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The Crystal Structure and Electronic Properties of the Bis(1,3-dimethyl-5-diazophenyl-6-amino uracilato) Copper(II) Complex, Dimethyl Sulfoxide Solvate – a New Pseudotetrahedral CuN_4 Complex

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Abstract

The crystal structure of the title complex has been determined by X-ray diffraction technique. The crystals are monoclinic, space group $P2_1/n$, with a = 12.878(2), b = 14.791(1), c = 17.268(2) Å, β = 109.79(1)°, Z = 4, R = 0.057 for 2514 reflections. There are two ligands of 1,3-dimethyl-5-diazophenyl-6-amino uracilato anions in bidentate coordination to a copper(II) ion per asymmetric unit. The ligands are in *cis*-arrangement to each other. The copper environment is pseudotetrahedral, with a dihedral angle ϕ of 39.7° between the two CuN_4 ligand planes. This geometry seems to result from steric interaction between the ligands. The coordination of each molecule of the ligand takes place through the nitrogen atom of the deprotonated 6-amino group and a nitrogen of the azo group. The structure is stabilised by extensive stacking interactions between the phenyl rings as well as the pyrimidine rings. A pair of hydrogen-bonded interactions between the solvent molecule and the two ligands further stabilise the structure. The magnetic moment, ESR and electronic reflectance spectrum are in accordance with the observed molecular structure. A linear correlation between the highest energy d–d transition and the dihedral angle for several pseudotetrahedral CuN_4 complexes has been proposed.

Introduction

Uracil derivatives play an important role in the field of biology as fundamental constituents of nucleic acids. 1,3-Dimethyl-6-aminouracil derivatives substituted at the 5-position by a cinnamoyl derivative group were found to be active against P388 leukemia *in vivo* and exhibited cytotoxic activity *in vitro* against L1210 leukemia [1]. The compounds present a polycyclic planar structure and could give a complete overlap of the DNA base pairs by intercalation in the double helix of the DNA as is the case with other polycyclic antitumor drugs like actinomycin or daunorubicin. This intercalation is responsible for the potential antitumour activity of these compounds. We have therefore synthesised several 6-amino-1,3-dimethyl-5-phenylazouracil derivatives, which are similar to the above mentioned cinnamoyl derivatives. These compounds also have a planar structure and are therefore capable of intercalation. Furthermore, 6-aminopyrimidine molecules having an arylazo group at the 5-position are active against acute leukemia. Thus the arylazo group promotes potential antitumour activity [2].

On the other hand, copper coordination chemistry has been growing in recent years because of the potential anticonvulsant, antiinflammatory, antiulcer and antitumour properties that certain copper complexes present [3–8].

For the above reasons the complexes formed between 5-phenylazouracil derivatives and the copper(II) cation are of interest. Although some X-ray structures of metal complexes of azobenzenes [9] and azylazooximes [10] have been published, no structural information is available on metal complexes of phenylazopyrimidines. In an attempt to obtain crystallographic evidence of the coordination sites of these compounds we have prepared and determined the structure of bis(1,3-dimethyl-5-phenylazouracil-6-aminato) copper(II) dimethyl sulfoxide solvate (hereafter abbreviated as $CuDZ_2DMSO$).

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Experimental

Preparation of the Ligand

6-Amino-1,3-dimethyl-5-phenylazouracil (DZH) was synthesised according to Todd *et al.* [11], using 6-amino-1,3-dimethyluracil and aniline as starting materials. After recrystallisation from pyridine the product was isolated as yellow needle-shaped crystals (yield = 70%, melting point (m.p.) 261–263 °C).

Preparation of $CuDZ_2DMSO$

The complex was prepared as previously reported [12]. Black plate-like crystals suitable for structure determination were obtained by slow evaporation of a saturated solution of the complex in DMSO. A crystal of dimensions 0.10 × 0.23 × 0.32 mm was used for data collection. All chemicals and organic solvents used were of reagent grade and were used without further purification.

Crystal Data

$Cu(C_{24}H_{24}N_{10}O_4)\cdot(C_2H_6SO)$, $M = 658.195$, monoclinic, space group $P2_1/n$, $a = 12.078(2)$, $b = 14.791(1)$, $c = 17.268(2)$ Å, $\beta = 109.79(1)^\circ$, $V = 2902.6(8)$ Å^3, $Z = 4$, $D_c = 1.506$ g cm^{-3}, $D_m = 1.53$ g cm^{-3} (method of flotation in $CHCl_3$ and CCl_4), Mo Kα radiation ($\lambda = 0.71073$ Å, $F(000) = 1356.00$, $\mu = 8.24$ cm^{-1}, $T = 293$ K.

