865. *Raman Effect and Solvent Extraction. Part II.*[1] *Spectra of the Tetrachloroindate and Tetrachloroferrate Ions.*

By L. A. Woodward and M. J. Taylor.

Ether extracts from solutions of indium chloride containing hydrochloric acid give a Raman spectrum which is attributed to the regular tetrahedral tetrachloroindate $InCl_4^-$ ion (ν_1 = 321 cm.$^{-1}$, strong, polarized; ν_2 = 89 cm.$^{-1}$, medium, depolarized; ν_3 = 337 cm.$^{-1}$, weak, diffuse, depolarized; ν_4 = 112 cm.$^{-1}$, medium, depolarized). The spectra of the aqueous solutions before extraction show that the tetrachloroindate ion is not the predominant indium-containing complex present. Extracts from gallium chloride solutions containing hydrochloric acid give the known spectrum of the tetrachlorogallate $GaCl_4^-$ ion. Extracts from ferric chloride solutions containing hydrochloric acid give a spectrum which is attributed to the tetrachloroferrate $FeCl_4^-$ ion and shows that its structure is regular tetrahedral (ν_1 = 330 cm.$^{-1}$, strong, polarized; ν_2 = 106 cm.$^{-1}$, medium; ν_3 = 385 cm.$^{-1}$, weak, diffuse; ν_4 = 133 cm.$^{-1}$, weak).

Extraction of Indium as $InCl_4^-$

Spectra of Extracts.—A 4M-aqueous solution (15 ml.) of indium chloride saturated with hydrogen chloride at room temperature was shaken with ether (22 ml.); two layers slowly formed. The volume of the ether layer was about 1 ml. larger than that of the original ether, and the aqueous layer showed a corresponding decrease in volume.

Table 1 gives the Raman frequencies observed for the solute in the ether extract. These were easily distinguishable from solvent frequencies, which are higher and relatively feeble.

TABLE 1. *Raman spectrum of extracts.*

$\Delta\nu$ (cm.$^{-1}$) From Hg 4358 Å	89	112	321	337
$\Delta\nu$ (cm.$^{-1}$) From Hg 4047 Å	89	112	320	336
Intensity, etc.	medium	medium	strong, sharp	weak, diffuse
Polarization	depol.	depol.	highly polarized	depol.

An identical spectrum was also observed for the ether layer obtained by extracting with an equal volume of ether an aqueous solution containing 0·85M-indium chloride and 8·5M-hydrochloric acid.

Attribution of Observed Spectrum to the Tetrachloroindate Ion.—The Raman spectrum shown in Table 1 is analogous to that previously reported [1] for the tetrabromoindate ion, and can be confidently attributed to the corresponding $InCl_4^-$ ion. From the totally symmetric stretching frequency ν_1 = 321 cm.$^{-1}$ we obtain $k_{In-Cl} = 2{\cdot}16 \times 10^5$ dynes/cm. for the stretching force constant.

Support for this attribution is obtained from a comparison with the spectra and stretching force constants of the isoelectronic species tetrachlorocadmate ion $CdCl_4^{2-}$ and stannic chloride (see upper half of Table 2). In particular, as the atomic number of the central

TABLE 2. *Spectra* (*cm.*$^{-1}$) *and stretching force constants* (*dynes/cm.*) *of isoelectronic species.*

Species XY_4	$\nu_2(E)$	$\nu_4(F_2)$	$\nu_1(A_1)$	$\nu_3(F_2)$	$10^{-5}k_{X-Y}$	Ref.
$CdCl_4^{2-}$	?	?	250	?	1·30	2
$InCl_4^-$	89	112	321	337	2·16	Present work
$SnCl_4$	104	134	366	403	2·80	3
$ZnCl_4^{2-}$	?	?	282	?	1·64	2
$GaCl_4^-$	114	149	346	386	2·50	4
$GeCl_4$	134	172	396	453	3·27	3

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[1] Woodward and Bill, *J.*, 1955, 1699, is considered to be Part I.

[2] Delwaulle, *Bull. Soc. chim. France*, 1955, 1294.

[3] Herzberg, " Infra-red and Raman Spectra," van Nostrand Co., New York, 1945, pp. 167 and 182.

