983. *Raman Spectra and Solvent-extractions of Cuprous Halides.*

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Extracts containing a high concentration of copper can be prepared by shaking diethyl ether with a solution of cuprous chloride in hydrochloric acid or of cuprous bromide in hydrobromic acid. Raman spectra of the extracts suggest the presence of the linear ions $CuCl_2^-$ (v_1 296 cm.$^{-1}$) and $CuBr_2^-$ (v_1 190 cm.$^{-1}$). The spectra of aqueous solutions show that the species in the extracts are not the predominant complexes of copper(I) in the aqueous phase before extraction.

WOODWARD *et al.*[1] recently demonstrated the use of Raman spectroscopy for the identification of the solute species extracted by diethyl ether from acidic aqueous solutions of metal halides. We have applied this technique in a study of the ether extraction of copper(I) from solutions of cuprous chloride in hydrochloric acid and of cuprous bromide in hydrobromic acid. As far as we are aware these extraction systems have not been described before.

Preparation of Extracts

Cuprous Chloride System.—Cuprous chloride dissolves in 6·0M-hydrochloric acid to the extent of 1·2M at 28°. When such solutions are shaken with an equal volume of diethyl ether, copper(I) is extracted into the organic phase with a distribution ratio ([Cu]$_{ether}$: [Cu]$_{aqueous}$) of 1·3 : 1. At higher acid concentrations, although the distribution ratio is smaller (1·0 for the extraction from 8·0M-acid), more concentrated extracts can be prepared because of the increased solubility of cuprous chloride. Above an initial 8·5M-acid concentration at 28°, complete miscibility of a saturated solution of cuprous chloride with an equal volume of ether occurs, and this phenomenon places an upper limit on the concentration of copper(I) which can be reached in an extract.

For a Raman investigation, an extract was prepared by shaking 20 ml. of a 3·0M-solution of cuprous chloride in 8·4M-hydrochloric acid with an equal volume of freshly distilled diethyl ether and a small quantity of copper powder. 23 ml. of extract were formed and found by analysis to be 1·6M in copper. The ratio Cu : Cl was found to be 1 : 3·0.

Cuprous Bromide System.—The solubility of cuprous bromide in 4·5M-hydrobromic acid at 28° is 1·0M and rises to 1·6M in 5·0M-acid. Efficient ether-extraction of copper(I) from saturated solutions of cuprous bromide begins when the hydrobromic acid concentration exceeds 4·0M, the distribution ratios for extraction from solutions in' 4·5M- and 5·0M-hydrobromic acid being

[1] (a) Woodward and Bill, *J.*, 1955, 1699; Woodward and Taylor, *J.*, (b) 1960, 4473; (c) 1962, 407.

0·8 : 1 and 1·1 : 1.   At acid concentrations greater than about 5·5M at this temperature, complete miscibility of saturated solutions of cuprous bromide with an equal volume of ether occurs.

A cuprous bromide extract for the Raman investigation was prepared by shaking 42 ml. of a 1·6M-solution of cuprous bromide in 5·0M-hydrobromic acid with an equal volume of freshly distilled ether and a small quantity of copper powder.   34 ml. of extract were formed and found to be 0·8M in copper, with a Cu : Br ratio of 1 : 2·1.

RESULTS AND DISCUSSION

Raman Spectra of Extracts.—Even on long exposure, only one Raman line could be found in the spectrum of each extract which could be attributed to a copper–halogen complex.   The other lines in the spectra, which occurred at greater displacements from

Extract	$\Delta\nu$ (cm.$^{-1}$)	Appearance polarization	f_{Cu-X} (10^5 dynes/cm.)
Cuprous chloride	296	Sharp, partially pol.	1·84
Cuprous bromide	190	Sharp, partially pol.	1·71

the exciting line, were all confidently assigned to the solvent (see below).   The observed Raman frequencies and the qualitative states of polarization of the Raman lines for the solute are given in the Table.

If it is assumed for each extract that this single line constitutes the complete Raman spectrum of the principal solute species (as seems likely since other lines could not be found in spectra where this one line was very strong) the observed Raman frequency may satisfactorily be assigned to the totally symmetric (a_{1g}) stretching vibration of the linear ion $(X-Cu-X)^-$ of point group $D_{\infty h}$, where X = Cl or Br.   This linear ion is the only possible halide complex (except Cu–X which can be discounted on the basis of known solubility data) for which only one line, partially polarized, is expected in the Raman spectrum.   The bond-stretching force constants in the Table, calculated for the species CuX_2 on the assumption of a simple valency force field (interaction force constants are neglected) are seen to decrease in the usual manner on passing from the chloride to the bromide complex.[1b]

The conclusion that the predominant species of copper(I) extracted into the ether phase are the ions $CuCl_2^-$ and $CuBr_2^-$, while admittedly depending somewhat on negative spectral evidence, is consistent with observations made on other acid–metal halide systems, where it is generally found [1,2] that the use of solvents of low dielectric constant (such as diethyl ether) results in the preferential extraction of complex anions bearing a single negative charge.   The anions are accompanied into the organic phase by hydrogen ions, and are probably associated with them in the form of ion pairs, in which the hydrogen ions are solvated.   The above conclusion is also in agreement with the Cu : Br ratio of 1 : 2·1 for the cuprous bromide extract, while in the case of the cuprous chloride extract the low Cu : Cl ratio of 1 : 3·0 is probably due to the simultaneous extraction of hydrochloric acid, a phenomenon which is often found to occur at high aqueous acid concentrations [2] [see, for example, the ether phase ratio Fe : Cl of 1 : 5 found in the extraction of $H^+(FeCl_4^-)$ from 8M-hydrochloric acid [3]].

