4)–C(5)	1.366(14)	C(6)–C(7)	1.518(12)
C(7)–C(8)	1.373(12)	C(8)–C(9)	1.397(16)
C(10)–C(11)	1.370(15)	C(10)–C(9)	1.378(17)

TABLE 4. Bond angles (°) for [Cu(DPM)$_2$]ClO$_4$

N(1)–Cu(1)–N(2)	94.4(3)	N(1)–Cu(1)–N(1a)	133.3(3)
N(2)–Cu(1)–N(1a)	110.6(3)	N(1)–Cu(1)–N(2a)	110.6(3)
N(2)–Cu(1)–N(2a)	114.6(4)	Cu(1)–N(1)–C(1)	117.9(5)
Cu(1)–N(1)–C(5)	118.1(5)	C(1)–N(1)–C(5)	118.1(7)
Cu(1)–N(2)–C(7)	117.6(5)	Cu(1)–N(2)–C(11)	124.6(6)
C(7)–N(2)–C(11)	117.7(7)	N(1)–C(1)–C(2)	121.9(7)
N(1)–C(1)–C(6)	117.0(7)	C(2)–C(1)–C(6)	121.2(7)
C(1)–C(2)–C(3)	118.8(7)	C(2)–C(3)–C(4)	119.0(8)
C(3)–C(4)–C(5)	118.6(9)	N(1)–C(5)–C(4)	123.5(7)
C(1)–C(6)–C(7)	113.9(7)	N(2)–C(7)–C(6)	115.9(6)
N(2)–C(7)–C(8)	123.3(8)	C(6)–C(7)–C(8)	120.8(7)
C(7)–C(8)–C(9)	117.6(9)	C(11)–C(10)–C(9)	119.0(10)
N(2)–C(11)–C(10)	123.2(9)	C(8)–C(9)–C(10)	119.1(10)

[Cu(DPM)$_2$](ClO$_4$)$_2$ (2) (Fig. 2)

Atomic coordinates and isotropic thermal parameters are given in Table 5. Bond lengths and bond angles are given in Tables 6 and 7. The copper atom is in a tetragonal environment with extremely long interaction with the perchlorate in the axial positions. The copper atom is located at the crystallographic center of symmetry with Cu–N distances of 2.011(4) Å, and Cu–O distance of 2.951 Å. As required by symmetry the metal center and the four nitrogen atoms form a plane. Consequently the N1–Cu–N2A angle is 92.4(2)°, a value slightly larger than 90.0°. The largest distortion from the 90.0° angles is displayed by the oxygen from the ClO$_4$ anion. The O3, Cu, O3A axis forms an angle of 90.5° with the N2, Cu, N2A axis and a 100.0° angle with the N1, Cu, N1A axis. This distortion is presumably

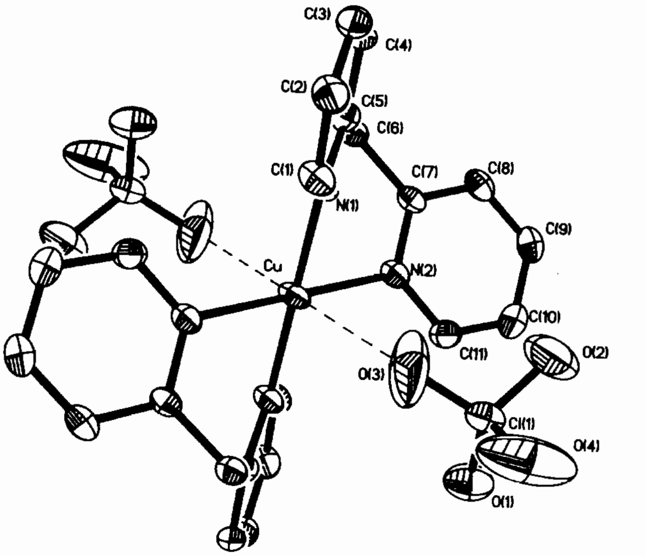

Fig. 2. A view of the molecule, $[Cu(DPM)_2](ClO_4)_2$ with atom numbering and hydrogen excluded for clarity.

