

7.60, 7.78, 8.05, 8.13, and 8.29 in a 1:1:1:1:3:3:3:3:2:1:6 ratio.

Pyrazole Complex of Diethylbis(1-pyrazolyl)boratodicyarbonyl-tungsten π -Allyl.—To 0.1 mol of $K(C_2H_5)_2B(pz)_2W(CO)_4$, prepared *in situ*, was added at room temperature 15 g of allyl bromide. On heating to 45°, 3.6 l. of gas was evolved. The solution was poured into 1 l. of ice water and the product was extracted with methylene chloride and purified by chromatography on alumina. There was obtained 32 g (58%) of air-stable yellow solid. It is very soluble in ether and halocarbons. Recrystallization from ethanol yielded yellow crystals, mp 147–148°. *Anal.* Calcd for $C_{18}H_{24}BN_6O_2W$: C, 39.2; H, 4.54; N, 15.2. Found: C, 39.7; H, 4.74; N, 15.5. Ir (cyclohexane): 1935 and 1846 cm^{-1} . Nmr: τ 2.1 d (with shoulder) ($J = 2.0$ Hz), 2.28 d ($J = 2.3$, $J' = 0.5$ Hz), 2.86 m, 3.80 t ($J = 2.2$ Hz), 6.8 m + s, 8.2 d ($J = 8$ Hz), ~ 9.1 m, 9.62 "s" in a 3:2:1:3:3:2:5:5 ratio.

Pyrazole Complex of Diphenylbis(1-pyrazolyl)boratodicyarbonyl-tungsten π -Allyl.—This compound was prepared as in the preceding experiment but using $Na(C_6H_5)_2B(pz)_2$ instead of $K(C_2H_5)_2B(pz)_2$. The product was obtained in 49% yield as yellow crystals and recrystallized from chloroform; mp 202–204°. *Anal.* Calcd for $C_{26}H_{24}BN_6O_2W$: C, 48.3; H, 3.72; N, 13.0. Found: C, 48.4; H, 4.62; N, 12.7.

Pyrazole Complex of Diethylbis(1-pyrazolyl)boratodicyarbonyl-molybdenum π -Allyl.—From the preparation of IIIb a 10% yield of a yellow solid, purified by chromatography and recrystallized from hexane, was obtained. This compound, mp 131–132°, was also obtained in 100% yield by the reaction of IIIb with 1 equiv of pyrazole. *Anal.* Calcd for $C_{18}H_{24}BMoN_6O_2$: C, 46.5; H, 5.39; N, 18.1. Found: C, 46.2; H, 5.50; N, 18.0.

The infrared spectrum showed, apart from carbonyl peaks at 1942 and 1857 cm^{-1} , the NH band at 3398 cm^{-1} . The nmr spectrum clearly demonstrated the presence of the $(C_2H_5)_2B(pz)_2$ ligand and of one additional pyrazole: τ 1.30 s (broad), 2.02 d

(unresolved), 2.21 d ($J = 2.0$ Hz), 2.31 d ($J = 2.4$ Hz), 2.94 d (unresolved), 3.83 t ($J = 2.2$ Hz), 5.8 m, 6.62 d ($J = 7.0$ Hz), 8.43 d ($J = 9.5$ Hz), ~ 9.1 m, 9.66 "d" in a 1:1:2:2:1:3:1:2:2:5:5 ratio. These were assigned to the NH, 3-H of pyrazole, 3-H's of ligand, 5-H's of ligand, 5-H of pyrazole, 4-H's of pyrazole and ligand, allylic 1-H, allylic 2-H, allylic 3-H, pseudoaxial ethyl, and pseudoequatorial ethyl, respectively.

Pyrazole Complex of Diphenylbis(1-pyrazolyl)boratodicyarbonyl-molybdenum π -Allyl.—To a stirred solution of 1.50 g of $(C_6H_5)_2B(pz)_2Mo(CO)_2$ π - C_2H_5 in 20 ml of methylene chloride was added 1 g (large excess) of pyrazole. The color changed immediately from orange to yellow. Evaporation of the solution and washing of the residue with aqueous methanol gave 1.65 g (96%) of yellow solid which was purified by recrystallization from a toluene-heptane mixture; mp 206–208° dec with prior darkening from $\sim 190^\circ$. *Anal.* Calcd for $C_{26}H_{24}BMoN_6O_2$: C, 55.7; H, 4.47; N, 15.0. Found: C, 55.5; H, 4.46; N, 14.9. Ir (cyclohexane): 1947, 1863 cm^{-1} .

Dihydrobis(3,5-dimethyl-1-pyrazolyl)boratocycloheptatrienyl-molybdenum Dicarboxylate.—To a freshly prepared solution of 13.7 g (0.05 mol) of cycloheptatrienylmolybdenum dicarbonyl iodide²¹ in 125 ml of DMF was added 14.1 g (0.06 mol) of $KH_2B(3,5-(CH_3)_2pz)_2$. The mixture was stirred at 50° until the color changed from greenish to deep red. The solution was poured into 500 ml of ice water and the precipitated product was isolated by filtration and purified by chromatography. It was obtained in 13.6-g (60%) yield and was recrystallized from ethyl acetate; mp 179–181° dec. *Anal.* Calcd for $C_{19}H_{23}BMoN_4O_2$: C, 51.2; H, 5.38; N, 12.5. Found: C, 51.2; H, 5.48; N, 12.4. Ir (cyclohexane): 1961, 1883 cm^{-1} . Uv: two superimposed bands at 333 $m\mu$ (ϵ 8170) and 305 $m\mu$ (ϵ 8300). The nmr spectrum has singlets at τ 4.30, 4.36, 4.76, 7.53, 7.58, 7.87, and 7.90 in 1:1:7:3:3:3:3 ratio.

