Reports

Mendelevium: Divalency and Other Chemical Properties

Abstract. *Mendelevium (element 101) is the first actinide element found to give a divalent ion stable in solution. Reduction from the 3+ oxidation state was accomplished with Zn dust, Zn-Hg amalgam, Cr^{2+}, Eu^{2+}, and V^{2+}; additionally, measurements of the equilibrium with V^{2+} provided an estimate of +0.2 volt for the couple, $Md^{2+} = Md^{3+} + e^-$. The chemical behavior of Md^{3+} is similar to that of the other trivalent actinides and lanthanides. Oxidation from the trivalent to higher valence states with sodium bismuthate was not detected.*

While the nuclear decay of the isotopes of mendelevium (element 101) was being studied, an anomaly became apparent in the chemical behavior of this element. After further experiments, we found that Md exhibits a 2+ valence state in acidic solutions, in addition to the normal 3+ state. Mendelevium is therefore the first divalent element found in solution within the series of 14 actinide elements. This finding is surprising, since the 3+ valence dominates in the preceding five actinides and only recently has their divalency been suggested (*1*). Within the first half of the actinide series, there is no reliable evidence for a stable 2+ oxidation state (*2*) other than in americium, which requires stabilization in a solid CaF_2 matrix (*3*).

From the time of discovery of Md in 1955 until now, the amounts made at any one time were limited to a few hundred atoms. That we were able to produce much larger quantities (from 10^5 to 10^6 atoms for each experiment) gave us an opportunity to investigate the chemical properties of Md conveniently. Several oxidation experiments were tried in order to test for valencies greater than 3+ and a series of experiments were aimed at the study of the Md^{2+} ion.

The main experiments were made to characterize the reduced ion as 2+ and to estimate the reduction potential of Md^{3+} by bracketing it with reductants of known potential. If Md^{3+} were reduced by a given reductant, the potential of the Md^{2+}–Md^{3+} couple would be less positive than that of the reductant; if not reduced, the potential would be greater. In the intermediate case, measurements of the equilibrium concentrations of the reactants allowed us to make a better estimate of the potential, a number which is a measure of the thermodynamic stability of the 2+ oxidation state. Spectroscopic or other instrumental methods of measurement are not possible with these tracer quantities.

Approximately 2500 disintegrations per minute (dis/min) of Md^{256} were prepared for each test by bombarding a 3-μg target of Es^{253} for 30 to 40 minutes with 38-Mev helium ions from the Berkeley heavy-ion linear accelerator. The transformed atoms of Md and Fm produced during the bombardments were physically separated from the bulk of the Es^{253} in the target by collecting them (as they recoiled from the nuclear reactions) on a second Be foil placed behind the thin Es target. In the range of 2 to 4×10^5 α-particles per minute of Es^{253} were carried over to the "catcher foil," providing a reference tracer for the behavior of a typical 3+ actinide ion in the chemical experiments. The Md^{256} produced by the (α,n) reaction on Es^{253} decays chiefly by electron capture with a 77-minute half-life to Fm^{256}, which in turn decays by spontaneous fission with a 157-minute half-life (*4*). The fission radioactivity of the Fm^{256} daughter was easily detected and showed with time a very marked growth before decaying when a freshly isolated sample of Md^{256} was repeatedly fission-counted (Fig. 1). The resolution of this growth and decay curve through a least-mean-squares fit, made with an iterating computer code, gave the amounts of Md^{256} and Fm^{256} in each sample.

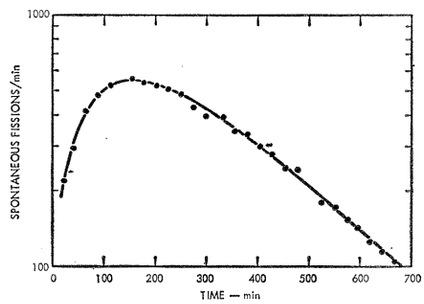

Fig. 1. Growth and decay of daughter Fm^{256} fission radioactivity in an initially pure sample of Md^{256}.

The chemical properties of Md^{2+} were expected to be very similar to those of the divalent lanthanides Eu^{2+} and Yb^{2+} and the "prelanthanide" Ba^{2+}, because the lanthanide series of elements is analogous to the actinides. These properties include insolubility of the sulfates and solubility of the hydroxides (*5*). In our work, the coprecipitation and carrying of 50 to 70 percent of the Md^{256} with barium and europous sulfates was assumed to indicate reduction and *divalency* (rather than monovalency). After the $BaSO_4$-$EuSO_4$ precipitates were separated, the supernatants were oxidized with hydrogen peroxide, and lanthanum fluoride was precipitated in order to measure the amounts of tracer not carried by $BaSO_4$.

