Electron Spin Resonance Study of Some Copper(II) Dithiocarbamates and their Mixed-ligand Complexes

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The e.s.r. spectra of seven copper(II) dithiocarbamates have been recorded in chloroform–ethanol mixtures at room temperature and at 113 K. It has been found that the addition of a range of salts to these dithiocarbamates destroys the complex forming a mixed-ligand complex, $[Cu(S_2CNR_2)X]$, with a new e.s.r. spectrum. When X is Cl or Br the additional interaction of the unpaired electron with a single halogen nucleus is observed. The $[Cu(S_2CNEt_2)Cl]$ complex forms a dipole–dipole coupled dimer and a computer simulation of the $\Delta M_s = 2$ absorption of this dimer has been obtained.

THE e.s.r. spectrum of copper(II) diethyldithiocarbamate in chloroform solution consists of a single, almost isotropic, absorption with a g value close to 2. However Gersmann and Swalen [1] have shown that in the temperature range 80—140 K a well resolved spectrum exhibiting a number of very sharp lines can be obtained in carefully selected mixed solvents. This work has been extended by Pilbrow *et al.*[2] to cover a wider range of mixed solvents. These latter workers noted that in a chloroform–toluene mixture a very broad spectrum was superimposed upon the well resolved, narrow-line, spectrum and was accompanied by a low intensity absorption at g *ca.* 4. The broad absorption at g *ca.* 2, and the accompanying low intensity absorption at g *ca.* 4, were attributed to a dimeric form of the complex with a dipole–dipole interaction between the two copper(II) ions.

In this paper we report the results of our examination of the low-temperature e.s.r. spectra of seven copper(II) dithiocarbamates in ethanol–chloroform. We also report the results of our investigation of the reaction of these complexes with a number of metal salts. These results are of interest in view of the recently reported reactions of copper(II) dithiocarbamates with halogens, and with a variety of salts, to form mixed-ligand complexes.[3-9] We have studied both the room- and low-temperature e.s.r. spectra of the products of these reactions and report the use of the third-derivative format in obtaining useful additional information from the e.s.r. spectrum of one of the reaction products. The computer simulation of the g *ca.* 4 absorption in copper(II) diethyldithiocarbamate before and after reaction with $CuCl_2$ has also been obtained.

RESULTS AND DISCUSSION

The e.s.r. spectra of seven copper(II) dithiocarbamate complexes were recorded in 50% (by volume) chloroform–ethanol over the temperature range 113—303 K. At low temperature, typically 113 K, the spectrum of each of these complexes consists of three distinct features. Two of these features occur in the g *ca.* 2 region of the spectrum where a narrow-line, well resolved absorption is superimposed on a very much broader featureless absorption. This region of the spectrum is shown in Figure 1 where the broad underlying absorption, although only just discernible, accounts for approximately 85% of the total absorption intensity in this region of the spectrum. The other feature in these spectra, the g *ca.* 4 absorption, exhibits hyperfine structure and is shown in Figure 2(*a*). These observations are in precise agreement with those of Pilbrow *et al.*[2] These workers have shown that the broad feature at g *ca.* 2 and the feature at g *ca.* 4 are both associated with a dipole–dipole coupled dimeric form of the complex and have obtained support for this view by the successful computer simulation of these two features for the copper(II) diethyldithiocarbamate complex. The g *ca.* 4 absorption has been assigned to a $\Delta M_S = 2$ transition, a feature often observed in complexes where there is a dipole–dipole interaction between two copper(II) ions.

