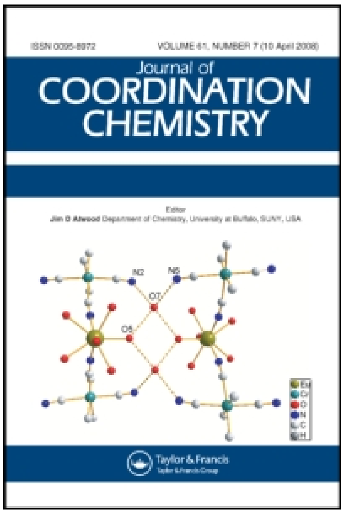

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EQUILIBRIA AND SPECIATION IMPORTANT IN HYDROMETALLURGY. PART IV. A STUDY OF THE SOLVENT EXTRACTION OF COPPER(II) BY LIX63

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EQUILIBRIA AND SPECIATION IMPORTANT IN HYDROMETALLURGY. PART IV. A STUDY OF THE SOLVENT EXTRACTION OF COPPER(II) BY LIX63

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The interaction of LIX63, primarily 5,8-diethyl-7-hydroxy-6-diodecanone oxime, with copper in sulphate media has been studied by E.S.R. spectroscopy. The results confirm that at a ligand to copper ratio of approximately 2:1 a monomeric complex, Cu(LIX63)$_2$, is formed. At lower ligand to metal ratios, a polymeric, E.S.R. silent species is formed. These results confirm those obtained from equilibrium studies.

INTRODUCTION

We have recently investigated the solvent extraction of copper(II) by varios commercial aromatic oxime reagents[1,2,3] using electron spin resonance. The presence of *bis*-chelated complexes in the organic phase and the formation of five-coordinate adducts with nitrogenous bases has been demonstrated.

LIX63 was the first commercial reagent to be marketed for copper(II) extraction and contains as the principal chelating agent 5,8-diethyl-7-hydroxy-6-dodecanone oxime (*I*).[4] Although not used commercially by itself for copper(II) extraction, LIX63 is used as an additive to LIX65N to give a commercial formulation known as LIX64N. LIX63 is the only α-hydroxy aliphatic oxime commercially available as a solvent extraction reagent and has attracted several studies of its coordination with copper(II). LIX63 reacts differently to the β-hydroxy aromatic oximes such as P5000, SME529 and LIX65N, (*II*). In the presence of excess oxime 1:2 complexes are formed by both aromatic and aliphatic oximes. However, with higher copper concentrations LIX63 appears to form a green polymeric species.[5]

In this paper we wish to report studies of the electron spin resonance spectra of copper(II) extracted by commercial LIX63, purified LIX63 and a pure synthesised sample of 5,8-diethyl-7-hydroxy-6-dodecanone oxime.

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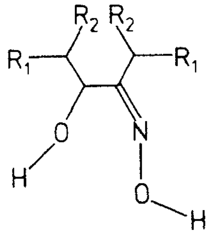

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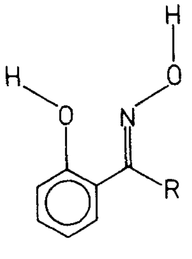


II

$R_1 = C_2H_5$

$R_2 = CH_3(CH_2)_3$

EXPERIMENTAL

LIX63 was donated by Henkel (Ireland) Ltd., and 5,8-diethyl-7-hydroxy-6-dodecanone oxime was prepared as reported earlier.[6] LIX63 was purified by preparation and subsequent hydrolysis of its copper(II) complex.[7,8] The solid complex was used in some experiments. The diluent used was 80% (v/v) 80-100 petrol/toluene. Reagent grade solvents were used without further purification. The copper(II) solution was prepared by dissolving $CuSO_4.5H_2O$ (BDH AnalaR) in water and adjusting the pH to 3.5 with H_2SO_4.

Extractions were carried out using a 1:1 phase volume ratio and stirring vigorously for 15 min. The phases were allowed to settle for 10 min and small aliquots taken from the organic layer.

ESR spectra were measured with a Varian E4 instrument at room temperature (close to 293K) and at 77K by immersion in liquid N_2. Spin Hamiltonian parameters were calculated by the method of Vanngard and Aasa.[9,10]

RESULTS AND DISCUSSION

Solutions of the copper(II) complex of the oxime were prepared using the three different sources of the ligand, commercial LIX63, purified LIX63 and the pure oxime. In general, similar results were obtained irrespective of the source of oxime and any significant differences are noted below.

