Inorganica Chimica Acta, 16 (1976) 113–120

An Investigation of the Structures of Copper(II) Polyamine Complexes in Aqueous Solution by a Combined Evaluation of the EPR and Thermodynamic Parameters

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Received May 19, 1975

A wide range of copper(II) polyamine complexes have been investigated by EPR and electronic spectroscopy in aqueous solution. All the compounds are found to be 4 + 2 or 4 + 1 species with a $d_{x^2-y^2}$ ground state. Species with only two nitrogen atoms coordinated have $g_{\parallel}$ values in the range 2.27–2.29, those with three nitrogens coordinated have values around 2.23 whilst those with four nitrogens coordinated have values around 2.20. These results are explained in terms of a different equatorial ligand field. By considering the enthalpy of Cu(II) complex formation to be connected with the strength of the coordinate bonds, the EPR and spectroscopic parameters are discussed together with the previously measured enthalpy and entropy values of the complexes considered.

Thus it is verified that the variations in $g_{\parallel}$ correspond closely to the variations in ΔH° for most of the complexes examined. For the other complexes a different structure from the 4 + 2 one normally found is invoked and substantiated by the entropy values. Also, a linear relationship between the $g_{\parallel}$ and ΔH° values is found.

Introduction

The complex formation reactions of the copper(II) ion with various polyamines in aqueous solution have been extensively investigated[1]. From the experimental values of the stability constants and of the heats of formation the thermodynamic parameters ΔG° and ΔH° have been obtained and hence by their combination the values of ΔS°. From an analysis of these three quantities reliable information about the structures of the complexes in solution has been obtained and it has also been possible to make deductions about the strength of the coordinate bonds formed by the different ligands which have been studied. Recently attempts have been made to correlate these thermodynamic quantities with certain spectroscopic parameters[2]. Thus EPR parameters have been determined and compared with the stability constants of the complexes in aqueous solution. A definite relationship between the stability constant K and the covalency parameter for σ-bonding, α^2, seems to be indicated[3]. In this study we have recorded the EPR and electronic spectra for several closely related series of polyamine complexes of the Cu^{2+} ion for which the thermodynamic parameters in aqueous solution have been previously determined[1]. We hoped in this way to obtain information about the electronic ground states of the complexes and about their stereochemistries and also to see if there is a simple relationship between the g and A values and the values of ΔH°, ΔG°, and ΔS°. The polyamines involved as ligands range from diamines to tetraamines so that a wide range of complexes having very different equatorial ligand field strengths have been investigated.

Experimental

Materials

The amines: en = ethylenediamine, diMeen = N,N′-dimethylethylenediamine, adiMeen = N,N-dimethylethylenediamine, Me_4en = N,N,N′,N′-tetramethylethylenediamine, Oden = bis-2-aminoethylether, NNOH = N-(2-hydroxyethyl)ethylenediamine, Sden = bis-2-aminoethylsulfide, 2,2-tri = 1,4,7-triazaheptane, 2,3-tri = 1,4,8-triazaoctane, 3,3-tri = 1,5,9-triazanonane, 2,3,2-tet = 1,4,8,11-tetraazaundecane, 3,2,3-tet = 1,5,8,12-tetraazadodecane, 3,3,3-tet = 1,5,9,13-tetraazatridecane, 2,2,2-tet = 1,4,7,10-tetrazadecane, CTH = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazaciclotetradecane, *meso* isomer; trien-Me_6 = hexamethyl-2,2,2-tet, are all commercially available. They were purified by precipitation as the hydrochlorides which were then recrystallised as described in references of Table I. Ethylene glycol was purchased from Merck. Copper(II) perchlorate was prepared by the action of perchloric acid on copper(II) carbonate. KOH solution was prepared as previously described[4]. Solutions of the complexes were prepared from decarbonated water. The preparation of the solid per-

TABLE I. Comparison of EPR with Stability Constants.

