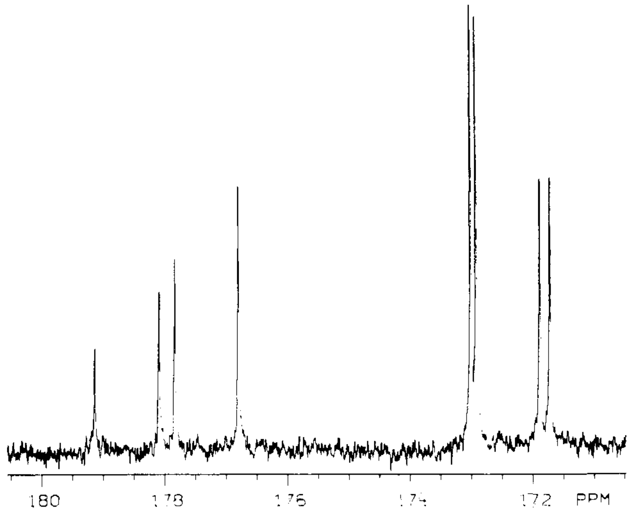

Figure 1. 121.5-MHz ^{31}P NMR spectrum of $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)_2(P(OCH_3)_3)]PF_6$.

^1H NMR spectral pattern observed in these and previously reported phosphite complexes.[3]

Reactivity Comparison of $[(\eta\text{-}C_5H_5)Fe(CH_3CN)_n(L)_{3-n}]^+$ and $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_n(L)_{3-n}]^+$. The cyclopentadienyliron acetonitrile compounds prepared here are in every case more reactive than the corresponding cyclopentadienylruthenium acetonitrile complexes that we have previously investigated. This difference in reactivity is most evident in the thermally unstable $(\eta\text{-}C_5H_5)Fe(CH_3CH)_3^+$ ion compared with the isolable ruthenium complex, $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_3]PF_6$. Addition of two-electron-donor ligands at room temperature to the ruthenium complex results in the replacement of exclusively one CH_3CN upon mixing. Further substitution of the complex $[(\eta\text{-}C_5H_5)Ru(CH_3CN)_2L]PF_6$ with an additional ligand proceeds slowly at room temperature. In contrast, the iron analogue $(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+$ reacts rapidly at room temperature in CH_3CN with a variety of two-electron-donor ligands to yield disubstituted complexes $(\eta\text{-}C_5H_5)Fe(CH_3CN)L_2^+$. The third acetonitrile ligand can be displaced in the disubstituted iron compounds in refluxing dichloromethane solution, while its replacement in the corresponding ruthenium complexes occurs in refluxing dichloroethane. Although these reactions proceed at similar rates, the Ru system is significantly less labile, as judged by the significantly higher boiling point of dichloroethane (44 °C difference). Finally, the increased reactivities of these iron acetonitrile complexes over the ruthenium analogues are consistent with the general observation that, in analogous first- and second-row complexes, reactions generally proceed more rapidly for the first-row transition-metal complex.

