

## The Effect of N-Alkylation on the Properties of Five-coordinate Copper(II) Complexes of Tetra-amine Ligands

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*Two series of five-coordinate copper(II) complexes have been investigated both in solution and in the solid state using EPR and electronic spectroscopy. The first series consists of the square pyramidal complexes of general formula [CutrienR<sub>6</sub>X]X (where trien is 1,4,7,10-tetraazadecane, R = H, CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub> and X = Cl, Br or I), while the other series consists of the trigonal bipyramidal complexes of general formula [CuR<sub>6</sub>trenX]X where tren is tris(2-aminoethane)amine.*

*The sensitivity of the geometry of the CuN<sub>4</sub>X<sup>+</sup> chromophores to N-substitution and the influence of the substituent groups on the spectroscopic parameters are evaluated. It appears that both N-alkylation and the nature of the halogen affect the bonding in both series of complexes. The geometry is only affected in the trien series of complexes.*

### Introduction

Whilst the Cu(II) ion in octahedral and tetrahedral environments has frequently been the object of EPR investigations, there have been relatively few studies of five-coordinate copper(II) species either in solution or in the solid state.

The present work reports EPR spectra and parameters for two series of such compounds of general formula CuLX<sub>2</sub>. In the first series the organic ligand L is either the tetra-amine trien, 1,4,7,10-tetraazadecane, trienMe<sub>6</sub> or trienEt<sub>6</sub>, whilst in the second series L is either the isomeric tetra-amine tren, tris(2-aminoethane)amine, or its hexamethyl or hexaethyl N-substituted derivatives Me<sub>6</sub>tren or Et<sub>6</sub>tren. In both series X is Cl, Br, or I. The ligand trien and its derivatives normally bind to Cu(II) at the corners of a square plane [1] whereas tren and its derivatives usually bind to Cu(II) at the corners of a trigonal pyramid [2].

It has been shown that an analogous trien complex [Cutrien(SCN)]NCS, contains the square pyramidal

cation [Cutrien(SCN)]<sup>+</sup> in the solid state [3] and that this cationic species also persists in methanolic solution [1, 4]. Similarly a crystal determination has shown that CuMe<sub>6</sub>trenBr<sub>2</sub> contains the trigonal bipyramidal cation [CuMe<sub>6</sub>trenBr]<sup>+</sup> in the solid state [5]. Solution studies of this complex and of some of its analogues have established that the solutions also contain five-coordinate trigonal bipyramidal species [6]. It is of considerable interest to see just how sensitive the geometry and electronic structure of CuN<sub>4</sub>X chromophore are to N-substitution.

### Experimental

#### Materials

The amine 1,4,7,10-tetra-azadecane (trien) was obtained commercially. The N,N,N',N'',N''',N''''-hexamethyl-1,4,7,10-tetraazadecane (trienMe<sub>6</sub>) was prepared by methylation of trien with a mixture of formic acid and formaldehyde [7]. Tris(2-aminoethane)amine and tris(2-dimethylaminoethane)amine were prepared by literature methods [6]. Tris(2-diethylaminoethane)amine was prepared by the method described previously [8]. N,N,N',N'',N''',N''''-hexaethyl-1,4,7,10-tetra-azadecane (trienEt<sub>6</sub>) was prepared by an analogous method to that reported for the isomeric amine Et<sub>6</sub>tren, by mixing, N,N'-diethylethylenediamine and N,N-diethyl chloroethylamine in an anhydrous solvent.

The solid compounds CutrienX<sub>2</sub> and CutrienMe<sub>6</sub>X<sub>2</sub> were prepared by literature methods [7, 9]. Although it did not prove possible to prepare the solid anhydrous compounds CutrienEt<sub>6</sub>X<sub>2</sub> we prepared solutions of the complexes by mixing a copper(II) salt with an equimolar amount of amine. Thus the chloride was prepared by dissolving copper(II) chloride in an equimolar amount of the amine. To prepare solutions containing the CutrienEt<sub>6</sub>Br<sup>+</sup> and CutrienEt<sub>6</sub>I<sup>+</sup> species we first added an equimolar amount of amine to a solution of CuSO<sub>4</sub> and then

TABLE I. Conductance and Spectral Data of the Trien and Tren Complexes.