Rigaku four circle diffractometer, graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), no absorption correction applied since a ϕ plot showed a deviation in F_o of within 4%, 2θ range: 3.0° to 50.0°, scan mode: ω scan for $2\theta < 30.0^\circ$ and ω–2θ scan for $2\theta > 30.0^\circ$ scan range $(1.0 + 0.5 \tan\theta)^\circ$, scan speed: 4°/min, index range: $0 \leqslant h \leqslant 14$; $0 \leqslant k \leqslant 16$; $-20 \leqslant l \leqslant 19$, standard reflections: 200, 040, and 008 were measured every 100 reflections, total number of reflections measured: 2884 of which 2514 had $F > 6\sigma(F)$, structure solution by a Patterson synthesis followed by a weighted Fourier synthesis, least-squares refinement using F magnitudes (SHELX-76), the function minimised was $w(|F_o| - |F_c|)^2$, where $w = 1/(\sigma^2(F) + 0.001F^2)$, anisotropic thermal parameters for non-hydrogen atoms, all hydrogen atoms located from a difference Fourier map and included in the structure factor calculations in the final cycles of refinement. The hydrogen atoms were assigned an equivalent isotropic temperature factor of the atom to which they are bonded. Anomalous dispersion corrections were applied to Cu(II) and S atoms. The final discrepancy indices were $R = 0.057$ and $R_w = 0.060$ for 2514 reflections. Atomic scattering factors from International Tables for X-ray Crystallography, 1974.

Physical Measurements

The reflectance spectrum of the solid complex was recorded using a Kontron-Uvicon 810 spectrophotometer with an integrating sphere attachment, using $BaSO_4$ as reference. Magnetic susceptibility data were obtained using an electrobalance Cahn 2000 coupling to a N 100 Oxford electromagnet with Faraday pole tips, and calibrated with mercury tetrakis (thiocyanato) cobaltate (susceptibility at 20 °C 16.44×10^{-6} cm^3 mol^{-1}). Data were corrected for diamagnetism of the ligand using Pascals constants [13]. ESR spectrum was recorded at X-band frequency with a Bruker 2000TT spectrometer. The microwave frequency was measured with a Racal-Dana frequency meter and the magnetic field with a Bruker gaussmeter.

Results and Discussion

Description of the Structure

The crystal structure of $CuDZ_2DMSO$ consists of $CuDZ_2$ and uncoordinated DMSO molecules. The fractional atomic coordinates of the non-hydrogen atoms with their e.s.d.s in parentheses are given in Table 1. Figure 1 shows the atom numbering of $CuDZ_2DMSO$, while the bond lengths and angles are given in Figs. 2 and 3, respectively. See also 'Supplementary Material'. Figures 4 and 5 give the molecular packing of $CuDZ_2DMSO$ down the *a* and *b* axes, respectively.

The structure of $CuDZ_2DMSO$ unit involves a four coordinate CuN_4 chromophore with a compressed tetrahedral geometry. The distortion was quantified [14] (Table 2). The value obtained indicates that the coordination geometry is intermediate between square-planar and tetrahedral.

The two symmetry independent A and B ligand anions in the $CuDZ_2$ molecule exhibit very similar geometries. The bond lengths and angles of the pyrimidine ring, except for the C5–C6 bond lengths, are in general agreement with those reported in the literature [15–17]. The geometry of the solvent molecule agrees well with the range of values observed in several other crystal structures [18, 19].

The torsion angles about the diazo N=N bond are −175.6(5) and −179.2(5)° for molecules A and B respectively and they give an idea of the relative orientation of the pyrimidine and the phenyl rings in the two molecules. The phenyl rings of the two molecules are however, not parallel to each other, the dihedral angle between them being 22.07(7)°.

The two crystallographically independent molecules of the pyrimidine base coordinate bidentately to the metal ion, in *cis* arrangement to each other, through the deprotonated amino nitrogen N6 and the diazo nitrogen N51. The environment around the metal atom is in the form of a compressed tetrahedron. Both the metal binding sites as well as the metal-centre environment are unusual.