The remaining feature in the spectrum, the well resolved group of lines apparent in Figure 1, is therefore assigned to that proportion of the complex existing in the monomeric form. The various parameters obtained from the e.s.r. spectra of the monomeric form for each of the seven copper(II) dithiocarbamate complexes studied are summarised in Table 1. The data for each complex have been obtained from spectra recorded at 113 K and, as can be seen in Figure 1, it is possible to obtain separate values for $a_{\parallel}$ for the two copper isotopes

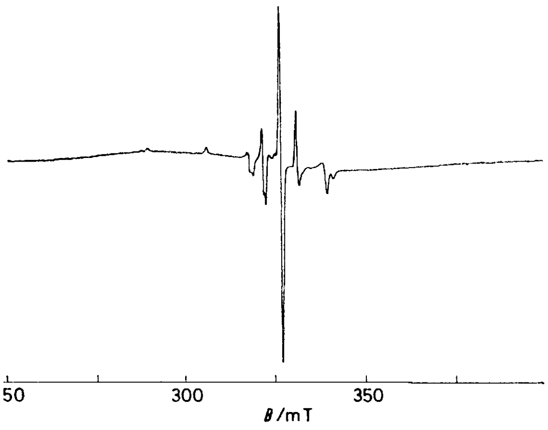

FIGURE 1 E.s.r. spectrum of copper(II) diethyldithiocarbamate (g *ca.* 2 region) in chloroform–ethanol at 113 K

at this temperature. The ratio of the hyperfine splitting constants for the two copper isotopes (1 : 1.05) is in reasonable agreement with that expected from the ratio of their nuclear magnetic moments (1 : 1.077).

It should be noted that we have recorded the e.s.r. spectra of these complexes in a chloroform–ethanol solvent mixture and therefore the complexes will be present in the form of their ethanol adducts. The relative ease of formation of these adducts and their influence on the e.s.r. spectra of copper(II) complexes has been nicely illustrated by Wisniewski and Wayland.[10] For example, the ethanol adduct of copper(II) bis(acetylacetonate), in a chloroform–toluene glass, has higher g values and smaller hyperfine splitting constants than its counterpart in an ethanol-free chloroform–toluene glass. A comparison of the g values and hyperfine splitting constants for the monomeric form of copper(II) diethyldithiocarbamate (see Table 1) with those obtained for the same complex in a chloroform–toluene glass[1] indicates an increase in the g values in the presence of ethanol. However the influence of ethanol adduct formation on the values of $a_{\parallel}$ and $a_{\perp}$ appears to be very slight. These results support the view that ethanol can act as a donor molecule forming bis adducts with planar copper(II) complexes and that the observed differences in g and a values are accountable in terms of the resulting axial perturbations.

TABLE 1

E.s.r. parameters for some copper(II) dithiocarbamate, $[Cu(S_2CNR_2)_2]$, complexes in ethanol–chloroform at 113 K

R_2	$g_{\parallel}$	$g_{\perp}$	$a_{\parallel}$ */mT	$a_{\perp}$/mT
Di-n-propyl	2.113	2.047	16.7, 17.6	4.4
Di-n-butyl	2.112	2.044	16.7, 17.6	4.4
Diallyl	2.100	2.036	16.7, 17.4	4.4
Diethyl	2.112	2.047	16.7, 17.6	4.4
Di-i-propyl	2.108	2.048	16.7, 17.5	4.5
Diphenyl	2.107	2.044	16.7, 17.4	4.4
Ethylphenyl	2.110	2.044	16.7, 17.5	4.4

* Results for the ^{63}Cu and ^{65}Cu isotopes respectively.

Of the two features associated with the dimeric form of these complexes, the $\Delta M_s = 1$ absorption at g *ca.* 2 would appear to reveal little useful information due to its very large linewidth. However the $\Delta M_s = 2$ absorption at g *ca.* 4 exhibits hyperfine structure and we have attempted a computer simulation of this absorption based on the principles described previously.[2] The principal features of this absorption are very similar for each of the copper(II) dithiocarbamates studied, and the computer simulation obtained can be considered to be an equally good fit to each of these. The best fit was obtained by continual variation of each of the six parameters involved and is shown in Figure 2(*b*). It was obtained using the following values: $a_{\parallel} = 17.6$ mT, $a_{\perp} = 2.14$ mT, $g_{\parallel} = 2.14$, $g_{\perp} = 2.04$, $r_{Cu-Cu} = 400$ pm, line width = 2.2 mT. Although this is the best fit we could obtain there are some minor features which are not entirely reproduced. However, further changes in any of the parameters failed to achieve any further improvement. A refinement to the computed simulation, allowing for the possibility of total anisotropy in these complexes, is possible. However this refinement would not appear justified in view of the line widths obtained in the experimental spectra reported here.