The general chemistry of the 2+ oxidation state is influenced by the ion being larger and having obviously less charge than the trivalent parent, a property we could also use for separation by an extraction method. The extractant chosen, di(2-ethylhexyl) orthophosphoric acid (HDEHP), behaves much like a liquid cation exchanger in which a partially ionized hydrogen in the extractant can be replaced by another positive ion. When this type of extractant is at equilibrium with a dilute acid solution of metal ions, its affinity for a particular ion is mainly dependent on the size and charge of the ion; thus, Eu^{3+} in 0.05*M* HCl is held 7.5×10^5 times better than Eu^{2+} by a similar phosphoric acid ester (*6*).

In our experiments multiple extractions were made with the column-elution technique of extraction chromatography in which 1.5*M* HDEHP in *n*-heptane was adsorbed on a bed of inert Kel-F powder. After being treated with a reducing agent, the tracers in 0.1*M* HCl were washed through the extraction bed. The first two to three column volumes of eluant contained nonabsorbed mono- or divalent ions, whereas the unreduced or trivalent Es, Fm, and Md were absorbed at the top of the column bed and were clearly separated from ions with lower oxidation states. For radiometric assay the absorbed tracers were stripped from the extractant with 3*M* HCl.

Table 1 shows the results of these coprecipitation and extraction experiments in which dilute acid solutions containing tracer Md^{256}, Fm^{255}, Es^{253},

and Eu-La carriers were treated with a variety of metal and ionic reductants. "Reduced" Md carries approximately ten times better on $BaSO_4$ than Es, Fm, and unreduced Md do, a result that seems consistent only with a Md^{2+} ion in the reduced solution. Moreover, extraction chromatography separated reduced Md by factors of 200 to 700 from Es and Fm, an indication that either a di- or monovalent mendelevium was partitioned between the extractant and acid phases. Our conclusion on the basis of these data is that Md^{3+} was reduced to Md^{2+} by Zn dust, Zn(Hg) amalgam, Cr^{2+}, Eu^{2+}, or V^{2+}. Very probably because of slow reaction rates, the Be foil and Ni powder did not appear to cause reduction.

The reductions with V^{2+} were only partially effective, thereby providing us with an opportunity to derive a rough value for the oxidation potential of Md^{2+}. The equation for the oxidation-reduction reaction can be written as

$$V^{2+} + Md^{3+} = V^{3+} + Md^{2+}$$

If it is assumed that the reaction has reached equilibrium, the equilibrium constant is given by the expression

$$K = [V^{3+}]\,[Md^{2+}]/[V^{2+}]\,[Md^{3+}],$$

where the brackets indicate activities of these ions. However, within our approximations, concentrations will serve as well as activities. The ratio $[Md^{2+}]/[Md^{3+}]$ was taken as ½ from Table 1; after the foregoing experiments we determined the ratio $[V^{3+}]/[V^{2+}]$ using solutions of similar composition, and the distinctive absorption spectra of vanadium in each oxidation state. Owing to the presence of a small quantity of nitrate ion in the lanthanum added as carrier, most of the vanadous ion was oxidized, resulting in a value of about 30 for the vanadic-vanadous ratio. Combining our ratios yields a value of about 15 for K, and the standard potential derived from the Nernst equation is

$$E^0 = 0.059 \log K = \approx 0.07 \text{ volt},$$

which means that V^{2+} is a better reducing agent than Md^{2+} by about 0.07 volt. Taking the potential of the V^{2+}–V^{3+} couple as +0.25 volt (*7*), we can then offer an estimate for the oxidation potential of mendelevium in the following half-reaction:

$$Md^{2+} = Md^{3+} + e^-, E^0 \simeq +0.2 \text{ volt}.$$

In comparison with the actinides, divalency within the lanthanide series is less rare and is mainly associated with the special stability given by the half-filled and fully filled *f*-electron shell. The lanthanide ions Eu^{2+} and Yb^{2+}, are accounted for under this rule, but Md^{2+} is not eligible for this extra stability, since the ion is at least one electron short of the supposedly stable $5f^{14}$ configuration. On the other hand, filling of the *5f* shell could occur if nobelium (element 102) formed a divalent state, which, in our opinion, is a reasonable possibility.