Isotropic ESR. A typical spectrum is shown in Figure 1 and the spin Hamiltonian parameters are summarised in the Table. The solid complex dissolved in petrol/toluene (80:20) produced a well resolved spectrum with four lines due to hyperfine coupling with copper ($I = 3/2$). Superhyperfine lines are superimposed in an approximately 1:2:3:2:1 ratio on the highest field component. This is the expected pattern for two equivalent nitrogens ($I = 1$).

The spectra of both commercial LIX63 and pure oxime solutions loaded with copper such that the [Cu(II)]:[oxime] ratio was approximately 1:2 are identical to that above

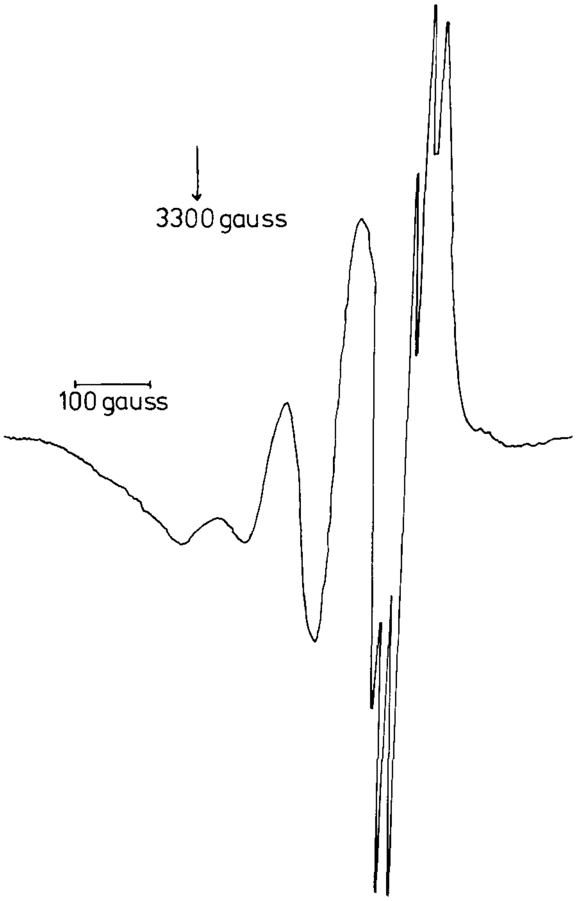


FIGURE 1 Isotropic spectra obtained on the dissolution of the solid LIX63-Copper(II) complex in Toluene/Petrol.

within experimental error. The dominant complex in all these solutions is hence the monomeric *bis*-chelate.

When any of these solutions is washed with further aliquots of aqueous copper sulphate (pH = 3.5) the ESR spectrum decreases in intensity but is otherwise unmodified. On continued washing a limiting intensity of about 1% of the original signal is reached. A

TABLE I
Typical E.S.R. Parameters for LIX63 Copper(II) Complexes.

Sample	g_{av}	A_{av}[a]	$g_{\parallel}$	$A_{\parallel}$[a]	g_{tr}
LIX63 (purified or as supplied) or pure oxime[b]	2.10(±0.01)	118(±3)	2.245(±0.005)	178(±5)	2.050(±0.001)
Second Species [LIX63] [Cu(II)]			2.285	160	

[a] 10^4 A cm^{-1}. [b] Maximum variation in $g_{\parallel}$ and A values observed for the various sources of oxime are given in parentheses.

careful study of such spectra revealed no evidence of a triplet (S = 1) species. These results are consistent with the formation of a polymeric complex in which coupling between adjacent metal centres is strong.

Anisotropic ESR. Under conditions such that the [Cu(II)] : [oxime] ratio is about 1:2, all sources of the oxime give rise to similar spectra. The results are summarised in the Table and a typical spectrum is shown in Figure 2.

Increasing copper(II) concentrations again merely decreased the intensity of the signal and no evidence for a triplet species could be obtained.