The parameters used in obtaining these simulations differ only slightly from those used in the simulation of the $\Delta M_s = 2$ absorption for copper(II) diethyldithiocarbamate in ethanol-free chloroform–toluene mixtures except for the value of $g_{\parallel}$. Our value ($g_{\parallel} = 2.14$) is significantly lower than that required in the absence of ethanol ($g_{\parallel} = 2.25$).[2] Certainly the use of the latter value produces an unsatisfactory simulation for the chloroform–ethanol spectrum. We also find a reduced value of r to be slightly more satisfactory. However the variation of r produced only minor changes in the com-

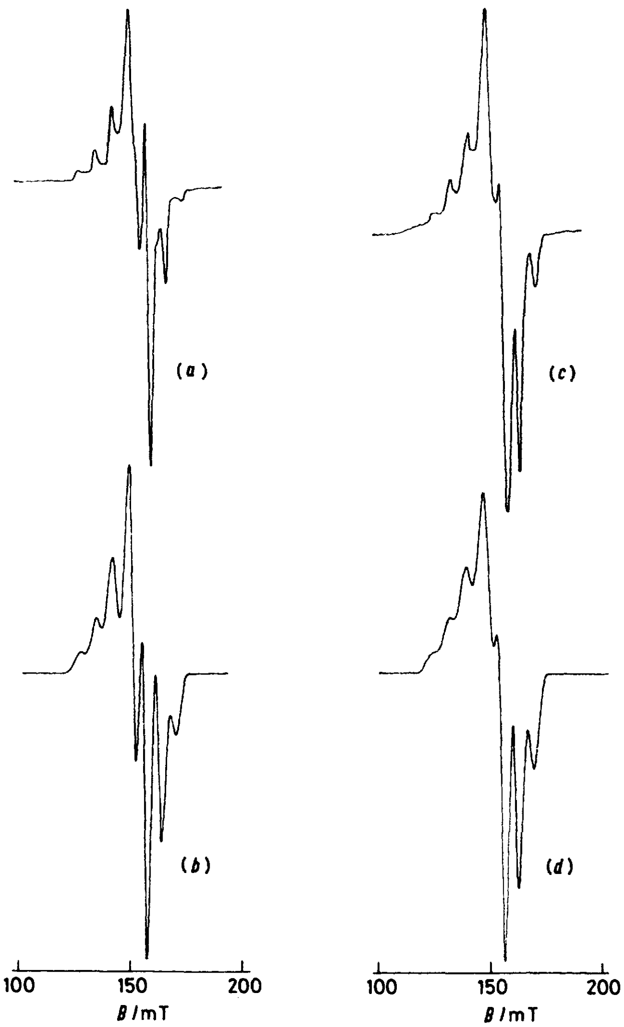

FIGURE 2 (*a*) E.s.r. spectrum of the $\Delta M_s = 2$ absorption of copper(II) di-n-butyldithiocarbamate in chloroform–ethanol at 113 K; (*b*) computer simulation of the spectrum in Figure 2(*a*) using the parameters given in the text; (*c*) e.s.r. spectrum of the $\Delta M_s = 2$ absorption in the $[Cu(S_2CNEt_2)_2]$–$CuCl_2$ mixture (ratio 1 : 1.5) in chloroform–ethanol at 113 K; (*d*) computer simulation of the spectrum in Figure 2 (*c*) using the parameters given in the text puter simulated spectra. This is unfortunate in so much that this approach would otherwise provide an alternative means of obtaining Cu–Cu distances in dimeric complexes of this type.