(21) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, New York, N. Y., 1965, p 141.

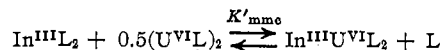
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Mixed-Metal Complexes between Indium(III) and Uranium(VI) with Malic, Citric, and Tartaric Acids¹

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The formation of mixed-metal complexes between indium(III) and uranium(VI) with various hydroxycarboxylic acids was studied using spectrophotometric, potentiometric, and solvent extraction methods. Over wide concentration ranges, it was shown that the reactions for the formation of the indium(III) uranium(VI) malate, citrate, and tartrate mixed-metal complexes can be written



where L is the hydroxycarboxylic acid ligand. At 25° and pH 4 values of K'_{mmc} are as follows: malate, 30; citrate, 720; tartrate, 31. In order to study these reactions, it was first necessary to investigate the polymerization of indium(III) and dimerization of uranium(VI) complexes.

Introduction

The formation of mixed-metal complexes (henceforward denoted mmc) between a hydroxycarboxylic acid and a variety of different metal ions has been reported

in the literature.^{2,3} It has been recently found that the basic malic acid structure is necessary for the formation of an mmc between Cr(III) and In(III).^{2a} Some mmc's have been assigned the formula ABL_2 where A

(2) (a) T. W. Gilbert, L. Newman, and P. Klotz, *Anal. Chem.*, **40**, 2123 (1968); (b) H. M. N. H. Irving and W. R. Tomlinson, *Chem. Commun.*, 497 (1968).

(3) R. C. Srivastava and T. D. Smith, *J. Chem. Soc. A*, 2192 (1968).

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(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

and B are two different metal ions and L is the hydroxycarboxylic acid ligand, but other formulas have also been reported.^{3,4}

Little is known, however, of the structure of these complexes or of the equilibria involved in systems where mmc's occur. The purpose of this study was to investigate thoroughly a selected set of systems and obtain quantitative data which would determine factors influencing the stability of these complexes. Since hydroxycarboxylic acids are widely used buffering agents, this information is also of practical importance.

Preliminary work showed that very stable mmc's are formed between U(VI) and In(III) in malic, citric, and tartaric acids at pH 4. Quantitative information on the dimerization of uranium(VI) malate, citrate, and tartrate, which is a competitive reaction to mmc formation, was available.⁵⁻⁷ These systems were therefore chosen for the study.

Experimental Section

Reagents.—Indium(III) perchlorate solutions were prepared from reagent grade (G. F. Smith) solid and standardized gravimetrically as the oxide. National Bureau of Standards U_3O_8 was dissolved in 1:1 HNO_3 and diluted to give a 0.1 M $UO_2(NO_3)_2$ stock solution. Stock solutions (4 M) of sodium chloride and sodium nitrate were prepared using analytical grade reagents. For adjustment of pH, sodium hydroxide solutions were prepared from analytical grade solid. A 2.5 M acetate buffer which gave a pH of ~ 4 upon fivefold dilution was prepared from analytical grade sodium acetate and glacial acetic acid. Solutions of malic acid (Aldrich) and citric and tartaric acids (both J. T. Baker Analyzed Reagent) were standardized by titration against standard alkali. In experiments where it was found necessary to reduce levels of metal ion impurities, which arose primarily from the sodium hydroxide solution used in adjusting the pH's of solutions, we resorted to the utilization of buffer solutions prepared from citric acid and analytical grade trisodium citrate dihydrate. Similarly, sodium hydrogen tartrate crystals were prepared by mixing equimolar quantities of analytical grade *d*-tartaric acid and disodium tartrate. The solution of sodium hydrogen tartrate was standardized by titration against sodium hydroxide.

Decimolar solutions of dicrotalic acid and DL-chlorosuccinic acid (both from K & K Laboratories); lactic acid (J. T. Baker); aspartic acid, succinic acid, and tricarballic acid (all Eastman White Label); and tartronic, citramalic, and β -hydroxypropionic acids (all Aldrich) were prepared from weighed amounts of the reagents.

The sources and methods of preparation of thenoyltrifluoroacetone (HTTA) and $^{114}In(III)$ have been previously described.^{2a}

Experimental Technique.—Spectra were recorded on a Cary Model 14 spectrophotometer. The measurement of pH was made using a Corning semimicro combination pH electrode in conjunction with an Orion Model 801 digital pH meter. In solvent extraction experiments, the pH was adjusted to 4.00 ± 0.01 with respect to a buffer prepared from analytical grade potassium hydrogen phthalate.

Solvent extraction experiments were carried out in stoppered, jacketed glass cells maintained at $25.0 \pm 0.05^\circ$. The aqueous phase was contacted with an equal volume of HTTA in benzene using magnetic stirring. The HTTA concentration was generally chosen to give a distribution coefficient (*D*) for In(III) of approximately unity. Contacting times were varied between

15 min and 1 hr without appreciably affecting measured "*D*" values. Phase separation was good, but if very large or small "*D*" values were anticipated, both phases were centrifuged separately. Aliquots of each phase were γ counted in a well-type scintillation counter. Distribution coefficients for U(VI) were measured by fluorometric analysis of the organic phase using a Jarrel-Ash fluorometer.

In solvent extraction studies where interference from metal ion impurities was feared, all solutions were prepared in doubly distilled water (Barnstead quartz still) and precontacted with HTTA in benzene to remove extractable metal ions. The sodium nitrate stock solution was also precontacted with HTTA in benzene. Hydroxycarboxylic acid buffers as described in the reagent section were used so that sodium hydroxide was only needed for the final slight pH adjustment.