Table 1. Comparison of the coprecipitation and extraction behavior of tracer Es, Fm, and Md after treatment with reducing agents. One-half milligram of Eu^{3+} was added before the reducing agent in all experiments; 0.5 mg of Ba^{2+} and 0.5 mg of La^{3+} carriers were added at the same point in the precipitation tests only. The column-elution method of extraction chromatography was used with the extractant, di(2-ethylhexyl)phosphoric acid (HDEHP), absorbed on a fixed column bed of Kel-F powder.

Conditions for reduction	Standard potential of reducing agent (volt)	Carried by $BaSO_4$ (%)		Not extracted by HDEHP column (%)	
		Md	Es-Fm	Md	Es-Fm
Be foil dissolved in 6*M* HCl, ~80°C, 7 min	+1.85	4.1	8.3		
Zn dust added to ~4*M* HCl over a 25-min interval, ~80°C	+0.763	52	8.0		
Ni powder added to ~4*M* HCl, ~80°C, 23 min	+0.250	1.1	1.5		
~0.6*M* Cr^{2+}, ~4*M* HCl, ~25°C, 1–2 min	+0.41	72	7 ± 2		
0.1*M* V^{2+}–V^{3+}, 1*M* HCl, 2–3 min, ~25°C	+0.256	46	7 ± 2		
0.2*M* V^{2+}–V^{3+}, 1*M* HCl, 2–3 min, ~25°C		36	2.0		
Zn(Hg) amalgam, 80°C, ~20 min, 0.1*M* HCl; Zn(Hg) amalgam in upper half of extraction column	+0.763			77	<0.10
0.01*M* Eu^{2+}, 0.1*M* HCl, ~2–3 min, 80°C; Zn(Hg) amalgam in upper half of extraction column	+0.43			75	<0.10
~0.6*M* Cr^{2+}, 0.1*M* HCl, ~2 min, 25°C; extraction column washed with 0.6*M* Cr^{2+} in 0.1*M* HCl	+0.41			99	0.56

If we now consider the properties of mendelevium in the 3+ oxidation state, a combination of all our experiences—including the chemical isolations of Md for nuclear experiments, points to a chemical behavior of Md^{3+} similar to that of the other trivalent actinides and lanthanides. The hydroxide and fluoride are insoluble and are quantitatively coprecipitated with lanthanum. As may be expected, Md^{3+} was not seriously differentiated from trivalent Cm, Es, and Fm by elution from cation-exchange resin with 6*M* HCl. Numerous elutions from cation exchange resin with solutions containing the chelate, ammonium α-hydroxyisobutyrate, confirmed the element elution sequence and Md-Fm separation described earlier for mendelevium (*8*).

The oxidation of Md^{3+} to higher oxidation states was attempted by heating solutions of Md-Es tracer in 1*M* and 6*M* nitric acid for about 20 min with sodium bismuthate (a strong oxidant). During this oxidation step, the 1*M* HNO_3 solution was extracted with an equal volume of pure tri-*n*-butyl phosphate: the 6*M* HNO_3 was extracted after oxidation with HDEHP diluted to 1.5*M* with *n*-heptane. Our knowledge of these extractants has expanded from years of wide use in many laboratories, and it is well known that they are quite selective. The HDEHP, for instance, prefers to extract small, highly charged ions such as tetravalent actinides (*9*). Over 90 percent of the Md, if in the tetravalent state, should have been extracted into the HDEHP at the acid concentration we selected. However, in this experiment less than 1 percent of the Md was found in the organic phase, and with either extractant Md was unseparated from Es in the acid and organic phases. Thus, we conclude that Md^{3+} is not easily oxidized.

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14 August 1967

Rabbit Hemoglobin Biosynthesis: Use of Human Hemoglobin Chains To Study Molecule Completion

Abstract. *A cell-free protein-synthesizing system made from rabbit reticulocytes was used to incorporate ^{14}C-amino acids into hemoglobin. Electrophoretic analyses of the soluble products of this cell-free system revealed a fraction containing rabbit ^{14}C-alpha chains in addition to the rabbit ^{14}C-hemoglobin. The addition of isolated human hemoglobin beta chains to this system during active synthesis inhibited the release of newly synthesized rabbit ^{14}C-beta chains into solution from the ribosome fraction. This inhibition was possibly a result of hybrid hemoglobin formation between rabbit alpha and human beta chains. A model of hemoglobin construction in which soluble alpha chains are intermediates is suggested. These alpha chains may aid in the release of beta chains from the polyribosomes during the completion of the hemoglobin molecule.*

The hemoglobin molecule is composed of two peptide α-chains, two peptide β-chains, and four heme groups. Biosynthesis of the individual chains in rabbit reticulocytes, apparently occurring on separate polyribosomes, is followed by release to the soluble phase (*1*). However, the exact mechanism of construction of the final hemoglobin molecule remains unknown.