Complex	Solid <sup>a</sup> (kK)	MeOH Solution <sup>b</sup> (kK)	Molar Conductance <sup>c</sup> (ohm <sup>-1</sup> cm <sup>2</sup> )
CutrienCl <sub>2</sub>	15.8	16.4 (140)	90
CutrienBr <sub>2</sub>	16.2	16.3 (200)	90
CutrienI <sub>2</sub>	16.3	16.0 (220)	102
CutrienMe <sub>6</sub> Cl <sub>2</sub>	sh., 14.7	14.5 (185)	75
CutrienMe <sub>6</sub> Br <sub>2</sub>	sh., 14.3	13.9 (284)	66
CutrienMe <sub>6</sub> I <sub>2</sub>	sh., 14.2	13.9 (306)	73
CutrienEt <sub>6</sub> Cl <sub>6</sub>	d	15.4 (233), 17.9 (200)	72
CutrienEt <sub>6</sub> Br <sub>2</sub>	d	15.2 (287), 16.7 (270)	77
CutrienEt <sub>6</sub> I <sub>2</sub>	d	16.1 (290)	78
CutrenCl <sub>2</sub>	d	11.3 (124), 13.6 sh.	91
CutrenBr <sub>2</sub>	14.2	11.2 (124), 13.8 sh.	96
CutrenI <sub>2</sub>	11.3 sh., 15.0	11.1 sh., 14.5 (191)	102
CuMe <sub>6</sub> trenCl <sub>2</sub>	10.8, 13.8	10.7 (416), 13.5 (163)	88
CuMe <sub>6</sub> trenBr <sub>2</sub>	10.0, 12.8	10.4 (430), 13.4 (186)	90
CuMe <sub>6</sub> trenI <sub>2</sub>	9.8, 13.1	9.8 (500), 13.0 (438)	103
CuEt <sub>6</sub> trenCl <sub>2</sub>	10.5, 13.4	10.4 (620), 13.3 (315)	70
CuEt <sub>6</sub> trenBr <sub>2</sub>	10.0, 13.0	10.1 (500), 12.9 (325)	72
CuEt <sub>6</sub> trenI <sub>2</sub>	10.0, 13.2	10.4 (390), 13.2 (243)	92

<sup>a</sup>sh = shoulder. <sup>b</sup>The values in parentheses are the molar extinction coefficients in l mol<sup>-1</sup> cm<sup>-1</sup>. <sup>c</sup>Reference values in MeOH are Et<sub>4</sub>Ni 103, <sup>n</sup>Bu<sub>4</sub>NBr 88, NaCl 95 for 1:1 electrolytes and BaCl<sub>2</sub> 126 ohm<sup>-1</sup> cm<sup>2</sup> for 1:2 electrolytes. <sup>d</sup>Not obtained in the anhydrous form (for CutrenCl<sub>2</sub> see also ref. 9).

added a hot solution of BaBr<sub>2</sub> or BaI<sub>2</sub>. The BaSO<sub>4</sub> which precipitated was filtered off after allowing the solution to cool. The filtrate was then used for the spectral measurements. The same spectra were obtained by dissolving in methanol the solid solvated compounds, CutrienEt<sub>6</sub>X<sub>2</sub>·nCH<sub>3</sub>OH, isolated from a methanolic solution by adding anhydrous ether. The compounds CutrenX<sub>2</sub> and CuMe<sub>6</sub>trenX<sub>2</sub> were prepared by literature methods [6, 9]. Solid CuEt<sub>6</sub>trenCl<sub>2</sub> was prepared by adding an alcoholic solution of CuCl<sub>2</sub> (1.3 mmol) to a methanolic solution of amine (1.5 mmol). After the solution had been concentrated, a small amount of isopropanol was added and the solution was then cooled. The product was recrystallised from ethanol. The compounds CuEt<sub>6</sub>trenBr<sub>2</sub> and CuEt<sub>6</sub>trenI<sub>2</sub> were obtained from an alcoholic solution of CuEt<sub>6</sub>trenCl<sub>2</sub> by adding a hot solution of either KBr or KI. The complex crystallised on cooling and was recrystallised from ethanol.

