sensitivity is 0.02 absorbance unit/division. This figure clearly shows the deepening of color mentioned above.

That complexation as an initial step is likely has already been proposed by Kemp and Waters,[11] who oxidized malonic acid with Mn(III), and by Amjad and McAuley,[5] who oxidized malonic acid with Ce(IV). The initial complex formed was moderately stable, taking several days to be lost via a redox step. We feel it is reasonable to assume that the monosubstituted acids also complex with Ce(IV) prior to the redox step, and so complexation steps (reactions 2 and 3) were included in the mechanism.

Equation VI indicates that the relative value of k_5/k_4 can be obtained by taking the ratio of the slope to the intercept from Figure 2. These values are 2.5 and 1.5 for methyl- and ethylmalonic acids, respectively, indicating that for both acids, steps 4 and 5 of the mechanism are of comparable importance. For malonic acid McAuley obtained a value of 0.22 for this ratio, showing that there is a considerably smaller acid dependency for the unsubstituted acid compared to that for the substituted acids. A comparison of the slopes (K_2k_5 for methylmalonic acid to K_2k_5 for ethylmalonic acid) and of the intercepts (K_2k_4 for methylmalonic to K_2k_4 for ethylmalonic acid) yields values of 1.8 and 3.0, respectively. The latter value contains an appreciable error since it is obtained from the extrapolated values of the intercepts. Since the methyl group is a more effective electron-donating group than the ethyl group, methylmalonic acid would be a somewhat stronger Lewis base than ethylmalonic acid, resulting in its having a larger value of K_2. This is consistent with the dissociation constants of the two acids; for methylmalonic acid $K_{a_1} = 0.87 \times 10^{-3}$ whereas for ethylmalonic acid $K_{a_1} = 1.3 \times 10^{-3}$. If this interpretation is correct, then the two acids would have similar k_4 and k_5 values. McAuley's results for malonic acid, however, are different from those for the substituted acids. This is not surprising, however, since malonic acid contains two methylene H atoms rather than one.

It is not possible to obtain a reasonable estimate of k_6. Only the product, $k_6K_2K_8$, could be obtained. The values 0.17 and 0.03 s^{-1} for methyl- and ethylmalonic acids, respectively, were the values that linearized the results shown in Figure 2. Their contributions are important only at the lowest acidities used. At acidities of 1 M and above, this product, $k_6K_2K_8$, had a negligible effect on the linearity of the plot.

More important is that the best fit value of $K_7 = 0.18$ M for the hydrolysis of Ce^{4+} is in excellent agreement with that found by McAuley. This is supportive of the correctness of the proposed mechanism.

The overall mechanism including the rate-determining step (rds) and subsequent steps is

$$Ce^{IV} + HCR(CO_2H)_2 \rightarrow \text{complex}$$

$$\text{complex} \rightarrow \cdot Cr(CO_2H)_2 + Ce^{III} + H^+ \quad \text{rds}$$

$$\cdot Cr(COOH)_2 + Ce^{IV} + H_2O \rightarrow RC(OH)(CO_2H)_2 + Ce^{III} + H^+$$

$$RC(OH)(CO_2H)_2 + Ce^{IV} \rightarrow \cdot HCO_2 + RC(O)(CO_2H) + Ce^{III} + H^+$$

$$\cdot HCO_2 + Ce^{IV} \rightarrow H^+ + CO_2 + Ce^{III}$$

where R = CH_3 or C_2H_5. This results in a CO_2:Ce(IV) mole ratio of 1:4.0, which was observed. Where R = H, the RC(O)(CO_2H) molecule is further oxidized to formic acid, resulting in a CO_2:Ce(IV) mole ratio of 1:3.0.

Registry No. Cerium, 7440-45-1; methylmalonic acid, 516-05-2; ethylmalonic acid, 601-75-2.

