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The Effect of Ligands on the Chemical Properties of Monovalent Cadmium Ions[1a]

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The effects of glycine, ethylenediamine, nitrilotriacetic acid, and ethylenediaminetetraacetic acid on the spectra of monovalent cadmium ions and on the specific rates of reaction of monovalent cadmium ions with nitrate, nitrite, bromate, and iodate ions have been determined. The results indicate that monovalent cadmium ions form complexes with these ligands. The mechanism of reduction by monovalent cadmium ions is discussed.

Monovalent cadmium ions, Cd^+, formed by the reaction of hydrated electrons with divalent cadmium ions, have been shown to be powerful reducing agents.[2-6] The specific rates of reduction of different inorganic compounds,[2-5] including a series of Co(III) complexes[6] by Cd^+, have been measured. It has been suggested that Cd^+ ions react as a reducing agent both *via* the outer- and inner-sphere mechanisms.[6]

It seemed of interest to study the effects of ligands on some specific rates of reaction of monovalent cadmium ions, in the hope of achieving a better understanding of the mechanisms involved. The ligands ethylenediaminetetraacetic acid, EDTA, and nitrilotriacetic acid, NTA, have been chosen for this study as they are known to form stable complexes with most cations. The effects of ethylenediamine, en, and glycine, gly, have been also studied as their functional groups are the same but they have much lower chelating capabilities. Furthermore, these ligands are relatively stable toward reducing agents and are therefore not reduced by monovalent cadmium ions.

The results indicate that Cd^+ forms complexes with EDTA and NTA and possibly with en and gyl too. It is concluded that the mechanism of reduction of several anions by the EDTA and NTA complexes does not involve coordination of the anion to the cation prior to reduction. Hydrated Cd^+ ions reduce some of these anions *via* the same mechanism, whereas NO_2^- seems to be reduced after penetration into the inner coordination sphere of the cation.

Experimental Section

Materials.—All solutions were prepared from triply distilled water and AR reagents. The ethylenediamine sulfate, glycine, nitrilotriacetic acid, and ethylenediaminetetraacetic acid disodium salt were supplied by K & K Laboratories.

Procedure.—The procedure of preparation of the samples, irradiation, observation of the optical changes, and calculation of the specific rate constants have been identical with those described earlier in detail.[5,6] The absorption spectra of the transients have been determined by splitting the light beam after it passed through the sample, so that a second monochromator could be used at a constant wavelength, as a monitor of pulse intensity. The absolute molar absorption coefficients were determined by pulse radiolyzing under exactly identical conditions a standard solution, the solution to be analyzed, and once again the standard solution. The standard solution chosen was 10^{-3} *M* $K_4Fe(CN)_6$ saturated with N_2O. The determination of $G\epsilon$ was based on $G[Fe(CN)_6^{3-}] = 6.1$ molecules/100 eV and $\epsilon[Fe(CN)_6^{3-}] = 1000\ M^{-1}\ cm^{-1}$ at 4200 Å. The accuracy of $G\epsilon$ thus determined is ±15%. The activation energy of the reactions has been determined by measuring the specific rates of reactions at temperatures between 3 and 90°.

Results

An attempt to measure the spectra of Cd(I) in the presence of the different ligands has been made. The absorption spectra of the transients formed in deaerated solutions containing 10^{-2} *M* $CdSO_4$ and excess of the ligand, L (0.2 *M* for en and gly, 0.02 *M* for EDTA and NTA), have been determined immediately after the pulse. Under these conditions three intermediates may result as shown by the reactions

$$e_{aq}^- + Cd^{II}L_n \longrightarrow Cd^IL_n \longrightarrow Cd^IL_m + (n-m)L \qquad (1)$$

where $n = 1$–3 depending on the ligand and $m \leq n$ as the complexes of Cd^+ are expected to be less stable than those of Cd^{2+} for poor π-electron-donating ligands

$$OH + L \longrightarrow P_1 \qquad (2)$$

$$H + L \longrightarrow P_2 \qquad (3)$$

P_1 and P_2 are organic radicals which might be identical if H and OH do abstract the same hydrogen atom from the organic ligand. If OH and H attack the organic ligand at more than one site more than two organic intermediates might be formed. The absorption spectra of the transients formed by pulse radiolyzing deaerated solutions of the organic ligand alone have been measured. As in the absence of Cd(II) the hydrated electron exists for about 50 μsec in these solutions contributing to the absorption of the transients, the absorption was measured 100 μsec after the pulse and extrapolated to time zero. (The decay of the organic radicals is relatively slow.) The spectra of the intermediates in the absence of Cd(II) were deducted as a blank from those observed in the presence of Cd(II), and the resulting spectra are attributed to Cd^IL_m.