Results

Spectrophotometric Evidence for Mixed-Metal Complex Formation between Uranium(VI) and Indium(III) with Some Hydroxycarboxylic Acids.—The spectra of U(VI) in the presence of an excess of malic or citric acid at pH 4 show a maximum in the region of 430 nm. This absorption is increased in the presence of In(III) indicating an interaction between the complexes of the two metal ions. Using metal ion concentrations of 2×10^{-3} M and a tenfold excess of ligand, a modification of the U(VI) peak in the presence of In(III) was taken as an indication of the formation of an mmc.

Clear effects were exhibited by citric, malic, tartaric, and citramalic acids. Of the acids lactic, dicrotalic, and aspartic, only lactic showed an effect, but a pH and ligand concentration dependence of the absorbance precluded a definite conclusion. Dicrotalic acid showed an increased absorption, less than for the first group of acids, possibly indicating a weak mmc. Spectra with aspartic acid were taken at a pH of 3.5 to prevent precipitation. A very slight (5%) increase in absorbance could be due to weak mmc formation. Tartronic and chlorosuccinic acids showed no evidence for mmc formation. Tricarballic, succinic, and β -hydroxypropionic acids gave precipitates in the presence of U(VI) and In(III) preventing the recording of spectra.

It has been reported⁸ that in the spectra of copper(II) citrate there is a peak characteristic of $Cu^{II}-RCOOH$ complexes and another peak found only in the citrate complex and therefore corresponding to a chelate containing the hydroxy group. The uranium spectra were therefore more closely examined by us. It was noticed that in malate, citrate, citramalate, and tartrate media, solutions containing both In(III) and U(VI) exhibited peaks at 555 and 660 nm. In corresponding solutions containing no In(III), the peaks were present in every case except for tartrate. The peaks at 555 and 660 nm were always much smaller than the ones at 430 nm. It is interesting that the spectrum of uranium(VI) tartrate does not contain these peaks. Normally, the above spectra were of solutions which had been stored in the dark for several hours. However, the spectrum of U(VI) in citramalic acid was recorded immediately after preparation and no peaks were observed at 555 and 660 nm. After standing for 2 hr, a spectrum of this solu-

(4) H. Flashka, J. Butcher, and R. Speights, *Talanta*, **8**, 400 (1961).

(5) I. Feldman, C. A. North, and H. B. Hunter, *J. Phys. Chem.*, **64**, 1224 (1960).

(6) K. S. Rajan and A. E. Martell, *Inorg. Chem.*, **4**, 462 (1965).

(7) K. S. Rajan and A. E. Martell, *J. Inorg. Nucl. Chem.*, **26**, 1927 (1964).

(8) R. C. Warner and I. Weber, *J. Amer. Chem. Soc.*, **75**, 5086 (1953).

tion showed the appearance of the two peaks. This aging process has been observed previously.⁴ Possibly in certain systems an initial complex, with a structure corresponding to uranium(VI) tartrate, rearranges to a more stable form. This point is considered more fully in the Discussion.

The Composition of the Mixed-Metal Complex.—

The absorption at 430 nm due to U(VI) was used to determine the composition of the citrate and malate mmc's. Corresponding experiments were not carried out with the tartrate mmc since solvent extraction data confirmed that this had the same general formula.

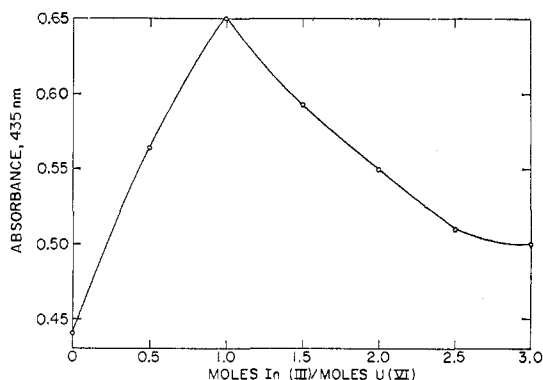
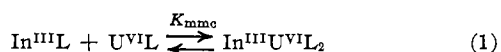


Figure 1.—Determination of the ratio of In(III) to U(VI) in the mixed-metal complex. Absorbance change due to the addition of In(III) to $2 \times 10^{-3} M$ U(VI) in $4 \times 10^{-3} M$ citric acid in the presence of $0.05 M$ acetate buffer at pH 4.00. Five-centimeter cells were employed.

Figure 1 shows the effect of adding In(III) to a solution of U(VI) in citric acid. The results of this experiment clearly demonstrate that the ratio of In(III) to U(VI) is 1:1. A $0.05 M$ acetate buffer maintained the pH at 4 and prevented precipitation at higher metal-ion concentrations. It has previously been shown that high concentrations of acetate can influence the composition of solutions such as these.^{2a} A separate experiment, however, showed that $0.05 M$ acetate had a negligibly small effect on the spectrum of uranyl citrate. The effect of varying malic and citric acid concentrations in $0.05 M$ acetate medium at pH 4 is shown in Figure 2. The results of these experiments demonstrate that the mmc's can be assigned the general formula $U^{VI}In^{III}L_2$, if the hydroxycarboxylic acid is denoted "L."