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Mixed-Ligand Chelate Extraction of Lanthanides with 1-Phenyl-3-methyl-4-acyl-5-pyrazolones

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A study of the equilibrium extraction behavior of series of representative tervalent lanthanide ions (La, Pr, Eu, and Yb) was carried out with either chloroform solutions of selected 1-phenyl-3-methyl-4-acyl-5-pyrazolones (acyl = decanoyl, phenacetyl, 3-phenylpropionyl, and *p-tert*-butylbenzoyl) (HP) alone or these solutions in combination with 1,10-phenanthroline (phen), trioctylphosphine oxide (TOPO), or methyltrioctylammonium chloride ($R_3R'NCl$). The results demonstrate that these lanthanides are extracted as LnP_3 or, in the presence of phen or TOPO, as LnP_3·phen or LnP_3·TOPO, or, in the presence of $R_3R'N^+Cl^-$, as $R_3RN^+LnP_4^-$. The extraction constants (K_{ex}), K_{ex}(phen), K_{ex}(TOPO), and K_{ex}, are discussed in terms of structure–behavior interrelations.

Introduction

As a part of a systematic evaluation of the use of chelating extractants in the separation of tervalent lanthanide ions, the equilibrium extraction behavior of a series of representative lanthanide ions with either chloroform containing 8-quinolinol (HQ), 5,7-dibromo-8-quinolinol (HQ′), and 1-phenyl-3-methyl-4-octanoyl-5-pyrazolone (HP) alone or these solutions in combination with 1,10-phenanthroline (phen) or methyltrioctylammonium chloride ($R_3R'NCl$) was studied in detail.[1–4] The extracted species were found to be the complexes $LnQ_3 \cdot nHQ$ (n = 2,3) for 8-quinolinol, LnQ_3·HQ for 5,7-dibromo-8-quinolinol, and LnP_3 for 1-phenyl-3-methyl-4-octanoyl-5-pyrazolone (HPMOP). In the presence of phen or $R_3R'NCl$, the formation of mixed-adduct and self-adduct ion pairs, LnQ_3·2HQ·phen and $R_3R'N^+$,LnQ_4^-·HQ, was observed for HQ whereas for HQ′ the formation of simple adducts and

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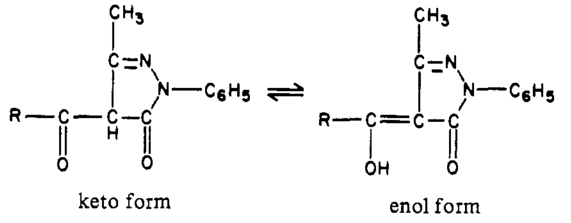
Table I. Characteristics of 1-Phenyl-3-methyl-4-acyl-5-pyrazolones

ligand	R	elemental anal.[a] % C	% H	% N	mp, °C	color[b]
HPMDP	C_9H_{19}	73.14	8.59	8.54	42.7–43.5	white
		73.22	8.79	8.44		
HPMPPP	$C_6H_5CH_2CH_2$	74.49	5.92	9.14	78.3–79.0	yellow
		74.40	5.90	9.24		
HPMPAP	$C_6H_5CH_2$	73.95	5.52	9.58	105–106	light yellow
		73.87	5.67	9.77		
HPMBBP	$(CH_3)_3CC_6H_5$	75.42	6.63	8.38	110–111	brownish yellow
		75.23	6.87	8.39		

[a] The first value given is the calculated value, and the second is the value found. [b] All the compounds formed needle-shaped crystals.

ion pairs, LnQ_3·phen and $R_3R'N^+,LnQ_4^-$, and for HPMOP, LnP_3·phen and $R_3R'N^+,LnP_4^-$ was observed.

Since in the 8-quinolinol series a stronger acid, HQ′, gave better extraction and separation, a comparative study was conducted with acylpyrazolones (A, 1-phenyl-3-methyl-4-acyl-5-pyrazolone), a family of chelating agents that are more strongly acidic than the 8-quinolinols. 1-Phenyl-3-methyl-4-decanoyl-5-pyrazolone (HPMDP) (A with R = C_9H_{19}), 1-phenyl-3-methyl-4-(3-phenylpropionyl)-5-pyrazolone (HPMPPP) (A with R = $C_6H_5CH_2CH_2$), 1-phenyl-3-methyl-4-(phenylacetyl)-5-pyrazolone (HPMPAP) (A with R = C_6H_5-CH_2), and 1-phenyl-3-methyl-4-(*p*-*tert*-butylbenzoyl)-5-pyrazolone (HPMBBP) (A with R = $(CH_3)_3CC_6H_5$) were chosen for this study because they can be compared with the widely used acylpyrazolone 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) (R = C_6H_5)[5-7] as well as an extractant described in the previous paper, octanoylpyrazolone (HPMOP) (R = C_7H_{15}),[4] so that the influence of acyl substituents could be gauged.



