

E.s.r. Properties of Some Copper(II) Polyamine Complexes in Nonaqueous Solvents

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An e.s.r. study of Copper(II) complexes with the following linear aliphatic polyamines: ethylenediamine, 1,3-diaminopropane, triethylenetetramine, 3,3'-diaminodipropylamine and N,N,N',N'',N''',N''''-hexamethyltriethylenetetramine has been carried out with the aim of providing information on the electronic ground state of the complexes. In addition information on the nature and extent of the interaction with the solvent has been obtained. Complementary data, namely electronic spectra and conductivity measurements, have been used to help provide the most reliable prediction of the stereochemistry of the complexes.

Introduction

E.s.r. spectroscopy can be used to determine the electronic ground state of a copper(II) complex in solution and hence, in conjunction with electronic spectroscopy, it can give us information about the possible stereochemistry of the complex. At a slightly more sophisticated level variations in the Spin Hamiltonian parameters of square planar and square pyramidal species can give us information about the nature and extent of axial interactions. We have examined a number of square planar and square pyramidal species for which the stereochemistry in the solid state is already known¹ in some cases, with the intention of studying their behaviour in different solvents. The polyamines used to prepare the Copper(II) complexes were: ethylenediamine (en), 1,3-diaminopropane (tn), triethylenetetramine (trien), 3,3'-diaminodipropylamine (dpt) and N,N,N',N'',N''',N''''-hexamethyltriethylenetetramine (trienMe₆). The solvents were N,N-dimethylformamide, methanol and nitroethane.

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Experimental

Materials

The amines ethylenediamine (en), 1,3-diaminopropane (tn), triethylenetetramine (trien) and 3,3'-diaminodipropylamine (dpt) were commercially available. The amine N,N,N',N'',N''',N''''-hexamethyltriethylenetetramine (trienMe₆) was prepared by methylation of trien with a mixture of formic acid and formaldehyde.¹

The solid compounds Cuen₂(SCN)₂, Cuen₂(SCN)(ClO₄), Cutn₂(SCN)₂, Cutn₂(ClO₄)₂, Cutrien(SCN)₂, Cutrien(SCN)(ClO₄), CutrienMe₆(SCN)(ClO₄) were prepared by literature methods.¹ The compound CudptBr₂ was prepared by an analogous method.

Visible Spectra

Absorption spectra were recorded at room temperature with a Beckman DK-2A spectrophotometer in 1 cm silica cells.

E.s.r. Spectra

First derivative e.s.r. X-band spectra were recorded at room temperature and at -140°C using a Decca X-3 spectrometer and a Hilger Microspin spectrometer. Magnetic field was measured using an n.m.r. probe. Simulated spectra for a Lorentzian line shape were obtained using Venables' programme.² The copper concentration as Cu(II) complex was about 10⁻³M.

E.s.r. Data Treatment

For square planar and square pyramidal copper(II) complexes the ground state is normally d_{x²-y²}, or more rarely d_{xy}, for which states it is found that g_{||} > g_⊥ > 2.04. Molecular orbitals can be constructed from the metal ion orbitals and the appropriate ligand symmetry orbitals using the LCAO method. From such MO expressions for the Spin Hamiltonian parameters can be derived and hence, knowing the experimental values of these parameters, the values of the MO coefficients can be calculated. The approximate forms of the ex-

pressions derived by Maki and McGarvey³ assuming axial symmetry are:

$$\begin{aligned} g_{||} &= 2.0023 - 8\rho(\alpha\beta_1^{-1/2}\alpha'(1-\beta_1^2)^{1/2}T(n)) \\ g_{\perp} &= 2.0023 - 2\mu(\alpha\beta - (1/2)^{1/2})\alpha'(1-\beta^2)^{1/2}T(n) \\ A_{||} &= P[(-4/7 - K_o)\alpha^2 + (g_{||} - 2) + 3/7(g_{\perp} - 2) \\ &\quad - 4\rho\alpha'(1-\beta_1^2)^{1/2}T(n) \\ &\quad - (3.2^{1/2}/7)\mu\alpha'(1-\beta^2)^{1/2}T(n)] \quad (1) \\ A_{\perp} &= P[(2/7 - K_o)\alpha^2 + 11/14(g_{\perp} - 2) - (11.2^{1/2}/ \\ &\quad 14)\mu\alpha'(1-\beta^2)^{1/2}T(n)] \end{aligned}$$