TABLE 5. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for $[Cu(DPM)_2](ClO_4)_2$ (**2**)

	x	*y*	*z*	*U*
Cu	0	0	0	40(1)*
N(1)	9163(5)	1893(4)	105(4)	40(2)*
N(2)	732(5)	768(4)	8300(4)	38(2)*
C(1)	9555(7)	2782(5)	1618(6)	47(2)*
C(2)	−1106(7)	4011(5)	1736(7)	51(2)*
C(3)	−2116(7)	4405(5)	277(7)	48(2)*
C(4)	−2449(5)	3556(5)	−1259(6)	43(2)*
C(5)	8202(5)	2300(5)	8677(5)	35(1)*
C(6)	−2113(6)	1324(5)	−2960(5)	41(2)*
C(7)	−336(6)	1363(4)	−2883(5)	36(2)*
C(8)	232(7)	2036(5)	−3954(5)	43(2)*
C(9)	1891(7)	2088(5)	−3816(6)	49(2)*
C(10)	2962(7)	1437(6)	7401(6)	50(2)*
C(11)	2327(6)	789(5)	8411(6)	45(2)*
Cl(1)	5085(2)	2975(1)	3022(2)	53(1)*
O(1)	−5575(6)	−1657(5)	−2583(6)	79(2)*
O(2)	−5030(8)	−3986(6)	−1907(7)	116(4)*
O(3)	3396(11)	2406(7)	2815(17)	234(10)*
O(4)	6488(12)	3931(8)	4587(7)	188(6)*

Starred items: the equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

caused by packing requirements of the molecule. In spite of the disorder, the perchlorate was refined with no constraints since the geometry of the major component is very close to tetrahedral. The dihedral angle formed by the two pyridyl rings in each ligand is 59.7° which correlates well with a tetrahedral geometry around the methylene carbon. Consequently all four pyridyl rings form an angle of about 42.0° with the CuN_4 plane (41.7° and 42.7°).

TABLE 6. Bond lengths (Å) for $[Cu(DPM)_2](ClO_4)_2$

Cu–N(1a)	2.011(4)	Cu–N(1c)	2.011(4)
Cu–N(2a)	2.026(5)	Cu–N(2b)	2.026(5)
N(1)–C(1)	1.356(7)	N(1)–Cua	2.011(4)
N(1)–C(5a)	1.351(6)	N(2)–C(11)	1.333(7)
N(2)–Cub	2.026(5)	N(2)–C(7a)	1.345(6)
C(1)–C(2a)	1.376(8)	C(2)–C(3)	1.377(7)
C(2)–C(1a)	1.376(8)	C(3)–C(4)	1.377(8)
C(4)–C(5b)	1.385(7)	C(5)–N(1b)	1.351(6)
C(5)–C(4a)	1.385(7)	C(5)–C(6a)	1.507(7)
C(6)–C(7)	1.498(8)	C(6)–C(5b)	1.507(7)
C(7)–C(8)	1.391(8)	C(7)–N(2a)	1.345(6)
C(8)–C(9)	1.372(9)	C(9)–C(10a)	1.396(7)
C(10)–C(11)	1.365(9)	C(10)–C(9a)	1.396(7)
Cl(1)–O(3)	1.333(11)	Cl(1)–O(4)	1.380(5)
Cl(1)–O(1a)	1.422(6)	Cl(1)–O(2a)	1.422(7)
O(1)–Cl(1a)	1.422(6)	O(2)–Cl(1a)	1.422(7)

TABLE 7. Bond angles (Å) for $[Cu(DPM)_2](ClO_4)_2$

C(1)–N(1)–Cua	120.3(3)	C(1)–N(1)–C(5a)	118.9(4)
C(11)–N(2)–Cub	120.5(3)	C(11)–N(2)–C(7a)	119.4(5)
N(1)–C(1)–C(2a)	122.1(5)	C(3)–C(2)–C(1a)	118.9(5)
C(2)–C(3)–C(4)	119.4(5)	C(3)–C(4)–C(5b)	119.8(4)
C(7)–C(6)–C(5b)	111.1(3)	C(6)–C(7)–C(8)	121.7(4)
C(6)–C(7)–N(2a)	117.7(5)	C(8)–C(7)–N(2a)	120.6(5)
C(7)–C(8)–C(9)	120.0(4)	C(8)–C(9)–C(10a)	118.4(6)
C(11)–C(10)–C(9a)	118.8(6)	N(2)–C(11)–C(10)	122.8(5)
O(3)–Cl(1)–O(4)	118.8(8)	O(3)–Cl(1)–O(1a)	108.7(4)
O(4)–Cl(1)–O(1a)	107.9(5)	O(3)–Cl(1)–O(2a)	106.7(6)
O(4)–Cl(1)–O(2a)	104.3(4)		