A Simple Model for the Calculation of Mixed-Metal Complex Stability Constants (K_{mmc}).—If only 1:1 complexes of indium and uranium with the hydroxycarboxylic acids (L) are formed, the reversible formation of the mmc can be written



The distribution coefficient (D_0) of In(III) by itself must first be measured between the aqueous phase and HTTA-benzene. The distribution coefficient (D) of In(III) from an aqueous phase also containing U(VI) is then measured. Sometimes a correction for a small amount of U(VI) extracted was also necessary. If L is

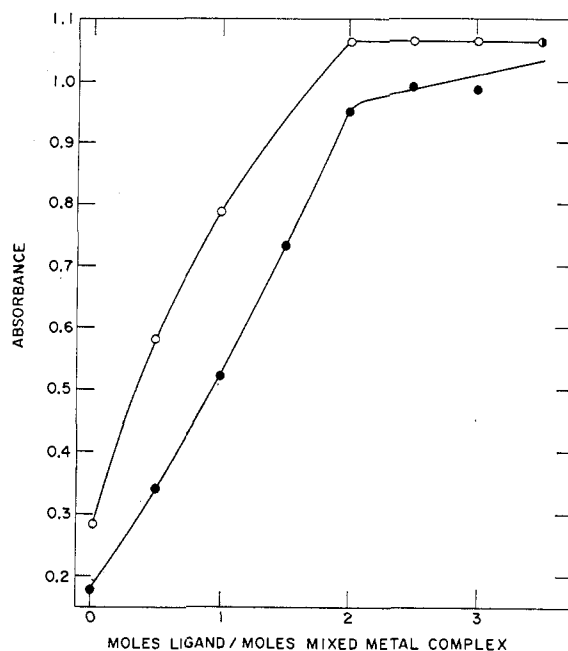


Figure 2.—Determination of the moles of ligand in the mixed-metal complexes. $[U(VI)] = [In(III)] = 3 \times 10^{-3} M$: open circles, absorbance at 433 nm for various malate solutions; solid circles, absorbance at 437 nm for various citrate solutions. Five-centimeter cells were employed.

present in sufficient excess to ensure essentially complete complexation

$$D_0 = [In]_{org}/[InL] \quad (2)$$

and

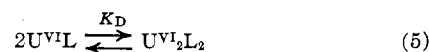
$$D = [In]_{org}/([InL] + [mmc]) \quad (3)$$

Applying eq 2 and 3 to the solution containing both In(III) and U(VI)

$$1/D = 1/D_0 + [mmc]/[In]_{org} \quad (4)$$

Using mass balance relationships and eq 3 and 4, the concentrations of $In^{III}L$, mmc, and free $U^{VI}L$ can be determined.

Values of K_{mmc} determined in this way, however, were found to depend upon $[In^{III}L]$, $[U^{VI}L]$, and $[L]$. Uranium(VI) malate, citrate, and tartrate are known to dimerize according to the general equation⁵⁻⁷



Correction of data using literature values for the equilibrium constants still did not give consistent K_{mmc} values. Our systems contained free uranium(VI) hydroxycarboxylate complexes almost invariably at considerably lower concentrations than those in the above studies. We therefore extended polymerization data to lower U(VI) concentrations using a solvent extraction technique.

Dimerization of Uranyl Malate, Citrate, and Tartrate.

—The extraction of U(VI) from aqueous malate, citrate, and tartrate media into HTTA-benzene was studied at 25° and pH 4 over the concentration range of 5×10^{-8} – $3 \times 10^{-3} M$ U. The U_2L dimers previously observed in solutions with $[U(VI)] > [L]$ were completely ab-

sent in our experiments since L was present in large excess. The D for U(VI) in the presence of excess L can be written

$$D = [U]_{\text{org}} / ([UL] + 2[U_2L_2]) \quad (6)$$

In dilute U(VI) solutions where no polymerization occurs

$$D_0 = [U]_{\text{org}} / [UL] \quad (7)$$

and in concentrated solutions

$$D = [U]_{\text{org}} / 2[U_2L_2] \quad (8)$$

At high U(VI) concentrations therefore $D \propto 1/[U(VI)]_{\text{aq}}^{1/2}$ and at low concentration $D = \text{constant} = D_0$. A plot of $\log D$ vs. $\log [U(VI)]_{\text{aq}}$ thus has a slope of -0.5 at high concentrations increasing gradually to zero as the dimer becomes more dissociated. Such plots are shown in Figure 3.

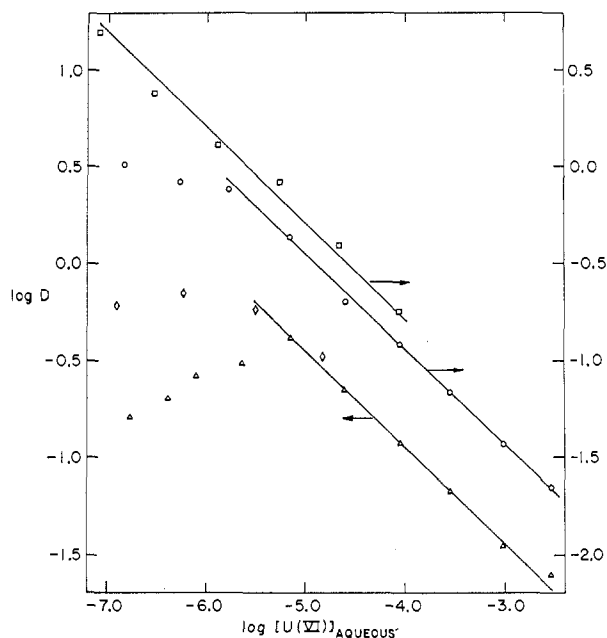


Figure 3.—The dimerization of uranium(VI) citrate, malate, and tartrate: squares, 0.08 M malate; circles, 0.1 M tartrate; triangles, 0.08 M citrate prior to reducing the level of metal ion impurities; diamonds, 0.08 M citrate after reducing metal ion impurities. Aqueous phase pH was maintained at 4.00 and ionic strength at 0.15 with sodium nitrate. Organic phase consisted of 0.10 M HTTA in benzene in all cases except the tartrate system which was 0.04 M HTTA.