where $\rho = \lambda\alpha\beta_1/\Delta E_{xy}$, $\mu = \lambda\alpha\beta/\Delta E_{xz}$, α' is the ligand coefficient of the ground state M.O., λ is the free-ion value of the spin-orbit coupling constant for Cu(II), ΔE_{xy} is the energy separation between the $d_{x^2-y^2}$ and d_{xy} orbitals, ΔE_{xz} is that between $d_{x^2-y^2}$ (or d_{xy} according to which is the ground state) and the d_{xz} , d_{yz} orbitals (assumed degenerate), α is the coefficient of the metal orbital in the ground state M.O. (σ -bonding), β_1 is the coefficient of the metal orbital in the in-plane π -bonding M.O., and β is the coefficient of the d_{xz} , d_{yz} in the degenerate pair out-of-plane π -bonding M.O., K_o is the hyperfine contact term (the omission of the overlap terms and ligand-ligand interactions from these expressions makes relatively little difference to the values of the metal ion coefficients which are obtained).

The addition of axial ligands to a square planar copper(II) species leads to an increase in the value of $g_{||}$. Thus it is well known experimentally^{4,5,6} that the value of $g_{||}$ for a square planar copper(II) species in solution increases with the basicity of the solvent. It has been shown⁷ that as the axial field increases the equatorial ligands are driven further from the metal. This increase in the length of the equatorial bonds is accompanied both by a decrease in the covalency of these bonds, *i.e.* by an increase in the value of α , and by a red-shift of the $d_{x^2-y^2} \rightarrow d_{xy}$ transition. Both these factors, as can be seen from equation (1) above, lead to an increase in the value of $g_{||}$. Smith has shown⁸ (for a series of salts of $\text{Cu}(\text{NH}_3)_4^{2+}$, chromophore CuN_4X_2) that there is a good correlation between the experimental values of $g_{||}$, and the overlap between the copper d_{z^2} orbital and the axial ligand np-orbitals. The change in g_{\perp} is usually much smaller and the observed increase in g_{iso} is largely due to the increase in $g_{||}$. The axial ligands are only weakly bound however and most of the bonding arises from interaction between the metal 4s and 4p-orbitals and the ligand σ -orbitals. Any increase in the 4s electronic population should lead to a decrease in the hyperfine contact term since the 4s-contribution to this term is of opposite sign to the main contribution which arises from spin polarisation of inner s-orbitals (core polarisation).^{8,9} Since the hyperfine terms are mainly determined by the contact term¹⁰ this should lead to a decrease in the A-

values. In fact a decrease in the value of $A_{||}$ has often been observed.¹¹

In square pyramidal species the copper(II) ion is usually raised out of the plane of the equatorial ligands. Relative to analogous square planar species this leads to a decrease in inplane bonding. This together with the presence of the single axial bond leads to a general red shift of the electronic transitions, *cf.* the data for $(\text{NH}_4)\text{Cu}(\text{NH}_3)_5(\text{PF}_6)_3$ given in ref. 12, and as a result to an increase in both $g_{||}$ and g_{\perp} . The addition of a solvent molecule in the sixth coordination position tends to bring the copper(II) ion back into the plane of the equatorial ligands with a consequent increase of the in-plane bonding, but it is also almost certainly accompanied by an increase in the length of the original axial bond. Thus the shifts in the values of g_{\perp} and $g_{||}$ will be not be the same and in fact will be somewhat unpredictable except insofar as the decrease in g_{\perp} will be expected to be the larger. As in the case of square planar complexes any increase in the 4s-population will lead to a decrease in the contact term. However, the effective symmetry of many square pyramidal species being low, some mixing of 4s into the ground state orbital may be allowed so that it will be difficult to predict the effect of solvent coordination on the contact term and hence on the A-values.