Complexes	% Species Obtained by EPR Spectra at −140° C			% Species Calculated by the Stability Constants				Ref.
	Cu^{2+}	CuL	CuL_2	Cu^{2+}	CuL	CuL_2	Other complexes	
Cuen	25.9	74.1		23.3	69.1	7.6		13
CudiMeen	12.0	90.1	7.9	11.5	92.5	6.0		13
CuadiMeen		86.0	14.0	8.4	86.6	5.0		13
$CuMe_4en$	8.7	91.3		15.2	84.8			13
CuOden		100.0		17.4	81.4		1.2	15
CuNNOH	27.0	73.0		30.0	70.0			16
CuSden	5.0	95.0						
Cu(2,2-tri)		100.0			100.0			17
Cu(2,3-tri)		100.0		0.1	99.9			a
Cu(3,3-tri)		100.0			99.4		0.6	b
Cu en_2			100.0			100.0		13
Cu $diMeen_2$		4.0	96.0		7.8	92.2		13
Cu $adiMeen_2$			93.0			90.2		13
Cu(2,3,2-tet)		100.0			100.0			c
Cu(3,2,3-tet)		100.0			100.0			d
Cu(CTH)		100.0						
Cu(2,2,2-tet)		100.0			99.9			e
Cu(3,3,3-tet)	9.0	91.0		11.3	88.7			26
Cu(2,2,2-tet-Me_6)		81.1	18.9					
$Cu(2,2\text{-tri})_2$			100.0		2.3	92.9	4.8	17

[a] R. Barbucci, L. Fabbrizzi and P. Paoletti, *Inorg. Chim. Acta, 7,* 157 (1973). [b] A. Vacca, D. Arenare and P. Paoletti, *Inorg. Chem., 5,* 1384 (1966). [c] D.C. Weatherburn, E.J. Billo, J.P. Jones and D.W. Margerum, *Inorg. Chem., 9,* 1557 (1970). [d] P. Paoletti, L. Fabbrizzi and R. Barbucci, *Inorg. Chem., 12,* 1861 (1973). [e] P. Paoletti, M. Ciampolini and A. Vacca, *J. Phys. Chem., 67,* 1065 (1963).

chlorates of $Cuen_2^{2+}$, $Cu(diMeen)_2^{2+}$, $Cu(adiMeen)_2^{2+}$, $Cu(2,2,2\text{-tet})^{2+}$, $Cu(2,3,2\text{-tet})^{2+}$, $Cu(3,2,3\text{-tet})^{2+}$, $Cu(3,3,3\text{-tet})^{2+}$ and of the complex $Cu(CTH)^{2+}$ have been described elsewhere[5]. Satisfactory analyses were obtained for all these compounds.

Measurements

EPR spectra were recorded using a Varian E-9 spectrometer. The EPR spectra were calibrated using DPPH as a g-marker. Glassy EPR spectra were recorded at −140° C and solution spectra at ambient temperature (25° C). 10^{-2} to $10^{-3}M$ solutions of the copper(II) salt in a 1:3 mixture of ethylene glycol–water were used for the measurement of the spectra. No dependence of the EPR parameters on the solvent composition was observed. Absorption spectra in solution were measured on a Beckmann DK-2A spectrophotometer.

Complexes in Solution

Solutions of the complexes were generally prepared by mixing weighed quantities of copper(II) perchlorate, amine hydrochloride and KOH (solutions of known titre) in a 10 ml flat bottomed flask. The quantities required were calculated using a FORTRAN programme which given the stability constants of the complexes, the protonation constants of the amine and the amounts of amine and Cu^{2+} added determines the percentages of the various complexes present for different amounts of KOH added and hence for different pH values. It was thus possible to determine the optimum conditions for the measurement of the spectra, *i.e.* the conditions which gave the maximum percentage of the complex whose spectrum was to be recorded. The complex stability constants and the amine protonation constants used are those given in the references quoted in Table I.

In the cases for which it was not possible to prepare solutions containing 100% of the desired species the EPR spectra obtained at low temperature showed the presence of more than one species (Figure 1). For the purposes of the present work it was necessary to know which set of lines belonged to which species. The relative amounts of the different species present in a given case were very different so that an approximate determination of the relative EPR intensities was sufficient to identify the species.