The C–NH_2 bond (in adenine, guanine and cytosine) is highly conjugated with the purine or

TABLE 1. Fractional atomic parameters of non-hydrogen atoms ($\times 10^4$) with e.s.d.s in parentheses and their equivalent isotropic temperature factors ($\times 10^4$)

Atom	x/a	y/b	z/c	U_{eq}
N1A	−26(5)	1173(7)	5990(4)	414
C1A	−657(8)	1116(8)	6584(7)	674
C2A	−710(7)	1138(6)	5160(5)	446
O2A	−1770(5)	1031(5)	4934(4)	719
N3A	−128(5)	1231(5)	4603(4)	405
C3A	−857(8)	1203(7)	3723(6)	619
C4A	1073(7)	1402(6)	4816(5)	442
O4A	1486(5)	1531(5)	4271(3)	738
C5A	1753(6)	1411(5)	5691(5)	342
N5A	2883(5)	1680(4)	5852(4)	312
N51A	3621(5)	1688(4)	6591(4)	301
C6A	1190(6)	1255(5)	6286(5)	325
N6A	1768(5)	1208(5)	7064(4)	367
C1AP	4739(6)	2055(5)	6640(5)	305
C2AP	5158(7)	2066(6)	5978(5)	449
C3AP	6244(8)	2422(7)	6072(5)	521
C4AP	6936(8)	2769(6)	6826(6)	533
C5AP	6552(8)	2761(6)	7472(5)	442
C6AP	5436(7)	2408(6)	7382(5)	360
N1B	4477(5)	1382(4)	10121(3)	351
C1B	3361(7)	1614(6)	10230(5)	533
C2B	5485(7)	1390(5)	10835(5)	404
O2B	5415(5)	1644(4)	11489(3)	529
N3B	6528(5)	1122(4)	10755(3)	392
C3B	7564(7)	1108(6)	11512(5)	603
C4B	6665(7)	856(5)	10016(5)	362
O4B	7628(5)	622(4)	10022(3)	525
C5B	5610(6)	854(5)	9295(4)	320
N5B	5762(5)	502(4)	8624(4)	323
N51B	4941(5)	465(4)	7912(3)	293
C6B	4488(6)	1148(5)	9349(4)	316
N6B	3533(5)	1162(4)	8705(3)	345
C1BP	5310(6)	52(5)	7301(4)	328
C2BP	6481(6)	72(5)	7327(5)	396
C3BP	6783(7)	−285(6)	6687(5)	462
C4BP	5941(7)	−640(6)	6010(5)	532
C5BP	4783(7)	−667(6)	5986(5)	584
C6BP	4463(6)	−314(5)	6627(5)	460
S	345(2)	987(2)	9118(1)	556
OS	1019(5)	1126(5)	8531(4)	589
C1S	−889(9)	1730(8)	8766(7)	811
C2S	−436(8)	−64(7)	8838(6)	537
Cu	3450(1)	1125(1)	7574(1)	325

pyrimidine ring and therefore is a poor ligand [20] and a poor protonation site compared to the ring nitrogens. In fact, there is no crystallographic evidence of the exocyclic amino group either participating in metal binding or acting as a protonation site. However, once the amino nitrogen is deprotonated, it becomes a good ligand [21] and this fact is supported by several crystal structures [22, 23]. Ordinarily, uracil (and thymine) is known to be a poor complexing agent with its exocyclic O2 or O4 atom usually being the ligating atom as long as the ring nitrogens N1 and N3 are not deprotonated. However, in the present case, it may be noted that none of the exocyclic oxygens participate in metal binding and the ring nitrogens being methylated, are not available for coordination. It seems probable that the ligating power of the deprotonated amino nitrogen as well as that of the diazo nitrogen supercedes that of the exocyclic carbonyl oxygen. Also, the Cu–N (amino or diazo nitrogen) distances in this complex are, in general, shorter than any of the Cu–N distances observed by Aoki [24] for the various ring nitrogens in purine and pyrimidine complexes of copper(II), supporting the possibility that the amino or diazo nitrogen is a better ligand than any of the ring nitrogens. Between the two, the deprotonated amino nitrogen seems to have more potential ligation power than the diazo nitrogen as is reflected by the N6A–Cu and N6B–Cu distances of 1.925(5) and 1.922(5) Å which are significantly shorter than the N51A–Cu and N51B–Cu distances of 1.963(7) and 1.956(5) Å, respectively. Thus, the introduction of N6 and the diazophenyl group on the uracil moiety seems to have greatly enhanced its complexing capabilities.