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(1) (a) Based on work performed under the auspices of the U. S. Atomic Energy Commission. (b) Reprint requests to be sent to D. Meyerstein, Nuclear Research Centre, Negev, Israel.

(2) (a) J. H. Baxendale and R. S. Dixon, *Z. Physik. Chem.* (Frankfurt), **43**, 161 (1964); (b) J. H. Baxendale, J. P. Keene, and D. A. Stott in "Pulse Radiolysis," Academic Press, London, 1965, p 107.

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(Further evidence for this assignment will be given below.) A major drawback of this procedure is that in the absence of Cd(II) the reaction

$$e_{aq}^- + L \longrightarrow P_3 \qquad (4)$$

$$e_{aq}^- + H_2O \longrightarrow H; \qquad H + L \longrightarrow P_2$$

might increase the absorption by the organic radicals.

The spectra of Cd^IL_m thus obtained in deaerated solutions of 0.01 *M* $CdSO_4$ and 0.2 *M* $enSO_4$ or 0.2 *M* gly are presented in Figures 1 and 2. In both cases the maxima of absorptions of Cd^IL_m are between 320 and 330 nm, which means a shift of about 25 nm to the red, relative to Cd^I(aq). The absorption of the organic radicals in the en blank solution is rather small and the accuracy of the spectrum of $Cd^I(En)_m$ is therefore relatively good. In the gly blank solution a much larger correction due to the organic radicals is necessary but mainly not in the region of maximum absorption. In the blank solutions of NTA and EDTA the absorption by the organic radicals approaches 50% that of the Cd^IL_m in the region of maximum absorption and it was, therefore, not possible to determine the maxima of the spectra for $Cd^I(NTA)_m$ and Cd^IEDTA accurately. However the results indicate a red shift, of the same order of magnitude, for these cases too.

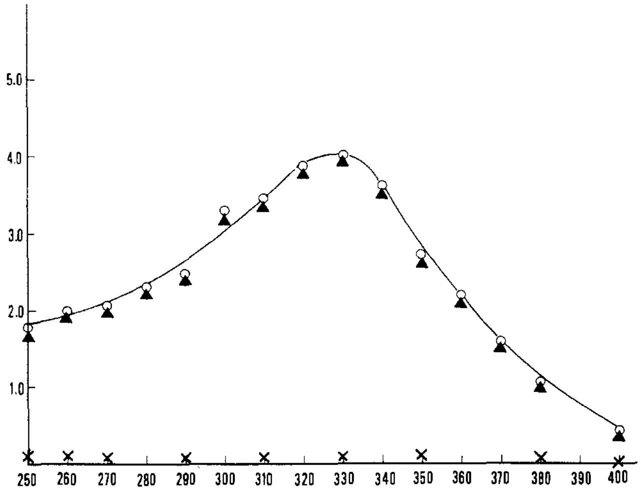

Figure 1.—The absorption spectrum of $Cd^I(en)_m$, the abscissa being in nm and the ordinate in arbitrary absorption units: ×, transient formed in a solution of 0.2 *M* $enSO_4$, pH 11.4; ○, transient formed in a solution of 0.01 *M* $CdSO_4$, 0.2 *M* $enSO_4$, pH 11.4; ▲, a difference curve (○ minus ×).

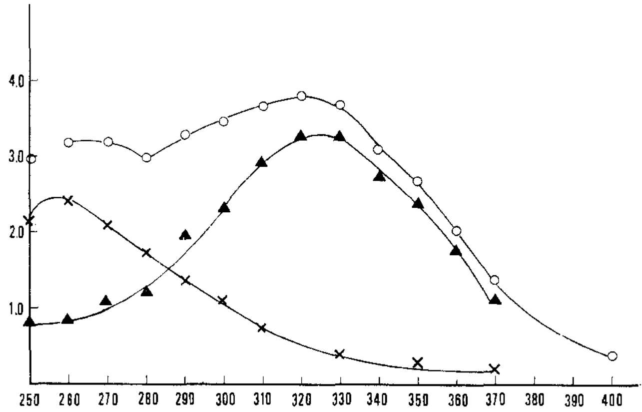

Figure 2.—The absorption spectrum of $Cd^I(gly)_m$, the abscissa being in nm and the ordinate in arbitrary absorption units: ×, transient formed in a solution of 0.2 *M* gly, pH 10.5; ○, transient formed in a solution of 0.01 *M* $CdSO_4$, 0.2 *M* gly, pH 10.5; ▲, a difference curve (○ minus ×).