The addition of $CuCl_2$ (in ethanol–chloroform) to a solution of copper(II) diethyldithiocarbamate produces some dramatic changes. The original deep orange-brown solution of the complex becomes a deep green when the $CuCl_2$: $[Cu(S_2CNEt_2)_2]$ ratio approaches 1 : 1. The changes in the room-temperature e.s.r. spectrum clearly reveal the formation of a new complex with $g = 2.070$ and $a_{Cu} = 7.5$ mT, see Figure 3(*a*) {*cf.* $[Cu(S_2CNEt_2)_2]$ at room temperature $g = 2.046$, $a_{Cu} = 7.7$ mT}. These parameters agree well with the observations of Yordanov and Shopov.[7] These changes are not unique to copper(II) diethyldithiocarbamate. We repeated the experiment with the di-n-butyl, di-n-propyl, and dibenzyl complexes and found similar changes. The addition of other copper(II) salts (*e.g.* $CuBr_2$ and $Cu[NO_3]_2$) also yielded deep green solutions at equimolar concentrations. Again the original $[Cu(S_2CNEt_2)_2]$ spectrum was replaced by a new e.s.r. spectrum upon addition of these salts. The spectrum obtained upon the addition of $CuBr_2$ [see Figure 3(*a*)] clearly indicates interaction of the unpaired electron with a single Br nucleus. In view of this observation we re-examined the spectrum obtained for the $[Cu(S_2CNEt_2)_2]$–$CuCl_2$ mixture [Figure 3(*b*)]. The room-temperature spectrum indicated some additional, but poorly resolved, structure on the $M_I = +\frac{3}{2}$ line, possibly due to interaction of the unpaired electron with a Cl nucleus. At 253 K [see Figure 4(*a*)] this structure is more apparent and would appear to consist of four equally intense lines. However this additional hyperfine structure is not well resolved at this temperature. In order to distinguish between various possibilities we recorded the third-derivative spectrum of the mixture at 253 K [see Figure 4(*b*)]. This third-derivative spectrum provides further information on the nature of the new complex. It clearly reveals that the additional structure on the $M_I = +\frac{3}{2}$ line consists of four equally intense equally spaced lines corresponding to the interaction of the unpaired electron with a single Cl nucleus. (The display of e.s.r. spectra in third-derivative format enhances the intensity of the narrow-line features in the spectrum when compared with the first-derivative format and hence the broader $M_I = -\frac{3}{2}$ and $M_I = -\frac{1}{2}$ lines are almost lost in the third-derivative spectrum.)

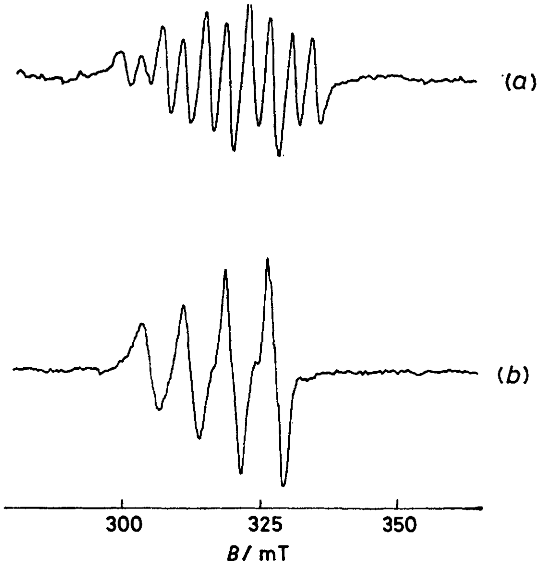

FIGURE 3 E.s.r. spectrum of (*a*) the $[Cu(S_2CNEt_2)_2]$–$CuBr_2$ mixture (ratio 1 : 1.1) and of (*b*) the $[Cu(S_2CNEt_2)_2]$–$CuCl_2$ mixture (ratio 1 : 1.1) in chloroform–ethanol at 293 K