Whereas in order to obtain the intensity of an EPR line accurately it is necessary to integrate the full absorption curve, *i.e.* to double integrate the first derivative curve, if the linewidths of two components are

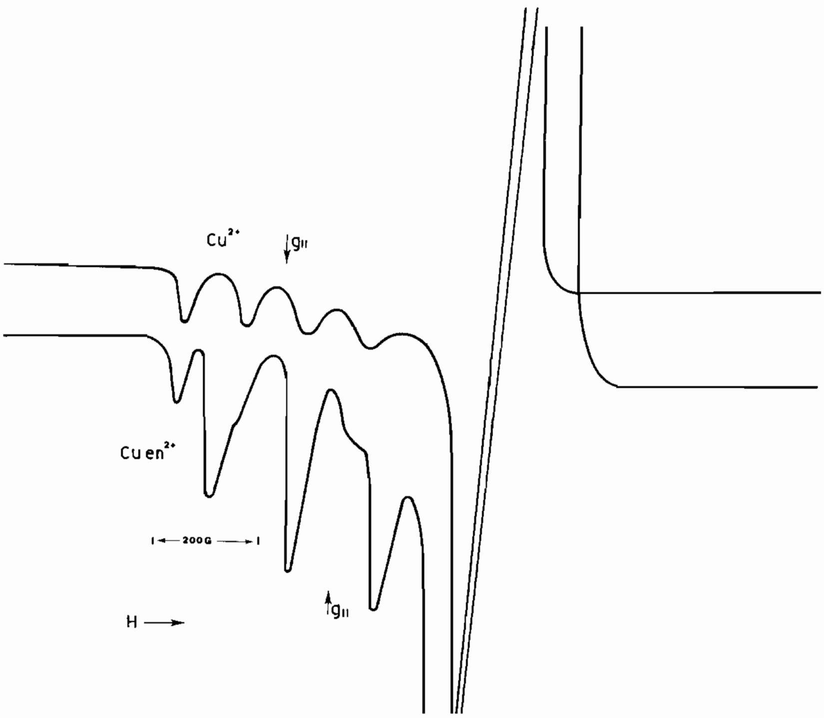

Figure 1. X-band (–140° C) EPR spectra for Cu^{2+} and $Cuen^{2+}$.

equal then the peak-to-peak amplitudes are proportional to the intensities. In the present work the linewidths of the various species present are approximately equal and it was therefore possible to adopt the latter procedure in order to obtain the relative amounts of the different species present to the required degree of accuracy.

From the areas subtended by a given hyperfine peak it was possible to determine experimentally the percentages of the different species present. There was good agreement between these values and those calculated by the stability constants (Table I). This verification of the calculated percentages of the species present is particularly important for aqueous solutions because of the doubt which might otherwise exist that on cooling from room temperature to –140° C the equilibrium could be shifted to such an extent that the species being examined was not the required one. In some cases spectra were also recorded for solutions obtained by dissolving the solid complex in the ethylene glycol–water mixture. No differences between the spectra obtained in this way and those obtained from mixtures of the amine, the copper(II) solution and KOH solution were found. A typical EPR spectrum is shown in Figure 1.

Simulated spectra for a Lorentzian line shape were obtained using Venable's programme[6] and it was found possible in all cases to fit the experimental spectra extremely closely. The EPR parameters given in Table II are the best-fit parameters for the final simulation.

The electronic spectra were measured using various ratios of metal ion to ligand in order to be able to calculate the limiting spectrum for each species in the way that we have previously described.[7]

Results and Discussion

All the EPR spectra can be fitted using an axial Spin Hamiltonian although it should be borne in mind that very small anisotropies of the g values in the xy-plane are almost impossible to detect experimentally in solution spectra because of the small in-plane hyperfine coupling constants and the relatively large linewidths. For tetragonal and square pyramidal copper(II) species – and all the species examined in the present work are thought to be 4 + 2 or 4 + 1 species in solution – the ground state is normally $d_{x^2-y^2}$, or more rarely d_{xy}, and for such states it is found that $g_{\parallel} > g_{\perp} > 2.04$[8]. As can be seen from the data in Table II all the species we have examined are in one of these ground states.