An attempt has been made to measure the absolute values of the molar extinction coefficients of Cd^IL_m at 350 nm. Using the technique described above, $G\epsilon_{350}$ has been determined with an error limit of ±15%; the results are summarized in Table I. It should be noted that the $G\epsilon_{350}$ values measured represent a combination for all the transients formed in each solution. In order to obtain $G\epsilon_{350}(Cd^IL_m)$, the value obtained for an identical solution but for the absence of $CdSO_4$ should be deducted. (The drawbacks of this procedure were discussed above.) In order to calculate $\epsilon(Cd^IL_m)$ the corresponding *G* values must be determined. The difficulty in measuring the accurate *G* values is that they are dependent on the $Cd^{II}L_n$ concentration and on $k(e_{aq}^- + Cd^{II}L_n)$. Thus for Cd^I(aq) it was found that $G\epsilon_{350}(Cd^I(aq))$ increases by about 40% when the $CdSO_4$ concentration is increased from 10^{-4} to 10^{-1} *M*. The yields in the presence of the organic ligands are expected to be lower than those in their absence, as the ligands decrease by one to three orders of magnitude the specific rates of reaction of e_{aq}^- with $Cd^{II}L_n$.[7,8] Assuming that $G(Cd^IL_m) \approx 3$, $\epsilon_{350}(Cd^IL_m)$ of the order of 8000 M^{-1} cm^{-1} is obtained for all the ligands. The latter value is significantly higher than that for ϵ_{350} $(Cd^I(aq))$. This increase reflects mainly the red shift of the corresponding absorption bands due to the organic ligands. The absorption coefficients at the peak seem to be of the same order or even a little smaller in the presence of the organic ligands.

TABLE I

DETERMINATION OF $G\epsilon_{350}$ VALUES[a]

Matrix	$G\epsilon_{350}$ No Cd(II)	 0.01 *M* Cd(II)
H_2O, pH 6.0	0	11,100
0.2 *M* en, pH 11.4	930	27,300
0.2 *M* gly, pH 10.5	2980	26,800
0.02 *M* NTA, pH 10.7	7840	29,300
0.02 *M* EDTA, pH 11.3	6510	13,100

[a] ϵ_{350} in units of M^{-1} cm^{-1}; maximal standard deviation ±15%. Based on $G\epsilon_{4200}$ = 6100 for $Fe(CN)_6^{3-}$ in 10^{-3} *M* $K_4Fe(CN)_6$ solutions saturated with N_2O.

The rates of disappearance of Cd^IL_m in the absence of added oxidants have been determined by following the decay of its absorption at 350 nm. At this wavelength the absorption of all organic radicals formed is smaller than 25% of that of Cd^IL_m (Table I). Furthermore, it was found that the organic radicals formed in solutions containing no $CdSO_4$ disappear much more slowly than Cd^IL_m. Therefore, for example, after all the Cd^IEDTA has disappeared, a residual absorption remains which decays very slowly. The decay of the absorption of Cd^IEDTA has been analyzed for first-

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[7] M. Anbar and D. Meyerstein, *Trans. Faraday Soc.*, **65**, 1812 (1969).

[8] D. Meyerstein and W. A. Mulac, *ibid.*, **65**, 1818 (1969).