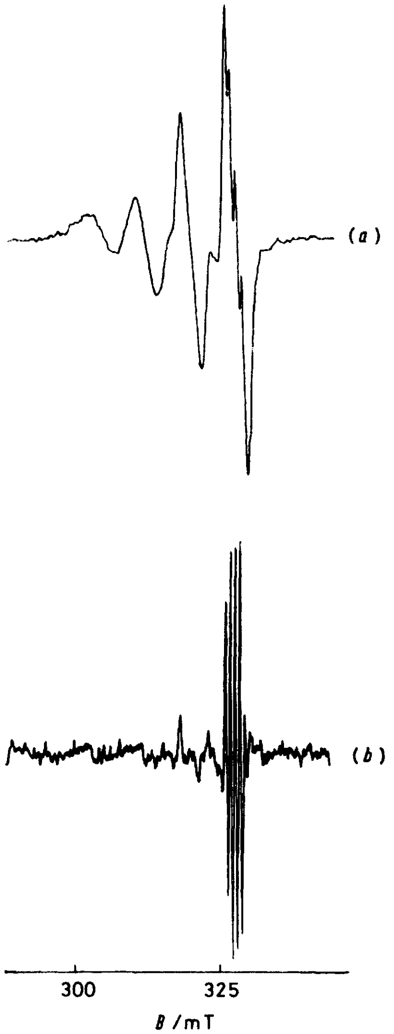

FIGURE 4 (*a*) E.s.r. spectrum of the $[Cu(S_2CNEt_2)_2]$–$CuCl_2$ mixture (ratio 1 : 1.1) in chloroform–ethanol at 253 K and (*b*) the third-derivative spectrum of the same solution at 253 K

This range of experiments was extended further by the addition of $NiCl_2$ and $CoCl_2$ solutions to $[Cu(S_2CNEt_2)_2]$. Again the solutions achieved a deep green colouration but with these two salts, larger salt : [Cu-

$(S_2CNR_2)_2]$ ratios were required. Additional splitting on the $M_I = +\frac{3}{2}$ line is just discernible on the spectrum of the $CoCl_2$–$[Cu(S_2CNEt_2)_2]$ mixture but unfortunately in the $NiCl_2$–$[Cu(S_2CNEt_2)_2]$ mixture the larger line width obscures any possible additional structure in the new complex.

The above results (summarised in Table 2) show that the addition of a range of different metal salts destroys the copper(II) dithiocarbamate complex. In particular this destruction is complete when the $CuX_2 : [Cu(S_2CNR_2)_2]$ ratio is 1 : 1 for X = Cl or Br. The room-temperature e.s.r. spectra reveal the interaction of the unpaired electron with a single halogen nucleus. In the case of the chlorine complex this interaction is only clearly evident in the third-derivative spectrum, and we believe that these experiments indicate the value of multiple-derivative formats in helping to elucidate the nature of hyperfine structure which is only partially resolved in first-derivative spectra. These results lead us to propose that a mixed-ligand complex involving a single halogen nucleus has been formed, equation (1). The higher

TABLE 2

E.s.r. parameters for some copper(II) diethyldithiocarbamate mixed-ligand complexes in ethanol–chloroform at 293 K

Complex	$g_{iso.}$	$a_{iso.}$/mT	a_x/mT
$[Cu(S_2CNEt_2)_2]$	2.046	7.7	
$[Cu(S_2CNEt_2)_2]$–$CuCl_2$	2.070	7.5	0.8
$[Cu(S_2CNEt_2)_2]$–$CoCl_2$	2.065	7.2	*ca.* 0.8
$[Cu(S_2CNEt_2)_2]$–$CuBr_2$	2.065	7.8	3.7
$[Cu(S_2CNEt_2)_2]$–$Cu[NO_3]_2$	2.083	7.1	
$[Cu(S_2CNEt_2)_2]$–$NiCl_2$	2.070	7.8	

$$[Cu(S_2CNR_2)_2] + CuCl_2 \longrightarrow 2[Cu(S_2CNR_2)Cl] \quad (1)$$

ratios required to achieve complete destruction of the original dithiocarbamate complex upon the addition of $CoCl_2$ and $NiCl_2$ reflect the stability of the original complex relative to that of the new complexes formed in these systems (see, for example, refs. 5 and 9).