It will also be noted from the data in Table II that the values of $g_{\parallel}$ decrease as the number of coordinated nitrogen atoms increases. Thus species with only two nitrogen atoms coordinated have values in the range 2.27–2.29, those with three nitrogens coordinated have

TABLE II. EPR, Electronic Spectral and Thermodynamic Data.

Compound	EPR Spectra								Electronic Spectra (kK)[d]	Thermodynamic values[e]	
	$g_{\parallel}$	$g_{\perp}$	$g_{\perp}'^{a}$	g_{iso}	$A_{\parallel}^{b}$	$A_{\perp}^{b}$	$A_{\perp}'^{b,c}$	A_{iso}^{b}		$-\Delta H°$ (kcal mol^{-1})	$\Delta S°$ (cal mol^{-1} deg^{-1})
Cuen	2.272	2.070	2.074	2.140	177	17	14	68	15.7(50)	12.6	6.3
CudiMeen	2.278	2.057	2.056	2.130	173	12	8	63	14.9(55)	11.1	9.0
CuadiMeen	2.273	2.060	2.069	2.137	172	22	12	65	15.1(63)	9.8	9.5
$CuMe_4en$	2.281	2.060	2.061	2.134	168	19	18	68	14.2(90)	6.2	13.0
CuOden	2.277	2.080	2.064	2.135	138	15			14.3(63)	9.5	9.1
CuNNOH	2.270	2.056	2.056	2.127	172	16	12	65	14.6(55)	11.1	10.1
CuSden	2.293	2.060	2.032	2.119	169	10	0.5	56	15.3(106)		
Cu(2,2-tri)	2.226	2.042	2.050	2.109	190	20	16	74	16.6(76)	18.0	12.2
Cu(2,3-tri)	2.230	2.043	2.050	2.110	177	11	8	64	16.9(135)	19.2	11.5
Cu(3,3-tri)	2.246	2.055	2.056	2.119	162	10	0.	54	16.3(93)	16.1	11.0
$Cuen_2$	2.200	2.045	2.052	2.101	200	19	20	80	18.3(62)	25.2	5.8
$CudiMeen_2$	2.206	2.045	2.056	2.106	195	33	26	82	17.6(110)	20.8	9.3
$CuadiMeen_2$	2.202	2.052	2.052	2.102	195	19	24	81	17.7(157)	19.3	9.9
Cu(2,3,2-tet)	2.193	2.035	2.043	2.093	196	34	31	86	19.0(66)	27.7	16.5
Cu(3,2,3-tet)	2.206	2.040	2.038	2.094	196	29	34	88	18.7(86)	25.9	13.1
Cu(CTH)	2.200	2.040	2.052	2.101	199	19	25	83	19.6(158)		
Cu(2,2,2-tet)	2.200	2.040	2.047	2.098	190	29	27	81	17.3(163)	21.6	19.5
Cu(3,3,3-tet)	2.217	2.060	2.054	2.108	183	14	24	77	16.8(169)	19.5	12.8
Cu(2,2,2-tet Me_6)	2.239	2.053	2.053	2.115	170	17	16	67	15.0(180)		
$Cu(2,2\text{-}tri)_2$	2.206	2.045	2.061	2.109	185	9	11	69	16.3(107)	26.2	7.5

[a] $g_{\perp}' = \frac{1}{2}(3g_{iso} - g_{\parallel})$. [b] All hyperfine coupling constants in units 10^{-4} cm^{-1}. [c] $A_{\perp}' = \frac{1}{2}(3A_{iso} - A_{\parallel})$. [d] The values in parentheses are the molar extinction coefficients. [e] The thermodynamic values are taken from Ref. 1.

values around 2.23, whilst those with four nitrogens coordinated have values around 2.20. It is well known that in cases where only σ-bonding is really significant the values of $g_{\parallel}$ fall in a fairly narrow range depending on the donor atom set involved. Thus in general the values of $g_{\parallel}$ decrease in the order $CuO_4 > CuO_2N_2 > CuON_3 > CuN_4$.