In the malate system no tailing of the plot was observed. Comparing these data to the corresponding plot for indium(III) tartrate dimerization (see below) where dissociation was observed, the dimerization constant (K_D) for uranium(VI) malate must be greater than 1×10^7 , under these conditions.

In the citrate system, values of D were found to reverse their trend at $10^{-5} M$ U(VI). This was attributed to the formation of U(VI) mmc's with metal ion impurities at the $10^{-5} M$ level. It was possible to reduce the concentration of these impurities by a factor of 10 (see Figure 3) using methods described in the Experimental Section. From the lower limit of the straight-

line portion in the figure it can be said that under these conditions K_D for uranyl citrate is greater than 1×10^6 .

A tailing of the plot was observed for uranyl tartrate when the uranium concentration fell below $1.5 \times 10^{-6} M$. If the tailing were caused by an impurity, a reversal of slope would be expected as the uranium concentration became smaller in comparison to the concentration of impurity. This was observed for uranium(VI) citrate. No such reversal was observed for tartrate and the tailing was assumed to be due to dissociation of the dimer. The data are not precise enough to determine a dimerization constant accurately, but an estimated value is 5×10^5 .

Polymerization of Indium(III) Malate, Citrate, and Tartrate.—The possible polymerization of solutions of $In^{III}L$ was investigated because (a) values of K_{mmc} were found to depend upon $[In(III)]$ and (b) polymerizations of $U^{VI}L$ complexes, $Cu^{II}L$ complexes,⁹⁻¹² chromium(III) citrate,^{2a} and vanadium(IV) tartrate¹³ have been observed. Using an analogous procedure to the $U^{VI}L$ dimerization experiments, the variation of the distribution at pH 4 of $In(III)$ into HTTA-benzene was studied as a function of $In(III)$ concentration in the presence of excess ligand. The results are illustrated in logarithmic form in Figure 4. Polymerization

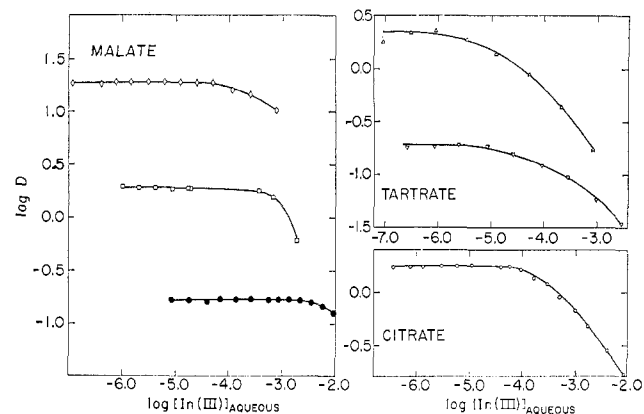


Figure 4.—The polymerization of $In(III)$ with citrate, malate, and tartrate: circles, 0.2 M citrate, 0.15 M HTTA; triangles, 0.02 M tartrate, 0.01 M HTTA; inverted triangles, 0.1 M tartrate, 0.015 M HTTA; diamonds, 0.2 M malate, 0.15 M HTTA; squares, 0.075 M malate, 0.03 M HTTA; filled circles, 0.5 M malate, 0.075 M HTTA. The pH of the aqueous phase was maintained at 4.00 and the ionic strength at 0.15 with sodium nitrate.

of the malate, citrate, and tartrate complexes is clearly observed. Using eq 6 and 7 and mass balance relationships, concentrations of monomeric and polymeric $In(III)$ can be calculated.

The results for indium(III) malate and citrate did not correspond to the formation of a single polymeric species. Fortunately in almost all mmc experiments

(9) K. S. Rajan and A. E. Martell, *J. Inorg. Nucl. Chem.*, **29**, 463 (1967).

(10) J. F. Boas, *et al.*, *J. Chem. Soc. A*, 94 (1969).

(11) R. E. Tapscott, R. L. Belford, and I. C. Paul, *Coord. Chem. Rev.*, **3**, 323 (1969).

(12) N. D. Chasteen and R. L. Belford, *Inorg. Chem.*, **9**, 169 (1970).

(13) R. E. Tapscott, R. L. Belford, and I. C. Paul, *ibid.*, **7**, 356 (1968).

involving malic and citric acids, polymerization of In(III) complexes could be considered negligible. The results for indium(III) tartrate taken over a 100-fold variation in the total indium concentration and at two tartrate concentrations show a dimerization reaction. This complex may be analogous to the previously identified copper(II) and vanadium(IV) tartrate dimers.⁹⁻¹³ Indium(III) tartrate dimerization was considerable in tartrate mmc experiments, but the use of dimerization data enabled constant mmc constants to be obtained over a wide range of In(III) concentrations.

From the results in Figure 4 at different ligand concentrations it can be seen that the extent of polymerization is greater at lower ligand concentrations. The ratio of In(III):L is therefore different in the monomeric and polymeric species. Previous workers have determined an In(III):citrate ratio of 1:1 in solutions approximately 10^{-3} M in indium(III) and citric acid. The possibility of polymerization was not considered. It seemed from our results (Figure 4) that, at least at pH 4, solutions of 10^{-3} M indium(III) citrate would be completely polymerized. Also values of K_{mmc} assuming that monomeric indium complexes had the general formula $In^{III}L$ exhibited an inverse dependence upon [L]. The composition of indium hydroxycarboxylate monomers at pH 4 was therefore determined under conditions where polymerization could be neglected.