It is often difficult to determine g_{\perp} and A_{\perp} from the frozen solution spectra directly. In order to simulate spectra, however, values of these entities are necessary, hence to obtain initial values we made use of the expressions:

$$\begin{aligned} g_{\text{iso}} &= \frac{1}{3}(g_{||} + 2g_{\perp}) \\ A_{\text{iso}} &= \frac{1}{3}(A_{||} + 2A_{\perp}) \end{aligned} \quad (2)$$

where A_{iso} and g_{iso} are the pseudoisotropic values of A and g found at room temperature in solution when the viscosity is such as to allow the molecules to tumble freely. The use of these expressions does presuppose that no change in structure or bond lengths occurs when the solutions are frozen which may not always be the case. In most cases however equations (2) give g_{\perp} to an accuracy of *ca.* $\pm 1\%$ and A_{\perp} to an accuracy of *ca.* $\pm 10\%$. In fact where independent checks have been made, *e.g.* by using a spectrometer with a higher microwave frequency, the agreement has been remarkably good. Thus Yokoi and Isobe⁶ using a K-band spectrometer found values of 2.050 and 2.052 for $\text{Cu}(\text{N}_2)(\text{ClO}_4)_2$ in 50% methanol-water using expression (2) and a K-band spectrometer respectively. Empirical values of the Fermi contact term K can be obtained from the expression:

$$K = \frac{A_{\text{iso}}}{P} + (g_{\text{iso}} - 2.0023) \quad (3)$$

In the absence of a 4s contribution to the ground state orbital it could be assumed that K would be equal to

α^2K_0 but if there is such a contribution than K will be equal to $\alpha^2K_0 - 4s$ contribution. Values of K are shown in Table III together with the g - and A -values.

Results and Discussion

The analytical data are shown in Table I, the electronic and e.s.r. spectral data in Table II and III.

$Cu_2(SCN)_2$ and $Cu_2(NCS)(ClO_4)$

Although X-ray studies have shown that in the solid state both complexes have tetragonal structures with weak axial bonding via the thiocyanate groups,^{13,14} it

has also been found that in methanolic solution the bis(thiocyanate) complex dissociates to give the square planar species¹⁵ Cu_2^{2+} . The measured equilibrium constant for the reaction: $Cu_2^{2+} + SCN^- \rightleftharpoons Cuen_2(SCN)^+$ in methanol¹⁶ is too small for any appreciable concentration of the latter species to be present in the solutions used for the e.s.r. measurements. It is quite clear that the perchlorate complex will also dissociate in methanolic solution to give the same Cu_2^{2+} cation.

Within experimental error, the e.s.r. data obtained for the two complexes in DMF solution are essentially identical and are typical for compounds with a $d_{x^2-y^2}$ ground state. The values of g_{iso} found in MeOH and

TABLE I. Summary of Analytical Data for Cu(II) Complexes.

	Found %				Calculated %			
	Cu	C	H	N	Cu	C	H	N
$Cu_2(SCN)_2$	21.3	24.0	5.7	28.5	21.2	24.0	5.4	28.0
$Cu_2(SCN)(ClO_4)$	18.6	17.3	4.9	20.4	18.6	17.6	4.7	20.5
$Cu_2(SCN)_2$	19.5	29.1	6.3	25.9	19.4	29.3	6.1	25.6
$Cu_2(ClO_4)_2$	15.3	17.9	5.0	13.9	15.5	17.5	4.9	13.6
$Cu_2(SCN)_2$	19.7	29.6	5.6	25.5	19.5	29.5	5.6	25.8
$Cu_2(SCN)(ClO_4)$	17.4	23.0	5.1	19.5	17.3	22.9	4.9	19.1
$Cu_2Me_6(SCN)(ClO_4)$	14.3	34.6	7.1	15.7	14.1	34.6	6.7	15.5
Cu_2Br_2	17.7	20.2	6.5	16.0	17.9	20.3	6.7	16.3

TABLE II.