Figure 6 shows the metal ion environment projected down a mean plane through the atoms involved in metal coordination and the metal ion. The coordination geometry around Cu takes the form of a compressed tetrahedron. A survey by Hathaway [25] shows that this is one of the less common geometries for divalent copper, the octahedral or square pyramidal geometries being the most favoured [26]. In the present structure, the distortion from tetrahedral geometry is so severe that it is almost half way between tetrahedral and square planar geometries, the angle between the plane containing N6A, Cu and N51A, and the plane containing N6B, Cu and N51B being 39.7(7)°. Table 3 gives a list of CuN_4 complexes with a compressed tetrahedral geometry together with the dihedral angle between the two CuN_2 coordination planes and energies of d–d transition of the reflectance spectrum. The distortion is normally due to steric interactions [26a–h]. In the title complex, the steric hindrance between the phenyl groups leads to a compressed tetrahedral geometry and prevents the adoption of a square-planar geometry more favoured by the effects of crystal field stabilisation energy. The balance between this energy and the steric hindrance also causes some distortion of the ligands from planarity. Thus, the angle between the phenyl rings and the C5A, N5A, N51A plane is 154.8(1)° for ligand A and 157.9(1)° for ligand B. Analogous distortions of the ligand have been observed in other CuN_4 complexes [26b, c].

The pyrimidine rings of the two independent ligands (A and B) are planar within 0.041 and 0.013 Å, respectively and the corresponding phenyl rings

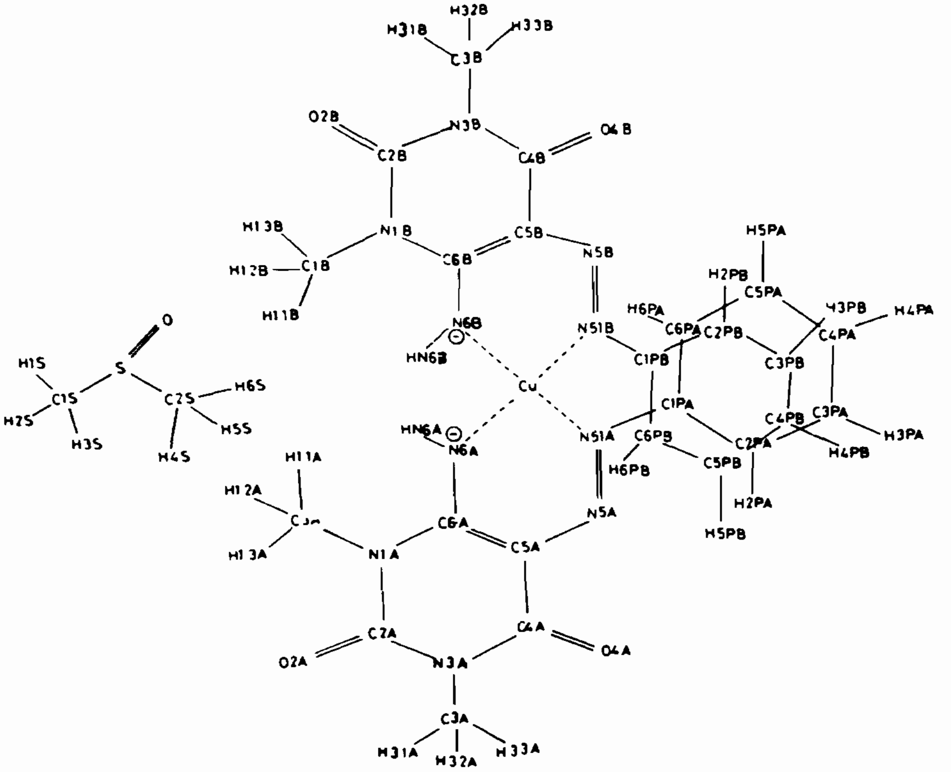

Fig. 1. Schematic diagram and numbering scheme of $CuDZ_2DMSO$.