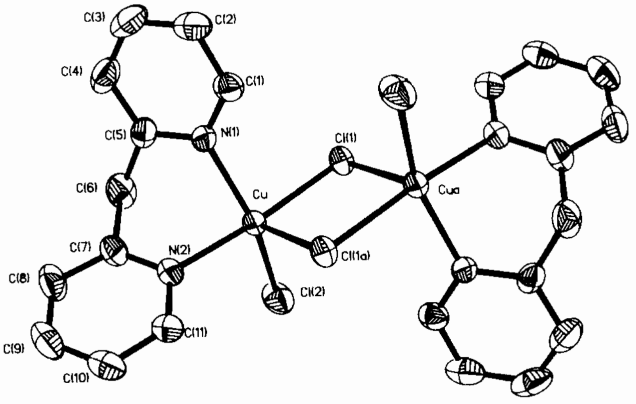

Fig. 3. A view of the molecule $[Cu(DPM)Cl_2]_2$ with atom numbering and hydrogen excluded for clarity.

$[Cu(DPM)Cl_2]_2$ (3) (Fig. 3)

Atomic coordinates and isotropic thermal parameters are given in Table 8. Bond lengths and bond angles are given in Tables 9 and 10. The molecule is dimeric, asymmetrically bridged by Cl atoms with Cu–Cl bond lengths of 2.315(1) and 2.629(1) Å. The geometry about the copper atom is five coordinate, approximating a distorted trigonal bipyramid. Cl1 and N2 occupy axial positions and form with copper a 175.4° angle. The

TABLE 8. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for $[Cu(DPM)Cl_2]_2$ (**3**)

	x	*y*	*z*	*U*
Cu	4516(1)	9248(1)	1202(1)	30(1)*
Cl(1)	5230(1)	8716(1)	−500(1)	33(1)*
Cl(2)	6878(1)	8797(1)	2407(1)	49(1)*
N(1)	2237(2)	8871(2)	409(2)	31(1)*
N(2)	3702(2)	9685(2)	2628(2)	33(1)*
C(1)	1506(3)	9213(2)	−681(2)	37(1)*
C(2)	−23(3)	8920(3)	−1216(3)	49(1)*
C(3)	−840(3)	8257(3)	−597(3)	57(1)*
C(4)	−109(3)	7937(2)	533(3)	53(1)*
C(5)	1443(3)	8247(2)	1019(2)	37(1)*
C(6)	2323(4)	7947(2)	2268(2)	48(1)*
C(7)	2758(3)	8976(2)	3004(2)	38(1)*
C(8)	2167(4)	9214(3)	3974(2)	52(1)*
C(9)	2562(4)	10189(3)	4569(2)	54(1)*
C(10)	3527(4)	10918(2)	4180(2)	48(1)*
C(11)	4063(3)	10634(2)	3210(2)	40(1)*

Starred items: the equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 9. Bond lengths (Å) for $[Cu(DPM)Cl_2]_2$

Cu–Cl(1)	2.315(1)	Cu–Cl(2)	2.261(1)
Cu–N(1)	2.033(2)	Cu–N(2)	2.034(2)
Cu–Cl(1a)	2.629(1)	Cl(1)–Cua	2.629(1)
N(1)–C(1)	1.339(3)	N(1)–C(5)	1.344(3)
N(2)–C(7)	1.341(3)	N(2)–C(11)	1.335(3)
C(1)–C(2)	1.377(3)	C(2)–C(3)	1.392(5)
C(3)–C(4)	1.370(4)	C(4)–C(5)	1.389(3)
C(5)–C(6)	1.513(4)	C(6)–C(7)	1.509(4)
C(7)–C(8)	1.385(4)	C(8)–C(9)	1.372(4)
C(9)–C(10)	1.376(5)	C(10)–C(11)	1.371(4)