A cell-free system from rabbit reticulocytes can incorporate ^{14}C-amino acids into soluble hemoglobin (*2*). This protein-synthesis system should be useful in exploring the terminal steps in completion of hemoglobin. We wanted to obtain information on the nature of the soluble chains involved in completion.

Bucci and Fronticelli showed that isolated undenatured α- and β-chains can be obtained from human hemoglobin by treatment with *p*-chloromercuribenzoate (*3*). Because of the excellent homology between rabbit and adult human hemoglobin chains (*6*), we decided to see if the addition of these isolated human chains to the rabbit cell-free system (*4, 5*) would affect the completion of rabbit hemoglobin in a specific manner.

The presence of human hemoglobin α- or β-chains in the rabbit system throughout the 60-minute incubation did not change the total incorporation of ^{14}C-valine into protein (Table 1). However, human β-chains, but not human α-chains, caused a shift in distribution of radioactivity between the soluble and ribosome-bound proteins. The presence of human β-chains resulted in a 30-percent decrease in the amount of protein radioactivity in solution. There was a corresponding increase in the amount of protein radioactivity in the ribosome fraction. This effect was not seen if the β-chains were incubated with an equal amount of α-chains, thereby forming human hemoglobin A (*7*) before addition to the rabbit system. Thus, the change in distribution of radioactivity between soluble and ribosome-bound protein was caused specifically by free human β-chains.

Table 1. Effect of human hemoglobin chains on protein synthesis in a cell-free system from rabbit reticulocytes. In the reaction mixture, each assay contained 4 mg of ribosomes and 0.1 μmole of ^{14}C-valine (1.0 mc/mmole) in a final volume of 1.4 ml; 0.37 mg of human α-chains or 0.39 mg of human β-chains were included as indicated. The mixture was incubated for 60 minutes at 37°C. After the incubation, the ribosomes were removed by centrifugation (105,000*g* for 90 minutes). Both the ribosome pellet and resulting supernatant (soluble fraction) were washed for counting of radioactive protein in a liquid-scintillation system (*14*).

Addition to reaction mixture	^{14}C-valine in protein (mμmole)		
	Total	Soluble	Ribosomes
None	6.12	4.89	1.23
α-Chains	6.20	4.97	1.23
β-Chains	6.00	3.24	2.76

To learn whether this shift in distribution of protein radioactivity could be explained by an inhibition of nascent rabbit α- or β-chain release into solution from the ribosomes, we prepared rabbit globin from each of the two labeled soluble phases (supernatant after centrifugation at 105,000*g*) isolated after cell-free incubations with and without added human β-chains. The α- and β-chains of these globins were separated on carboxymethylcellulose columns (*8*). The presence of human β-chains in the incubation mixture caused a 45-percent decrease in the amount of radioactivity found in the rabbit β-chain peak. The amount of radioactivity in the rabbit α-chain remained the same. Thus, human β-chains appeared to inhibit selectively the release of newly synthesized rabbit β-, but not α-, chains into the soluble phase from the ribosome fraction (*9*).

We investigated the question of whether the human chains added during active synthesis were able to form hybrid hemoglobins (*10*) with the newly synthesized rabbit ^{14}C-chains. Forty percent of the soluble ^{14}C-protein radioactivity traveled with the carrier α_2^{RAB} β_2^{A} hybrid band when human β-chains had been present during active synthesis (Fig. 1a). Conversely, 55 percent of the soluble ^{14}C-protein radioactivity was located in the carrier α_2^{A} β_2^{RAB} band when human α-chains were present (Fig. 1b). Furthermore, chain-separation chromatography of the globins eluted from these hybrid bands showed that in both cases the ^{14}C radioactivity was located in the particular rabbit chain consistent with the formation of a true hybrid hemoglobin.

Formation of these hybrids was accompanied by a corresponding decrease in the amount of ^{14}C-protein radioactivity in the pure rabbit hemoglobin band. (See Fig. 2a for a typical electrophoretic pattern of the soluble phase from an incubation without added human chains.) Figure 1 also shows that the human chains did not induce the breakdown of already formed rabbit ^{3}H-hemoglobin included in the incuba-