Equilibria and Speciation of Metal Complexes Important in Hydrometallurgy. Part 3.[1] Studies of the Copper(II) Complexes of 5-Nonylsalicylaldoxime (Acorga P50), the Effect of 4-Nonylphenol and the Formation of Five-co-ordinate Adducts with Nitrogenous Bases ‡

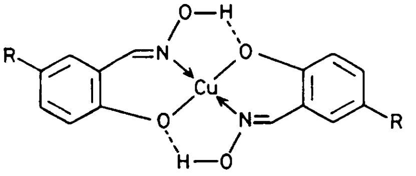
Brian McCudden, Paul O'Brien,* and John R. Thornback *,†
Department of Chemistry, Chelsea College, Manresa Road, London SW3 6LX

Copper complexes of the 'Acorga P5000' series of reagents have been studied by electronic and e.s.r. spectroscopy. The P5000 series solvent extraction reagents contain as the major complexing agent 5-nonylsalicylaldoxime; this ligand forms a stable bis-chelated complex with copper(II) in the organic phase. The common additive 4-nonylphenol does not interact with the first co-ordination sphere of the copper(II) complex in the organic phase. In contrast, both pyridine and ammonia form five-co-ordinate adducts with the complex. The equilibrium constant has been determined as 40 dm^3 mol^{-1} for the binding of pyridine to the bis(salicylaldoxime) complex in toluene.

Hydrometallurgical methods for the processing of copper are becoming increasingly important.[2] Several of the commercially available reagents are substituted aromatic oximes (HL) derived from salicylaldoxime; some of these are shown in Table 1. The extraction process involves the equilibrium (i).

$$2HL(org) + Cu^{2+}(aq) \rightleftharpoons [CuL_2](org) + 2H^+(aq) \qquad (i)$$

The product in the organic phase is a *trans* square co-planar complex of the type (1), stabilized by hydrogen bonding.[3-5]



(1)

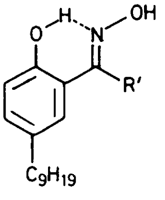
We have recently investigated by e.s.r. the speciation of copper in organic phases obtained by extraction with the Shell reagent SME 529. On addition of nitrogenous bases (L′) five-co-ordinate adducts were formed, equation (ii).

$$[CuL_2](org) + L'(org) \rightleftharpoons [CuL_2(L')](org) \qquad (ii)$$

The facile formation of such complexes had not been considered in earlier work, although the transfer of ammonia into the organic phase by such reagents had been noted.[6-8]

In this paper we have studied, using electronic and e.s.r. spectroscopy the P5000 series of reagents, marketed by Acorga.[8-10] These reagents contain 5-nonylsalicylaldoxime (hereafter P50) as the main chelating agent for copper(II); this is mixed with varying percentages of 4-nonylphenol (Table 1). The phenol alters both the equilibrium and kinetic performance of the system.[11] The main advantage of its addition is that copper(II) may be stripped from the organic phase at lower (more economic) concentrations of acid. The activity of 4-nonylphenol in these systems could be due to either an interaction of the phenol with the copper(II) complex in the organic phase or to the disruption of hydrogen bonding in the solution.[3,12,13] E.s.r. spectroscopy is sensitive to changes in the first co-ordination sphere of such complexes.[1,5] We have used this technique to investigate the effect of adding 4-nonylphenol to the copper(II) P50 complex. Adduct formation by [Cu^{II}(P50)$_2$] with both pyridine (py) and ammonia has been shown to occur; for the pyridine complex the equilibrium constant was determined spectrophotometrically.

Table 1. Some aromatic *o*-hydroxyoxime reagents



HL

Reagent L	R′	Supplier and notes
LIX 65	C_6H_5	General Mills (now Henckel)
SME 529	CH_3	Shell
P50	H	Acorga
P5100	H	+48% 4-nonylphenol, Acorga
P5300	H	+70% 4-nonylphenol, Acorga

Results

Electron Spin Resonance.—Isotropic (*ca.* 293 K) and anisotropic (77 K) spectra of copper in the organic phase, toluene–light petroleum (20 : 80), obtained by solvent extraction with the P5000 series reagents (at 1% and 10% dilutions), have been recorded.