Compound	Electronic Spectra (kK)		
	Solid	Solution ^a	
$Cu_2(SCN)_2$	19.4	17.5(83)	MeOH ^b
		17.2(90)	DMF
$Cu_2(SCN)(ClO_4)$	18.5	17.7(86)	MeOH
		17.5(79)	DMF
$Cu_2(SCN)_2$	19.2	16.3(140)	MeOH ^c
		16.2(156)	DMF
		15.7(127)	EtNO ₂ ^c
$Cu_2(ClO_4)_2$	17.8	17.9(118)	MeOH ^c
		17.5(125)	DMF
$Cu_2(SCN)(NCS)$	17.4	16.0(240)	MeOH ^c
		15.5(180)	DMF
		15.6(172)	EtNO ₂ ^c
$Cu_2(SCN)(ClO_4)$	16.2	16.3(169)	MeOH ^c
		15.8(177)	DMF
		15.3(139)	EtNO ₂ ^c
$Cu_2Me_6(NCS)(ClO_4)$	16.0	15.9(255)	MeOH ^c
		15.6(267)	DMF
		15.6(253)	EtNO ₂ ^c
Cu_2Br_2	10.8sh, 14.9	14.9(122)	DMF
		13.8(460),	EtNO ₂
		10.8sh	

^a The values in parentheses are the molar extinction coefficients. ^b Ref. 15. ^c Ref. 1.

TABLE III.

Compound		E.s.r. Spectra						
		$g_{ }$	g_{\perp}	g_{iso}	$A_{ }$ ($cm^{-1} \times 10^{-1}$)	A_{\perp}	A_{iso}	k^b
Cuen ₂ (SCN) ₂	MeOH			2.106			80	0.32
	DMF	2.209	2.051 ^a	2.104	195	~24 ^a	82	0.32
Cuen ₂ (SCN)(ClO ₄)	MeOH			2.108			82	0.33
	DMF	2.207	2.051 ^a	2.103	197	~22 ^a	80	0.32
Cutn ₂ (SCN) ₂	MeOH			2.117			75	0.32
	DMF	2.227	2.065 ^a	2.119	192	~10 ^a	71	0.31
Cutn ₂ (ClO ₄) ₂	MeOH			2.111			84	0.34
	DMF	2.220	2.046 ^a	2.104	193	~27 ^a	82	0.33
Cutrien(SCN)(NCS)	MeOH	2.214	2.062 ^a	2.113	172	~24 ^a	73.5	0.315
	DMF	2.209	2.059 ^a	2.109	175	~10 ^a	65	0.29
Cutrien(SCN)(ClO ₄)	MeOH	2.206	2.058 ^a	2.107	182	~24 ^a	77	0.32
	DMF	2.204	2.045 ^a	2.098	183	~15 ^a	71	0.29
CutrienMe ₆ (NCS)(ClO ₄)	MeOH	2.219	2.066 ^a	2.117	153	~36 ^a	75	0.32
	DMF	2.227	2.055 ^a	2.112	181	~22 ^a	74	0.32
	EtNO ₂	2.22±0.01	2.078 ^c (2.068 ^c)	2.125	~200±10		71	
CudptBr ₂	DMF	2.246	2.072 ^a	2.115±.015	164	~30 ^a	~75	
	EtNO ₂	~2.22	2.10 ^c	2.127±.013			~75	

^a Calculated from (2). ^b Calculated from (3). ^c Taken directly from spectrum.

DMF solutions are significantly different but the A_{iso} values are the same within the limits of experimental error (Table III).

Unfortunately we were unable to obtain resolved spectra in frozen methanol solution. We interpret the increase in g_{iso} as probably due to an increase in $g_{||}$. A possible explanation for the fact that A_{iso} does not change may be that the decrease in K resulting from the increased axial bonding is balanced by the increase in the term $(g_{||} - 2)$ because of the increased value of $g_{||}$.

Although Yokoi and Isobe do report¹⁷ a value of $g_{||}$ of 2.209 for Cuen₂(ClO₄)₂ in MeOH which is not significantly different from the value we find in DMF for our two complexes, we are reluctant to compare this value with our data since they do not report a value for g_{iso} and it is notoriously difficult to keep MeOH water-free so that the two samples may well differ in the amount of water present.

