TABLE 1 — REACTIONS OF Hf(OPr$^i$)$_4$.Pr$^i$OH WITH ALKALINE EARTH METALS (Mg, Ca, Sr or Ba)

| Reactants (g) | | Reaction time (hr) | b.p. (°C/0. mm) and yield (%) | Product | Found (Calc.) (%) | | |
|---|---|---|---|---|---|---|---|
| Metal | Hf(OPr$^i$)$_4$. Pr$^i$OH | | | | Metal | Hf | Isopropoxy |
| | | | 1:4 MOLAR RATIO | | | | |
| Mg (0·09) | 4·63 | 65 | 165/0·1 (55) | Mg[Hf$_2$(OPr$^i$)$_9$]$_2$ | 1·34 (1·33) | 39·56 (39·62) | 59·21 (59·05) |
| Ca (0·09) | 4·12 | 165 | S. 180-90/0·1 (40) | Ca[Hf$_2$(OPr$^i$)$_9$]$_2$ | 2·16 (2·20) | 39·42 (39·26) | 57·96 (58·44) |
| Sr (0·25) | 5·33 | 10 | S. 180-5/0·05 (60) | Sr[Hf$_2$(OPr$^i$)$_9$]$_2$ | 4·64 (4·66) | 38·20 (38·28) | 57·70 (57·06) |
| Ba (0·25) | 3·47 | 20 | S. 230-40/0·05 (35) | Ba[Hg$_2$(OPr$^i$)$_9$]$_2$ | 7·14 (7·17) | 37·35 (37·28) | 54·95 (55·55) |
| | | | 1:3 MOLAR RATIO | | | | |
| Mg (0·03) | 1·78 | 60 | 180/0·1 (60) | Mg Hf$_3$(OPr$^i$)$_{14}$ | 1·74 (1·73) | 38·58 (38·61) | 59·82 (59·65) |
| Ca (0·08) | 2·97 | 170 | S. 190-5/0·05 (50) | Ca Hf$_3$(OPr$^i$)$_{14}$ | 2·84 (2·83) | 38·01 (38·17) | 59·12 (59·98) |
| Sr (0·19) | 3·12 | 15 | S. 210-20/0·1 (40) | Sr Hf$_3$(OPr$^i$)$_{14}$ | 6·10 (6·04) | 36·87 (36·91) | 56·94 (57·05) |
| Ba (0·26) | 2·71 | 25 | S. 250-60/0·05 (30) | Ba Hf$_3$(OPr$^i$)$_{14}$ | 9·15 (9·13) | 35·82 (35·71) | 55·35 (55·16) |

The NMR spectra (Varian-60) of I and II exhibited only a single methyl doublet suggesting rapid interchange between bridging and terminal isopropoxy groups.

All the manipulations were carried out under anhydrous conditions.

Hafnium isopropoxide isopopanolate was prepared by ammonia method[2] from anhydrous HfCl$_4$.

Isopropoxy group was estimated by the oxidation of potassium dichromate[3]. Hafnium, magnesium, calcium, strontium and barium were estimated gravimetrically as HfO$_2$, MgNH$_4$PO$_4$.6H$_2$O, CaC$_2$O$_4$.H$_2$O, SrSO$_4$ and BaSO$_4$ respectively.

*Reaction of mgnesium with Hf(OPr$^i$)$_4$.Pr$^i$OH in molar ratios 1:4* — Magnesium (0·09 g) was dissolved in a solution of Hf(OPr$^i$)$_4$.Pr$^i$OH(4·63 g)$_4$. in isopropanol (~40 ml) in the presence of HgCl$_2$ (0·01 g) as catalyst, by refluxing for 65 hr. The white crystals appeared after leaving overnight. Excess of the solvent was removed and the product dried under reduced pressure. The white crystalline solid Mg [Hf$_2$(OPr$^i$)$_9$]$_2$ obtained could be distilled at 165°/0·1 mm in 55% yield.

Analyses of this product and the details of other similar reactions are given in Table 1.

*Reaction in molar ratio 1:3* — Magnesium (0·03 g) was dissolved in the solution of Hf(OPr$^i$)$_4$.Pr$^i$OH (1·78 g) in isopropanol (≈ 40 ml) in presence of HgCl$_2$ (0·008 g) as catalyst. This mixture was refluxed for about 60 hr. After leaving this solution overnight, a white crystalline product appeared. Excess of the solvent was removed and the residue was dried *in vacuo* to give a white crystalline product, MgHf$_3$(OPr$^i$)$_{14}$, which could be distilled at 180°/0·1 mm in 60% yield.