All the compounds and the amines synthesized gave satisfactory C, H, N, analyses.

#### Electronic Spectra

Absorption spectra were recorded at room temperature with a Beckmann DK-2A spectrophotometer using 1 cm silica cells. Reflectance spectra were obtained by a method analogous to that reported by Venanzi *et al.* [10].

#### Conductivities

Molar conductivities were measured at 25 °C with a WTW model LBR/B conductance bridge.

#### EPR Spectra

First derivative EPR X-band spectra were recorded at room temperature and at -140 °C using a Varian E-9 spectrometer and were calibrated using diphenylpicrylhydrazyl (DPPH) as a g-marker. Simulated spectra for a Lorentzian lineshape were obtained using our variant of Venable's program [11] and in all cases it was possible to fit the experimental spectra closely. The EPR parameters given in Table II, III are the best-fit parameters for the final simulation.

#### Calculation of K Values

The free-ion value of K, the Fermi contact term, is 0.43 cm<sup>-1</sup> but experimentally determined values in complexes are usually lower [1]. For the square pyramidal species we obtained empirical values of K using the equation:

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

For the trigonal pyramidal tren complexes we used the expressions for A<sub>||</sub> and A<sub>⊥</sub> recently derived [12], which include terms involving the halogen spin-orbit coupling constant. Values of K were obtained separately from each equation. In view of the approximations which had to be made the agreement between the pairs of values was very good for the chlorides and bromides. In the case of the iodides the agreement was not quite so good but the mean values lie in the right range. In all cases we found that the equations could only be fitted to the experimental values if A<sub>||</sub> was taken as positive and A<sub>⊥</sub> as negative. This is contrary to the conclusions previously made

TABLE II. Trien Complexes. EPR Spectral Data.

Compound	$g_{\perp}$	$g_{\parallel}$	$g_{iso}$	$A_{\perp}(G)$	$A_{\parallel}(G)$	$A_{iso}(G)$	$\times 10^{-4}$ $A_{\perp}(cm^{-1})$	$\times 10^{-4}$ $A_{\parallel}(cm^{-1})$	$\times 10^{-4}$ $A_{iso}(cm^{-1})$	$K (cm^{-1})$
CutrienCl <sub>2</sub>	2.085	2.185	2.100	45	175	67	44	178	66	0.257
CutrienBr <sub>2</sub>	2.084	2.181	2.103	40	170	75	39	173	74	0.280
CutrienI <sub>2</sub>	2.081	2.186	2.103	35	140	75	34	143	74	0.278
CutrienMe <sub>2</sub> Cl <sub>2</sub>	2.079	2.223	2.103	15	167	72	15	173	68	0.265
CutrienMe <sub>6</sub> Br <sub>2</sub>	2.069	2.233	2.078	30	158	90	29	165	87	0.299
CutrienMe <sub>6</sub> I <sub>2</sub>	2.090	2.233	2.117	15	158	65	15	165	87	0.338
CutrienEt <sub>6</sub> Cl <sub>2</sub> <sup>a</sup>	2.060	2.224	(2.09) <sup>c</sup>	15	148	(86)	14	154	(84) <sup>c</sup>	(0.303) <sup>c</sup>
CutrienEt <sub>6</sub> Cl <sub>2</sub> <sup>b</sup>	2.060	2.168	(2.09) <sup>c</sup>	15	197	(86)	14	199	(84) <sup>c</sup>	(0.303) <sup>c</sup>
CutrienEt <sub>6</sub> Br <sub>2</sub> <sup>a</sup>	2.052	2.220	2.116	15	158	81	14	164	80	0.319
CutrienEt <sub>6</sub> Br <sub>2</sub> <sup>b</sup>	2.058	2.161	2.089	15	212	89	14	214	87	0.310
CutrienEt <sub>6</sub> I <sub>2</sub>	2.050	2.224	2.096	15	171	90	14	176	88	0.319