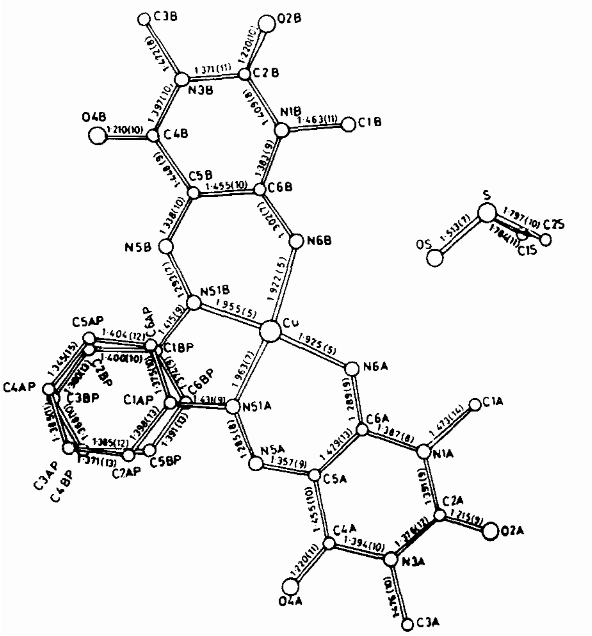

Fig. 2. Bond lengths in $CuDZ_2DMSO$.

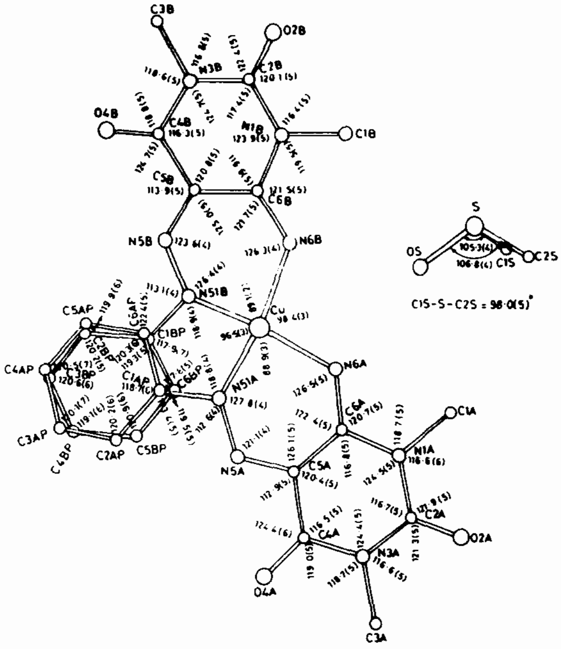

Fig. 3. Bond angles in $CuDZ_2DMSO$.

are planar within 0.008 and 0.041 Å, respectively. The planarity of the pyrimidine and phenyl rings has also been observed in several analogous complexes of 6-aminouracil derivatives [27].

The unit cell packing of $CuDZ_2DMSO$ viewed down *a* and *b* (Figs. 4 and 5) show that the crystal structure is stabilised by extensive stacking interactions between the pyrimidine rings as well as

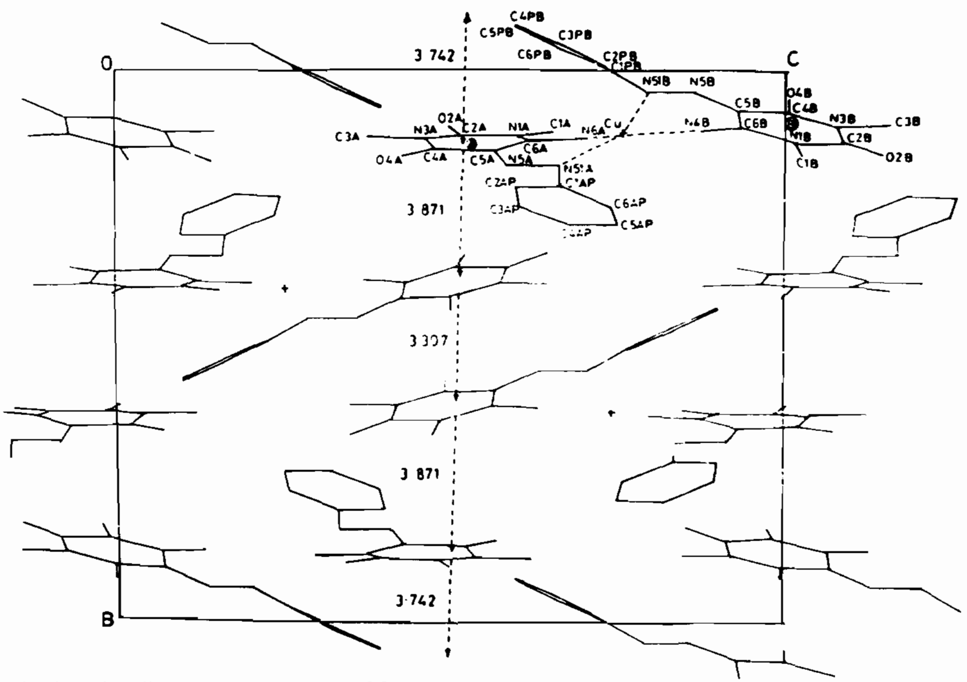

Fig. 4. Unit cell packing of CuDZ$_2$DMSO down the *a* axis.

