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Study of Halogenometallate(II) Anions Absorbed on an Ion-Exchange Resin by Far-Infrared Spectroscopy

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It is now some years since we demonstrated how it was possible to identify the nature of the species absorbed on an ion-exchange resin from tin(II) solutions in hydrochloric acid, using infrared spectroscopy in the far-infrared (80–450 cm^{-1}) region [1]. Surprisingly, no further reports using this technique appear to have been published, yet the method has potential for studying metal ion/halide ion equilibria, and for identifying new halogenometallate anions. In order to explore the general applicability of the technique, a range of metal(II)/halide ionic systems have been investigated.

Experimental

The method used was essentially that described in the earlier work [1], although since there was no need to prevent oxidation, no attempts were made to exclude air. The resin used was 'Isopor' De-acidite FF-IP (Permutit Co. Ltd.), either 14–52 or 100–200 mesh (3–5% or 7–9% cross-linking, respectively). A small amount (2–3 cm^3) of the resin in the chloride form was placed in a tube and washed thoroughly with high grade de-ionised water. The metal halide solution in the corresponding hydrohalic acid was added and the tube shaken vigorously. The solution was then decanted, and the resin carefully dried (temperatures less than 60 °C). In some cases the resin was washed with acetone before drying. The halide ion to metal ion ratio in the original solution varied from 0 to more than 10.

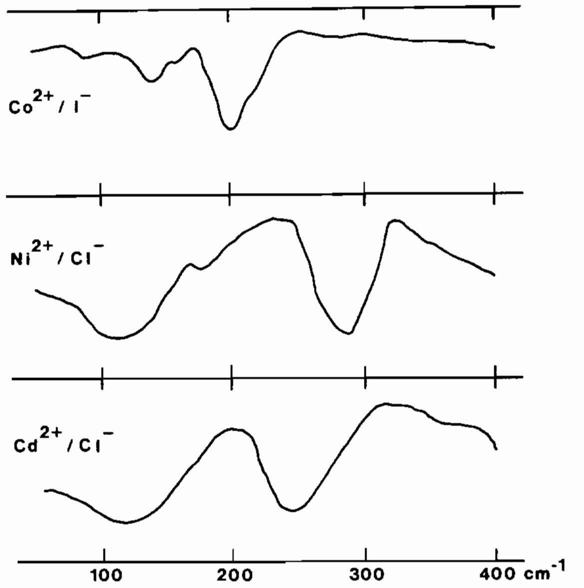

Fig. 1. Far-infrared spectra of species absorbed on an ion-exchange resin from M^{2+}/X^- solutions. The parent resin, in the halide form, shows no discernable bands in the region studied.

A small amount of the finely ground resin (5–10 mg) was intimately mixed with powdered polyethene (25–30 mg) and pressed into a disc.

Spectra of the discs were obtained using a Beckman FS-720 Fourier spectrometer over the range

TABLE I. Far-Infrared Data (cm^{-1}).

System	Observed[a]		Literature[b] on $[MX_4]^{2-}$		
	ν(MX)	δ(MX)	ν(MX)	δ(MX)	Ref.
Co^{2+}/Cl^-	305, 290	*ca.* 135 br	311, 291	135	[2]
Co^{2+}/Br^-	*ca.* 230 br		231, 222	96	[2]
Co^{2+}/I^-	200, 140		202, 194	56	[3]
Ni^{2+}/Cl^-	287	*ca.* 110 br	294, 280	119	[2, 3]
Cu^{2+}/Cl^-	*ca.* 280 br	*ca.* 125 br	267, 248	136, 118	[3, 4]
Cd^{2+}/Cl^-	245	*ca.* 120 br	250	104	[5]
Hg^{2+}/Cl^-	220 br	*ca.* 105 br	229	110	[6]
Hg^{2+}/I^-	*ca.* 115 br		123	60	[7]

[a] br = broad; w = weak. [b] I.r. data on ν_3 and ν_4, generally of salts in the solid state, taken from the references given.

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50–400 cm^{-1} at both room temperature and at *ca.* 50 K in some cases.

Results and Discussion

In all cases examined, spectra were obtained showing bands in the corresponding metal–halide stretching regions, although the quality was variable (see Fig. 1). The results obtained are summarised in Table I.

While there appeared to be some subtle variations in band profiles in experiments carried out using different relative concentrations of metal and halide ions, it was not possible in these preliminary experiments to confirm or rationalise the effects. Washing of the resin with acetone after absorption of the metal halide species had no observable effect on the spectrum.

In all cases studied, the main features of the spectra can be explained as arising from the corresponding tetrahalogenometallate(II) anion. Band positions observed are all close to those found for solid $[MX_4]^{2-}$ salts with cations such as $[Et_4N]^+$, the differences not apparently being of significance bearing in mind the breadth of the bands observed in the present case (Fig. 1) and the common variation of anion band frequencies with changing cation.

For the Hg^{2+}/Cl^- system, there was indication also of a weak band at *ca.* 280 cm^{-1} under some conditions. This observation is of some interest since ν(HgCl) of terminal Hg–Cl bands in $[Hg_2Cl_6]^{2-}$ dimers occurs in this region (280 and 292 cm^{-1} for $[Et_4N]^+$ and $[Pr_4N]^+$ salts, respectively) [8], thus affording some evidence for analogous species absorbed on the resins.

With the system Co^{2+}/I^-, a clear future is observed at 140 cm^{-1} (Fig. 1), the origin of which is unknown but is likely to be an iodocobaltate(II) species other than $[CoI_4]^{2-}$.

Conclusions

The preliminary data reported herein demonstrate that it is possible to obtain vibrational spectra, in the far-infrared region, of halogenoanions of metals absorbed on ion-exchange resins *in situ*. Moreover, the nature of the species so absorbed may also be determined. With refinement, the prospect might emerge of using the method to study ionic equilibria involving ion-exchange resins.

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