In order to obtain further information on the reactions which occur upon addition of the various salts we also recorded the low-temperature spectra of the same mixtures. The changes observed in the e.s.r. spectrum of $[Cu(S_2CNEt_2)_2]$ upon addition of the above salts at low temperature (113—133 K) are more dramatic than those observed at room temperature. For example, the intensity of the $\Delta M_s = 2$ absorption of the $[Cu(S_2CNEt_2)_2]$ complex decreases upon addition of $CuCl_2$ and is replaced by a new absorption which increases in intensity upon addition of further $CuCl_2$ (see Figure 5). Addition of $CuCl_2$ beyond a 1 : 1 ratio produces no further change in the intensity of any of the features in the spectrum but results in a spectrum in which these features are present together with the spectrum of unreacted $CuCl_2$. We find that the copper(II) di-n-butyl-, di-n-propyl-, and dibenzyl-dithiocarbamate complexes behave in exactly the same manner. These results support the conclusion drawn from the room-temperature experiments that a new complex, $[Cu(S_2CNR_2)X]$, has been formed and that this complex is stable to further additions of $CuCl_2$.

It is apparent that at 113 K the $\Delta M_s = 2$ absorption of the new complex is different from that of the original $[Cu(S_2CNEt_2)_2]$. We have again obtained a computer simulation of the $\Delta M_s = 2$ absorption and find that the parameters giving the best fit to the experimental spectrum are: $a_{\parallel} = 18.7$ mT, $a_{\perp} = 0$, $g_{\parallel} = 2.22$, $g_{\perp} = 2.07$, $r_{Cu-Cu} = 450$ pm, linewidth = 2.4 mT.

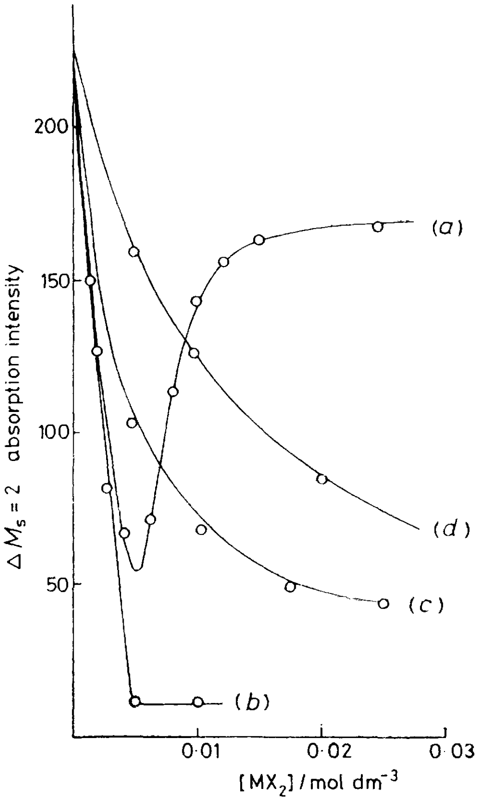

FIGURE 5 The variation of the area of the $\Delta M_s = 2$ absorption in $[Cu(S_2CNEt_2)_2]$ (0.01 mol dm^{-3}) upon addition of (*a*) $CuCl_2$, (*b*) $Cu[NO_3]_2$, (*c*) $CoCl_2$, and (*d*) $NiCl_2$

The addition of increasing concentrations of $CuBr_2$, $Cu[NO_3]_2$, $CoCl_2$, and $NiCl_2$ to $[Cu(S_2CNEt_2)_2]$ also resulted in a rapid decrease in the intensity of the $\Delta M_s = 2$ absorption at low temperature (see Figure 5) indicating destruction of the original complex. As can be seen in Figure 5 no new $\Delta M_s = 2$ absorptions appear upon further increasing the $Cu[NO_3]_2$, $CoCl_2$, and $NiCl_2$ concentrations. Figure 5 also shows that the $CoCl_2 : [Cu(S_2CNEt_2)_2]$ and $NiCl_2 : [Cu(S_2CNEt_2)_2]$ ratios required to completely destroy the $\Delta M_s = 2$ absorption are much greater than for the copper(II) salts. These results are again in accord with the room-temperature observations.