The hyperfine coupling constants also show a regular trend which in general is the reverse of that shown by the values of $g_{\parallel}$. Experimentally a decrease in the value of $|A_{\parallel}|$ with increasing axial interaction has often been observed[9]. The axial ligands are only weakly bound and most of the bonding arises from interaction between the metal 4*s* and 4*p* orbitals and the ligand σ-orbitals[10]. Any increase in the 4*s* electronic population will lead to a decrease in the size of the hyperfine coupling constant. This is because the main contribution to the hyperfine terms is a contact term arising from core polarisation and the sign of the 4*s* contribution to this term is positive while the net contribution of the inner *s* orbitals (1*s*, 2*s*, 3*s*) is negative.

The contribution from the inner *s* orbitals is much the larger so that the sign of the hyperfine terms is negative[11]. For octahedral M(II) species of the first row elements it has been observed that a general decrease in core polarisation occurs with increasing covalency in the metal–ligand bonds[12].

Complexes containing a Single Bidentate Ligand

In those species with only two nitrogens coordinated to the metal ion the remaining coordination positions will be occupied by solvent molecules, *i.e.* by water or ethylene glycol molecules both of which have oxygen donor atoms. We are thus dealing with *cis*-CuO_4N_2 species. For the complexes of ethylenediamine and its derivatives diMeen, adiMeen, and Me_4en, there is a steady increase in $g_{\parallel}$ and decrease in $A_{\parallel}$ with methyl substitution. This can be interpreted in terms of increased axial bonding resulting from a decrease in metal–nitrogen bonding. This is certainly compatible with the measured enthalpies[13] of formation of these species (Table II) but is somewhat surprising in view of the known +I effect of the methyl group[14].

Complexes with Tridentate Ligands

The value of $g_{\parallel}$ for $Cu(Oden)^{2+}$ falls in the same range as those of the complexes with a single N_2 bidentate ligand. Even if it has been ascertained that the etheral oxygen is coordinated the chromophore is expected to be the same and the maximum in the electronic absorption spectrum is very close to those of these latter complexes. The value of $A_{\|}$ is however exceptionally low and the value of $g_{\perp}$ relatively high. These two facts taken together suggest a square pyramidal structure with a chromophore CuO_3N_2 with 2 water molecules coordinated. The value of $\Delta S°$ found for this complex[15] is compatible with the formation of a complex having a smaller number of coordinated solvent molecules than a 4+2 complex. A comparison with another complex in which the chelating ligand has the same donor atoms is therefore particularly desirable. $Cu(NNOH)^{2+}$ is such a complex and both its EPR parameters and thermodynamic data[16] are similar to those found for the en series (Table II); in particular the data closely parallel those for the diMeen and adiMeen complexes. Thus the alcoholic oxygen contributes little to the stabilisation of the Cu^{2+} complex.

In general substitution of S for O as donor atom results in lower values of $g_{\|}$ because of the increased covalency whilst the effect on $A_{\|}$ is rather more complicated and is not readily predictable. In the case of $Cu(Sden)^{2+}$ the value of $g_{\perp}$ is smaller than that in $Cu(Oden)^{2+}$ while somewhat surprisingly the value of $g_{\|}$ is larger. Similarly the value of $A_{\|}$ is larger in $Cu(Sden)^{2+}$ whilst the value of $A_{\perp}$ is smaller and may even be of opposite sign to $A_{\|}$. An explanation may be sought in the greater nephelauxetic effect of the sulphur atom which may lead to an increase in the Cu–N and $Cu–OH_z$ bond lengths.