TABLE 10. Bond angles (°) for $[Cu(DPM)Cl_2]_2$

Cl(1)–Cu–Cl(2)	93.7(1)	Cl(1)–Cu–N(1)	89.5(1)
Cl(2)–Cu–N(1)	150.7(1)	Cl(1)–Cu–N(2)	175.3(1)
Cl(2)–Cu–N(2)	90.5(1)	N(1)–Cu–N(2)	85.8(1)
Cl(1)–Cu–Cl(1a)	86.2(1)	Cl(2)–Cu–Cl(1a)	106.6(1)
N(1)–Cu–Cl(1a)	102.7(1)	N(2)–Cu–Cl(1a)	94.7(1)
Cu–Cl(1)–Cua	93.8(1)	Cu–N(1)–C(1)	123.1(2)
Cu–N(1)–C(5)	117.7(1)	C(1)–N(1)–C(5)	119.2(2)
Cu–N(2)–C(7)	118.0(2)	Cu–N(2)–C(11)	123.6(2)
C(7)–N(2)–C(11)	118.4(2)	N(1)–C(1)–C(2)	122.2(3)
C(1)–C(2)–C(3)	118.9(2)	C(2)–C(3)–C(4)	118.9(2)
C(3)–C(4)–C(5)	119.5(3)	N(1)–C(5)–C(4)	121.3(2)
N(1)–C(5)–C(6)	115.9(2)	C(4)–C(5)–C(6)	122.7(3)
C(5)–C(6)–C(7)	110.1(2)	N(2)–C(7)–C(6)	115.8(2)
N(2)–C(7)–C(8)	121.2(2)	C(6)–C(7)–C(8)	122.9(3)
C(7)–C(8)–C(9)	119.6(3)	C(8)–C(9)–C(10)	119.2(3)
C(9)–C(10)–C(11)	118.3(3)	N(2)–C(11)–C(10)	123.3(3)

equatorial positions are occupied by Cl2, symmetry generated Cl1A, and N1. Together with copper these atoms define a plane with a deviation of no more than 0.015 Å. This plane is essentially perpendicular (92.0°) to the plane defined by the two copper atoms of the dimer and the two bridging chlorine atoms. The angles between the equatorial and axial atoms deviate from 90.0° by no more than 4.2°. Attempts to define a square pyramidal geometry with Cl1, Cl2, N1, N2 as a base gives a poorly defined plane with a deviation of more than 2 Å for most of the atoms. The dihedral angle between the pyridyl rings of the ligand is 64.8° which corresponds to one of the largest folds observed so far.

The structures of **1** and **2** are representative of the geometries preferred by copper(I) and copper(II) ions, respectively. The dimeric compound is best described as a distorted trigonal bipyramid. All structures involve C–N bonds which have relatively constant lengths of 2.0 Å.

Compounds **1** and **2** show a tetrahedral geometry of the bridgehead methylene carbon atom leading to the dihedral angle of approximately 60.0° between the pyridyl units of the di-(2-pyridyl)methane ligands. The dihedral angle between the pyridyl rings of the ligand in the dimeric chloro complex is 64.8°. The corresponding dimeric bromo complex [6] has a smaller dihedral angle of 62.6°. Similar values of the dihedral angle are found for the $[Cu(DPM)(DPMA)Cl]ClO_4$ complex [2] (DPMA corresponds to di-(2-pyridyl)methanol). The values are 61.1° for the di-(2-pyridyl) ligand and 64.9° for the di-(2-pyridyl)methanol ligand. A value of 63.7° is obtained for this same angle in the bis(di-(2-pyridyl)-methane)diolcopper(II) chloride complex [5].

Magnetic properties of $[Cu(DPM)Cl_2]_2$

The variation of the magnetic susceptibility with temperature for the dimeric copper(II) complex (interpreted in terms of a singlet–triplet equilibrium) is given by the Bleaney–Bowers equation [7].

$$\chi_m = [Ng^2\mu_B^2/3k(T-\theta)][1+1/3\exp(-J/kT)]^{-1}$$

A study of the variation of the magnetic susceptibility with temperature allows a value for the singlet–triplet separation to be determined. The magnetic susceptibility values as a function of temperature are given in Table 11.

The parameters which gave the best fit of the experimental values are $g = 2.06$, $\theta = 0.87$ K and $J = +1.55$ cm^{-1}. This indicates that the copper atoms are ferromagnetically coupled. Other examples of complexes with such a magnetic behavior are $[Cu(DMG)Cl]_2$ (DMG = dimethylglyoxime) [8–10], $[Cu(dien)Cl]_2(ClO_4)_2$ (dien = diethylenetriamine) [11, 12], $[Cu(Et_3en)Cl_2]_2$ ($(Et)_3en$ = *N*,*N*,*N*′-triethylethylenediamine) [13]. Other dimeric complexes with chloro bridges that have been studied are antiferromagnetically coupled [14]. The typical values for the exchange of these chloro-bridged dimers are between −1.05 and −8.3 cm^{-1} [15].