In solutions of the commercial LIX63 such that [oxime] $\gg$ [Cu(II)] significantly different spectra were obtained. In the parallel region of the spectrum a second complex is seen to be present (Figure 3 and Table). This species is not present in solutions prepared from the pure ligand or purified reagent under similar conditions. We have not to date identified this complex, although it is possibly an adduct of the type we have identified in related systems.[1,2,3]

Electron spin resonance enables us to confirm that the major species formed on the extraction of copper(II) from moderately acidic aqueous solutions by LIX63 is the monomeric *bis*-oximato complex. In marked contrast to the aromatic oximes studied by us previously, solutions of the *bis*-aliphatic oxime complex may extract further copper(II) to form a strongly exchange coupled polymer. ESR spectra provide direct evidence for this species and enable us to discuss its structure.

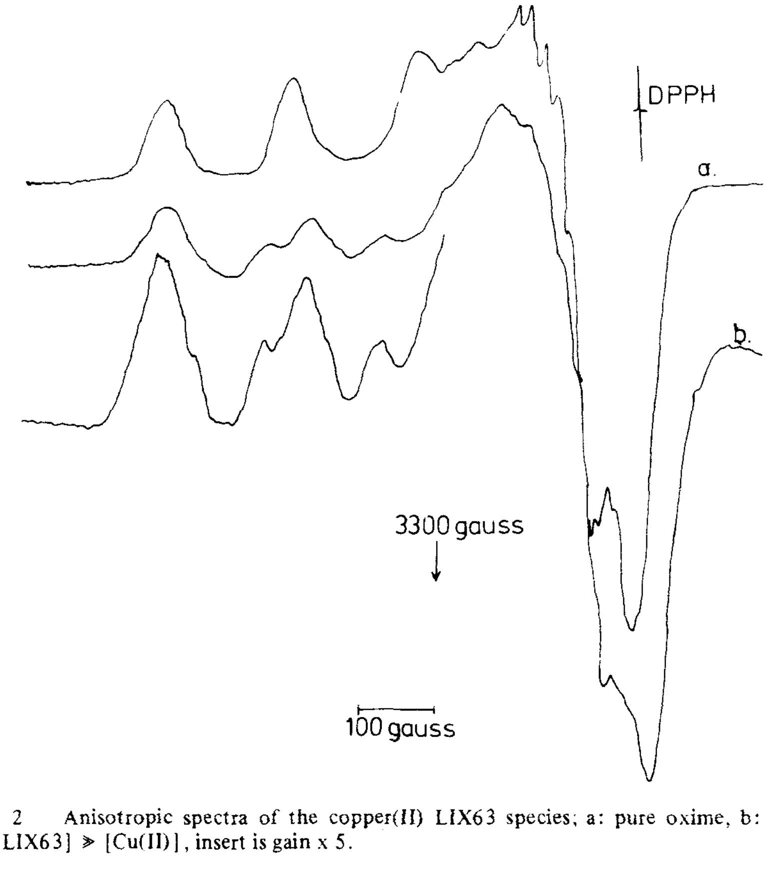
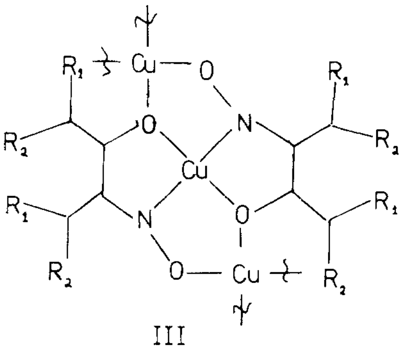


FIGURE 2 Anisotropic spectra of the copper(II) LIX63 species; a: pure oxime, b: commercial LIX63, [LIX63] $\gg$ [Cu(II)], insert is gain x 5.

The aliphatic oxime is capable of forming an extended two dimensional system of five membered chelate rings (*III*). The planar arrangement allows strong coupling between adjacent copper(II) centres. This is in marked contrast to the aromatic oximes (*II*) in which analogous polymerization would lead to adjacent five and six membered rings. This system cannot be flat; the strong coupling between the copper centres is only possible for the aliphatic oxime and provides an extra driving force for polymerisation.

There is an impurity in the commercially provided reagent which, at high ligand to copper ratios, leads to the formation of a new species. Our attempts to identify this complex have been unsuccessful but it seems unlikely to be important under commercial operating conditions.



III

$R_1 = C_2H_5$ $R_2 = CH_3(CH_2)_5$

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