The complexes of the triamines 2,2-tri, 2,3-tri and 3,3-tri involve three nitrogen donor atoms and the values of $g_{\|}$ increase regularly with the length of the aliphatic chain whilst the $A_{\|}$'s decrease in the same order. These trends contradict those found for the thermodynamic data[17,18,19] and for the maxima of the electronic absorption spectra (Table II). Thus the values of $-\Delta H°$ and of $\bar{\nu}$ both follow the trend Cu(2,3-tri) > Cu(2,2-tri) > Cu(3,3-tri). However the $\Delta S°$ values are very similar for the three complexes in contrast to the trend in the enthalpy values, and this implies a differing spatial arrangement of the tridentate ligand in the three complexes.

Complexes with Four or More Nitrogen Atoms

The $g_{\|}$ and $A_{\|}$ values for the complexes having two molecules of en or of its dimcthyl derivatives coordinated to the Cu^{2+} ion show the same trends as for the complexes having only one molecule of these ligands coordinated to the metal ion. Thus the en complex has the lowest $g_{\|}$ and the highest $A_{\|}$ value, the diMeen complex has the highest $g_{\|}$ value whilst its $A_{\|}$ value is essentially identical to that of the adiMeen complex. This can be accounted for by supposing that the en complex has shorter Cu–N bonds and less axial bonding. This is compatible with the available X-ray data[20] and with the measured enthalpies of formation of these species (Table II).

For the complexes of the tetraamines 232-, 323-, 222- and 333-tet the $g_{\|}$ values decrease in the order:

$$Cu(2,3,2\text{-tet}) < Cu(2,2,2\text{-tet}) < Cu(3,2,3\text{-tet}) < Cu(3,3,3\text{-tet})$$

and this trend is the same as that of the enthalpy values except for the position of Cu(3,2,3-tet) whose value of $-\Delta H°$ is larger than that of Cu (2,2,2-tet)[21]. The EPR parameters obtained for Cu(222-tet) are in line with the values obtained for [Cu(222-tet)(SCN)](NCS)[22] in solvents such as MeOH and DMF when due allowance is made for the greater donor strength of water. Now [Cu(222-tet)(SCN)](NCS) is known to have a square pyramidal structure[23] which allows a relatively strain free configuration to be adopted by the amine which, as has been shown by several X-ray structure determinations, normally cannot place the nitrogen atoms in the appropriate positions for square planar coordination without introducing considerable strain[24]. The formation of a pentacoordinate complex in aqueous solution too is borne out by the relatively low values of $A_{\|}$ and the relatively high value of $\Delta S°$[25] compared with complexes having similar values of $g_{\|}$ (Table II). The formation of a square pyramidal complex leads to the liberation of a greater number of water molecules than does the formation of a 4+2 complex. In the case of Cu(3,3,3-tet) the larger value of $g_{\|}$ and the smaller value of $A_{\|}$ taken in conjunction with the relatively small $\Delta S°$[26] value clearly indicate a stronger axial interaction in a 4+2 complex rather than the formation of a 4+1 complex. Similarly the EPR data for the complex of the hexamethylated 222-tet, $Cu(222\text{-tetMe}_6)$, seem to indicate strong axial bonding and relatively weak Cu–N bonds. This is comparable to the behaviour of $CuMe_4en$ relative to Cuen. The $g_{\|}$ and $A_{\|}$ values of the macrocyclic complex $Cu(CTH)^{2+}$ are virtually identical to those of $Cuen_2$ and not very different from those of Cu(232-tet). The structure of the macrocycle does not allow variations in the lengths of the equatorial bonds and an X-ray structure determination has show that these are equal to those of ethylenediamine complexes[27]. Thus, the similarity of the EPR parameters for these two complexes shows that the extent of the axial interaction whith the solvent must also be the same for each in this solvent mixture. Finally we come to the complex $Cu(2,2\text{-tri})_2$ which has six nitrogen donor atoms available. The value of $g_{\|}$ is in the range found for the CuN_4 complexes but the relatively low value of $A_{\|}$ compared with the values found for complexes having similar values of $g_{\|}$ indicates a stronger axial interaction than would be expected from solvent molecules alone. Therefore the assumption that a fifth nitrogen atom is coordinated to the metal ion would appear to be valid and is borne out by the values of $\Delta H°$ and $\Delta S°$ [17].