<sup>a</sup>Square pyramidal species.<sup>b</sup>Square planar species.<sup>c</sup>Average value (see text).

about their relative signs from a consideration of the equation:

$$A_{iso} = 1/3(A_{\perp} + 2A_{\parallel}) [13].$$

## Results and Discussion

### Complexes of the Trien Series of Ligands

The conductivity data for methanolic solutions of these compounds show that, in this solvent at least, they all behave as 1:1 electrolytes and should therefore be formulated [CutrienX]X or [CutrienR<sub>6</sub>X]X (Table I). The electronic spectra of the solid compounds and of the solutions are very similar and in the d-d region consist of a single band whose maximum shows a small shift to lower wave numbers in conformity with the position of X in the spectrochemical series. These data are compatible with a square pyramidal structure for the cationic species [1].

The EPR data obtained for all the complexes in MeOH solution are typical for compounds with a  $d_{x^2-y^2}$  (or possibly a  $d_{xy}$ ) ground state (Table II). It will be noted from the data in Table that there is a steady increase in  $g_{\parallel}$  and decrease in  $A_{\parallel}$  with N-alkylation.

The [CutrienX]<sup>+</sup> species have slightly lower values of  $g_{\parallel}$  and higher values of  $g_{\perp}$  than does the [Cutrien(SCN)]<sup>+</sup> complex. This suggests that the [CutrienX]<sup>+</sup> species have strictly square pyramidal structures. However the observation that the values of  $A_{\parallel}$  decrease as X becomes more polarisable suggests that the Cu-X bonds are essentially covalent and that this is reflected in an increasing population of the Cu 4s-orbital. Any increase in the 4s electronic population will lead to a decrease in the hyperfine contact term since the 4s contribution is positive and therefore of opposite sign to the main contribution arising from spin polarisation of inner s-orbitals (core polarisation) which is negative. Since the hyperfine terms are mainly determined by the contact term this will lead to a decrease in the  $A_{\parallel}$  values. As far as the [Cutrien-Me<sub>6</sub>X]<sup>+</sup> species are concerned, it is worth noting that  $g_{\parallel}$  and  $A_{\parallel}$  for the chloride are not very different from the values found for the square pyramidal species [CutrienMe<sub>6</sub>NCS]<sup>+</sup>. Also in this series the value of  $A_{\perp}$  decreases as X becomes more polarisable.

N-alkylation of trien might be expected to have two effects on the electronic spectra. Firstly steric hindrance between alkyl groups could lead to a change in geometry with a consequent change in position of the d-levels. The steric hindrance could be relieved by a movement of the Cu(II) back into the equatorial plane and this would probably be accompanied by a slight increase in the axial bond length. The crystal field model then predicts a decrease in the energy of all d-d transitions. In fact the maxima in

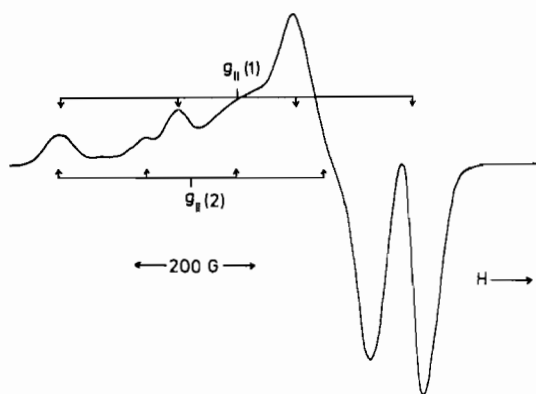


Figure 1. EPR Spectrum of CutrienEt<sub>6</sub>Cl<sub>2</sub> in methanol at -140 °C.