Details of this and other similar reactions are given in Table 1.

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## Solvent Extraction Behaviour of Tris(oxalato)Co(III) with Long-chain Amines: Part II — Extraction from Hydrochloric & Sulphuric Acid Solutions

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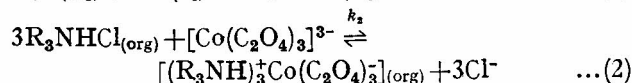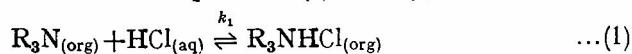Chemistry Division, Bhabha Atomic Research Centre Trombay, Bombay 400085

**Extraction of tris(oxalato)Co(III) anion into long-chain amines, viz. primene JMT, Amberlite LA-2, tri-n-hexylamine and triisooctylamine, in xylene, toluene, CCl$_4$ or nitrobenzene as diluents from hydrochloric and sulphuric acid solutions has been studied. In dilute solutions of the amines, the extraction follows the order primary > tertiary > secondary from HCl solutions, while the order primary ≃ secondary > tertiary is followed for extraction from H$_2$SO$_4$ solutions. On the other hand, for concentrated solutions of the same amines (2%), the order of extraction is reversed. The results indicate that salts of Amberlite LA-2 and triisooctylamine are monomers, whereas primene JMT and tri-n-hexylamine form aggregates to a certain extent. Nitrobenzene (as diluent) is found to increase the extraction, except in the case of primene JMT whereas carbon tetrachloride decreases the extraction in all the cases.**

IN continuation of our work[1] on extraction of tris(oxalato)Co(III) anion by several long-chain amines from essentially perchloric acid solutions,

we report here the results of studies on the extraction of this compound from hydrochloric acid and sulphuric acid systems.

*Materials and methods* — The amines employed were primene JMT, Amberlite LA-2, tri-*n*-hexylamine (THA) and triisooctylamine (TIOA). The diluents used were xylene, toluene, carbon tetrachloride and nitrobenzene. Potassium tris(oxalato)Co(III), tagged with $^{60}$Co, was prepared and purified as described earlier[1]. The concentration of the complex was always kept at $1 \times 10^{-3} M$. The experimental procedure including the method of measurement was the same as described earlier[1].

*Results and discussion* — The extraction of anionic complex by a tertiary amine from hydrochloric acid involves the equilibria (1) and (2).

$$R_3N_{(org)} + HCl_{(aq)} \overset{k_1}{\rightleftharpoons} R_3NHCl_{(org)} \qquad ...(1)$$

$$3R_3NHCl_{(org)} + [Co(C_2O_4)_3]^{3-} \overset{k_2}{\rightleftharpoons}$$
$$[(R_3NH)_3^+Co(C_2O_4)_3^-]_{(org)} + 3Cl^- \qquad ...(2)$$

Examining Eq. (2) in the light of the treatment given earlier[1], one gets:

$$\log E = \log k_2 - 3 \log [Cl^-] + 3 \log [R_3NHCl] \qquad ...(3)$$

From Eq. (1)

$$k_1 = \frac{[R_3NHCl]_{org}}{[R_3N]_{org}[HCl]_{aq}} \qquad ...(4)$$

At constant [HCl],

$$\log [R_3NHCl] = \log C_1 + \log [R_3N] \qquad ...(5)$$

and at constant [amine],

$$\log [R_3NHCl] = \log C_2 + \log [HCl] \qquad ...(6)$$

Substituting Eq. (5) in Eq. (3) one gets, at constant [Cl⁻],

$$\log E = 3 \log [R_3N] + C \qquad ...(7)$$

Thus, a plot of log $E$ against log $[R_3N]$ should give a slope of 3 if no other parameter interferes with the extraction.

Similarly at constant [amine] substitution of Eq. (6) in Eq. (3) gives

$$\log E = C + 3 \log [HCl] - 3 \log [Cl^-] \qquad ...(8)$$

The term log [Cl⁻] represents the competition from the anion whereas the term log [HCl] represents dependency on the conversion of the amine into amine salt. Earlier[1] it was shown that chloride and sulphate ions, at the concentrations obtained in these experiments, do not compete with the complex for extraction and the term log [Cl⁻] can be neglected. Hence Eq. (8) may be reduced to Eq. (9).

$$\log E = C_1 + 3 \log [HCl] \qquad ...(9)$$

A plot of log $E$ against log [HCl] should be linear with slope equal to 3. Under the experimental conditions one can use concentration instead of mean activity of the acid.