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Registry No. $[(\eta\text{-}C_5H_4CH_3)Fe(\eta\text{-}p\text{-}xyl)]BF_4$, 85709-81-5; $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_3)_3)_2]PF_6$, 85701-91-3; $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(CNC(CH_3)_3)_2]PF_6$, 85701-93-5; $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(2,6\text{-}DMP)_2]PF_6$, 85701-95-7; $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_2CH_3)_3)_2]PF_6$, 85701-97-9; $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OPh)_3)_2]PF_6$, 33307-64-1; $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(diphos)]PF_6$, 83172-78-5; $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2(2,6\text{-}DMP)]PF_6$, 85701-99-1; $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)(2,6\text{-}DMP)_2]PF_6$, 85702-01-8; $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)_2(P(OCH_3)_3)]PF_6$, 85702-03-0; $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)(P(OCH_3)_3)_2]PF_6$, 85702-05-2; $[(\eta\text{-}C_5H_5)Fe(P(OCH_3)_3)_2(P(OPh)_3)]PF_6$, 85702-07-4; $[(\eta\text{-}C_5H_5)Fe(CH_3CN)(P(OCH_3)_3)(2,6\text{-}DMP)]PF_6$, 85702-09-6; $[(\eta\text{-}C_5H_5)Fe(P(OCH_2CH_3)_3)(P(OCH_3)_3)(2,6\text{-}DMP)]PF_6$, 85702-11-0; $[(\eta\text{-}C_5H_5)Fe(\eta\text{-}p\text{-}xyl)]PF_6$, 34978-37-5; $P(OCH_3)_3$, 121-45-9; CH_3CN, 75-05-8; $CNC(CH_3)_3$, 7188-38-7; 2,6-DMP, 2769-71-3; $P(OCH_2CH_3)_3$, 122-52-1; $P(OPh)_3$, 101-02-0; diphos, 1663-45-2; $(\eta\text{-}C_5H_5)Fe(CD_3CN)_3^+$, 85702-12-1; CD_3CN, 2206-26-0; $(\eta\text{-}C_5H_5)Fe(CH_3CN)_3^+$, 85702-13-2; thallium cyclopentadienide, 34822-90-7.

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Sublimation of Bis(1,3-propanedial) Chelates of Palladium(II) and Chromium(III)

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The bis(1,3-propanedial) chelates of palladium(II) and chromium(III) have been synthesized and characterized, and their volatility has been studied. Both chelates sublime below 120 °C in a fractional sublimator in a stream of air at 1 torr and are recoverable, but not quantitatively. Sublimation of the Pd(II) chelate was accompanied by a partial decomposition with Pd metal deposited as a mirror. It is proposed that the Pd(II) chelate may be used in the preparation of palladium front-surface mirrors in spectroscopic instrumentation and for the deposition of catalytic palladium in porous supports. Attempts to synthesize the bis(1,3-propanedial) chelates of Al(III), Co(II), Co(III), Cu(II), Fe(III), Ni(II), Mn(II), Mn(III), Pt(II), and Rh(III) were unsuccessful.

Numerous β-diketone ligands have been investigated in this laboratory for their ability to form volatile metal chelates, but of all the ligands studied, 1,3-propanedial (malonaldehyde) is unique. Malonaldehyde (MDA) is the simplest molecule capable of providing the basic 1,3-diketo structure, which may enolize and thereby coordinate with metal ions to form β-diketo chelates, but unlike other 1,3-diketones it will coordinate with a very limited number of ions and forms a palladium chelate with unusual sublimation characteristics.

MDA has been extensively studied by organic chemists but has been almost ignored as a possible chelating agent. Schuster[1] used the metal chelates of MDA as models in LCAO–MO calculations on the enol form of acetylacetone and its metal complexes, but the chomium(III) complex of MDA is the only chelate of the ligand reported in the literature as having been isolated and characterized. Kwon and Watts[2]

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postulated the presence of the iron(III) chelate but were unable to isolate the compound. Hall and Swile[3] have presented the ^{1}H NMR spectrum of the trimethylplatinum derivative of MDA, which they consider to be dimeric.

The present investigation was undertaken to determine whether MDA would chelate with common metal ions and if the bis(malonaldehyde) chelates were volatile. It was thought that the chelates of MDA might be more volatile than the β-diketo chelates of ligands of higher molecular weight. The uniqueness of MDA as a chelating agent was confirmed.

Experimental Section

Reagents. 1,1,3,3-Tetramethoxypropane, 99+% pure (Aldrich Chemical Co.), was distilled twice at reduced pressure before use. All other reagents and metal salts employed were reagent grade.