The Composition of the Monomeric Indium(III) Complexes at pH 4.—In these experiments the In(III) was kept within the 10^{-5} – 10^{-6} M range to eliminate polymeric species. The distribution of indium between the aqueous phase containing various ligand concentrations at pH 4 and an organic HTTA–benzene phase was measured. The ionic strength was kept approximately constant by interchanging $NaNO_3$ and Na^+L^- . The ligand concentrations used ($1 \times 10^{-2} < [\text{malate}] < 9 \times 10^{-2}$ M, $1 \times 10^{-2} < [\text{citrate}] < 2 \times 10^{-1}$ M, $1 \times 10^{-2} < [\text{tartrate}] < 1.5 \times 10^{-1}$ M) duplicated the range of ligand concentrations investigated in mmc experiments. Under these experimental conditions

$$D = [In]_{org}/[InL_n] = [In]_{org}/K[In][L]^n \quad (9)$$

where K is a pseudo constant at pH 4 defined as

$$K = [In(III)L_n]/[In(III)][L]^n \quad (10)$$

If the pH remains constant at 4, the ratio $[In]_{org}/[In]$ is constant and a plot of $\log D$ against $\log [L]$ has a slope of $-n$. The plots are shown in Figure 5 and in all three systems $n = 2$. Therefore, the In(III) monomeric complexes all have the general formula $In^{III}L_2$ at pH 4. We were not able to extend our studies down to ligand concentrations comparable to those used in ref 15. We consider it likely, however, in the light of the present work, that the earlier study was made under conditions where a high proportion of polymeric species was present.

Values of the Equilibrium Constants for the Mixed-Metal Complexes.—Under the conditions used in

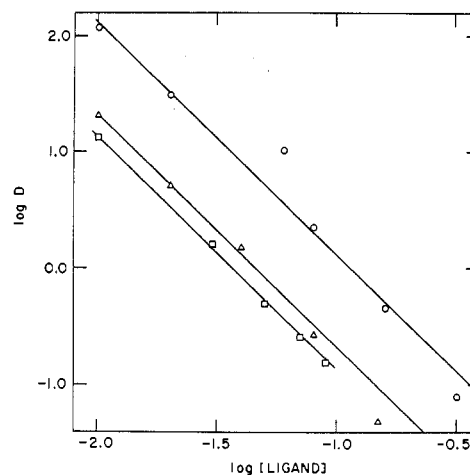
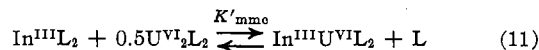


Figure 5.—Determination of the ligand to indium ratio in the monomeric indium citrate, malate, and tartrate complexes: circles, varying citrate, 0.075 M HTTA; triangles, varying tartrate, 0.015 M HTTA; squares, varying malate, 0.015 M HTTA. The pH of the aqueous phase was maintained at 4.00 and the ionic strength of the citrate system was 1.0, the malate system was 0.2, and the tartrate system was 0.15. The In(III) concentration was 10^{-6} M in the citrate system, 10^{-6} M in the malate system, and 2×10^{-6} M in the tartrate system.

these experiments, the formation of the mmc's can be written



Experimentally the distribution coefficient of In(III) alone was measured under conditions where there was no significant polymerization. Then

$$D_0 = [In]_{org}/[InL_2] \quad (12)$$

The distribution coefficient of In(III) was then measured in a more concentrated solution (call this solution 2) also containing U(VI). The free ligand concentration and pH were held constant. Now

$$D = [In]_{org}/([InL_2] + n[In]_n + [mmc]) \quad (13)$$

Now for solution 2

$$[InL_2] = \frac{[In]_{org \text{ in soln } 2}}{D_0} \quad (14)$$

Data on In(III) polymerization allow one to calculate the concentrations of $[In]_n$ from the values of $[InL_2]$ obtained from eq 14. Since

$$[In]_{aq} = [In]_{initial} - [In]_{org} = [InL_2] + n[In]_n + [mmc] \quad (15)$$

we can calculate the [mmc] in solution 2 from eq 15. Finally

$$[U]_{free} = 2[U_2L_2] = [U]_{initial} - [U]_{org} - [mmc] \quad (16)$$

Substituting the calculated values for the concentrations of each of the species in eq 11 yielded values of K'_{mmc} at 25° and pH 4 which are summarized in Table I.

In all experiments the ionic strength was kept approximately constant by interchanging $NaNO_3$ with NaL . All results are listed in Table I including some values of K'_{mmc} which, especially in the citrate system, vary quite markedly from the mean figure. The citrate