Though the equations are derived for a tertiary amine and HCl system, these hold good for other amines as well as sulphuric acid system. Only difference is that instead of molarity, normality of sulphuric acid is used in plotting the data.

*Acid-dependency on extraction into amines using xylene as the diluent* — Fig. 1 shows the acid-depen-

dency on extraction of the complex into different amines in xylene from HCl. The corresponding plots for sulphuric acid systems are similar. The order of extraction with 2% amine solutions is secondary > tertiary > primary. When log $E$ was plotted against log [acid], a slope of 3 was obtained for TIOA and LA-2 from both HCl and $H_2SO_4$ solutions. The slope for THA was approximately 5 and that for primene JMT 6·5. Considering that the anion is trivalent a slope of 3 is expected. The higher value in the case of JMT could be due to amine aggregation as primary amines are known to aggregate to a greater extent than secondary and tertiary amines[2]. However, the slope observed in the case of THA is difficult to explain. If the aggregation is due to hydrogen bonding only, then a straight-chain amine like THA may have a larger aggregation than the branched-chain amines like LA-2 or TIOA.

*Amine-dependency on extraction in toluene from hydrochloric and sulphuric acid solutions* — Plots of log $E$ against log amine (%) in $0·01N$ HCl solutions are shown in Fig. 2 for different amine solutions in toluene. A slope of 3 was obtained for TIOA, THA and LA-2, which means that the requirements of stoichiometry have been met and hence the chlorides
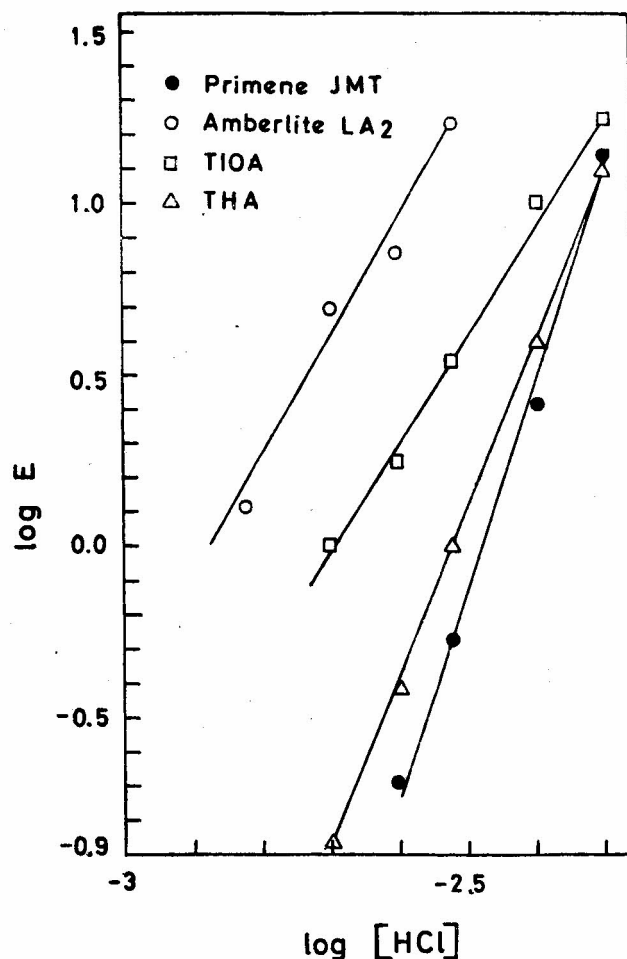


Fig. 1 — Extraction of $Co(C_2O_4)_3^{3-}$ into different amines from hydrochloric acid: dependence on hydrochloric acid concentration