A

Experimental Section

Apparatus and Reagents. The apparatus as well as materials such as the lanthanide salts, arsenazo III, and 1,10-phenanthroline used here have been described previously.[1] 1-Phenyl-3-methyl-4-acyl-5-pyrazolones were synthesized from 1-phenyl-3-methyl-5-pyrazolone (ICN Pharmaceuticals) and the corresponding acid chloride as described by Jensen[8] (Table I). Decanoyl chloride, 3-phenylpropionyl chloride, phenylacetyl chloride, and *tert*-butyl chloride were obtained commercially (Aldrich). 3-Phenylpropionyl chloride, phenylacetyl chloride, and *p*-*tert*-butylbenzoyl chloride were synthesized from 3-phenylpropionic acid (Aldrich), phenylacetic acid (Aldrich), and *p*-*tert*-butylbenzoic acid (Eastman Kodak), respectively, and thionyl chloride (J. T. Baker) as described by Cason.[9]

Methyltrioctylammonium chloride (Aliquat 336S, Henkel Corp.) was dissolved in chloroform just prior to use. Trioctylphosphine oxide (Eastman Organic Chemical) and all the other chemicals of analytical reagent grade were used without further purification.

Procedure. Lanthanides with an initial concentration of 2×10^{-5} M were extracted in the presence of 2×10^{-3} M succinic acid and various amounts of sodium hydroxide. The ionic strength of the aqueous solution was controlled at 0.1 with sodium perchlorate except in the presence of the alkylammonium salt, when sodium chloride was added. Equal volumes (10 mL) of aqueous and chloroform solutions were placed in a glass vial and mechanically shaken vigorously at room temperature for 60 min, a time found to be adequate for equilibration. The pH value of the aqueous phase after extraction was taken as the equilibrium pH value. After phase separation, an aliquot of the organic phase was shaken with 0.1 M sodium formate–formic acid buffer at a pH of 2.0–2.6. The concentration of lanthanide back-extracted into the aqueous solution was determined by the arsenazo III method described previously.[1] The metal ion concentration in the aqueous phase was determined by the same method. Distribution ratios were calculated from the concentrations of lanthanide in organic and aqueous phases in the usual manner.

Results and Discussion

A traditional and effective means of obtaining both stoichiometric and equilibrium constant information about extraction processes, called "slope analysis", is based on an examination of the variation of *D*, the distribution ratio, with relevant experimental variables. A log–log plot of the extraction in the form of *D* vs. a concentration variable indicates the stoichiometry of the formation of the extractable complex and thus leads to the derivation of a suitable equilibrium expression and then to the calculation of equilibrium constants.

From such a slope analysis of the extraction data (a detailed data summary is available from authors), slopes of all the log *D* vs. pH plots were found to be close to 3, indicating that the extracted species contains three ligand anions. This was confirmed directly for europium by the observation that the slope of the log *D* vs. log $[HP]_o$ plot gave values of 3 in all cases. (The subscript o designates concentration in the organic phase.) This latter observation also signifies that the extracted complexes are simple chelates rather than adducts. Thus, the extraction reaction can be written as

$$Ln^{3+} + 3HP(o) \overset{K_{ex}}{\rightleftharpoons} LnP_3(o) + 3H \qquad (1)$$

Values of K_{ex}, shown in Table II, increase as expected with increasing lanthanide atomic number, reflecting mainly the increasing chelate stability, β_3, in each ligand. The behavior of the auxiliary ligands, phen and TOPO (B), giving complexes containing only one B molecule (note that the log *D* vs. log $[B]_o$ slope is very close to unity for each ligand), leads to the equation

$$Ln^{3+} + 3HP(o) + B(o) \overset{K_{ex}(B)}{\rightleftharpoons} LnP_3{\cdot}B(o) + 3H^+ \qquad (2)$$

By substracting eq 1 from eq 2, the adduct formation in the organic phase can be isolated:

$$LnP_3(o) + B(o) \overset{K_{AD}(B)}{\rightleftharpoons} LnP_3B(o) \qquad (3)$$

The effect of adduct formation is to increase the extraction equilibrium constant, $K_{ex}(B)$, by a factor given by the adduct formation constants $K_{AD}(B)$. As seen in Table II, the enhancement is much greater when phen is used than is the case