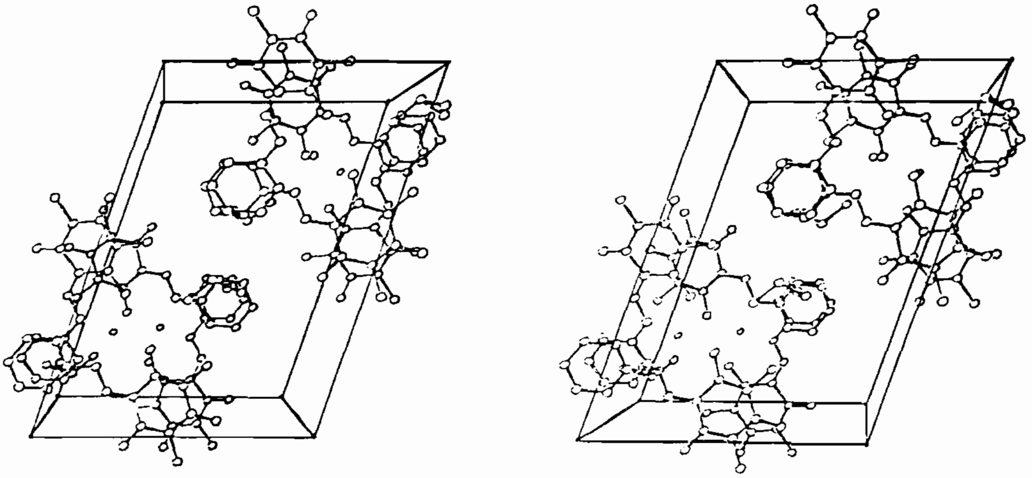

Fig. 5. Unit cell packing of CuDZ$_2$DMSO viewed along the *b* axis.

between the phenyl rings and by the two hydrogen bonds between the solvent molecule and the base. The pyrimidine rings stack alternately in pairs along the *b* axis in the sequence A–A–B–B–A–A, etc., the pairs A–A and B–B being related by a centre of inversion and the pairs A–B and B–A being related by the two-fold screw along the *b* axis. The stacking distance for the A–A pair is 3.74 Å and that for the B–B pair is 3.31 Å. The stacking distance for the A–B or the B–A pair is 3.87 Å. The stacking distance between the phenyl rings is 4.48 Å. The pyrimidine rings stack in such a way as to form infinite columns extended along the *b* axis. The columns are located approximately at ($x = 0.5$, $z = 0$) or ($x = 0$, $z = 0.05$), so that each unit cell contains four such columns.

Apart from the stacking interactions, the sulfonyl oxygen atom of the solvent DMSO accepts two hydrogen bonds from each of the deprotonated amino nitrogens of the two independent molecules A and B. The donor to acceptor distances for A and B molecules are 2.967(13) and 2.949(9) Å, respectively.

Electronic Properties

The polycrystalline ESR spectrum (Fig. 7) of CuDZ$_2$ is not clearly axial and it seems to be pseudo-

TABLE 2. Coordination polyhedron around copper atom: experimental vs. theoretical dihedral angles (°) calculated for tetrahedral (*Td*) and square-planar (D_{4h}) geometry; distortion estimated according to ref. 14

Dihedral angles	D_{4h}	Experimental	*Td*
N4B–N4A–N51A–N51B	0	34.93	70.32
N51A–N4A–N4B–N1B	0	37.58	70.32
N4A–N51A–N4B–N51B	180	127.70	70.32
N4A–N4B–N51B–N51A	0	34.91	70.32
N51A–N4A–N51B–N4B	180	127.59	70.32
N4A–N51A–N51B–N4B	0	37.90	70.32
ΔD [a]	100	49.65	0

[a] The dihedral distortion (%) was calculated as follows:

$$\Delta D = \frac{1}{n}\sum_{j}\left|\frac{\sum_{j}(\delta_i - \delta_j)}{(\delta_{j1} - \delta_{j2})}\right| \times 100$$

where n = number of dihedral angles; δ_i = experimental dihedral angle; δ_{j1} = theoretical dihedral angle for *Td*; δ_{j2} = theoretical dihedral angle for D_{4h}.