Cutn₂(SCN)₂ and Cutn₂(ClO₄)₂

In this case too both complexes have tetragonally distorted structures in the solid state.^{1,18} However as reported in a previous paper,¹ they have different stereochemistries in MeOH solution as shown by the conductivity and spectral data. The perchlorate gives the square planar cation Cutn₂²⁺ whilst the bis(thiocyanate) gives the same pentacoordinate cation Cutn₂(NCS)⁺ as does Cutn₂(NCS)ClO₄.¹

For each complex the electronic spectra in MeOH and DMF are very similar (Table II) so that it is rea-

sonable to suppose that for each of them the molecular structure is the same in both solvents. From the e.s.r. data in DMF it is clear that both complexes have a $d_{x^2-y^2}$ (or d_{xy}) ground state in this solvent (Table III, Fig. 1). This, together with the electronic spectrum, leads us to the conclusion that the structure of Cutn₂(NCS)⁺ in DMF solution must be essentially square pyramidal. This contrasts with the essentially trigonal bipyramidal structure found for this cation in the solid complex Cutn₂(NCS)ClO₄ by Cannas *et al.*,¹⁹ but is highly probable that the solid state structure is determined by packing requirements.

Although it is true that the structures of 5-coordinate complexes often depart from the idealized forms it is nevertheless true that even distorted trigonal bipyramidal species, *e.g.* the Cu(bipyridyl)₂I⁺ cation,²⁰ are found to have essentially d_{z^2} ground states.

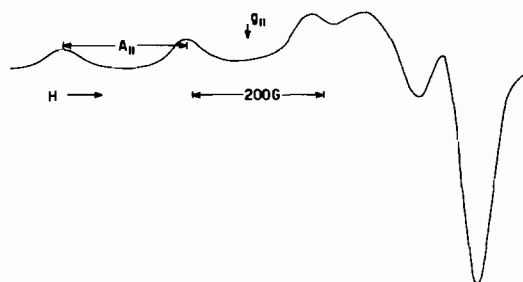


Figure 1. E.s.r. spectrum (X-band) of frozen solution of Cutn₂(ClO₄)₂ in DMF at -140°C.

The value of $g_{||}$ found for Cutn_2^{2+} is higher than that for Cuen_2^{2+} , *i.e.* it is closer to the value predicted by the ionic model. The greater stability of Cuen_2^{2+} compared with Cutn_2^{2+} has been attributed to stronger coordinate bond formation by nitrogen in the 5-membered ring, a view to which the measured enthalpy values²¹ lends support. This in itself may be sufficient to explain the larger value of $g_{||}$ but it is also true that weaker in-plane bonding will lead to a greater degree of axial bonding. The value of g_{iso} for the perchlorate in MeOH is higher than in DMF and this is probably due to the stronger axial interaction in MeOH which should result in a larger $g_{||}$ but we were unable to confirm this as we could not obtain a resolved spectrum in the frozen solution. As for the two en complexes the values of A_{iso} in the two solvents are essentially identical. Yokoi and Isobe¹⁷ again report a value of $g_{||}$ for this compound in MeOH which is identical with our value in DMF but again they report no value of g_{iso} .

The values of both $g_{||}$ and g_{\perp} for $\text{Cutn}_2(\text{NCS})^+$ in DMF are higher than for the perchlorate. These shifts can be explained, as we have already pointed out in the section "e.s.r. data treatment" by the weaker in-plane bonding and the red shifts in the d-d transitions. It is noticeable that the values of A_{iso} are appreciably smaller than for the square planar species. This is possibly due to a small amount of 4s mixed into the ground state since the strict symmetry is C_{2v} . However the effective symmetry may be as high as C_{4v} in which case the 4s-population will arise from bonding with the solvent molecule coordinated in the sixth coordination position.

