Magnetic Susceptibility and Electron Spin Resonance of Some Copper(II) Unsaturated Carboxylates

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The magnetic susceptibility of some complexes of the type $Cu(O_2CR)_2$, $Cu(O_2CR)_2L$, and $[Cu(O_2CR)_2L_2]$ (where R is an unsaturated carboxylic acid and L is either pyridine or pyrazine) are reported. The measurements show that the $Cu(O_2CR)_2$ and $Cu(O_2CR)_2L$ complexes are dimeric and that the $[Cu(O_2CR)_2L_2]$ complexes are monomeric. In the case of the dimeric complexes a study of the temperature variation of the magnetic susceptibility and of the intensity of the e.s.r. absorption has been used to determine values of the exchange integral (J). The results indicate that the e.s.r. approach provides a useful alternative for determining the value of J, particularly in dilute solution.

A NUMBER of copper(II) unsaturated aliphatic acid complexes have been shown to have subnormal magnetic moments at room temperature. Molecular weight, spectrophotometric, and conductivity data indicate that these complexes are dimeric.[1] This behaviour is, of course, typical of a very wide range of copper(II) complexes [2-6] of which copper(II) acetate monohydrate is perhaps the best known example.[7] The monopyridine adducts of these complexes are also dimeric which again is a typical consequence of pyridine co-ordination. For example, the co-ordination of pyridine to copper(II) acetate produces no significant change in magnetic character.[8,9]

In a previous publication [10] we examined the low-temperature electron spin resonance (e.s.r.) spectra of a number of these copper(II) unsaturated-acid complexes together with their adducts of the type $Cu(O_2CR)_2L$ (where L is a donor ligand). The e.s.r. spectra were interpreted in terms of dimeric species in which the two copper atoms are exchange coupled. This conclusion is in accord with the room-temperature magnetic susceptibility measurements of Edmundson and Lever.[1]

A study of the variation of the magnetic susceptibility with temperature allows a value for the singlet–triplet separation, J, to be determined. Values of J have indeed been determined in this way for a wide range of dimeric copper(II) complexes.[9,11,12] However there is also a possibility of determining J from the temperature variation of the intensity of the e.s.r. absorption. There appears to have been little previous attempt to compare, in a systematic manner, values of J determined by these two alternative approaches. In some respects the e.s.r. approach appears to offer advantages. First, the intensity of the e.s.r. absorptions are such that measurements can be quite readily made using dilute solutions. Gouy magnetic susceptibility measurements, however, are best made on a polycrystalline sample and therefore require a reasonable quantity of the complex. Additionally, magnetic impurities in the sample, which often interfere with magnetic susceptibility measurements, would not normally interfere in the e.s.r. spectrum. One disadvantage of the e.s.r. method, however, is the limited accuracy to which the area beneath the e.s.r. absorption can be determined. It was hoped that by determining values of J by these two different techniques it might be possible to establish the usefulness of the e.s.r. method.

RESULTS AND DISCUSSION

The variation of the magnetic susceptibility with temperature for a dimeric copper complex (interpreted in terms of a singlet–triplet equilibrium) is given by expression (1) [13] where χ_{Cu} is the average magnetic

$$\chi_{Cu} = \frac{\bar{g}^2 L \mu_B^2}{kT}[3 + \exp(-J/kT)]^{-1} + N\alpha \qquad (1)$$

susceptibility per copper atom. The usual method of determining J from this equation is to find the best fit to the magnetic susceptibility data over a temperature range by varying $\bar{g}$, J, and $N\alpha$. $N\alpha$ represents the temperature-independent paramagnetism and is usually considered to be close to 60×10^{-6} c.g.s. units for octahedral copper(II) complexes. In addition the values of $\bar{g}$ for the complexes under investigation have been previously determined independently from their e.s.r. spectra.[10] Consequently the experimental data can be used to find the best fit to equation (1) by varying J only. The presence of a paramagnetic impurity in the samples can be allowed for by incorporating the term $0.43/T + N\alpha$ into equation (1) to give the experimentally determined χ_{Cu} [equation (2)] where x is the mol fraction of the