The Relationship between Thermodynamic and EPR Parameters

As we have shown above the variations in $g_{\|}$ correspond closely to the variations in ΔH° for most of the complexes we have examined. It will be seen from Figure 2 that a plot of $g_{\|}$ against ΔH° gives a moderately good straight line represented by:

$$g_{\|} = 2.319–0.00479(–\Delta H^\circ) \qquad (1)$$

That there should be a linear relationship is not too surprising since the major factor causing both quantities to vary with the amine nitrogen atoms in the first coordination sphere of the copper(II) ion is the covalent interaction between the metal ion and nitrogen. Thus for a square planar species with a $^2B_{1g}$ state the value of $g_{\|}$ is given approximately by: [28]

$$g_{\|} = 2.0023–8\varrho\,(\alpha\beta_1–f(\beta_1)) \qquad (2)$$

where $\varrho = \lambda\alpha\beta_1/\Delta E_{xy}$, α is the coefficient of the metal b_{1g} orbital in the ground state molecular orbital (σ-bonding), β_1 is the coefficient of the metal b_{2g} orbital in the in-plane π-bonding molecular orbital, λ is the metal spin-orbital coupling constant, ΔE_{xy} is the energy separation between the b_{1g} and b_{2g} orbitals and $f(\beta_1)$ is a function of β_1 and is usually quite small. In the case of saturated aliphatic amines the amount of in-plane π-bonding involving nitrogen is very small and β_1 is approximately equal to 1. Thus variations in the value of $g_{\|}$ for a related series of compounds will largely reflect changes in α and ΔE_{xy}. A decrease in the amount of equatorial bonding and an increase in the amount of axial bonding leads to a decrease in ΔE_{xy} and an increase in the value of α leading to an overall increase in the value of $g_{\|}$. In the case of our data the deviations from the linear relationship (1) are greatest for complexes having ligands in which there is considerable steric hindrance about the nitrogen donor atoms. For these ligands the process of desolvation is greater and the extent of interaction with the molecules of solvent is less. Thus in order for these complexes to obey the linear relationship they would need to have larger values of $–\Delta H^\circ$. It is significant that Cu(2,2-tri)$_2$ is among the complexes which deviate most from the linear relationship.

An attempt to find a similar linear relationship between $A_{\|}$ and ΔH° was not quite so successful. However a fairly good straight line is obtained for the tetraamine series represented approximately by:

$$A_{\|} = 160.0 + 1.3(–\Delta H^\circ) \qquad (3)$$

where $A_{\|}$ is in units of 10^{-4} cm^{-1}. The complexes containing a single molecule of en or one of its methyl substituted derivatives also have values falling on this line although perhaps surprisingly the complexes containing two molecules of en or one of its derivatives fall on a line of similar slope but displaced to higher values