[Cutrien(SCN)]NCS, [Cutrien(NCS)]ClO₄ and [CutrienMe₆(NCS)]ClO₄

In MeOH and EtNO₂ solutions the conductivity and electronic spectral data show that these complexes all give square pyramidal 5-coordinate ions as has already been reported¹ (Table II). The electronic spectral data in DMF are similar to those previously obtained in the other two solvents. Similarly the e.s.r. data (Table III) show that they all have either a $d_{x^2-y^2}$ or a d_{xy} ground state (Fig. 2). Hathaway's study²² of an undiluted single crystal of $[\text{Cutrien}(\text{SCN})]\text{NCS}$, in which he reported both the e.s.r. and the polarised electronic spectra, led him to assign this complex a d_{xy} ground state. He suggested that this ground state, previously found only in the presence of π -bonding chelate ligands, may be the result of the accumulated angular distortion of the three methylene groups in the trien ligand. It is therefore probable that all three of the above complexes also have this ground state in solution (in solution e.s.r. spectroscopy does not allow us to distinguish between d_{xy} and $d_{x^2-y^2}$ ground states).

It is noteworthy that contrary to expectations the spectral data for the two trien complexes are far from

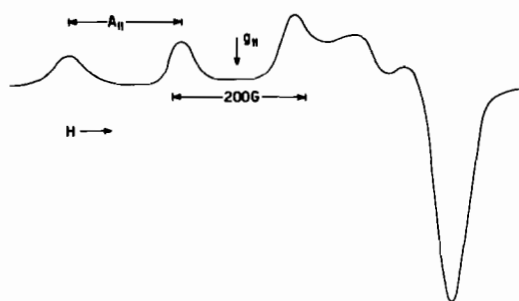


Figure 2. E.s.r. spectrum (X-band) of frozen solution of $\text{Cutrien}(\text{SCN})_2$ in DMF at -140°C .

being identical (see Table III). The most likely hypothesis is that in $[\text{Cutrien}(\text{SCN})]\text{NCS}$ we have S-bonded thiocyanate whereas in the perchlorate complex we have N-bonded thiocyanate.

It has been observed in the case of $\text{VO}(\text{Acac})_2$ that the value of A_{iso} is particularly sensitive to the nature of the solvent.²³ Unfortunately in addition to the coordinate strength of the solvent, its capacity to form hydrogen bonds and its dielectric constant are factors which affect this sensitivity and there is little available data on the values of dielectric constants at low temperature. From the data in Table III it is seen that for both trien compounds the values of A_{iso} and g_{iso} vary appreciably with solvent whereas for both compounds the value of $A_{||}$ is not much affected by change of solvent. The higher values of $g_{||}$ and lower values of $A_{||}$ found for the bis(thiocyanate) are compatible with a bigger axial interaction.

The g -values are in fact larger than those reported for the solid state²² ($g_z = 2.2044$, $g_x = 2.0504$ and $g_y = 2.0400$) as would be expected if the axial bonding with a solvent molecule were fairly strong. The relatively long Cu-S bond which must reflect fairly weak bonding and ligand-metal electron transfer would lead one to expect a fairly strong interaction with solvent molecules.

On the other hand an N-bonded thiocyanate would be more strongly bonded with the result that solvent interaction would be weaker. This is confirmed by the lower $g_{||}$ and higher $A_{||}$ values found for the perchlorate complex. In the case of the bis(thiocyanate) the larger value of $g_{||}$ in MeOH and relatively small increase in g_{\perp} relative to the values in DMF suggest that the effect of MeOH as an axial ligand is greater than that of DMF, as already found in the case of $\text{VO}(\text{acac})_2$,²³ but that there is little change in geometry. The significant changes in g_{iso} , A_{iso} and g_{\perp} found with change of solvent for the perchlorate, accompanied by insignificant changes in $g_{||}$ and $A_{||}$, can best be interpreted by assuming a greater change in the geometry of the complex when the solvent is changed than is found for the bis(thiocyanate).