Significant changes were also observed in the *g ca.* 2 region of the e.s.r. spectrum of the same solutions at low temperature (113—133 K) upon addition of the various salts. In the $Cu[NO_3]_2$–$[Cu(S_2CNEt_2)_2]$ mixture the new spectrum at g *ca.* 2 appears to be that of a single species [see Figure 6(*a*)]. However in the $\mathrm{CuCl_2}$–, $\mathrm{CuBr_2}$–, and $\mathrm{CoCl_2}$–$[\mathrm{Cu(S_2CNEt_2)_2}]$ mixtures the spectrum in this region consists of two components [see Figure 6(*b*)]. One component in these spectra undoubtedly has the same g and a values as obtained in the $\mathrm{Cu[NO_3]_2}$–$[\mathrm{Cu(S_2CNEt_2)_2}]$ mixture [$a_{\parallel} = 16.0, 15.0$ mT ($^{65}\mathrm{Cu}$, $^{63}\mathrm{Cu}$), $a_{\perp} = 2.8$ mT, $g_{\parallel} = 2.19$, and $g_{\perp} = 2.06$]. The second component contains additionalsplitting due to the interaction of the unpaired electron with a single halogen nucleus [$a_{\parallel} = 17.4, 15.0$ mT ($^{65}\mathrm{Cu}$, Cu^{63}), $a_{\perp} = 2.9$ mT, $a_{\mathrm{Cl}} = 1.5$ mT ($a_{\mathrm{Br}} = 4.7$ mT), $g_{\parallel} = 2.17$, and $g_{\perp} = 2.05$]. Attempts to obtain conditions under which the second component alone was presented failed, *e.g.* further addition of $\mathrm{CuCl_2}$ to the $\mathrm{CuCl_2}$–$[\mathrm{Cu(S_2CNEt_2)_2}]$ mixture merely resulted in further absorptions in the spectrum which could be readily assigned to unreacted $\mathrm{CuCl_2}$.

