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Equilibria and Speciation of Metal Complexes Important in Hydrometallurgy. Part 1. Bis anti-5-nonyl-2-hydroxyacetophenone Copper(II) and Its Pyridine Adduct

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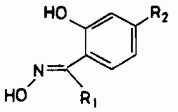
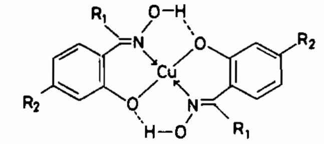
Hydrometallurgical methods are becoming increasingly important [1]. The solvent extraction system marketed by Shell [2] (Shell Metal Extractant 529) contains as the principle chelating agent for copper(II) anti-5-nonyl-2- hydroxyacetophenone oxime (I) (henceforth SME 529). The complex in the organic phase is believed to be the bis chelate (II). Extraction with this reagent shows a marked dependence on pH, concentration of ammonia in the aqueous phase and concentration of SME 529 in the organic phase [2]. Van der Zeeuw has suggested [3] that in extraction from ammoniacal solutions a complex of doubly deprotonated SME 529 may account for the difficulty in back washing copper(II). The possibility of the formation of 5 coordinate adducts (III) in the organic phase has been overlooked. In view of the widespread occurrence of such adducts [4, 5] for square planar copper(II) complexes, this is surprising. In this paper we report studies of the pyridine adduct of Cu(SME 529)$_2$ as a model system for solvent extraction processes.

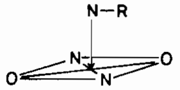


(I)

$R_1 = CH_3$
$R_2 = C_9H_{19}$



(II)



N–R = Pyridine, NH_3, etc.

(III)

Results

The complex was prepared by direct reaction of the ligand with ethanolic solutions of copper acetate; the pyridine adduct by reacting Cu(SME 529)$_2$ with pyridine in petrol. Pyridine was lost relatively easily from the adduct; hence it was not subjected to conventional microanalysis. The presence of pyridine in the complex was confirmed by infra-red spectroscopy. Characteristic bands 1220, 755 and 695 cm^{-1} were observed [6]. Thermogravimetric analysis (10 °C min^{-1}) showed a weight loss of ~11% 70–235 °C, unfortunately this overlapped with decomposition ~238 °C. Isothermal studies at 125 °C revealed a weight loss of 11.5%, close to the theoretical 11.37% required for the loss of one mole of pyridine per mole of complex for a 1:1 adduct. The complex obtained after such heating was identical with Cu(SME 529)$_2$ by IR and ESR; all IR bands characteristic of pyridine having disappeared.

Eelectron Spin Resonance

Both the complex and pyridine adduct were studied in the solid state, solutions (80–100 petrol) and glasses (80–100 petrol 77 K). For the pyridine adduct identical spectra were obtained by adding excess pyridine to solutions of Cu(SME 529)$_2$ or dissolving the solid adduct, no evidence for the formation of higher adducts or other complexes was obtained.

TABLE I. ESR Parameters for Cu(SME 529)$_2$ and Its Pyridine Adduct.[a]

	g_o	$a_{A_o}^{Cu}$	$a_{A_o}^{N}$	$g_\parallel$	$a_{A_\parallel}^{Cu}$	$a_{A_\parallel}^{N}$	$g_\perp$	$a_{A_\perp}$ Cu	
Cu(SME 529)$_2$	–	–	–	2.194	210	~10	2.050	~34.5	solid room temperature
Cu(SME 529)$_2$	2.098	93	17	–	–	–	–	–	solution room temperature
Cu(SME 529)$_2$	–	–	–	2.173	213	~12	2.060	~33	glass in 80–100 petrol 77 K
Cu(SME 529)$_2$·py	–	–	–	~2.21	–	–	~2.08	–	solid room temperature
Cu(SME 529)$_2$·py	2.115	74	15	–	–	–	–	–	solution room temperature
Cu(SME 529)$_2$·py	–	–	–	2.211	196	~10	2.067	~13	glass in 80–100 petrol 77 K

[a] a = cm^{-1} × 10^{-4}.

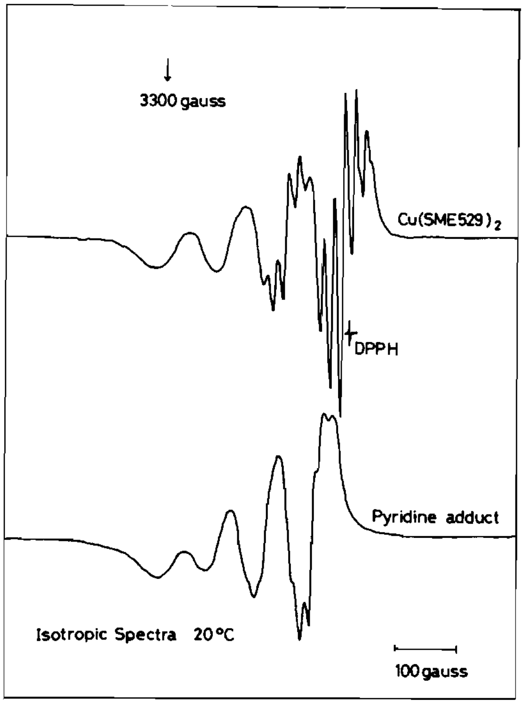


Fig. 1. Isotropic Spectra (~20 °C) of Cu(SME 529)$_2$ and its pyridine adduct.