TABLE I
MIXED-METAL COMPLEX FORMATION BETWEEN
INDIUM AND URANIUM

$n[\text{In}]_n$, M	$[\text{InL}_2]$, M	$2[\text{U}L_2]$, M	$[\text{mmc}]$, M	$[\text{L}]$, M	K'_{mmc} , $M^{1/2}$
Malate					
5.1×10^{-6}	7.3×10^{-5}	1.3×10^{-4}	1.0×10^{-2}		41
1.6×10^{-6}	6.4×10^{-5}	1.4×10^{-4}	2.0×10^{-2}		30
1.8×10^{-6}	7.3×10^{-5}	2.8×10^{-4}	4.0×10^{-2}		32
1.1×10^{-4}	4.4×10^{-4}	5.3×10^{-4}	7.5×10^{-2}		25
5.9×10^{-6}	1.6×10^{-4}	2.3×10^{-4}	7.5×10^{-2}		33
3.3×10^{-5}	8.9×10^{-5}	1.0×10^{-4}	7.5×10^{-2}		25
2.5×10^{-4}	5.4×10^{-4}	4.7×10^{-4}	1.5×10^{-1}		25
Citrate					
1.0×10^{-7}	4.8×10^{-6}	9.8×10^{-6}	1.0×10^{-2}		610
2.1×10^{-7}	4.8×10^{-6}	9.5×10^{-6}	2.0×10^{-2}		570
1.4×10^{-7}	1.0×10^{-5}	9.6×10^{-6}	2.0×10^{-2}		600
2.9×10^{-7}	1.1×10^{-5}	9.4×10^{-6}	4.0×10^{-2}		560
4.1×10^{-7}	5.1×10^{-4}	9.1×10^{-6}	4.0×10^{-2}		560
6.7×10^{-7}	1.1×10^{-5}	9.3×10^{-6}	8.0×10^{-2}		480
8.6×10^{-7}	5.4×10^{-6}	8.3×10^{-6}	8.0×10^{-2}		470
1.3×10^{-4}	8.5×10^{-5}	8.1×10^{-4}	2.0×10^{-1}		170
1.2×10^{-6}	9.0×10^{-4}	9.8×10^{-5}	2.0×10^{-1}		760
2.7×10^{-6}	8.9×10^{-3}	9.9×10^{-4}	2.0×10^{-1}		780
4.8×10^{-6}	2.0×10^{-3}	9.9×10^{-4}	2.0×10^{-1}		1400
4.0×10^{-5}	9.8×10^{-3}	8.9×10^{-4}	2.0×10^{-1}		640
2.6×10^{-5}	6.7×10^{-4}	2.9×10^{-4}	2.0×10^{-1}		1200
7.6×10^{-7}	8.6×10^{-4}	9.8×10^{-5}	2.0×10^{-1}		1300
Tartrate					
1.2×10^{-6}	3.6×10^{-6}	2.3×10^{-5}	2.0×10^{-2}		33
3.2×10^{-6}	6.0×10^{-6}	4.3×10^{-5}	4.9×10^{-2}		36
8.5×10^{-6}	1.0×10^{-5}	7.6×10^{-5}	1.1×10^{-1}		36
1.8×10^{-5}	4.0×10^{-5}	1.1×10^{-4}	8.1×10^{-1}		28
4.3×10^{-5}	6.9×10^{-5}	2.0×10^{-4}	1.8×10^{-1}		26
1.3×10^{-4}	1.3×10^{-4}	4.4×10^{-4}	5.4×10^{-1}		29

system was the most widely studied. The mean K'_{mmc} value of 720 has a relatively large deviation but was determined from data in which $[\text{In}]_{\text{free}}$ varied by a factor of 1000, $[\text{U}]_{\text{free}}$ by a factor of 2000, and $[\text{L}]$ by a factor of 20. No trends in K'_{mmc} are readily observable, and the results, despite their scatter, confirm that eq 9 best describes the equilibria in these solutions over wide concentration ranges. The correct identification of the species in eq 9 is also confirmed by these calculations of K'_{mmc} . The results in the tartrate system are especially gratifying in view of the competitive formation of dimeric indium tartrate.

Values of K_{mmc} calculated on the basis of eq 1, which would be extremely valuable from the point of view of a comparison of the relative strengths of the malate, citrate, and tartrate mmc's, cannot be calculated since the solvent extraction techniques used were not able to give values for the constants

$$K_{2,\text{In}} = [\text{In}^{\text{III}}L_2]/[\text{In}^{\text{III}}L][L]$$

and

$$K_{\text{D,U}} = [\text{U}^{\text{VI}}L_2]/[\text{U}^{\text{VI}}L]^2$$

However minimum values of some constants can be calculated and are summarized in Table II.

Discussion

Despite some spectrophotometric evidence for an interaction between In(III) and U(VI) complexes of certain hydroxycarboxylic acids, the previous finding^{2a} that the skeletal structure of malic acid is necessary for the formation of strong mmc's still holds.

The existence of several polymeric metal ion-hydroxycarboxylic acid complexes has been mentioned

TABLE II
ESTIMATES OF DIMERIZATION AND
MIXED-METAL COMPLEX CONSTANTS

Complex	Constant, M^{-1}
$\text{U}^{\text{VI}}_2(\text{malate})_2$	$K_{\text{D}} > 1 \times 10^7$
$\text{U}^{\text{VI}}_2(\text{citrate})_2$	$K_{\text{D}} > 1 \times 10^6$
$\text{U}^{\text{VI}}_2(\text{tartrate})_2$	$K_{\text{D}} \geq 5 \times 10^5$
$\text{U}^{\text{VI}}\text{In}^{\text{III}}(\text{malate})_2$	$K_{\text{mmc}} > 1 \times 10^8$
$\text{U}^{\text{VI}}\text{In}^{\text{III}}(\text{citrate})_2$	$K_{\text{mmc}} > 5 \times 10^8$
$\text{U}^{\text{VI}}\text{In}^{\text{III}}(\text{tartrate})_2$	$K_{\text{mmc}} > 2 \times 10^6$

earlier. In the U(VI)-In(III) systems studied, the individual metal polymers (especially uranium dimers) have extremely high stabilities at a pH of 4. Data show, however, that the corresponding mmc's acquire additional stability from some source. It is very tempting to assume that the mmc forms an analogous structure to the U(VI) dimer by simply replacing UO_2^{2+} by In^{3+} . This view is supported by the similar spectra of uranium(VI) malate and citrate dimers and the mmc's. The additional stability of the mmc's could arise from stereochemical and size considerations which result in less strained structures. The UO_2^{2+} ion has up to six equatorial coordination sites whereas In^{3+} has both equatorial and axial sites. Molecular models show that only tridentate chelation of citric acid is possible in $(\text{U}^{\text{VI}}(\text{citrate}))_2$ but that quadridentate chelation can occur in the $\text{In}^{\text{III}}\text{U}^{\text{VI}}(\text{citrate})$ complex. The fact that three protons per citrate are liberated during dimer formation and four protons per citrate during mmc formation strengthens this belief. X-Ray crystallographic data have shown that all tartrate hydroxy groups are ionized in the complex $(\text{U}^{\text{VI}}(\text{tartrate}))_2^{2-}$.¹³ It therefore seems more reasonable to assume that the hydroxy groups become ionized in interpreting the above potentiometric data. We observed three indications that dimeric uranium(VI) tartrate may have a structure different from the malate and citrate dimers: (a) the absence of peaks at 555 or 660 nm in the spectrum of $(\text{U}^{\text{VI}}(\text{tartrate}))_2$, (b) the slow appearance of these peaks for the citramalate complex, and (c) the fact that the $(\text{U}^{\text{VI}}(\text{tartrate}))_2$ dimer seems to be weaker than the citrate and malate dimers.