Anisotropic spectra. The compounds P50, P5100, and P5300 gave identical values for the parallel components of the spin-Hamiltonian ($g_{\parallel}$ and $A_{\parallel}$); these are summarized in Table 2. Dilution with 4-nonylphenol of a 10% P50 extraction produced no significant variation in the numerical values of $g_{\parallel}$ and $A_{\parallel}$ (Table 2). The resolution of spectra was improved by the phenol, presumably because a better glass of higher magnetic dilution was produced by its addition. A typical spectrum is shown in Figure 1; nitrogen superhyperfine structure in an approximately 1 : 2 : 3 : 2 : 1 ratio is clearly observed on the low-field components of $A_{\parallel}$.

Isotropic spectra. Typical copper(II) isotropic spectra were observed for all the reagents and mixtures studied. In all cases four lines of equal area were observed due to splitting by copper ($I = \frac{3}{2}$ for ^{63}Cu and ^{65}Cu). In each case the highest field component was clearly split into five equally spaced lines of approximately 1 : 2 : 3 : 2 : 1 intensity ratio, indicative of two equivalent nitrogen donors at copper(II).[14] 4-Nonylphenol

---

† *Present address:* Department of Chemistry, Loughborough University of Technology, Loughborough LE11 3TU.

‡ *Non-S.I. unit employed:* 1 G = 10^{-4} T.

Table 2. Selected e.s.r. parameters for aromatic oxime extractants

Sample [a]	$g_{\parallel}$	$10^4 A_{\parallel}/\mathrm{cm}^{-1}$
P50	2.187	0.0211
P5300	2.188	0.0209
P5100	2.187	0.0209
P50 + 4-nonylphenol (50%)	2.188	0.0212
P50 + 4-nonylphenol (90%)	2.188	0.0212
P50 + py	2.261	0.0188
P50 + py [+ 4-nonylphenol (90%)]	2.261	0.0188
P50 + ammonia	2.256	0.0180
SME 529 [b]	2.160	0.0212
SME 529 [b] + py	2.211	0.0196
SME 529 [b] + ammonia	2.207	0.0196

[a] All at a reagent concentration of *ca.* 10 g dm^{-3} in toluene–light petroleum (20 : 80) at 77 K, except dilutions with 4-nonylphenol as indicated. [b] Refs. 1 and 5.

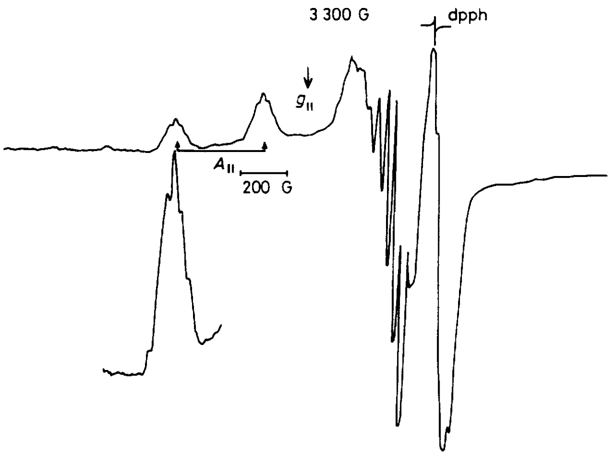


Figure 1. Anisotropic e.s.r. spectrum of [Cu(P50)$_2$]: P5300 reagent concentration 1%, saturated with copper(II); insert is × 5, recorded as a glass at 77 K

did not effect $g_{\mathrm{av.}}$ and $A_{\mathrm{av.}}$ values; however, lineshapes were again altered, again due to less free tumbling of the complex in this highly viscous solvent.

Adduct Formation.—On addition of pyridine to a solution of copper(II) in P50, 1% in toluene–light petroleum (20 : 80), a smooth change to the spectrum (shown in Figure 2) was observed. No evidence for the formation of more than one adduct was observed; an excess of pyridine produced no further change. Isotropic spectra were also modified; however, five superhyperfine lines in a 1 : 2 : 3 : 2 : 1 ratio were still observed on the highest-field component of A_{av}. This existence implies a 1 : 1 adduct with two equivalent nitrogens in the square plane. Spin-Hamiltonian parameters for the adduct were again unaffected by the addition of large excesses (9 : 1 dilution) of 4-nonylphenol.