isotropic, like that of the complex Cu(2,2'-bipyridylamine)$_2$(ClO$_4$) [28]. However, $g_{\parallel}$ can be observed without any difficulty in 2800–3200 G. The approximate $g_{\parallel}$ and $g_{\perp}$ values are 2.227 and 2.054, respectively. These values are similar to those found for the [Cu(bipy)$_2$][PF$_6$] complex [26h]. As $g_{\parallel} > g_{\perp} > 2.03$, a $d_{x^2-y^2}$ (or d_{xy}) orbital ground state might be proposed. The flattening of the coordination tetra-

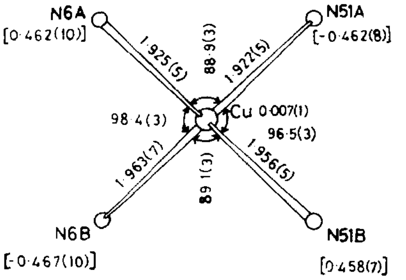

Fig. 6. Metal environment in CuDZ$_2$DMSO. The numbers in brackets are atom deviations from a mean plane through Cu, N6A, N6B, N51A and N51B.

TABLE 3. Geometrical parameters and optical bands of the compressed tetrahedral CuN$_4$ complexes

Complex	Dihedral angle (°)	Reference	d–d Band (kK)	Reference
[Cu(*trans*[14]diene)][ClO$_4$]$_2$	0.0	26k	19.96[d]	31
[3,7,14,18,23,24-hexaazatricyclo(18.2.1.1)tetracosane-2,7,9,11,13,18,20,22-octaene-N^3,N^7,N^{23},N^{24}] copper(II)	30.0	26i	17.50	26i
[Cu(*cis*[18]dieneN$_4$)](ClO$_4$)$_2$	36.6	26f	17.18[c]	26f
Cu(DZ)$_2$DMSO	39.6	[a]	17.10[b]	[a]
Bis(2,2'-bipyridyl) copper(II) bis(hexafluorophosphate)	44.6	26h	16.95[b] 15.04	26h
Bis(2-pyridyl-2pyrimidylamine) copper(II) diperchlorate	53.8	26d	15.90[b] 10.30 7.50	30
Bis(2,2'-bipyridylamine) copper(II) diperchlorate	55.6	26b	15.70[c] 13.50 10.40 7.50	34
Bis(3,3'-dimethyl-2,2'-dipyridylamine) copper(II)	57.4	26c		26d
Bis(di-2-pyridylamine) copper(II)	58.8	26g	15.60 9.90	30
Bis(*N*-tert-butyl-pyrrole-carbaldimino) copper(II)	60.0	26g	15.50[d]	29
Bis(diethyl-3-3',5,5'-tetramethyl-dipyrromethene-4,4'-dicarboxylate) copper(II)	68.0	26a		
Bis(4-phenylamine-2-phenyliminopent-3-enato-*N*,*N*') copper(II)	67.0	26e		

[a] This work. [b] Shoulder. [c] Polarised single crystal values. [d] Solution spectrum.

hedron causes the splitting of both the excited ^2E and ground $^2T_2$ levels, so that four d–d transitions are expected. However, normally only two d–d bands are observed in the reflectance spectrum.

The reflectance spectrum of CuDZ$_2$DMSO consists of a main broad band at 19.2 kK with a clear but unresolved shoulder at 17.1 kK and a clearly resolved shoulder at 12.4 kK. Other bands are at 22.0, 27.1, 31.2 and 41.6 kK. Bands occurring above 18 kK are believed to be due to intraligand and/or copper–ligand charge transfer transitions. Bands at 17.1 and 12.4 kK are assigned to d–d transitions. The crystal field energy is much smaller in the tetrahedral geometry than in the square one. Thus the energy of d–d transitions increases progressively as the dihedral angle between the two N–Cu–N planes varies from 90° (perfect tetrahedral geometry) to 0° (square-planar geometry). This effect can be clearly observed in the complexes listed in Table 3.