$$\chi_{Cu} = \frac{0.43x}{T} + \frac{(1-x)\bar{g}^2 L \mu_B^2}{kT}[3 + \exp(-J/kT)]^{-1} + N\alpha \qquad (2)$$

impurity. In order to obtain values of J from this equation we have employed the graphical method described by Herring *et al.*[11] In this method a function, F, is introduced [equation (3)] and equation (2) can be rearranged to give (4). Hence a plot of $\ln(F - 3)$ *vs.*

$$F = 3 + \exp(-J/kT) \qquad (3)$$

$$F = \frac{\bar{g}^2 L \mu_B^2}{kT}(1 - x)(\chi_{Cu} - 0.43\,x/T - N\alpha)^{-1} \qquad (4)$$

$1/T$ should be linear with a slope of $|J|/k$. A least-squares procedure can therefore be employed treating x and J as variables and using the e.s.r. $\bar{g}$ values.

In addition to the above approach values of J have also been determined from the e.s.r. spectra of the complexes using expression (5) where A is the relative

$$A \propto 1/T[3 + \exp(-J/kT)] \qquad (5)$$

intensity of the e.s.r. absorption, and again employing a least-squares fit procedure.

TABLE 1

Magnetic susceptibilities ($10^6\chi_{Cu}$) in c.g.s. units

T/K	$Cu(va)_2$	$Cu(va)_2(py)$	$Cu(va)_2(pz)$	$[Cu(va)_2(py)_2]$	$Cu(ac)_2$	$Cu(ac)_2(py)$	$[Cu(ac)_2(py)_2]$	$Cu(aa)_2$	$Cu(aa)_2(py)$
113	515	525	224	3 469	434	496	3 308	251	214
123	535	535	271	3 340	468	532	3 058	318	282
133	564	562	318	3 163	514	567	2 811	367	337
143	597	590	381	2 883	570	605	2 666	430	388
153	645	616	434	2 733	626	635	2 474	478	432
163	699	646	500	2 480	669	665	2 288	522	490
173	729	685	553	2 366	708	700	2 147	590	527
183	768	702	578	2 260	791	746	1 871	614	575
193	810	729	638	2 154	802	771	1 922	647	602
203	821	744	666	2 032	812	784	1 824	699	643
213	862	758	716	1 911	827	808	1 751	713	670
223	880	772	744	1 848	848	825	1 675	728	690
233	882	783	750	1 739	860	833	1 621	728	711
243	892	794	775	1 673	871	849	1 552	747	738
253	897	804	810	1 625	870	855	1 515	752	741
263	900	798	819	1 585	871	858	1 414	760	751
273	897	809	832	1 519	871	860	1 355	779	768
283	900	809	850	1 456	868	860	1 308	786	772
293		812	857	1 390		868	1 261		772
303		809	869			849	1 232		775
313		809	866			846	1 225		775

py = Pyridine, pz = pyrazine.

The magnetic susceptibilities of the copper(II) complexes investigated in this study are given in Table 1. Two complexes, bis(acrylato)bis(pyridine)copper(II) and bis(pyridine)bis(vinylacetato)copper(II), have normal magnetic moments and our results indicate that these two complexes are monomeric. However the results for the remaining complexes indicate that they are dimeric. The previously reported e.s.r. spectra of these dimeric complexes indicate that a paramagnetic impurity is present to a different extent in each complex. The presence of this impurity has been taken into account as per equation (4) and the values of x required to give the best fit to the ln ($F - 3$) *vs.* $1/T$ plots are summarised in Table 2. Each plot (using the values of x reported) gave a good straight line passing through, or very close to, the origin. Two plots requiring rather different values of x have been selected for illustration in the Figure. As a check on possible errors in the method, plots were also obtained using the magnetic susceptibility data for bis(pyridine)tetrakis(vinylacetato)dicopper(II) but varying the value of $\bar{g}$ from 2.16 to 2.26. Again good linear plots were obtained. The different values of $\bar{g}$ had a slight effect on the intercept but made no measurable difference to the slope and hence to the value of J. Varying the value of $N\alpha$ had a similar effect. Consequently the method cannot be used as a check on e.s.r. $\bar{g}$ values as an error in $\bar{g}$ could be counterbalanced by an opposite error in $N\alpha$.