The effect of shaking a solution of P50, 1% in toluene–light petroleum (20 : 80), with saturated aqueous ammonia (specific gravity 0.880) was investigated. The solution turned green and the anisotropic e.s.r. spectrum is shown in Figure 2. The effect of 4-nonylphenol on the spectrum was the same as that reported above for the 1 : 1 pyridine adduct. It should also be noted that the intensity of the e.s.r. spectrum was, in all the above experiments, unaffected by the addition of 4-nonylphenol.

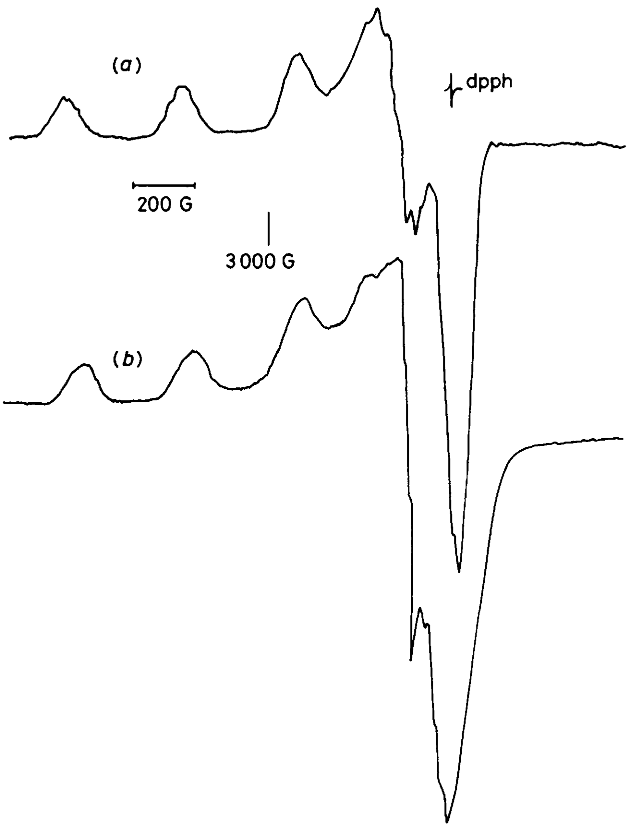


Figure 2. Anisotropic spectra of 1 : 1 adducts of [Cu(P50)$_2$] with (*a*) pyridine and (*b*) ammonia: P50 reagent concentration 1%, plus excess nitrogenous base; recorded as a glass at 77 K

Electronic Spectra.—The reagents all showed similar visible spectra with a single broad absorption (between 11.8 × 10^3 and 18.2 × 10^3 cm^{-1}) at 14.7 × 10^3 cm^{-1} (ε *ca.* 93 dm^3 mol^{-1} cm^{-1}).* The addition of excess pyridine to such solutions causes absorbance increases at 16.7 × 10^3 and 13.2 × 10^3 cm^{-1}, peaks in the visible spectrum now being 17.1 × 10^3 (ε *ca.* 91) and 14.3 × 10^3 cm^{-1} (ε *ca.* 89 dm^3 mol^{-1} cm^{-1}). Application of the method of continuous variation to solutions of [Cu(P50)$_2$] and pyridine produced no observable changes in the electronic spectrum from that of [Cu(P50)$_2$].

A solution of [Cu(P50)$_2$] (*ca.* 0.01 mol dm^{-3} in toluene) was titrated with neat pyridine. A smooth change to the spectrum of the green pyridine adduct described above was observed; tight isosbestic points at 18.2 × 10^3, 15.3 × 10^3, and 14.4 × 10^3 cm^{-1} were observed. From plots of log$_{10}$[($A_{\mathrm{obs.}} - A_0$)/($A_{\infty} - A_{\mathrm{obs.}}$)] *versus* log$_{10}$[py], equation (iii), values of *n* [the number of moles of pyridine bound per mole of bis(salicylaldoximate)] and the equilibrium constant *K* may be determined.

$$\log_{10}K = \log_{10}\frac{[\mathrm{Cu(P50)_2(py)}_n]}{[\mathrm{Cu(P50)_2}]} - n\log_{10}[\mathrm{py}] \qquad \text{(iii)}$$

Two wavenumbers, 16.7 × 10^3 and 13.2 × 10^3 cm^{-1}, both with relatively large changes in absorbance were used in the analysis. A least-squares procedure led to estimates of 1.15 for *n* and 40 dm^3 mol^{-1} for the equilibrium constant, with a correlation coefficient of 0.999. The equilibrium is hence accurately described by equation (iv). Similar changes in electronic spectrum

$$[\mathrm{Cu(P50)_2}] + \mathrm{py} \rightleftharpoons [\mathrm{Cu(P50)_2(py)}] \qquad \text{(iv)}$$

---

* Molar absorption coefficients are calculated per mol of copper(II).