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Table II. Extraction Constants and Separation Factors

ligand		eq no.	extraction const La	Pr	Eu	Yb	separation factors La/Pr	Pr/Eu	Eu/Yb
HPMDP	$\log K_{ex}$	1	−10.26	−8.74	−7.27	−5.42	1.52	1.47	1.85
	$\log K_{ex}$(phen)	2	−3.42	−1.14	0.26	1.90	2.28	1.40	1.64
	$\log K_{AD}$(phen)	3	6.84	7.60	7.53	7.32			
	$\log K_{ex}$(TOPO)	2	−5.80	−4.05	−2.73	−0.78	1.75	1.32	1.95
	$\log K_{AD}$(TOPO)	3	4.46	4.69	4.54	4.64			
	$\log K_{ex}'$	4	−7.03	−5.24	−3.92	−3.60	1.79	1.32	0.32
	$\log(K_{ex}'/K_{ex})$	5	3.23	3.50	3.35	1.82			
HPMPPP	$\log K_{ex}$	1	−9.45	−7.86	−6.62	−4.95	1.59	1.24	1.67
	$\log K_{ex}$(phen)	2	−2.51	−0.42	1.10	2.03	2.09	1.52	0.93
	$\log K_{AD}$(phen)	3	6.94	7.44	7.72	6.98			
	$\log K_{ex}$(TOPO)	2	−4.94	−3.53	−2.00	−0.28	1.41	1.53	1.72
	$\log K_{AD}$(TOPO)	3	4.51	4.33	4.62	4.67			
	$\log K_{ex}'$	4	−5.65	−3.80	−2.80	−2.28	1.85	1.10	0.52
	$\log (K_{ex}'/K_{ex})$	5	3.80	4.06	3.82	2.67			
HPMPAP	$\log K_{ex}$	1	−8.76	−7.29	−6.03	−4.62	1.47	1.26	1.41
	$\log K_{ex}$(phen)	2	−1.96	−0.22	1.50	2.47	1.74	1.72	0.97
	$\log K_{AD}$(phen)	3	6.80	7.07	7.53	7.09			
	$\log K_{ex}$(TOPO)	2	−4.40	−3.10	−1.74	0.25	1.30	1.36	1.99
	$\log K_{AD}$(TOPO)	3	4.36	4.19	4.29	4.87			
	$\log K_{ex}'$	4	−5.03	−3.57	−2.35	−1.75	1.46	1.22	0.62
	$\log (K_{ex}'/K_{ex})$	5	3.73	3.72	3.68	2.87			
HPMBBP	$\log K_{ex}$	1	−8.13	−6.72	−5.67	−4.56	1.41	1.05	1.11
	$\log K_{ex}$(phen)	2	−1.77	−0.01	1.54	2.44	1.76	1.55	0.90
	$\log K_{AD}$(phen)	3	6.36	6.71	7.21	7.00			
	$\log K_{ex}$(TOPO)	2	−3.66	−2.47	−1.20	0.50	1.19	1.27	1.70
	$\log K_{AD}$(TOPO)	3	4.47	4.25	4.47	5.06			
	$\log K_{ex}'$	4	−4.20	−2.53	−1.63	−1.27	1.67	0.90	0.36
	$\log (K_{ex}'/K_{ex})$	5	3.03	4.10	4.04				

Table III. Comparison of Extraction Constants and Separation Factors

		extraction const La	Pr	Eu	Yb	separation factors La/Pr	Pr/Eu	Eu/Yb
HPMPPP	$\log K_{ex}$	−9.45	−7.86	−6.62	−4.95	1.59	1.24	1.67
HPMPAP		−8.76	−7.29	−6.03	−4.62	1.47	1.26	1.41
HPMBBP		−8.13	−6.72	−5.64	−4.56	1.41	1.05	1.11
HPMBP[7]		−7.28	−6.17	−5.33	−4.24	1.11	0.84	1.09
HPMDP		−10.26	−8.74	−7.27	−5.42	1.52	1.47	1.85
HPMOP[4]			−8.49	−6.97	−5.20		1.52	1.77
5,7-dibromo-8-quinolinol[2]	$\log K_{ex}\beta_{10}$		−11.32	−10.38	−8.37		0.94	2.01
8-quinolinol[1]	$\log K_{ex}\beta_{20}$		−15.86	−14.02	−12.50		1.84	1.52