There is no evidence in the Raman spectra of the extracts to suggest further co-ordination between the copper halide complexes and molecules of the solvent.   In addition to the single line attributed to the species CuX_2^-, the Raman spectra of each extract contained other lines which we have attributed to the solvent.   It is true that this " solvent " spectrum differed slightly from that of pure ether, in particular by the presence of a strong doublet ($\Delta\nu$ = 1077, 1103 cm.$^{-1}$) in a region where the Raman lines of pure ether are relatively weak.   A spectrum identical with the extract solvent spectrum was, however, obtained from a mixture of equal volumes of ether and 12M-hydrochloric acid

[2] Diamond and Tuck, *Progress in Inorg. Chem.*, 1960, **2**, 109.
[3] Nachtrieb and Conway, *J. Amer. Chem. Soc.*, 1948, **70**, 3547.

and it seems certain that the differences in these spectra from that of pure ether should be attributed to the participation of ether molecules in hydrogen-ion solvation rather than (in the case of the extracts) in co-ordination to copper.

Raman Spectra of Aqueous Solutions.—Raman spectra were also recorded from aqueous solutions of cuprous chloride (2·4M in cuprous chloride, 6·7M and 11·9M in hydrochloric acid) and of cuprous bromide (1·4M in cuprous bromide, 5·0M in hydrobromic acid; 1·0M in cuprous bromide, 9·0M in hydrobromic acid). In each case the spectrum consisted only of a broad diffuse band, whose position did not appear to change with variation of acid concentration. This band was extremely broad in the case of the cuprous chloride solutions, extending from the exciting line to roughly $\Delta\nu = 220$ cm.$^{-1}$, while for the cuprous bromide solutions a broad line ($\Delta\nu = 160 \pm 5$ cm.$^{-1}$, partially polarized) was found.

Although the symmetric vibration frequencies of the ions $CuCl_2^-$ and $CuBr_2^-$ are expected to be slightly lower (10—15 cm.$^{-1}$) in aqueous than in ethereal solution,[4] it appears from the spectra that these ions are not present in appreciable concentrations in the aqueous solutions. The low frequencies of the observed bands are consistent rather with more highly co-ordinated species such as CuX_3^{2-} or CuX_4^{3-}, or with bridged complexes such as $Cu_2X_3^-$. The broadness of the spectral bands probably arises from the overlapping of the strongest lines of a number of such species in equilibrium, the situation being similar to that found in the case of aqueous solutions of indium(III) halides.[1a] Stability constants [5] indicate that $CuCl_3^{2-}$ should predominate over $CuCl_2^-$ in the aqueous chloride solutions examined here, but no such information is at present available for other chloro- or bromo-complexes of copper(I).

EXPERIMENTAL

Raman Spectra.—Solutions of cuprous halides and their extracts are colourless, but are very susceptible to oxidation and rapidly become green on exposure to air. For the Raman investigations, solutions were therefore contained in a special closed Raman tube flushed with argon. The slight oxidation which occurred while filling the tube was reversed by shaking the solution with copper powder in a side-arm separated from the Raman cell by a sintered-glass disc.

Spectra were excited by Hg 4358 Å from a 1 kw Toronto arc source and were recorded on Kodak Special Scientific (103a, E) plates. The longest exposures (6 hr., slit width 0·17 mm., for the cuprous chloride extract; 5 hr., slit width 0·07 mm., for the cuprous bromide extract: sample volume 16 ml.) were continued to a point where the continuous spectral background appeared strongly in the spectrograms. The spectrograph was a Huet two-prisms instrument with F/8 camera and a dispersion of 100 cm.$^{-1}$ in the region of 4358 Å. Frequencies were calculated by reference to an iron-arc spectrum and are estimated to be accurate to ± 2 cm.$^{-1}$.

Analysis.—Copper was estimated as copper(II) by iodometry after oxidation of copper(I) with hydrobromic acid and potassium permanganate and removal of the excess of bromine by boiling. Hydrogen ion was determined by titration with standard potassium hydroxide solution. Since H^+ and Cu^+ were the only cations present in the solution, the sum of the concentrations of these was taken to be equal to the total concentration of free and complexed chloride or bromide ion.

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[4] Allen and Warhurst, *Trans. Faraday Soc.*, 1958, **54**, 1786.
[5] " Stability Constants," *Chem. Soc. Special Publ.*, No. 7, 1958, p. 99.