Our data show that at pH 4, the dimeric U(VI) complexes are essentially undissociated down to the 10^{-6} M level. This is at variance with other work.⁵⁻⁷ Our measurements were made at much lower U(VI) concentrations than those of other workers and additional work at higher concentrations and a variation of pH may clear up this discrepancy. Polymerization can proceed further than dimerization as shown in the present work with indium(III) malate and citrate. The trimerization of $\text{Fe}^{\text{III}}(\text{malate})_2$ has also been observed in this laboratory.¹⁴ The results of the present study indicate, however, that no mmc's other than the binuclear $\text{In}^{\text{III}}\text{U}^{\text{VI}}L_2$ species are formed.

A comparison of our results for the formation of indium(III)-hydroxycarboxylate complexes with those of earlier workers¹⁵ shows that In:L ratios were measured in solutions which probably contained a high pro-

(14) A. Adin, P. Klotz, and L. Newman, unpublished work.

(15) V. D. Cozzi and S. Vivarelli, *Z. Elektrochem.*, **58**, 907 (1954).

portion of polymeric species. Our results at pH 4 are wholly consistent with an equilibrium of monomeric $\text{In}^{\text{III}}\text{L}_2$ complexes with polymeric species and mmc's. We observe that the ratio of $\text{In}:\text{L}$ in polymeric complexes is less than 0.5. The degree of polymerization is much reduced at values of pH less than 4³ but the extent of mmc formation also becomes much less. Nothing is known of the structure of the $\text{In}^{\text{III}}\text{L}_2$ complexes which exist in very dilute solutions of pH 4, but both ligands are quite tightly bound to the metal ion since no dissociation of these complexes was detected when the concentration of free ligand was as low as $10^{-2} M$.

The general picture which emerges from this investigation is one of the coexistence of very stable polymeric complexes of each metal ion with an mmc where the most stable species is the mmc. The data allow estimations of monomeric, polymeric, and mmc concentrations to be made in solutions containing either or both $\text{In}(\text{III})$ and $\text{U}(\text{VI})$ in malate, citrate, or tartrate media. These calculations and the experimental results show that mmc formation and polymerization can drastically affect the distribution coefficient of a metal ion present in concentrations at the $10^{-6} M$ level (under certain conditions the distribution coefficient of $\text{In}(\text{III})$ was reduced by a factor of 10^2).

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Preparation and Some Reactions of Alkoxides of Gadolinium and Erbium

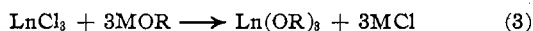
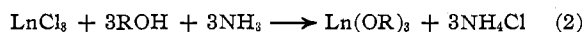
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Convenient methods for the preparation of alkoxides of gadolinium and erbium have been described. The pure isopropoxides can be obtained in quantitative yields by treating the 2-propanolates of the respective lanthanide chlorides with stoichiometric amounts of alkali isopropoxide. Alcoholysis of isopropoxides yields higher alkoxides. Reactions of isopropoxides with dry hydrogen chloride, *tert*-butyl acetate, and phenol were also carried out to yield chloride alcoholates, *tert*-butoxides, and phenoxides, respectively. Molecular complexity data show the soluble alkoxides to be oligomers in boiling benzene. Further identification of the products was made by infrared spectra.

In spite of considerable interest in the chemistry of alkoxides¹ of transition elements during the last decade only a few scattered references are available on similar derivatives of inner transition elements²⁻⁹ but these do not include any on gadolinium or erbium.

Experience in our laboratories and elsewhere^{1,8} suggested that the following general methods might be applicable for the preparation of the alkoxides of gadolinium and erbium

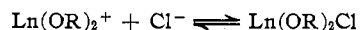
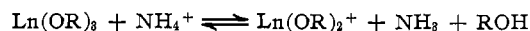


where Ln is lanthanide metal or ion, M is an alkali metal ion, and R is an alkyl group.

Method 1 has been used for the preparation of isopropoxides of dysprosium and ytterbium⁸ by treating

metal shavings with isopropyl alcohol in the presence of the catalyst mercuric chloride. The method was attempted a number of times for gadolinium and erbium but was not pursued as the products could not be purified to a sufficient degree.

In method 2 also, the gadolinium and erbium products were found to be contaminated with appreciable amounts of chloride. This behavior is understandable with the analogy of similar observations in the case of thorium alkoxides.¹⁰ As gadolinium and erbium alkoxides are more basic than ammonia, the following equilibria may be feasible



However, method 3 employing alkali metal alkoxides and anhydrous metal chlorides was found to be of general applicability for the preparation of pure soluble isopropoxides and insoluble methoxides of lanthanum, praseodymium, neodymium,⁵ and samarium⁶ and after a little modification was used for the preparation of alkoxides of gadolinium and erbium.

Results and Discussion

Soluble Alkoxides.—When gadolinium and erbium (hereafter described as lanthanide, abbreviated as Ln) chlorides suspended in benzene-isopropyl alcohol were

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