TABLE 11. Magnetic susceptibilities of $[Cu(DPM)Cl)_2]_2$ as a function of temperature

No.	T (K)	$\chi'_m \times 10^3$ (emu mol^{-1})
1	4.99	112.7
2	6.00	89.88
3	7.00	73.37
4	8.00	62.22
5	9.00	53.97
6	10.00	47.61
7	12.00	38.61
8	14.00	32.45
9	16.00	27.71
10	18.01	24.38
11	20.00	21.76
12	25.00	17.10
13	30.00	14.00
14	35.00	12.01
15	40.03	10.48
16	45.07	9.298
17	50.12	8.310
18	60.24	6.880
19	70.60	5.813
20	80.55	5.069
21	90.75	4.491
22	100.95	4.030
23	120.70	3.374
24	152.15	2.672
25	179.90	2.191
26	220.15	1.800
27	256.25	1.558
28	289.45	1.336

The introduction of a Curie–Weiss parameter, θ, into the denominator of the above equation indicates that interactions between dimers exist.

A similar ferromagnetically coupled ground state ($\theta = 2.6$ K) is observed for the dibromo[di-(2-pyridyl)methane]copper(II) dimer [16]. This complex has a distorted square pyramid geometry around the metal centers, which differentiates it from the complex studied here. However, the magnetic properties are similar.

Electronic spectra

The copper(II) perchlorate complex **2** exhibits an absorption in the solid state at 19 230 cm^{-1} [17]. This value is corroborated by the crystal structure determination, which indicates a tetragonal environment, with extremely long interaction distances between the copper(II) and the perchlorate oxygen in the axial positions (Cu–O 2.951 Å). In acetonitrile, a solution of compound **2** behaves as a 2:1 electrolyte (300 Ω^{-1} cm^2 mol^{-1}) and its visible spectrum exhibits a single asymmetric absorption band at 17 900 cm^{-1}, ($\epsilon = 100$ M^{-1} cm^{-1}). This suggests an tetragonal environment for the metal ion, $[Cu(DMP)_2(solvent)_2]^{2+}$.

The dimeric chloro complex **3** behaves as a non-electrolyte in acetonitrile solution, and its visible spectrum in this solvent is identical with the reflectance spectrum. The absorption band is located at 13 500 cm^{-1} ($\epsilon = 230$ M^{-1} cm^{-1}) with a shoulder at lower energies for the solution spectrum, and for the solid. The existence of an absorption maximum with a low energy shoulder has been used as a criterium to assign a square pyramidal geometry for five-coordinate copper(II) [18, 19]. However, compound **3** is better described as a distorted trigonal bipyramid.

The copper(I) complex **1** does not show a metal to ligand charge transfer absorption band in the visible spectrum. The corresponding 2,2′-bipyridine and 1,10-phenanthroline copper(I) complexes absorb in the visible region at 22 727 cm^{-1}, with $\epsilon = 4800$ and 7000 M^{-1}, respectively [20, 21]. The results are associated with the relative orbital energies between a vacant π^* orbital of the ligand and the d orbital of the copper(I) ion. 2,2′-Bipyridine and 1,10-phenanthroline are ligands with a planar configuration and a conjugated electronic structure, while di-(2-pyridyl)methane presents a fold at the methane center, which is observed in the dihedral angle of the two pyridyl rings (59.1°). This fact makes the di-(2-pyridyl)methane ligand a poorer π-acceptor than 2,2′-bipyridine or 1,10-phenanthroline [22a].

Redox behavior

The ligand is redox inert in the range studied. The cyclic voltammograms for the mononuclear cupric complex **2** show only one wave in the +0.7 to −0.5 V range. Both reduction and oxidation peaks can be seen for the copper(II)/copper(I) couple. The cyclic voltammograms do not show reversible electrochemical behavior. The average peak separation increases for scan rates between 20 and 500 mV s^{-1} (Table 12).

The fact that for lower scan rates the E_c value is more positive can be explained by the change in geometry that must take place during the reduction. The tetragonally distorted octahedral coordination geometry of the copper(II) ion must be reorganized to the tetrahedral geometry required for the copper(I) ion.