[4] Woodward and Nord, *J.*, 1956, 3721.

metal atom progressively increases, the values of k_{X-Y} show the type of non-linear increase which (as pointed out by Woodward [5]) is characteristic of such isoelectronic triads. The lower half of Table 2 gives the corresponding comparison for the analogous isoelectronic triad $ZnCl_4^{2-}$, $GaCl_4^-$, and $GeCl_4$. The similarity with the triad including tetrachloroindate is obvious.

Comparison with tetrabromo- and tetraiodo-indate also supports the view that the observed spectrum is due to the tetrachloroindate ion (see upper half of Table 3). Moreover there is a close similarity with the corresponding data for the halide complexes of gallium (lower half of Table 3).

TABLE 3. *Spectra (cm.$^{-1}$) and stretching force constants (dynes/cm.) of analogous ions.*

Ion XY_4	$\nu_2(E)$	$\nu_4(F_2)$	$\nu_1(A_1)$	$\nu_3(F_2)$	$10^{-5}k_{X-Y}$	Ref.
$InCl_4^-$	89	112	321	337	2·16	Present work
$InBr_4^-$	55	79	197	239	1·83	1
InI_4^-	42	58	139	185	1·44	6
$GaCl_4^-$	114	149	346	386	2·50	4
$GaBr_4^-$	71	102	210	278	2·08	7
GaI_4^-	52	73	145	222	1·57	6

The results show that the indium is extracted by ether in the form of the ion pair $(H^+)(InCl_4^-)$, in which the H^+ is doubtless solvated. The two ether extracts which gave the Raman spectrum of Table 1 were analyzed chemically for indium and chlorine and the atomic ratio Cl/In was found to be 4·7 ± 0·1 in both. The excess over 4 can be explained as due to extraction of some hydrochloric acid into the ether layer. Some aqueous solutions with a high concentration of acid relative to that of indium chloride (*e.g.* 1·6M-indium chloride + 15M-hydrochloric acid and 1·2M-indium chloride + 12M-acid) were completely miscible with equal volumes of ether.

Raman Spectra of Aqueous Solutions.—The aqueous solutions before extraction showed no trace of the spectrum of the tetrachloroindate ion: even the most intense line (ν_1 = 321 cm.$^{-1}$) was absent. Evidently the tetrachloroindate ion is by no means the predominant indium-containing species. Thus the case is analogous to that of indium bromide solutions; [1] but quite different from corresponding acid aqueous solutions of gallium chloride or bromide, which show only the spectra of tetrachloro- and tetrabromogallate ions respectively.[4,7]

The principal feature of the Raman spectrum of aqueous 4M-indium chloride saturated with hydrogen chloride was a band (or broad line) centred at about 283 cm.$^{-1}$. There were also indications of feebler lines at about 130 and 175 cm.$^{-1}$. Solutions with lower concentrations of indium showed only the principal band. A series was investigated in which the concentration of indium chloride was kept constant at 1·2M and that of hydrochloric acid was progressively increased from 0·4 to 15M. The centre of the Raman band moved gradually to lower frequencies (from about 295 to about 275 cm.$^{-1}$) as the acid concentration was increased. In the solutions of highest acid concentrations the band became noticeably sharper.

These spectra must be due to complexes other than the tetrachloroindate ion, and it appears probable that pentachloroindate $InCl_5^{2-}$ and hexachloroindate $InCl_6^{3-}$ are principally concerned. The most intense Raman features will be due to symmetrical In–Cl stretching, and the frequencies will be expected to decrease in the order $InCl_4^- > InCl_5^{2-} > InCl_6^{3-}$. On the assumption that the most intense stretching frequency of the pentachloroindate ion is about 295 cm.$^{-1}$ (which is reasonable in relation to that of the tetrachloroindate ion and to the value, 356 cm.$^{-1}$, for the isoelectronic species antimony

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[5] Woodward, *Trans. Faraday Soc.*, 1958, **54**, 1271.
[6] Woodward and Singer, *J.*, 1958, 716.
[7] Woodward and Nord, *J.*, 1955, 2655.

pentachloride[8]) and that the symmetrical In–Cl stretching frequency of hexachloroindate ion is about 275 cm.$^{-1}$ (which is reasonable in relation to the value, 311 cm.$^{-1}$, for the isoelectronic hexachlorostannate[9] species $SnCl_6^{2-}$), the observed progressive displacement of the unresolved Raman band to lower frequencies with increasing concentration of hydrochloric acid is understandable in terms of a progressive increase in the concentration of hexachloroindate at the expense of pentachloroindate. The presence of two other feebler frequencies at high concentrations of indium and acid is consistent with the presence of regular octahedral hexachloroindate ion with the Raman-active frequencies $\nu_1(A_1) \sim 275$, $\nu_2(E) \sim 175$ and $\nu_5(F_2) \sim 130$ cm.$^{-1}$ (cf. isoelectronic hexachlorostannate[9] with $\nu_1 = 311$, $\nu_2 = 229$, and $\nu_5 = 158$ cm.$^{-1}$).