Table 3. E.s.r. parameters for the P5000 series of reagents and SME 529 *

Sample	$g_\parallel$	$10^4A_\parallel$/cm^{-1}	$g_\perp$	$g_{av.}$	$A_{av.}$(Cu)/cm^{-1}	$A_{av.}$(N)/cm^{-1}
$[Cu(P50)_2]$	2.187	211	2.05	2.095	97.8	18.5
$[Cu(P50)_2(py)]$	2.261	188	2.07	2.130	77.6	14.9
$[Cu(P50)_2(NH_3)]$	2.256	180	2.04	2.110	88.5	16.6
$[Cu(SME\ 529)_2]$	2.173	213	2.06	2.098	93	17
$[Cu(SME\ 529)_2(py)]$	2.211	196	2.07	2.115	74	15

* Values for SME 529 are from ref. 5.

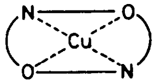
are observed when $[Cu(P50)_2]$ solutions are shaken with ammonia.

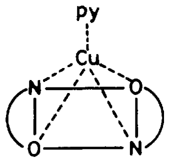
Discussion

The equilibrium study reported here supports our earlier conclusion,[1,5] based on spectroscopic and synthetic studies, that only 1 : 1 adducts of copper(II) bis(salicylaldoximate) complexes are formed under moderate conditions.

The e.s.r. spectra observed for the P50 series of reagents are consistent with the formation of bis(5-nonylsalicylaldoximato)-copper(II) in the organic phase. 4-Nonylphenol does not interact with the first co-ordination sphere of the complex (Table 2). In Table 3 are presented e.s.r. parameters which characterize the complex $[Cu(P50)_2]$ found in all solutions studied. The values reported are similar to those observed for the closely related Shell reagent SME 529 [1,5] and compare favourably with those recently reported for a series of five substituted salicylaldoximes [15] and the parent, bis(salicylaldoximato)-copper(II).[14]

On adduct formation (with NH_3 or py) the changes observed in the e.s.r. spectrum are typical of those observed for the formation of 1 : 1 adducts [15] [18] of approximately square-pyramidal geometry. Changes in parallel components are greatest, $A_\parallel$ decreases and $g_\parallel$ increases. This is consistent with a movement of copper(II) out of the square plane, as illustrated below. A decrease of in-plane bonding concurrent with such a change leads to the positive shift in $g_\parallel$ and marked decrease in $A_\parallel$; the results are again summarized in Table 3. The observation of five lines due to N-hyperfine interactions for all complexes (adducts and bis-chelated) provides firm evidence for the two nitrogens of the salicylaldoxime remaining approximately in a square plane.[19] [21]





Experimental

Materials.—The reagents P50, P5100, P5300, and 4-nonylphenol were a gift from I.C.I., all other chemicals were B.D.H. AnalaR grade. Toluene and light petroleum (b.p. 80—100 °C) were used without further purification.

Methods.—*Electron spin resonance spectra*. Spectra were recorded with a Varian E4 instrument at room temperature (close to 293 K) and 77 K. Diphenylpicrylhydrazyl (dpph) was used as a standard. All low-temperature spectra were axial, or nearly so (Figures 1 and 2). The parallel components of the spin-Hamiltonian parameters, $g_\parallel$ ($\sim g_z$) and $A_\parallel$ ($\sim A_z$) can be determined directly from the anisotropic spectra with reasonable accuracy.[22] Exact analysis of the high-field portion of anisotropic spectra is difficult particularly if $g_x \neq g_y$ and/or $A_x \neq A_y$. Average parameters g_{av} and A_{av} may be determined from isotropic (room temperature) spectra. The parameters $g_\perp$ and $A_\perp$ may then be estimated [22] by equations (v) and (vi). This presumes a small temperature

$$3g_{av} = g_\parallel + 2g_\perp \qquad (v)$$

$$3A_{av} = A_\parallel + 2A_\perp \qquad (vi)$$

dependence of spin-Hamiltonian parameters; however, in all cases reported $g_\perp$ calculated from the above was close (within 0.02) to that measured as the maximum of the anisotropic spectrum.