the spectra of the [CutrienMe<sub>6</sub>X]X complexes show a shift of *ca.* 2000 cm<sup>-1</sup> to lower energies compared to the trien complexes. The second effect expected to follow from N-alkylation is an increase in the polarisability of the N donor atom leading to larger values of  $\epsilon$  because of increased covalency in the Cu-N bonds. Such an increase in the  $\epsilon$  values is in fact observed. The situation with regard to the trienEt<sub>6</sub> complexes is somewhat more complicated. The electronic spectra of the chloride and bromide consist of a band with a shoulder on the high energy side. The EPR spectrum at -140 °C shows the presence of two distinct species in roughly equal amounts (Fig. 1) of which the parameters are reported in Table II.

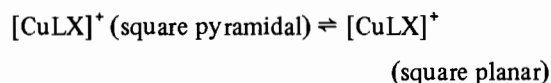
One of the species (labelled 2) is probably square pyramidal like the corresponding trien and trienMe<sub>6</sub> complexes. In fact the EPR parameters are consistent with those found for these complexes. For the second species the  $g_{||}$  values are lower while the  $A_{||}$  values are higher, indicating a stronger equatorial interaction. In view of this result we believe that the maximum in the electronic spectrum of this second species whose presence is revealed in frozen solution has to be placed under the shoulder on the high energy side.

For some Cu(II)-N,N'-dialkylethylenediamine complexes it was noted that the bulkier amines inhibit the approach of adjacent molecules and decrease the axial interaction, resulting in stronger in-plane bonding. In these cases the d-d bands of the electronic spectra move to higher energy with increasing bulkiness of the amine [14].

Tentatively we can suppose that the structure of this second species which is most compatible with all the data (conductivity, electronic spectra, EPR spectra) is a square planar chromophore CuN<sub>3</sub>X<sup>+</sup> in which one arm of the amine is free.

The electronic and EPR spectra of the iodide complex indicate the presence of only one species, a species of square pyramidal geometry, in methanolic solution.

The two species present in solutions of the chloride and bromide are presumed in equilibrium:



but the rate of exchange must be very different in the two cases. At room temperature the EPR spectrum of the bromide shows two sets of hyperfine lines, one for each species, so that the interconversion time must be long compared with the EPR time scale, *i.e.* it must be longer than *ca.* 10<sup>-6</sup> seconds. The EPR spectrum of the chloride on the other hand shows only an averaged spectrum at room temperature with a single set of sharp hyperfine lines, therefore the interconversion time must be less than 10<sup>-8</sup> seconds.

The overall picture is thus of fast interconversion for the chloride slower interconversion for the bromide and infinitely slow interconversion for the iodide. Such a trend could be explained by an increasing barrier to the movement of the halide into the equatorial plane with increasing size of the halide.

The square pyramidal trienEt<sub>6</sub> complexes have values of  $g_{||}$  very similar to those of the trienMe<sub>6</sub> series but markedly lower values of  $g_{\perp}$ . Even more noticeable is the fact that the trend in values of  $A_{||}$  for the trienEt<sub>6</sub> series is the opposite to that found for the other two series. This can be explained by supposing that in the case of the trienEt<sub>6</sub> complexes we have particularly weak, essentially electrostatic, Cu-X bonds resulting in very little involvement of the Cu 4s-orbital in the bonding.