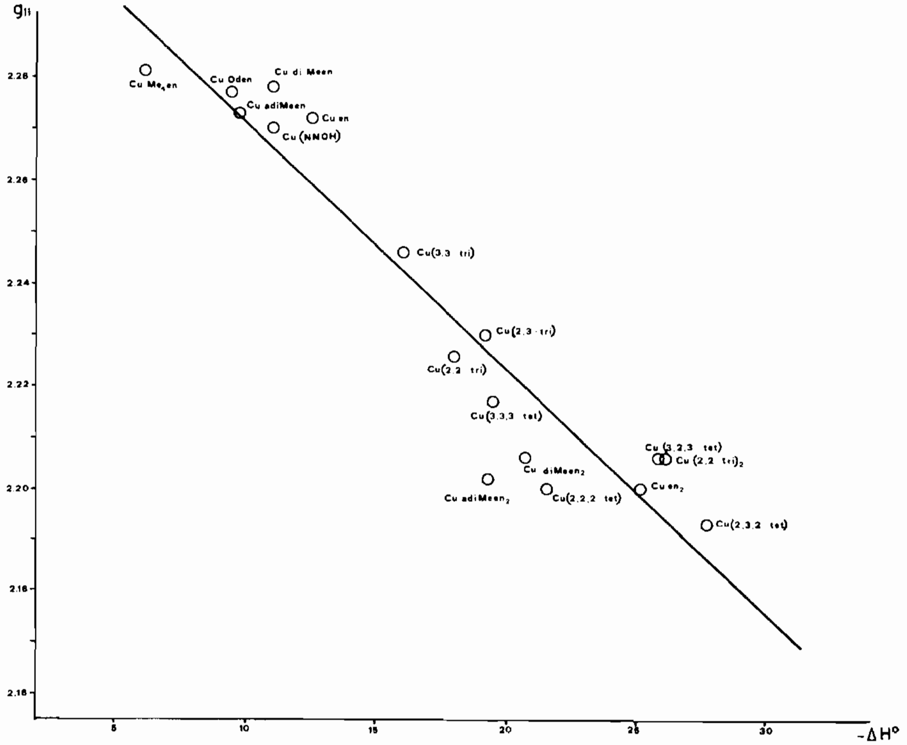

Figure 2. Relationship between $g_{\|}$ and $–\Delta H^\circ$ for Cu(II) polyamine complexes.

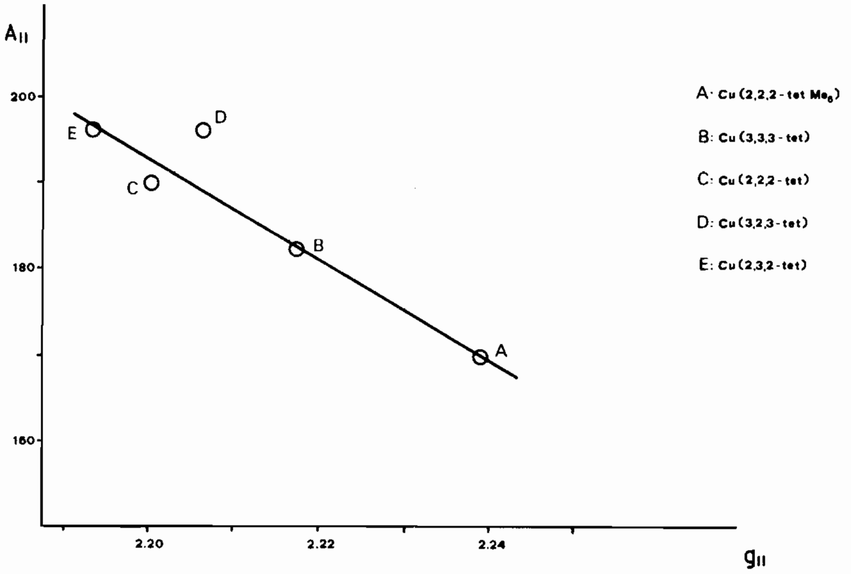

Figure 3. Relationship between $g_{\parallel}$ and $A_{\parallel}$ for Cu(II) tetraamine complexes.

of $A_{\parallel}$. An approximate expression for $A_{\parallel}$ is given by:[28]

$$A_{\parallel} = P(\alpha^2(-4/7-K_o) + (g_{\parallel}-2.0023) + 3/7(g_{\perp}-2.0023) + f_2) \quad (4)$$

where f_2 is usually a very small term. Thus $A_{\parallel}$ also depends on the values of α and ΔE_{xy} although its dependence on α is the more important since α^2 $(-4/7-K_o)$ is the largest term in the expression. However the variation of K_o, the contact term, with the population of the 4*s* orbital is not explicitly included in this equation. That the variations of $g_{\parallel}$ and $A_{\parallel}$ for the tetraamine series have a common origin is shown by the good straight line obtained for a plot of these quantities one against the other (Figure 3).

Acknowledgement

The authors thank Professor P. Paoletti for helpful discussion and criticism and Dr. C. Mealli for assistance in obtaining the graph plots of the simulated spectra.

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