Despite the relatively low concentration of tetrachloroindate in the aqueous solution, as compared with pentachloro- and hexachloro-indate ions, it is the tetrachloroindate ion that is preferentially (and apparently exclusively) extracted into ether. The explanation is doubtless concerned with an adverse effect of the higher anionic charges in aggregates of the type $(H^+)_2(InCl_5^{2-})$ and $(H^+)_3(InCl_6^{3-})$ as compared with $(H^+)(InCl_4^-)$.

Extraction of Gallium as $GaCl_4^-$

Aqueous solutions of gallium chloride containing hydrochloric acid show only the Raman spectrum of the tetrachlorogallate ion.[4] Ether extracts from these solutions were found, as expected, to show the same spectrum. The measured frequencies are given in Table 4. Within the limits of experimental error they are the same in ether layers as in water. (The ν_3 line is diffuse and its frequency difficult to measure precisely.)

TABLE 4. *Raman frequencies of* $GaCl_4^-$ (*cm.*$^{-1}$).

	ν_2	ν_4	ν_1	ν_3
Aqueous solutions	114	149	346	386
Ether extracts	116	150	345	381

By analogy we conclude that the frequencies given in Table 1 for the tetrachloroindate ion (observed only in ether extracts) are not subject to any appreciable effect of environment.

Extraction of Iron as $FeCl_4^-$

In 1892 Rothe[10] discovered that iron is extracted by ether from aqueous solutions of ferric chloride containing hydrochloric acid. This appears to have been the first example of the solvent extraction of an inorganic complex to be reported, and it has subsequently been studied in detail by a number of workers. Axelrod and Swift[11] concluded from analyses that the formula of the extracted species was $HFeCl_4$; and this was confirmed by Nachtrieb and his co-workers,[12] who also studied the absorption spectra of the extracts. Later studies establishing the presence of the tetrachloroferrate ion in the organic layer were made by Friedman[13] and by Myers, Metzler, and Swift.[14] Hitherto no determination of the structure of this ion in solution appears to have been made.

Raman Spectra of Ether Extracts.—15 ml. of a 0·7M-aqueous solution of ferric chloride containing 6M-hydrochloric acid were shaken with an equal volume of ether. The resulting ether layer had a volume of about 16 ml., and the water layer about 14 ml. The ether extract was pale greenish-yellow, in contrast to the much deeper yellow colour of the aqueous solution. Owing to absorption it was not possible to use either the blue mercury

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[8] Redlich, Kurz, and Stricks, *Monatsh.*, 1937, **71**, 1.

[9] Woodward and Anderson, *J.*, 1957, 1284.

[10] Rothe, *Stahl u. Eisen*, 1892, **12**, 1052.

[11] Axelrod and Swift, *J. Amer. Chem. Soc.*, 1940, **62**, 33.

[12] Nachtrieb and Conway, *J. Amer. Chem. Soc.*, 1948, **70**, 3547; Nachtrieb and Fryxell, *ibid.*, p. 3552; *idem, ibid.*, 1952, **74**, 897.

[13] Friedman, *J. Amer. Chem. Soc.*, 1952, **74**, 5.

[14] Myers, Metzler, and Swift, *J. Amer. Chem. Soc.*, 1950, **72**, 3767.

line (4358 Å) or the violet line (4047 Å) to excite the Raman spectrum, but excitation with the green line (5461 Å) gave the spectrum shown in Table 5. Owing to its deeper colour the aqueous solution was not investigated.