The voltammetric behavior of compound **1** in acetonitrile solution is similar to the observed for compound **2**. If the cyclic voltammogram is scanned at the same rate of 50 mV s^{-1} between −0.5 and +1.0 V, the

TABLE 12. Cyclic voltammetric behavior of $[Cu(DPM)_2](ClO_4)_2$ in acetonitrile

Scan rate (mV/s)	E (V)	$E_c/2$	E_a (V)	$E_a/2$	I_c (A)	$I_c/v^{1/2}$
20	0.21	0.315	0.32	0.24	41	9.25
50	0.18	0.300	0.34	0.25	62	8.77
200	0.10	0.290	0.36	0.26	110	8.04
500	0.075	0.280	0.365	0.25	166	7.42

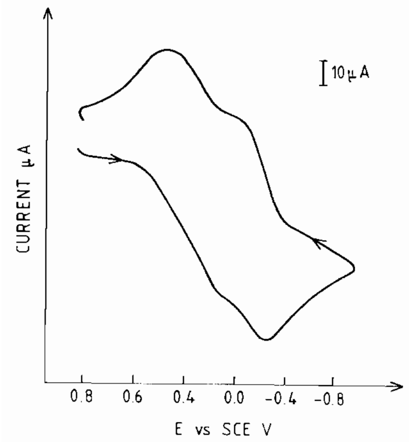

Fig. 4. Cyclic voltammogram for $[Cu(DPM)Cl_2]_2$ in acetonitrile solution (scan speed: 50 mV s^{-1}).

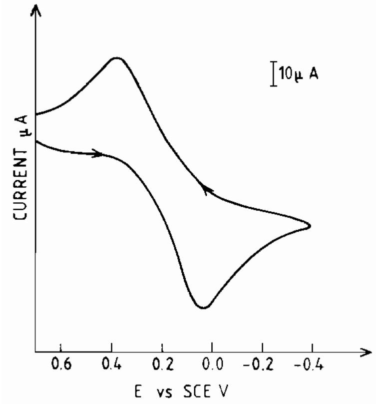

Fig. 5. Cyclic voltammogram for $[Cu(DPM)Cl_2]_2$ in dimethylacetamide solution (scan speed: 50 mV s^{-1}).

anodic peak at +0.34 V and the cathodic peak at +0.15 V are obtained. However, the shift of the peaks with increasing scan rates is not as drastic as for the copper(II) complex, probably due to the fact that copper(II) tolerates a tetrahedral environment more readily than copper(I) accepts an octahedral one. Copper(II) shows a greater 'plasticity' in its coordination geometries than copper(I) as expected for an ion with Jahn–Teller active ground states [22b].

If the cyclic voltammogram of **1** in acetonitrile is scanned in the +1.0 to −1.2 V range, two anodic and two cathodic peaks are observed. A sharp irreversible wave is observed in the more negative potential range. This wave, with a cathodic value of −0.82 V and anodic value of −0.34 V, corresponds to the redox copper(I)/copper(0) couple. The other wave has an anodic value of +0.34 V and a cathodic value of +0.15 V, corresponding to the redox copper(II)/copper(I) couple.

For the chloro dimer **3** it is possible to observe two reduction peaks and two oxidation peaks. These can be interpreted as a stepwise reduction from a Cu(II)–Cu(II) species to Cu(II)–Cu(I) and from Cu(II)–Cu(I) to the Cu(I)–Cu(I) complex [23]. The E_c values are +0.18 and +0.04 V, respectively, while the E_a values are +0.18 V and +0.48 V (Fig. 4).

The first reduction potential for the dimer is identical with the reduction potential found for the monomeric diperchlorate copper(II) complex (+0.18 V for a scan rate of 50 mV s^{-1}). This behavior is different from that observed for the binuclear copper(II) complex, $[Cu(BP)OH]_2^{2+}$ which has a more positive reduction potential for the first copper(II) ion in comparison to the mononuclear bis-2,2′-bipyridine complex, $[Cu(BP)_2]^{2+}$ (0.04 and 0.06 V, respectively) [24]. Compared with the positive E_c values obtained for **3**, electrochemical studies have shown that, in general, negative potentials (versus SCE) prevail for binuclear copper(II) complexes [25–34].

The stabilization of the mixed valence species observed in acetonitrile is lost if the redox behavior of the complex is studied in dimethylacetamide. Only one wave is obtained in the potential range studied (Fig. 5). Coulometric analysis of the reduction process indicates that almost two electrons per mole (1.8 *e*) are transferred, which suggests the formation of two copper(I) ions.

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