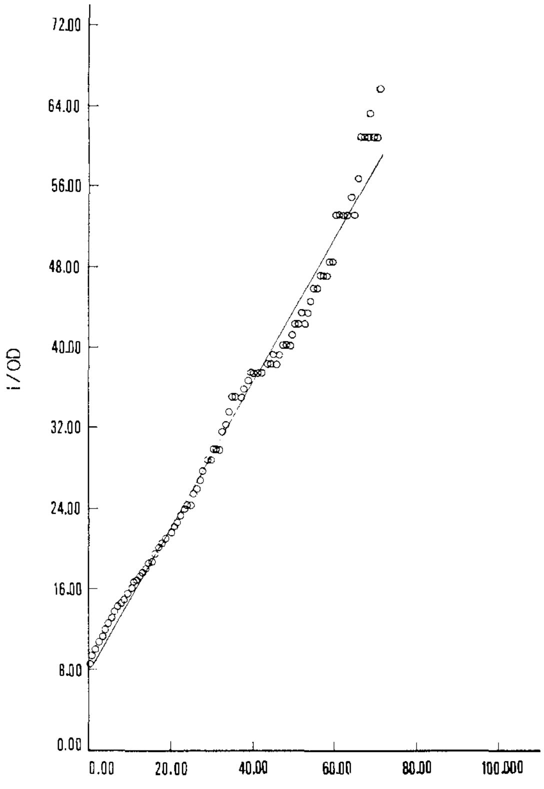

Figure 3.—Second-order decay plot for Cd^{I}EDTA in the absence of oxidants.

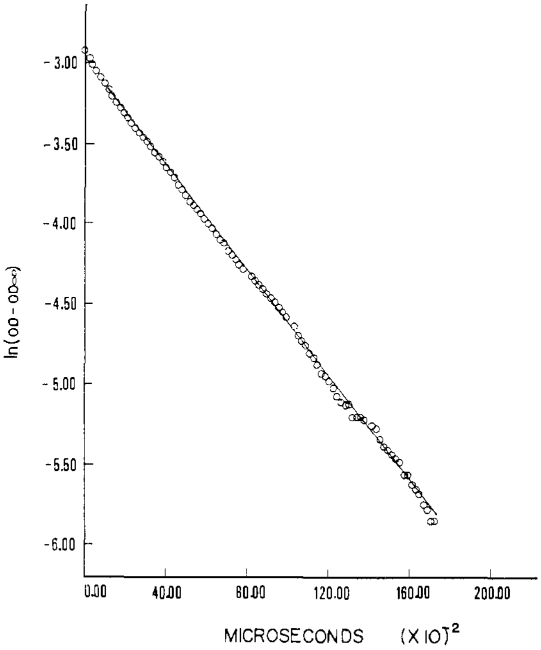

Figure 4.—First-order decay plot for the reaction Cd^{I}EDTA + NO_2^-.

and second-order mechanisms. It was found (Figure 3) that Cd^{I}EDTA disappears by a second-order mechanism. The rate of the reaction has been determined as $k/\epsilon_{350} = (5.8 \pm 1.5) \times 10^3$ and $k = (4 \pm 2) \times 10^7$ M^{-1} sec^{-1}. The large error limit is mainly due to the uncertainty in the exact value of the residual absorption and of the molar extinction coefficient of Cd^{I}EDTA. Similar results have been obtained for Cd^I(NTA)$_m$ where $k/\epsilon_{350} = (1.2 \pm 0.4) \times 10^5$ and $k = (8 \pm 4) \times 10^8$ M^{-1} sec^{-1}. For Cd^I(gly)$_m$ and Cd^I(en)$_m$ first-order disappearance mechanisms have been observed; these might be due to impurities in the ligands added.

The specific rates of reaction of Cd^{I}L$_m$ with NO_3^-, NO_2^-, BrO_3^-, and IO_3^- have been determined by following the decay of the absorption due to Cd^{I}L$_m$ at 350 nm in solutions containing 10^{-2} M Cd^{II}L$_m$ and 5×10^{-5}–2×10^{-4} M oxidating additive. The residual absorptions in these experiments have been found to be significantly smaller than in the absence of the oxidants. The disappearance of Cd^{I}L$_m$ in these experiments has been analyzed for both first- and second-order mechanisms. Pseudo-first-order rates of reaction of Cd^{I}L$_m$ with the oxidants have been calculated only when a good first-order plot has been obtained for at least 2 half-lives (see, for example, Figure 4). The results were corrected for the disappearance of Cd^{I}L$_m$ in the absence of oxidants when needed. The results are summarized in Table II and have an accuracy limit of ±20%. The specific rates of reaction of Cd^I(aq) with the same oxidants are included for comparison. It should be noted that the latter results were obtained at pH 4.5 and not in basic solutions.