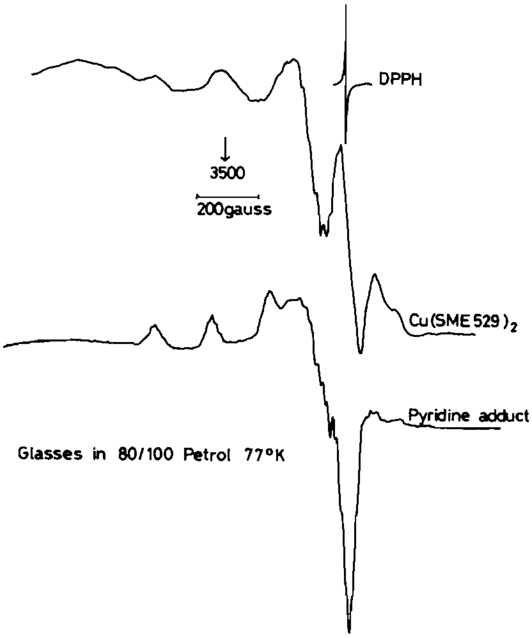


Fig. 2. Anisotropic Spectra of Cu(SME 529)$_2$ and its pyridine adduct.

Isotropic spectra (~20 °C in 80–109 petrol) for the adduct and parent complex are reported (Fig. 1), both complexes show five components due to nitrogen hyperfine on the high field line. Parameters g_o, A_o^N and A_o^{Cu} are reported (Table I). The ESR spectra of the above solutions frozen to glasses at 77 K are reported (Fig. 2), both spectra are typical of axial copper(II) (square coplanar and square pyramidal) and are hence accurately described by two g values. At high gain five hyperfine lines due to nitrogen could be observed on the parallel component of both complexes. This is the expected result for 2 equivalent nitrogens and strongly suggests a five coordinate adduct (III) in which the pyridine occupies an axial position. ESR parameters are reported (Table I).

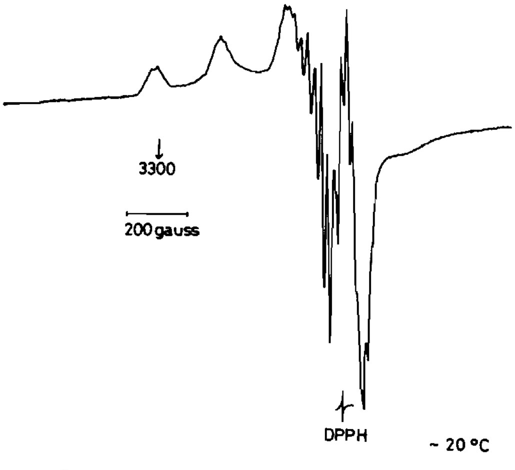


Fig. 3. Spectrum of Solid Cu(SME 529)$_2$.

The spectra of the solid at room temperature were recorded. The spectrum of the parent Cu(SME 529)$_2$ complex is quite remarkable; showing (Fig. 3) very high resolution for a complex which has *not* been diluted into a diamagnetic host lattice. The spectrum of the pyridine adduct is a typical broad powder spectrum, ESR parameters for this and the parent complex are again summarised in Table I.

Discussion

All the observed ESR spectra are consistent with square coplanar or square pyramidal geometries with a $dx^2 - y^2$ ground state [7]. The identity of the pyridine adduct in solution is confirmed by the dissolution of the 1:1 pyridine adduct in solution. We have hence shown that with pyridine the equilibrium:

$$Cu(SME\ 529)_2 + py \rightleftharpoons Cu(SME\ 529)_2 \cdot py$$

is important. Preliminary results indicate that similar adducts may form with ammonia; this should be appreciated in studies of such solvent extraction systems.

Experimental

Copper(II)acetate monohydrate was BDH Analar grade, SME 529 was used as supplied by Shell, 80–100 reagent grade petrol was used without further purification.

Preparation of Cu(SME 529)$_2$

Copper acetate (0.02 mol) was dissolved in ethanol and the solution gently warmed. On the dropwise addition of excess SME 529 the complex precipitated as a fine brown/green powder. The complex was washed extensively with ethanol and water and dried *in vacuo* over $CaCl_2$.

Preparation of Cu(SME 529)$_2$·py

The copper complex (0.001 mol) was dissolved in 20 ml of warm 80–100 petrol. A slight excess (0.0015 mol) of pyridine was added. The volume was reduced to 5 ml under a stream of nitrogen and the solid pyridine adduct filtered off and air-dried. The pyridine adduct was reasonably stable in a stoppered vial, if stored in the open lab (~22 °C) pyridine was lost totally in about one week.

Methods

Electron spin resonances were measured with a Varian E4 spectrometer; powder and solution spectra were measured at room temperature (close to 293 K), glossy spectra at liquid nitrogen temperatures (77 K).

Thermogravimetric analysis was carried out with a Stanton Redcroft TG 750 instrument. Infrared spectra were recorded with a Perkin Elmer 254 instrument and nujol mulls between CsI plates.

ESR parameters were calculated as described by Kneubühl [8], the method of Vanngard and Aasa [9, 10] being used for well resolved anisotropic spectra. Diphenylpicrylhydrazyl (DPPH) was used as a standard. For the pyridine adduct identical spectra were obtained by dissolving the solid adduct in solution or adding excess pyridine to Cu(SME 529)$_2$, no spectral evidence for other than 1:1 adduct was observed.

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