EtNO₂ is a relatively poorly coordinating solvent and we therefore anticipate little solvation in this solvent. Although the low temperature e.s.r. spectrum of CutrienMe₆(NCS)ClO₄ in this solvent is poorly resolved so that the values of $g_{||}$ and $A_{||}$ are known with less certainty than is the case for the other data in Table III, there is no doubt that relative to the values in MeOH and DMF the values of g_{\perp} and $A_{||}$ are higher and the value of $g_{||}$ little different. This suggests that in EtNO₂ there is indeed little interaction with the solvent and also that the Cu(II) ion is probably lifted well out of the plane of the equatorial ligands. The larger value of g_{iso} reflects the large value of g_{\perp} and the small value of A_{iso} indicates the low value of A_{\perp} . In MeOH the value of g_{\perp} is still relatively big suggesting that the geometry is not very different from that in EtNO₂ but the value of $A_{||}$ is exceptionally low, a fact for which we are unable to offer a satisfactory explanation. The empirical K calculated from equation (3) is no smaller however than those of the other complexes indeed it is larger than those of the trien compounds. Using equation (4) (see final section) produces a markedly smaller value of α^2 as might be expected since the methylated N-donor atoms should be more polarisable than unmethylated N-donors (indeed the first charge transfer band does occur at a lower frequency than for the trien complexes). The higher $g_{||}$ and $A_{||}$ values found in DMF together with a lower value of g_{\perp} can best be explained on the assumption of an appreciable change in geometry in this solvent – probably involving the Cu(II) ion being brought more nearly into the plane of the equatorial ligand donor atoms.

CudptBr₂

The e.s.r. spectrum of the powdered solid CudptBr₂ is rather unusual and difficult to interpret but the most likely interpretation is of a $d_{x^2-y^2}$ (or d_{xy}) ground state with both elongated rhombic symmetry, *i.e.* three g -values, and misalignment of the molecular axes of separate Cu(II) chromophores in the unit cell. The approximate g -values are $g_1 = 2.20$, $g_2 = 2.11$ and $g_3 = 2.06$ in terms of this interpretation.

This complex dissolves undissociated in both EtNO₂ and DMF as shown by the conductivity measurements, but its electronic spectrum in each of the two solvents is very different (Table II). Not only is the absorption maximum displaced to lower frequency in EtNO₂ solution but the molar extinction coefficient is much higher in this solvent. The e.s.r. spectra in the two solvents are quite similar and are only compatible with $d_{x^2-y^2}$ (or d_{xy}) ground state (Table III, Fig. 3). Thus taken in conjunction with the electronic spectrum this rules out a trigonal bipyramidal structure in DMF solution so that most likely structures are square pyramidal or square planar with one arm of the organic ligand uncoordinated. It is noteworthy that the struc-

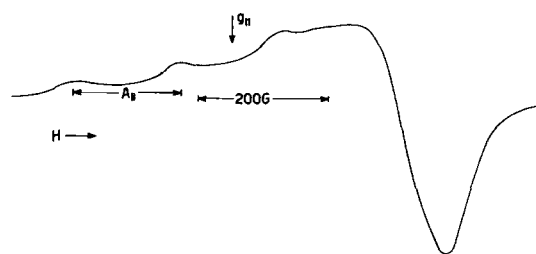


Figure 3. E.s.r. spectrum (X-band) of frozen solution of CudptBr₂ in DMF at -140°C .

ture in the solid state of Cudpt(NCS)₂ has recently been determined and the CuN₅ chromophore has a square pyramidal structure.²⁴ The EtNO₂ solution e.s.r. spectra is poorly resolved and the values of $g_{||}$ and $A_{||}$ are known with rather less certainty than in the case of the DMF solution. In both DMF and EtNO₂ solutions g_{\perp} is readily obtained directly from the spectrum rather than from the use of equation (2), and whatever the reason it is clear that the value of this parameter is larger in EtNO₂ solution. The most likely reason for the higher extinction coefficient in this solvent is lower symmetry with more resultant mixing-in of metal 4p-orbital into the ground state. With the two Br atoms in *trans*-equatorial positions the symmetry is C_{2v} whereas with one Br axial the symmetry is only C_s for the square pyramidal case. It is possible that in DMF the first structure is present whereas in EtNO₂ the second is present. It is also conceivable that in DMF the square planar structure is present – this would also have C_{2v} symmetry.