TABLE 2

Values of J obtained from magnetic susceptibility [equation (2)] and e.s.r. [equation (5)] measurements

	E.s.r.		Magnetic susceptibility	
Complex	Powder $-J$/cm^{-1}	Frozen solution $-J$/cm^{-1}	$-J$/cm^{-1}	x (mol %)
$Cu(a)_2 \cdot H_2O$ [a]	279	269	275—305 [b]	
$Cu(va)_2$	296	327	346	6
$Cu(va)_2(py)$	322	348	362	8
$Cu(va)_2(pz)$	342	358	370	0
$Cu(ac)_2$	259	333	308	1
$Cu(ac)_2(py)$	310	345	335	4
$Cu(aa)_2$	268	335	351	0
$Cu(aa)_2(py)$	363	344	362	0

[a] a = Acetate. [b] Taken from refs. 2 and 9.

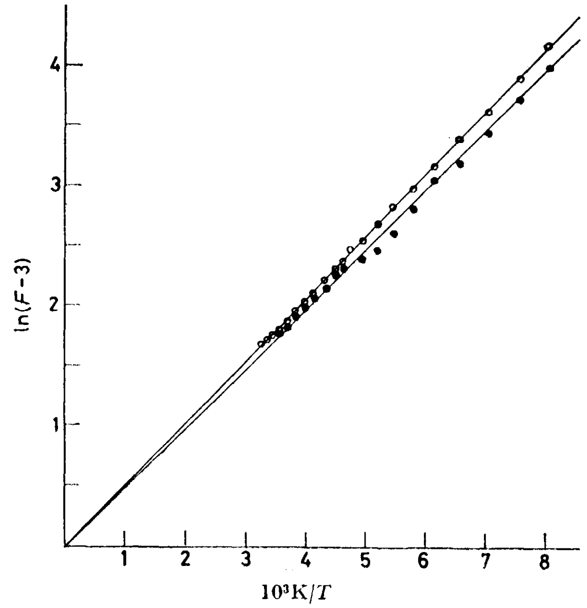
The e.s.r. data for the dimeric complexes is summarised in Table 3. Here it has been possible to make measurements on both a dilute solution and on a polycrystalline sample of each complex. All the e.s.r. absorption areas have been normalised to 100 units at 113 K. The temperature range available for the study of the frozen-solution spectra is fairly narrow, typically 113 to 153 K. The temperature range used for the polycrystalline samples was typically 113 to 173 or 193 K. As a check on the validity of the e.s.r. approach values of J were determined for copper(II) acetate monohydrate employing exactly the same procedure. The values obtained for the area beneath the e.s.r. absorption are included in Table 3 and the values of J in Table 2. In the case of the polycrystalline sample of copper(II) acetate, values of J were determined using area measurements made on the high- and the low-field absorption. The values agreed to within 5 cm^{-1} and lay within the typical range of values determined from magnetic susceptibility measurements. In general the J values obtained by the e.s.r. method are rather lower than those obtained from magnetic susceptibilities. The agreement between the two techniques is, in fact, rather better for the measurements made on frozen solutions than for those made on polycrystalline samples. This may reflect the fact that the e.s.r. absorptions in the frozen-solution spectra are narrower and, consequently, the areas more accurately determined. We believe that these results establish the usefulness of the e.s.r. method particularly for measurements on dilute solutions.

It has been established that the addition of pyridine to a range of dimeric copper carboxylates yields a dimeric complex with an increased *J* value.[9,12] Examination of the results summarised in Table 3 for the copper(II) unsaturated acid complexes studied appears to support this conclusion. An increase in *J* can be seen for the frozen-solution and polycrystalline e.s.r. measurements and for the magnetic susceptibility measurements.