TABLE II

EFFECT OF LIGANDS ON SPECIFIC RATES OF REACTION OF Cd(I)[a]

Matrix	μ[b]	NO_3^-	NO_2^-	BrO_3^-	IO_3^-
0.02 M CdSO$_4$, pH 4.5	0.08	3.5×10^8	2.0×10^9	1.25×10^8	2.3×10^9
0.01 M CdSO$_4$, 0.2 M enSO$_4$, pH 11.4	0.64	4.5×10^8	1.12×10^9	1.28×10^8	2.5×10^9
0.01 M CdSO$_4$, 0.2 M gly, pH 10.5	0.21	2.4×10^8	8.5×10^8	6.1×10^7	1.8×10^9
0.01 M CdSO$_4$, 0.02 M NTA, pH 10.7	0.10	4.5×10^7	4.2×10^7	1.02×10^7	6.1×10^8
0.01 M CdSO$_4$, 0.02 M EDTA, pH 11.3	0.16	1.66×10^7	3.2×10^6	8.9×10^6	2.7×10^8

[a] In units of M^{-1} sec^{-1}; maximal standard deviation ±20%. [b] The ionic strength.

The salt effects on the specific rates of reaction with NO_2^- and IO_3^- have been measured and are summarized in Table III. The activation energies 3.0 ± 0.4 kcal/mol for the reaction Cd^I(aq) + NO_2^- and 3.2 ± 0.4

TABLE III

SALT EFFECTS ON THE RATE OF REACTIONS OF Cd(I) WITH NO_2^- AND IO_3^-

Matrix	μ without added salt	μ with added salt[a]	Salt effect[b] NO_2^-	Salt effect[b] IO_3^-	Charge of Cd^{I}L$_m$[c]
0.01 M CdSO$_4$, pH 4.5	0.04	0.54	−16	−23	+1
0.01 M CdSO$_4$, 0.2 M enSO$_4$, pH 11.4	0.64	1.14	−12	−12	+1
0.01 M CdSO$_4$, 0.2 M gly, pH 10.5	0.21	0.71	+1	−6	0
0.01 M CdSO$_4$, 0.02 M NTA, pH 10.7	0.10	0.60	+34	+36	−2
0.01 M CdSO$_4$, 0.02 M EDTA, pH 11.3	0.16	0.66	+25	+40	−2 (−3)

[a] μ was changed by adding 0.5 M NaClO$_4$. [b] The magnitude of the salt effect on the specific rate constants in per cent from the specific rate in the absence of the added salt. A minus sign means a decrease in the specific rate of reaction. [c] Estimated charge of Cd^{I}L$_m$, from the salt effect (see text).

kcal/mol for the reaction $Cd^I(aq) + BrO_3^-$ have been measured as well as those of 2.0 ± 0.3 kcal/mol for the reaction $Cd^IEDTA + NO_2^-$ and 1.1 ± 0.3 kcal/mol for the reaction $Cd^IEDTA + BrO_3^-$.

Discussion

The results indicate that the monovalent cadmium ions formed by the reaction of e_{aq}^- with Cd(II) complexes retain, at least in part, their ligand shell. This can be concluded from the effect of the different ligands on the specific rates of reaction of Cd^IL_m with the different oxidants (Table II). Thus for example the relative rates of reaction of $Cd^I(aq)$ and Cd^IEDTA with IO_3^-, BrO_3^-, NO_3^-, and NO_2^- are, respectively, 8.5, 14, 21, and 625. If the EDTA effect would have been due to some change in the medium, *e.g.*, a change in the ionic strength, all the specific rates of reaction should have been affected to the same degree. Furthermore, the salt effects on the rates of reaction of Cd^IL_m indicate that whereas $Cd^I(en)_m$ is a cation as expected, $Cd^I(gly)_m$ seems to be neutral and $Cd^I(NTA)_m$ and Cd^IEDTA are anions. From the absolute values of the salt effects it seems that the charge of Cd^INTA is −2, the effect being larger than that for $Cd^I(aq)$, which conforms with the formula $CdNTA^{2-}$. For Cd^IEDTA a similar charge is suggested though a charge of −3 is expected from the formula $CdEDTA^{3-}$. This discrepancy might be due to ionic association in these concentrated solutions. The results further suggest that glycine forms a 1:1 complex with Cd(I) under the given conditions and a similar formula seems reasonable for the ethylenediamine complex. $Cd^I(aq)$ seems to be not complexed by sulfate as can be deduced from the salt effects and from the fact that using $Cd(ClO_4)_2$ instead of $CdSO_4$ has no effect on its specific rates of reaction.[5]

The small red shift of the absorption band of Cd(I) due to complexing seems difficult to explain by assuming that the band is due to a charge transfer to solvent transition.[9,10] Therefore, the suggestion that it is a $5^2S_{1/2} \rightarrow 5^2P_{3/2 \text{ or } 1/2}$ transition[11,12] seems more likely though more work is needed in order to elucidate the origin of this transition.