Molecular Orbital Coefficients and the Value of K_o

Although in principle the M.O. coefficients can readily be obtained using equations (1), in practice the difficulty arises that the values of ΔE_{xy} , ΔE_{xz} and K_o are uncertain. The absorption spectra of the complexes examined in this study consist in all cases of a broad undifferentiated band.^{1,15} However use may be made of the single crystal results¹² to estimate the relative positions of ΔE_{xy} and ΔE_{xz} , bearing in mind that the general effect of axial coordination on the energy levels of square planar and square pyramidal species is a shift of all transitions to lower energies and at the same time a decrease in the difference between ΔE_{xy} and ΔE_{xz} . The second problem is the value of $K_o \cdot K_o$, the Fermi contact term, is often given the value 0.43 but it has been shown that it cannot be constant³ and attempts to determine its empirical value have given values as low as 0.0254.²⁶

Low values are attributed to 4s-character in the ground state, arising either through zero field mixing-in resulting from low symmetry, or as a result of the interaction of the metal 4s-orbital with axial ligands.

The most satisfactory situation is that in which the ¹⁴N hyperfine splitting is known. In this case α' can

be evaluated directly and hence by means of the normalisation equation so can the value of α . Unfortunately in the present work none of the spectra showed resolved nitrogen hyperfine splitting. However Yokoi and Isobe¹⁷ found that in 50% MeOH/H₂O the spectra of Cuen₂(ClO₄)₂ and Cutn₂(ClO₄)₂ had ¹⁴N hyperfine splittings of 10.5 and 12.6 × 10⁻⁴ cm⁻¹ respectively (these are really A_{N||} but the A_{N⊥} values can be assumed to be not too different) which give values of 0.29 and 0.35 for α' . Using a reasonable value for the group overlap integral (0.146) the respective values of α^2 are 0.850 and 0.806. With these values and an estimate of ΔE_{xy} (Yokoi and Isobe use 15200 cm⁻¹ for the en complex and 14600 cm⁻¹ for the tn complex) values for β_1^2 , the in-plane π -bonding coefficient, are found to be of the order 0.6. Even if the manifestly too large value of 20000 cm⁻¹ is used for ΔE_{xy} the values of β_1^2 are still in the region of 0.8. In the absence of resolved hyperfine we have resorted to an iterative procedure for solving equations (1) and we also find values of α^2 and β_1^2 of the same order. These results appear to suggest that there is extensive in-plane π -bonding. This is at variance with the commonly held view that aliphatic amines are incapable of π -bonding. Thus the reduction factors obtained from single crystal data have interpreted²⁵ on the assumption that $\beta_1 = 1$, i.e. no in-plane π -bonding, to yield values of α for en complexes including Cuen₂(ClO₄)₂ and Cuen₂(SCN)₂ in the range 0.70–0.75 with the corresponding β values in the range 0.94–1.0. Yokoi and Isobe¹⁷ suggested hyperconjugation as a possible explanation but the values for [CutrienMe₆(NCS)](ClO₄) are very similar to those for the trien compounds.

The iterative procedure on equations (1) produces values of K₀ which lie in the range 0.20–0.26. As can be seen from Table III these are appreciably lower than those found from equation (3). Because in the expressions for A_{||} and A_⊥ K₀ is assumed to be simply proportional to α^2 , a 4s-contribution to the experimental K would cause the calculated values of α^2 to be too high which in turn would lead to calculated values of β_1 which would be too small. However no amount of juggling with the figures can produce a value of β_1 close to unity. One is therefore led to question the use of the free ion value of λ in the expressions for g_{||} and g_⊥.

It is possible to rearrange the equations for A_{||} in such a way as to eliminate K altogether but with the introduction of A_{iso}³:

$$\alpha^2 = 1.75 \left[\frac{|A_{||}|}{P} - \frac{|A_{iso}|}{P} + 2/3 g_{||} - 5/21 (g_{\perp}) - 6/7 \right] \quad (4)$$

If a 4s-contribution is included α^2 is replaced by $\alpha^2 f^2$ where f² is the fraction of 3d. Using (4) gives values of α^2 of the order 0.73–0.78.

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