TABLE 3

E.s.r. absorption areas (normalised to 100 units at 113 K)

		T/K							
		113	123	133	143	153	163	173	193
$Cu(a)_2 \cdot H_2O$	Polycrystalline	100	123	139	154	167	177	191	
	Frozen solution	100	121	132	139	162			
$Cu(va)_2$	Polycrystalline	100		148		188		208	
	Frozen solution	100	133	163	197	210	228		
$Cu(va)_2(py)$	Polycrystalline	100		165		223		264	289
	Frozen solution	100	142	169	206	233	259		
$Cu(va)_2(pz)$	Polycrystalline	100	136	165	192	227	242		
	Frozen solution	100	132	165	195				
$Cu(ac)_2$	Polycrystalline	100	120	135	147	154	164		
	Frozen solution	100	119	153	183	198	225		
$Cu(ac)_2(py)$	Polycrystalline	100		149		195		222	
	Frozen solution	100	139	169	208	231	253		
$Cu(aa)_2$	Polycrystalline	100		126		149		173	
	Frozen solution	100	144	160	209	231	246		
$Cu(aa)_2(py)$	Polycrystalline	100		157		241		284	341
	Frozen solution	100	143	178	199	221			



Plots of ln $(F - 3)$ against $1/T$ for tetrakis(allylacetato)bis(pyridine)dicopper(II) (●) (no paramagnetic impurity) and for tetrakis(vinylacetato)bis(pyridine)dicopper(II) (○) (8% paramagnetic impurity)

The addition of an extra donor (*i.e.* pyridine or pyrazine) molecule adds a further conjugated system to the complex. This would be expected to reduce the positive charge on the copper atom thus enhancing the exchange interaction.

The addition of two donor ligands per copper atom forms complexes of the type $[Cu(O_2CR)_2L_2]$ with normal magnetic susceptibilities (see Table 1). The addition of a second pyridine ligand appears therefore to destroy the dimeric nature of the complex to give a normal six-co-ordinate monomeric complex. These monomeric complexes, however, appear to be relatively unstable and lose pyridine on standing, reverting to the dimeric $Cu(O_2CR)_2L$. These changes were detected by a study of the e.s.r. spectrum of the copper(II) complex with vinylacetic acid and pyridine. A chloroform solution of bis(pyridine)tetrakis(vinylacetato)dicopper(II) give the e.s.r. spectrum previously reported.[10] The gradual addition of pyridine to this solution results in the decrease in the intensity of the dimer spectrum and a simultaneous increase in the intensity of the monomer spectrum (at *g ca.* 2). The e.s.r. spectrum corresponding to the dimeric complex $Cu(O_2CR)_2L$ completely disappears when the Cu : L ratio reaches 1 : 2, but slowly reappears when the resulting solution is allowed to stand for several hours indicating the presence of the equilibrium (6).

$$2[Cu(O_2CR)_2L_2] \rightleftharpoons [Cu_2(O_2CR)_4L_2] + 2L \quad (6)$$

EXPERIMENTAL

Preparations.—The copper complexes reported in this study were all prepared as previously described.[10] The C, H, and N analyses of the complexes were performed by the Microanalytical Laboratory, Manchester and agreed well with those calculated for the appropriate complex. Chloroform was washed with water and distilled off P_2O_5 before use.

E.S.R. Measurements.—E.s.r. spectra were recorded from 113 to 193 K on a Varian E3 Spectrometer employing a Varian E4557 variable-temperature unit. Spectra of a polycrystalline sample and of a chloroform solution of each copper complex were recorded. The derivative spectra were integrated using an I.C.L. 1905F computer to give the absorption spectra. Areas beneath the absorption curve were obtained to an accuracy of *ca.* 5% for the frozen solutions and *ca.* 10% for the polycrystalline samples [except for $Cu(va)_2$, $Cu(ac)_2$, and $Cu(aa)_2$ where the accurate drawing of a sloping baseline created an additional problem] (va = vinylacetate, ac = acrylate, aa = allylacetate).

Magnetic Measurements.—Magnetic susceptibility measurements were obtained on a Newport Instruments Magnetic (Gouy) Balance with 10.2 cm pole pieces employing a Newport Instruments cryostatic cooling system. Mercury cobalt thiocyanate and nickel chloride solution were used as calibrants.

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