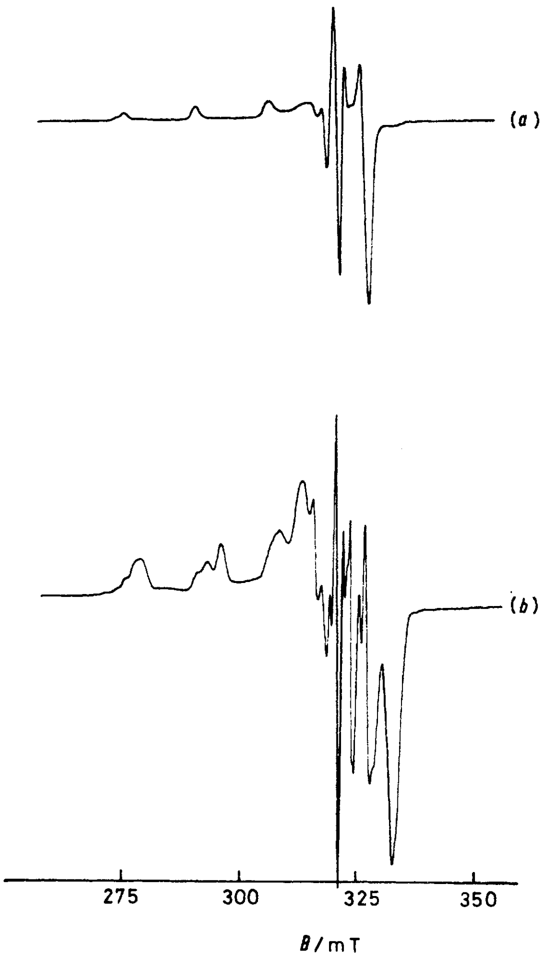

FIGURE 6 E.s.r. spectrum of the g *ca.* 2 region (*a*) of the $[\mathrm{Cu(S_2CNEt_2)_2}]$–$\mathrm{Cu[NO_3]_2}$ mixture (ratio 1 : 1.1) and (*b*) of the $[\mathrm{Cu(S_2CNEt_2)_2}]$–$\mathrm{CuCl_2}$ mixture (ratio 1 : 1.1), both at 113 K

The previously proposed dissociation of the mixed-

$$[\mathrm{CuXY}] \rightleftharpoons [\mathrm{CuX}]^+ + \mathrm{Y}^- \tag{2}$$

ligand complex,[11] equation (2), does not appear to proceed substantially in the $\mathrm{CuCl_2}$–$[\mathrm{Cu(S_2CNEt_2)_2}]$, $\mathrm{CuBr_2}$–$[\mathrm{Cu(S_2CNEt_2)_2}]$, and $\mathrm{CoCl_2}$–$[\mathrm{Cu(S_2CNEt_2)_2}]$ mixtures. This view is supported by conductivity measurements which indicate that, at room temperature, only a minor proportion of the complex is ionised. However the low-temperature e.s.r. spectra of the $\mathrm{CuBr_2}$–, $\mathrm{CoCl_2}$–, and $\mathrm{CuCl_2}$–$[\mathrm{Cu(S_2CNR_2)_2}]$ mixtures are consistent with the presence of two species. The spectrum of one component clearly reveals the interaction of the unpaired electron with a single halogen nucleus and clearly arises from the mixed-ligand complex. The spectrum of the second component present in these three mixtures shows no interaction with any magnetic nuclei other than $\mathrm{Cu^{II}}$ and is identical with the spectrum obtained from the $\mathrm{Cu[NO_3]_2}$–$[\mathrm{Cu(S_2CNEt_2)_2}]$ mixture. It is possible therefore that this second component in the spectrum arises from the $[\mathrm{Cu(S_2CNR_2)}]^+$ ion.

Mixed-ligand complexes, $[\mathrm{Cu(S_2CNEt_2)X}]$, have been suggested as 'intermediates' in the preparation of $[\mathrm{Cu(S_2CNEt_2)X_3}]^{2-}$ complexes by the reaction of $[\mathrm{Cu(S_2CNEt_2)_2}]$ with halogens and are reported to be 'brown-green'.[3,5] This colouration is consistent with that observed in our experiments. Brinkhoff[4] has reported room-temperature spectra similar to those in Figure 3 ($a_{\mathrm{Cu}} = 7.4$ mT, $a_{\mathrm{Cl}} = 0.8$ mT and $a_{\mathrm{Cu}} = 8$ mT, $a_{\mathrm{Br}} = 4$ mT), except that the additional hyperfine structure clearly arises from interaction with two equivalent chlorine (or bromine) nuclei. These spectra, which quite clearly arise from different species to those reported in this paper, have been attributed to $[\mathrm{Cu(S_2CNEt_2)X_2}]^-$ complexes.

EXPERIMENTAL

Preparations.—The copper(II) dithiocarbamate complexes were prepared by the addition of an aqueous solution of the appropriate sodium salt to an aqueous solution of copper(II) chloride in the correct molar ratios. The complex was filtered and purified by Soxhlet extraction with chloroform followed by careful precipitation, by the addition of ethanol, from the resulting chloroform solution. Finally, the crystals were dried over $\mathrm{P_2O_5}$.

Electron Spin Resonance Measurements.—Electron spin resonance spectra were recorded on a Varian E3 spectrometer employing a Varian E4557 variable-temperature unit. Third-derivative spectra were obtained in conjunction with a Telmore Instruments Ltd. 100-kHz subharmonic generator.

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