All the specific rates of reaction measured are very high though they are not diffusion controlled, with the exception of some of the reactions with iodate. The effects of the ligands are therefore relatively small and reduce the possibility of deducing from them the mechanism of reduction. Still it seems to us that some suggestions can be made.

The very small activation energies for the reactions of Cd^IEDTA with NO_2^- and BrO_3^- suggest that the anions do not penetrate the inner ligand sphere of Cd^IEDTA prior to the reactions. These activation energies are much smaller than those expected by comparison for the exchange of a ligand of Cd(I). Such an exchange should be the rate-limiting process if penetration into the inner sphere is needed for the formation of the transition state, as the reactions of $Cd^I(aq)$ with NO_2^- and BrO_3^- are faster and have higher activation energies.

If the suggestion that the oxidants do not penetrate the inner coordination sphere of Cd^IEDTA is correct, it is reasonable to assume that the reductions of NO_3^-, BrO_3^-, and IO_3^- by $Cd^I(aq)$ and the other complexes of Cd(I) studied proceed *via* the same mechanism, as the ligand effects on the specific rates of reaction are relatively small. Still the possibility that small contributions of another mechanism exist cannot be excluded. The increased specific rates of reaction of the $Cd^I(en)_m$ complex relative to the $Cd^I(aq)$ complex though the salt effect should have caused a decrease in the specific rates are attributed to the increase in the free energies of reaction. (Ethylenediamine and the other ligands which are poor π-electron donors are expected to stabilize the higher oxidation state.) The effects of gly, NTA, and EDTA as ligands on the specific rates of reaction with NO_3^-, BrO_3^-, and IO_3^- seem to be due to a combination of the increased free energies of reaction, the change in the charge of the reactant, and the salt effects.

From the specific rates of reaction determined (Table III), it is clear that the specific rate of reaction of Cd(I) with NO_2^- is affected by the different ligands more than all the other reactions. Thus the reaction of $Cd^I(aq)$ with NO_2^- is diffusion controlled and significantly faster than the reactions of $Cd^I(aq)$ with NO_3^- and BrO_3^-, whereas the reaction of Cd^IEDTA with NO_2^- is significantly slower than those of Cd^IEDTA with NO_3^- and BrO_3^-. This change in the relative reactivities of Cd(I) due to ligation cannot be explained by changes in the free energies of the corresponding reactions. It has to be assumed, therefore, that the reaction of $Cd^I(aq)$ with NO_2^- proceeds *via* a different mechanism than the reactions of $Cd^I(aq)$ with BrO_3^- and NO_3^-. It is suggested that the reaction $Cd^I(aq) + NO_2^-$ proceeds after penetration of the NO_2^- into the inner sphere of Cd(I). This would explain the relatively large effect of ligands on the reactivity of Cd(I) toward NO_2^-, which seems to be due to a change in the mechanism of reduction. The contribution of the penetration of NO_2^- into the inner sphere of Cd(I) to the mechanism of reduction seems to decrease from $Cd^I(aq)$ to $Cd^I(en)_m$, $Cd^I(gly)_m$, Cd^INTA, and Cd^IEDTA.

The question whether the oxyanion penetrates the inner coordination sphere of a reducing metal ion prior to reaction or not seems to be identical with the question of whether the metal ion is an inner- or outer-sphere reductant. The results therefore suggest that Cd^IEDTA is an outer-sphere reductant, whereas $Cd^I(aq)$ may react *via* both mechanisms. The later suggestion is in accordance with earlier conclusions.[6]

It is of interest to compare the relative reactivities of different reducing agents toward nitrite and nitrate.