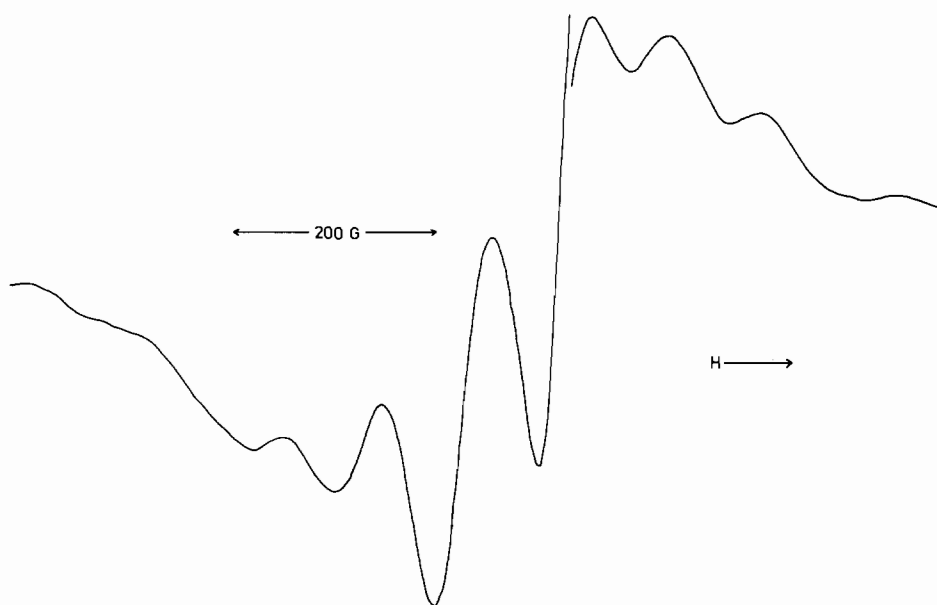
This is borne out by the noticeably higher values of the maxima in the electronic spectra of the trienEt<sub>6</sub> square pyramidal species compared with those found for the trienMe<sub>6</sub> species. In conclusion it does appear that N-alkylation affects both the geometry and the bonding in the trien series of complexes. The differences between the positions of the maxima in the electronic spectra of the trien and trienMe<sub>6</sub> species are sufficient to account for the differences between the  $g_{||}$  values. In the case of the square pyramidal [CutrienEt<sub>6</sub>X]<sup>+</sup> species this is not the case, and the higher  $g_{\perp}$  values relative to those of the [CutrienX]<sup>+</sup> complexes must have another origin.

#### Complexes of the Tren Series of Ligands

The electronic spectra of the solid compounds are consistent with a trigonal bipyramidal structure [6], and are very similar to each other (Table I). They all have bands at *ca.* 10-11 kK and 13-14 kK. In methanolic solution they all behave as 1:1 electrolytes and the absorption and reflectance spectra are essentially identical. The small shifts within each series are those expected from the position of X in the spectrochemical series (in methanol the [CutrienX]<sup>+</sup> complexes also show this behaviour) and thus all may be assumed to involve cations of essentially the same

TABLE III. Tren Complexes. EPR Spectral Data.

Compound	$g_{\perp}$	$g_{\parallel}$	$g_{\text{iso}}$	$A_{\perp}(\text{G})$	$A_{\parallel}(\text{G})$	$A_{\text{iso}}(\text{G})$	$\times 10^{-4}$ $A_{\perp}(\text{cm}^{-1})$	$\times 10^{-4}$ $A_{\parallel}(\text{cm}^{-1})$	$\times 10^{-4}$ $A_{\text{iso}}(\text{cm}^{-1})$	$K(\text{cm}^{-1})$
CutrenCl <sub>2</sub> (H <sub>2</sub> O)	2.209	2.001	2.117	106	69	60	109	64	59	0.335
CutrenBr <sub>2</sub>	2.210	2.00	2.110	111	67	50	115	63	49	0.355
CutrenI <sub>2</sub>	2.204	1.930	2.108	102	93	60	105	84	59	(0.33)
CuMe <sub>6</sub> trenCl <sub>2</sub>	2.181	2.00	2.128	90	?	47 ± 3	92	?	47 ± 3	0.284
CuMe <sub>6</sub> trenBr <sub>2</sub>	2.185	1.937	2.105	95	85	56 ± 5	97	77	55 ± 5	0.282
CuMe <sub>6</sub> trenI <sub>2</sub>	2.191			116			119			
	2.224	1.889	2.110	103	114	50	107	100	50	(0.33)
CuEt <sub>6</sub> trenCl <sub>2</sub>	2.185	2.00	2.122	77	80	79	79	75	78	0.263
CuEt <sub>6</sub> trenBr <sub>2</sub>	2.188	1.940	2.112	83	86	83	85	78	82	0.294
CuEt <sub>6</sub> trenI <sub>2</sub>	2.205	1.930	2.110	98	93	79	101	86	78	(0.34)