Electronic spectra. These were measured at 22 ± 1 °C using a Perkin-Elmer 402 scanning spectrophotometer, with toluene–light petroleum (20 : 80) in the reference beam.

Titrations. In general, a 1% or 10% solution of the reagent, in toluene–light petroleum (20 : 80) was saturated with copper using a 1 g dm^{-3} solution of copper(II) (prepared from $CuSO_4 \cdot 5H_2O$) at a pH of 3.5 (adjusted with H_2SO_4). Concentrations of the oxime in such solutions are 0.03 and 0.3 mol dm^{-3} respectively, and hence 0.015 and 0.15 mol dm^{-3} of copper(II) respectively.

For the titration a solution of P50 (in toluene) was standardized potentiometrically.[23] A solution (*ca.* 0.02 mol dm^{-3}) of the salicylaldoxime saturated with copper was then prepared and titrated with pyridine. Dilution which did not exceed 5% was not corrected for in subsequent calculations.

Acknowledgements

We should like to thank Drs. R. Price and J. Leng (I.C.I., Manchester) for helpful discussions and providing the Acorga reagents used in this study, and Professor M. J. Perkins (Chelsea College) for access to e.s.r. facilities.

References

1 Part 2, P. O'Brien and J. R. Thornback, *Hydromet.*, 1982, **8**, 331.
2 G. M. Ritcey and A. W. Ashbrook, 'Solvent Extraction, vol. II. Principles and Applications of Process Metallurgy,' Elsevier, Amsterdam, 1979.
3 J. W. Hoskins and N. M. Rice, *Hydromet.*, 1978, **3**, 217.
4 M. A. Jarski and E. C. Lingafelter, *Acta Crystallogr.*, 1964, **17**, 1109; L. L. Merritt, C. Guare, and A. E. Lesser, *Acta Crystallogr.*, 1956, **9**, 253.
5 P. O'Brien and J. R. Thornback, *Inorg. Chim. Acta*, 1981, **64**, L35.
6 'SME 529 Basic Performance Data,' Shell Preliminary Technical Information, INT 74 : M1.
7 A. J. Van der Zeeuw, *Erzmetall*, 1977, **30**, 139.
8 J. A. Tumilty, R. F. Dalton, and J. P. Massam, 'Advances in Extractive Metallurgy,' Institute of mining and metallurgy, London, 1977, p. 123.
9 J. A. Tumilty, G. W. Seward, and J. P. Massam, *CIM*, 1979, Spec. vol. **21**, 542 (*Chem. Abstr.*, 92:97242r).

10 R. F. Dalton, F. Hauxwell, and J. A. Tumilty, *Chem. Ind.*, 1976, **6**, 187.

11 C. Hanson, M. A. Hughes, J. S. Preston, and R. J. Whewell, *J. Inorg. Nucl. Chem.*, 1976, **38**, 2306.

12 D. R. Spink and D. N. Okuhara, *Int. Symp. Hydromet.*, 1973, 497.

13 D. S. Flett and D. W. West, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1365.

14 A. K. Wiersema and J. J. Windle, *J. Phys. Chem.*, 1964, **68**, 2316.

15 I. Rani, K. B. Pandeya, and R. P. Singh, *J. Inorg. Nucl. Chem.*, 1981, **44**, 2743.

16 K. Falk, E. Ivanova, B. Ross, and T. Vanngard, *Inorg. Chem.*, 1970, **9**, 556.

17 A. F. Garito and B. B. Wayland, *J. Am. Chem. Soc.*, 1969, **91**, 866.

18 H. J. Stoklosa, H. L. Huffman, and J. R. Wasson, *J. Inorg. Nucl. Chem.*, 1973, **35**, 2584.

19 B. B. Wayland and V. K. Kapur, *Inorg. Chem.*, 1974, **13**, 2517.

20 S. Ooi and Q. Fernando, *Chem. Commun.*, 1971, 532.

21 R. S. Drago, ' Physical Methods in Chemistry,' W. B. Saunders, New York, 1975, p. 2584.

22 T. Vanngard and R. Aasa, *Proc. Int. Conf. Paramagn. Reson.*, 1962, 509.

23 Acorga Mining Chemical Technical Information, MC 3, 80.

Received 26*th October* 1982; *Paper* 2/1815