Attribution of Spectrum to Regular Tetrahedral Tetrachloroferrate Ion.—The four-line pattern, with one highly polarized intense line, is that expected for a regular tetrahedral species of XY_4 type, and the spectrum can be confidently attributed to the tetrachloroferrate ion with this structure. The only unusual feature is the weakness of the 133 cm.$^{-1}$ line. From $\nu_1 = 330$ cm.$^{-1}$ we obtain $k_{\text{Fe}-\text{Cl}} = 2{\cdot}28 \times 10^5$ dynes/cm. for the bond-stretching force constant.

TABLE 5. *Raman spectrum of the tetrachloroferrate ion.*

$\Delta\nu$ (cm.$^{-1}$)	106	133	330	385
Intensity, etc.	medium	weak	strong, sharp	weak, diffuse
Polarization	—	—	highly polarized	—

The most nearly related species for which data are available is titanium tetrachloride, and the comparison is shown in Table 6. As expected, the frequencies and force constant of the negatively charged tetrachloroferrate ion are all lower than those of the neutral titanium tetrachloride molecule. In support of the force constant of the ion we note that the ratio of its value to that of titanium tetrachloride (*i.e.* 2·28/3·11 = 0·73) is nearly the same as the ratio of the corresponding force constant of the singly negative tetrachlorogallate ion to that of the neutral germanium tetrachloride molecule (*i.e.* 2·50/3·27 = 0·76; see Table 2).

TABLE 6. *Comparison of the tetrachloroferrate ion and titanium tetrachloride.*

Species XY_4	$\nu_2(E)$	$\nu_4(F_2)$	$\nu_1(A_1)$	$\nu_3(F_2)$	$10^{-5}k_{X-Y}$	Ref.
$FeCl_4^-$	106	133	330	385	2·28	Present work
$TiCl_4$	120	141	386	495	3·11	3

The spectrum shows that the tetrachloroferrate has the regular tetrahedral structure. This is in accordance with expectation[15] for a weak-field spin-free d^5 arrangement of the *d*-electrons of the central iron atom, as verified by the observation that the magnetic moment has the normal spin-free value (5·95 Bohr magnetons) in an ether extract.[16]

As with indium chloride, the iron is preferentially (and apparently exclusively) extracted as the singly charged complex ion, although (as is evident from the different colour) this is not the only species, and possibly not the predominant one, present in the aqueous solution from which the extract is made.

EXPERIMENTAL

Preparation of Aqueous Solutions.—Indium chloride solutions were prepared by dissolving weighed quantities of pure indium metal in excess of concentrated hydrochloric acid. The higher concentrations of acid were obtained by passing in hydrogen chloride. To prepare gallium chloride solutions, metallic gallium (previously granulated by shaking the molten metal in warm water) was dissolved in concentrated hydrochloric acid. Ferric chloride solutions were prepared by dissolving the pure anhydrous compound in hydrochloric acid.

Extraction.—The aqueous solutions were shaken for at least 2 min. at room temperature with the appropriate volumes of pure peroxide-free ether.

Chemical Analyses of Indium Extracts.—Indium was determined as In_2O_3 by the method used in Part I.[1] Chlorine was determined as silver chloride. Triplicate analyses gave consistent results. The limits of error of Cl : In ratios are about ±0·1.

Raman Spectra.—Solutions were filtered carefully through paper (or, where this was impracticable owing to high acid concentration, through sintered glass) into the Raman cell.

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[15] Gillespie and Nyholm, *Quart. Rev.*, 1957, **11**, 339.
[16] Metzler and Myers, *J. Amer. Chem. Soc.*, 1950, **72**, 3776.

The spectra were excited by suitable lines from a Toronto-type mercury-arc source, other primary lines being suppressed by appropriate filters. All the spectra were recorded photographically, a Hilger E 612 two-prism spectrograph being used with F 5·6 camera (dispersion about 95 cm.$^{-1}$ per mm. in the region of lines excited by Hg 4358 Å and about 160 cm.$^{-1}$ per mm. in the region of lines excited by Hg 5461 Å). For each solution a number of spectra were photographed with different exposure times on Kodak Special Scientific (Oa, G) plates. Frequencies were measured in the usual manner with an iron-arc spectrum as standard. The limits of error of $\Delta\nu$ values are approx. ± 2 cm.$^{-1}$ for strong sharp lines. For weak and diffuse features the errors may be somewhat larger. States of polarization of lines were determined qualitatively by the method of polarized incident light.

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THE INORGANIC CHEMISTRY LABORATORY,
SOUTH PARKS ROAD, OXFORD.

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