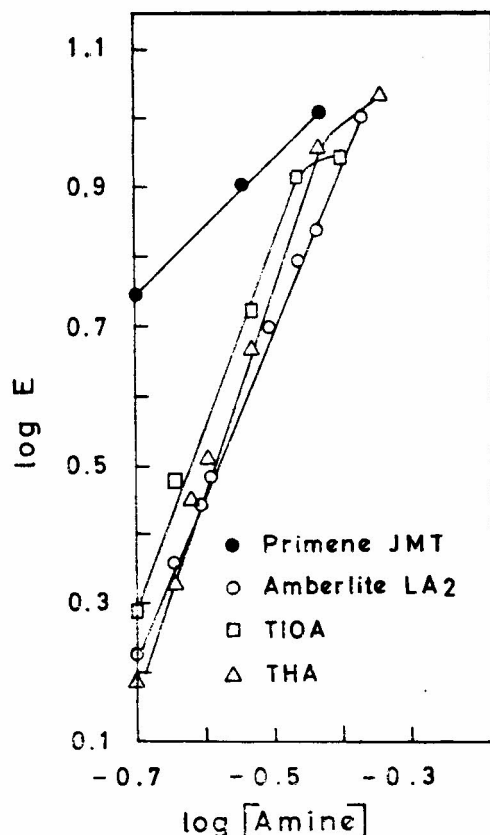Fig. 2 — Extraction of $Co(C_2O_4)_3^{3-}$ into different amines from hydrochloric acid: dependence on amine concentration

Table 1 — Extraction of Tris(oxalato)Co(III) into 2% TIOA in Nitrobenzene from HCl Solutions of Different Normality

| [HCl] $N \times 10^3$ | $\dfrac{\text{Normality of acid}}{\text{Normality of complex}} \times \dfrac{100}{3}$ | $K$ | Extraction (%) |
|---|---|---|---|
| 1·2 | 40 | 0·74 | 40·23 |
| 1·8 | 60 | 1·476 | 59·6 |
| 2·4 | 80 | 3·34 | 76·9 |
| 3·0 | 100 | 10·6 | 91 |

tris(oxalato)Co(III) was studied from different HCl solutions into TIOA in nitrobenzene. It was seen that the equilibrium (Eq. 2) shifts completely towards the right hand side. The extraction into 2% TIOA in nitrobenzene, from different HCl solutions, without pre-equilibrating the organic layer, is given in Table 1. It can be seen that the extraction is dependent on the stoichiometric ratio of amine hydrochloride to complex concentration (Table 1).

Extraction into a mixed solvent of toluene and nitrobenzene was studied from 0·003$M$ HCl by variation method. A plot of $E$ against ratio of nitrobenzene to total volume was linear in the case of TIOA and Amberlite LA-2.

For THA, the extraction was similar to that for TIOA in initial stages but afterwards, the effect is not very prominent. Nitrobenzene did not have any effect in the extraction with primene JMT indicating that nitrobenzene has less or negligible influence in systems where amines aggregate.

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of these amines can be monomeric. In the case of primene JMT, the slope is 1. The order of extraction obtained was primene JMT > TIOA > THA ≃ LA-2.

The extraction of tris(oxalato)Co(III) decreased with the increase in concentration of primene JMT in xylene, at fixed aqueous phase concentration (0·003$N$) of HCl and $H_2SO_4$. The decrease in the extraction of the complex may be due to amine aggregation which may explain also the low slope value of 1 obtained in the case of primene JMT in earlier experiments.

Somewhat similar results were obtained with 0·01$N$ $H_2SO_4$ also. For TIOA and THA, a slope of 3 was obtained. But with primene JMT and LA-2, the extraction was more than 90% even with 0·2% solutions of amines and hence it was difficult to make graphical analysis. The order of extraction was primene JMT ≃ LA-2 > TIOA ≃ THA.

When log $E$ was plotted against log amine (%) in the case of extraction with $CCl_4$, the slopes were similar to those obtained in the case of toluene but extraction was less.

*Extraction with amines using nitrobenzene as the diluent* — The amine salts usually exist as ion-pairs in organic diluents of low dielectric constants. The degree of the ion-pair formation depends on the nature of amine salt and the organic diluent. If the ion-pair formation is more in diluents having high dielectric constants, the extraction may also increase. To study this effect, the extraction of

## Exchange Studies of Complexes of Co(II) with Oximes of 2-Hydroxyacetophenone, Resacetophenone & 5-Nitroresacetophenone

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Isotopic exchange data of the complexes of Co(II) with 2-hydroxyacetophenone oxime, resacetophenone oxime and 5-nitroresacetophenone oxime in methyl ethyl ketone are reported. In all the three cases the exchange obeyed second order kinetics. The energy of activation in the case of 2-hydroxyacetophenone oxime complex is determined to be 16·55 kcal/mole. Differences in exchange rates were explained in terms of substituent effects.

STUDY of the exchange of metal ions between the complex containing the metal and the free metal ion gives evidence on the nature of bonding in the complex. Exchange reactions of the transition metal complexes with the oximes of 2-hydroxy-