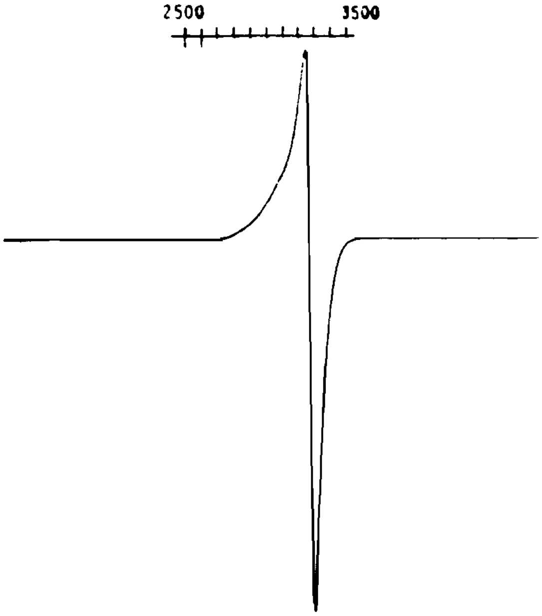

Fig. 7. Polycrystalline ESR spectrum of CuDZ$_2$DMSO at 293 K.

Battaglia *et al.* [33] correlated the dihedral angle with the highest-energy d–d transition in the electronic spectra of some tetrachlorocuprates with compressed tetrahedral D_{2d} symmetry. For these anions the variation of the dihedral angle with the highest energy d–d transition was linear. A similar relationship must be obtained for the CuN$_4$ complexes with compressed tetrahedral geometry, using the values of Table 3. The graph of the dihedral angle (ϕ) versus the highest energy d–d transition (ν_{max}) is given in Fig. 8. The least-squares equation for this line is: $\phi = -13.381\ \nu_{max} + 267$ with a correlation coefficient $r^2 = 0.997$.

Gouge and Geldard [30] have also proposed a correlation between the dihedral angle and observed energies of d–d transitions for several pseudotetrahedral CuN$_4$ complexes whose crystal structures have been determined, but the range of the dihedral angle was restricted to 53.8 to 58.8° by which its use is limited. The corrected magnetic moment at 293 K is 1.94 μB within the normal range for Cu(II) com-

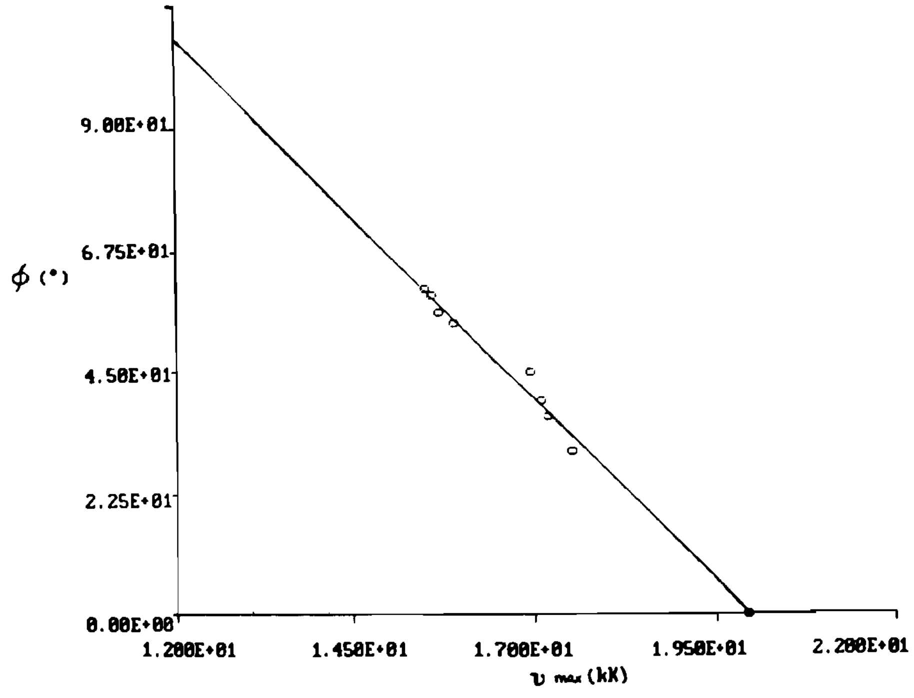

Fig. 8. Linear correlation between the dihedral angle and the highest d–d energy.

plexes lacking metal–metal interactions (1.7–2.2 μB). In square-planar and tetrahedral geometries different degrees of orbital contribution are expected. In the former geometry, because it has a non-degenerate ground state, there is no orbital contribution. However, in the latter geometry an orbital contribution is expected due to the $^2T_2$ ground state. The magnetic moment of the complex $CuDZ_2$-DMSO is essentially the spin only value with some degree of orbital contribution, in accordance with the compressed tetrahedral geometry for this complex.

Supplementary Material

The coordinates, bond lengths and angles involving the hydrogen atom are available from the authors on request.

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