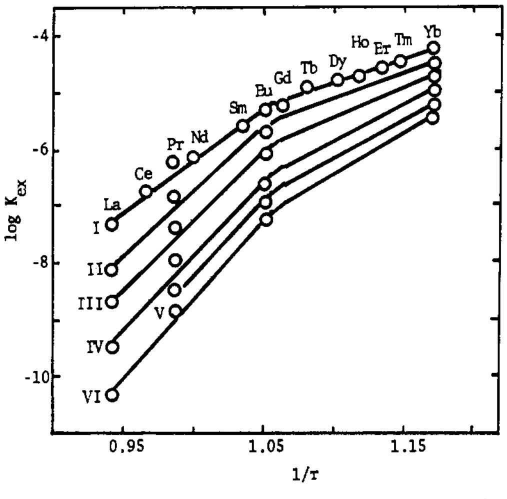

Figure 1. Relationship of log K_{ex} to the inverse reciprocal of the ionic radii (r) of lanthanide ions: (I) HPMBP; (II) HPMBBP; (III) HPMPAP; (IV) HMPPPP; (V) HPMOP;[4] (VI) HPMDP.

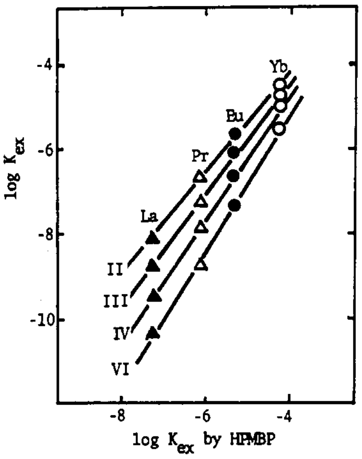

Figure 2. Comparison of log K_{ex} of the other acylpyrazolones to log K_{ex} of HPMBP: (II) HPMBBP; (III) HPMPAP; (IV) HPMPPP; (V) HPMDP.

with TOPO. Thus, it would seem that phen reacts as a bidentate ligand.

In the presence of a quaternary ammonium salt, slope analysis of the data confirms the occurrence of the reaction

$$\mathrm{Ln^{3+} + 4HP(o) + R_3R'N^+,Cl^-(o) \xrightleftharpoons{K_{ex}'} R_3R'N^+,LnP_4^-(o) + 4H^+ + Cl^-} \quad (4)$$

which, when eq 1 is subtracted, describes ion-pair complex formation in the organic phase:

$$\mathrm{LnP_3(o) + HP(o) + R_3R'N^+,Cl(o) \xrightleftharpoons{K_{ex}'/K_{ex}} R_3R'N^+,LnP_4^-(o) + H^+ + Cl^-} \quad (5)$$

It may be observed (Table II) that formation of an anionic chelate accompanied by ion pair extraction also significantly

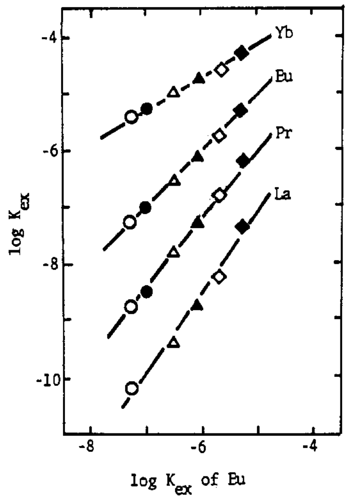

Figure 3. Comparison of log K_{ex} of various lanthanides to log K_{ex} of Eu: (○) HPMDP; (●) HPMOP; (△) HPMPPP; (▲) HPMPAP; (◇) HPMBBP; (◆) HPMBP.[7]

enhances lanthanide extraction ($K_{ex}' > K_{ex}$). The values of K_{ex}', like those of K_{ex}, increase with increasing atomic number. Closer examination reveals that this reflects an override of the influence of β_3, referred to earlier, because the values of K_{ex}'/K_{ex} (from eq 5) show a reverse trend, namely that the fourth ligand anion, as reflected in K_{ex}'/K_{ex}, becomes less favored with increasing atomic number, possibly because of crowding around smaller metal ions.