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The specific rates of reaction of e_{aq}^- [13] and $Cd^{I}EDTA$ with NO_3^- are higher than those with NO_2^-, whereas the specific rates of reaction of H atoms,[13] $Cd^{I}(aq)$,[5] and $Ni^{I}(aq)$[5] with NO_2^- are higher than those with NO_3^-. The hydrated electrons are expected to be outer-sphere reducing agents, and a similar mechanism has been suggested for $Cd^{I}EDTA$. Hydrogen atoms are most likely an inner-sphere reducing agent,[6,14–16] and the same mechanism has been suggested for $Ni^{I}(aq)$ and $Cd^{I}(aq)$.[6] It is, therefore, suggested that the relative reactivities toward NO_3^- and NO_2^- might be used as one of the guides for determining the mechanism of reduction by strong reducing agents.

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Volatile Chelates of Quadrivalent Actinides[1]

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Tetrakis β-diketonates were synthesized with quadrivalent thorium, uranium, neptunium, and plutonium and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione (fod) and with Th^{4+} and U^{4+} and 2,2,6,6-tetramethylheptane-3,5-dione (thd) and then characterized by elemental analysis. X-Ray diffraction data showed $Th(fod)_4$, $U(fod)_4$, and $Np(fod)_4$ were isomorphous, but $Pu(fod)_4$ had a different structure. Vapor pressures measured by a modified Knudsen effusion method were *ca.* 10^{-3} mm at 125° for all fod chelates and at 195° for both thd chelates. ΔH_{subl} increased from 33.1 kcal/mol for $Th(fod)_4$ to 36.4 kcal/mol for $Pu(fod)_4$. ΔS_{subl} values increased nearly linearly with Z for Th^{4+}, U^{4+}, and Np^{4+} fod chelates; the value for ΔS_{subl} for $Pu(fod)_4$ was larger than the value predicted by a linear increase with Z, probably because of the different crystal structure of $Pu(fod)_4$.

Introduction

Lanthanide chelates of the sterically hindered β-diketones 2,2,6,6-tetramethylheptane-3,5-dione (thd)[3] and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione (fod)[4] have sufficient volatility to permit gas chromatographic separation of the chelates of adjacent lanthanides.[3,4] Some lanthanide ions have been separated by fractional sublimation of $Ln(thd)_3$ chelates. The possibility of similar separations of actinides led to the study reported in this paper. In this study, $Th(thd)_4$, $U(thd)_4$, and $M(fod)_4$ (M = Th, U, Np, Pu) were prepared, and their vapor pressures and some other physical properties were determined. The preparation and study of the spectra of the fod chelates of Th^{4+} and U^{4+} were reported[5] while this paper was in preparation.

Previous workers[6,7] have prepared over 30 β-diketonates of U^{4+} and obtained some measure of their volatility. In general, the substitution of fluorine for hydrogen ($-CF_3$ for $-CH_3$) and replacement of normal alkyl groups with branched alkyl groups increased volatility. However, the most volatile of these chelates, $U(CF_3COCHCOCF_3)_4$, was too unstable for any practical use. The greater shielding of the M^{4+} ions by the bulky thd and fod ligands offers the possibility for both increased volatility and stability toward oxidation.

Experimental Section

$M(thd)_4$.—$Th(thd)_4$ and $U(thd)_4$ were prepared[3] by mixing ethanol–water solutions of the NaOH-neutralized β-diketonate and thorium nitrate or $[(C_2H_5)_4N]_2UCl_6$.[8] The chelates precipitated immediately upon mixing the solutions and were purified by recrystallization from petroleum ether (bp 20–40°) and vacuum sublimation. Analytical data are given in Table I.

Attempts to synthesize $Np(thd)_4$ and $Pu(thd)_4$ by the same procedure yielded products that were probably mixtures of $M(thd)_4$ and hydrocarbon-soluble oxidation products, perhaps including $MO_2(thd)_2$. Attempts to obtain pure $Np(thd)_4$ or $Pu(thd)_4$ from the mixture by fractional crystallization were also unsuccessful. An attempt to prepare $Pu(thd)_3$ in the presence of air resulted in the immediate oxidation of Pu^{3+} to higher plutonium oxidation states.

$M(fod)_4$.—$M(fod)_4$ compounds were prepared by the procedure of Springer, *et al.*,[4] rather than that of Wiedenheft.[5] Methanol–water solutions of the NaOH-neutralized β-diketonate and $[(C_6H_5)_4N]_2MCl_6$ or MCl_4 were mixed, and the crude $M(fod)_4$

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