Figure 2. EPR Spectrum of CutrenI<sub>2</sub> in methanol at -140 °C.

$C_{3v}$  symmetry. The molar extinction coefficients for the  $R_6$ tren complexes are much higher than those for the tren complexes. Because of the +I effect N-alkylation might be expected to increase the polarisability of the N donor atoms, as we have seen to happen for the  $[\text{Cutrien}R_6X]^+$  complexes, and this is probably the main source of the increased intensity. The more even distribution of intensity between the two transitions found for the iodide complexes may indicate some contributions from the highly polarizable iodine atom (the  $\epsilon$  value for the Cutren iodide is also larger than the value found for the corresponding chloride and bromide). The EPR data are compatible with the presence of the unpaired electron in a  $d_{z^2}$  orbital (the unusual EPR spectrum of the  $\text{CuMe}_6\text{trenI}^+$  cation has already been discussed) [13] and can be interpreted

in terms of an axial Spin Hamiltonian (Table III). The Spin Hamiltonian parameters reveal a number of interesting features. The  $|A|$  values increase with the atomic number of the halogen but do not vary greatly from series to series although the difference between  $A_{\parallel}$  and  $A_{\perp}$  is more marked for the tren complexes. The tren complexes also have somewhat higher  $g$ -values. Finally the most striking fact is that several of the complexes have values of  $g_{\parallel}$  markedly smaller than the free electron  $g$ -factor, which has been explained in terms of the contributions arising from the spin orbit coupling with the halogen [12]. The values of  $K$  for the tren series of complexes fall in the same range as those for the trien series, showing that the 4s contribution is probably similar in both series. However it must be said that we may be over-

estimating this contribution in both series since like other workers we have used the free ion value of  $P(\langle r^{-3} \rangle_{3d})$ . The K values for the tren series do appear to be significantly larger than those for the  $R_6$  tren series. The increase of |A| values within a series from Cl to I is essentially the result of the influence of the halogen spin-orbit coupling constant.

The frozen solution spectra of the tren series of complexes all exhibit one other feature worth comment. The linewidths of individual hyperfine components vary with the value of  $M_I$ . Thus in the perpendicular region the component at lowest field ( $M_I = +3/2$ ) is the broadest line while the component at highest field ( $M_I = -3/2$ ) is the narrowest. (Figure 2). We initially attributed this to residual motion in the frozen glass but samples cooled to 30 K gave identical spectra to those at 133 K and we therefore conclude that the explanation of the phenomenon must be sought elsewhere. In the expression for the intensity, only quadrupolar terms involve  $M_I$  to the first power and it therefore seems that a complete description of the spectrum must include such terms.

To conclude, it is clear that there are important differences between the parameters found for the tren complexes themselves and those found for the N-alkylated tren complexes. The most important difference seems to be the larger crystal field splittings in the tren compounds which also affect the g-values. However covalency effects also appear to be important and are mainly reflected in the intensities of the d-d transitions. The variations in the |A| values found within each series on the other hand appear to originate mainly in the terms which depend on the halogen spin-orbit coupling constant.

## Acknowledgement

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