It is interesting to observe that the K_{ex} values of the lanthanides for each of the reagents studied exhibit the well-known increase with reciprocal ionic radius of the metal ion (Figure 1), which ~~probably reflects~~ the importance of the stability constant, β_3, of the acylpyrazolones studied; the K_{ex} values for HPMBP are largest, probably because its relatively low pK_a (4.1) translates into the largest proton displacement constant. In the other members of the series, which are almost equally acidic, HPMBBP displays the highest K_{ex}, possibly because of the higher distribution constants of its chelates.

Logarithmic plots of K_{ex} for the extractants in this series vs. that for HPMBP (Figure 2) result in a series of converging lines which indicate that the greatest change in extraction constant from one acylpyrazolone to another occurs with the metal ion having the lowest K_{ex} (i.e. with La). The K_{ex} value increases with the atomic number, but the difference from one reagent is the series to another decreases.

How structural changes affect selectivity can best be seen by a series of log-log plots comparing log K_{ex} values for Eu with those of the other lanthanides (Figure 3). The lines describing the behavior of La and Pr are essentially parallel to one another as well as to that for Eu, indicating a selectivity in this group that is insensitive to structure modifications. The slope of the line for Yb, however, is significantly different from the others, and one can observe that selectivity (as Δ log K_{ex}) is highest at low K_{ex} values (i.e. with HPMDP).

In the presence of phen, however, the behaviors of Yb, Eu, and Pr shown by a similar plot are more nearly parallel with the differences for La becoming more pronounced. With TOPO, on the other hand, the separation of Yb from the other lanthanides becomes significantly larger. Finally, the use of the quaternary ammonium ion shifts the K_{ex} values to favor a greater separation for La from the other three.

This study demonstrates the usefulness of the acylpyrazolones as extractants for separation of the lanthanides as well as the need to carefully specify the pair of metal ions involved when one tries to characterize "reagent selectivity".

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Ligand-Exchange Reactivity Patterns of Oxotechnetium(V) Complexes

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The ligand-exchange reactions of various oxotechnetium(V) complexes with 1,2-dithiols have been investigated. The complexes $[TcO(OCH_2CH_2O)_2]^-$ (**1**), $[TcO(O_2C_6H_4)_2]^-$ (**2**), and $[TcO(SCH_2CH_2O)_2]^-$ (**3**) all react with 2 equiv of 1,2-ethanedithiol to ultimately form $[TcO(SCH_2CH_2S)_2]^-$ (**4**). However, different mechanisms and/or intermediates are observed in each case. The reaction of **1** proceeds without evidence for the formation of intermediates. In the reaction of **2**, an intermediate is detected, which is probably a mixed-ligand oxotechnetium monomer; and in the reaction of **3** the spectrum of the intermediate formed is similar to that of the dimer species $[(TcO)_2(SCH_2CH_2S)_3]$ (**5**). The relation of these results to ligand-exchange reactions of 1,2-dithiols with citrate complexes of technetium is discussed. Reaction of 1,3-propanedithiol with $[TcOCl_4]^-$ gives a compound formulated as $[(TcO)_2(SCH_2CH_2CH_2S)_3]$, which does not react with further amounts of ligand to form the bis(1,3-dithiolato) monomer, as would be anticipated from the sequential formation of **4** from **5** in the reaction of $[TcOCl_4]^-$ with 1,2-ethanedithiol.

We have previously reported the synthesis and characterization[2] of a number of oxotechnetium(V) complexes with core structures $TcOS_xO_{4-x}$ (x = 0, 2, 4). X-ray structural studies of at least one member of the series for each value of x have shown square-pyramidal coordination of Tc to be the rule. Each of these Tc(V) complexes has been prepared from aqueous solution or has been shown (x = 0) to be stable in aqueous solution in the presence of excess ligand, the situation occurring in radiopharmaceutical kits.[3] The conjecture[4] that all ^{99m}Tc radiopharmaceuticals probably contain Tc(IV) has been shown to be unlikely.

The preparation of citrate[5] and gluconate[6] complexes of Tc(V) has been reported. These complexes, prepared in situ by Sn(II) reduction of $[TcO_4]^-$ in the presence of an excess

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