Fractional Sublimation Apparatus and Procedure. Specifications for the fractional sublimator used in this work were reported earlier.[4,5] Briefly, the apparatus consists of a 1-m (12 mm o.d.) Pyrex tube with a temperature gradient maintained along its length, evacuated to 1 mm of mercury pressure, with a carrier gas (air) flowing from the high- (180 °C) to low- (40 °C) temperature end of the sublimator. Samples were placed in small aluminum boats between glass-wool plugs in the high-temperature end of the sublimation tube before the pressure was reduced and heated for 2 h at reduced pressure. The volatilized chelate was entrained in the stream of air and carried through the tube until condensation occurred. The recrystallized (sublimed) chelates were found in reproducible temperature condensation zones. Individual chelates were recovered by cutting the sublimation tube into selected segments and dissolving the chelate in ether or chloroform.

Preparation of the Metal Chelates. Bis(1,3-propanedialato)palladium(II). In a small test tube, 0.10 g (0.60 mmol) of tetramethoxypropane, 2 mL of water, and 1 drop of 1 N HCl were mixed and heated on a steam bath until the mixture became homogeneous and turned pale yellow. The solution was cooled in an ice bath, and the pH was adjusted to about 5 with 1 M NaOH. The solution was then added to a cold suspension of 18 mg (0.10 mmol) of palladium(II) chloride and 15 mL of ethyl ether in a 25 mL Erlenmeyer flask equipped with a magnetic stirring bar and cooled in an ice–salt bath. The contents were stirred for 1 h. The ether layer gradually became yellow and was removed by decantation. Additonal 15-mL portions of ether were added, and the process was continued until the ether layer remained colorless (three ether portions).

The ether extracts were combined and dried over magnesium sulfate for 2 h. The solution was decanted and evaporated in a stream of dry N_2 until yellow needles formed. The suspension was centrifuged and the liquid drawn off with a pipette. The crystals were washed with a few drops of cold (0 °C) ether and dried at room temperature under a stream of nitrogen to yield 8.7 mg (0.035 mmol) of yellow crystals (yield 35%). The yellow crystals gradually decomposed to a gray substance when dried for several hours in air at atmospheric pressure and 107 °C but were purified by sublimation in the fractional sublimator at 180 °C in a stream of air at 0.5 torr in 30 min with about 30% of the crude product recovered as fine yellow needlelike crystals. A carbon–hydrogen analysis of the sublimate gave the following results. Anal. Calcd for $C_6H_6O_4Pd$: C, 28.98; H, 2.44. Found: C, 28.35; H, 2.41. In the mass spectrum, the molecular ion and metal-containing fragments down to the free metal itself showed the distinctive isotope pattern of palladium (five major isotopes 104, 105, 106, 108, 110). The infrared spectrum (KBr pellet) showed major bands at 1590, 1490, 1430, 1360, 1325, 635, and 457 cm^{-1}. The NMR spectrum ($CDCl_3$) showed a triplet at 5.62 ppm and a doublet at 7.18 ppm.

Tris(1,3-propanedialato)chromium(III). This chelate was prepared by the procedure suggested by Collman[6] and also by the procedure used to prepare the palladium chelate. The yield was 38% by the Collman method and 31% by the method described above. The product was purified by sublimation, and the long red crystals melted at 182–183 °C (lit. mp 182–183 °C). A carbon–hydrogen analysis of the sublimate gave the following results. Calcd for $C_9H_9O_6Cr$: C, 40.76; H, 3.42. Found: C, 41.00; H, 3.72. In the mass spectrum, the molecular ion and fragments due to loss of one and two ligand molecules were present. The infrared spectrum (KBr pellet) showed major bands at 1600, 1490, 1440, 1370, 1310, 692 and 463 cm^{-1}.

Results and Discussion

Attempts were made to chelate the following metal ions with MDA: aluminum(III), cobalt(II), cobalt(III), copper(II), nickel(II), iron(III), manganese(II), manganese(III), platinum(II), and rhodium(III). In all cases it appeared that the metal ion was involved in the reaction with the ligand because of drastic color changes in the system or modified chemical behavior of the metal ion but none of the products could be isolated and identified as metal chelates. The infrared spectra of those solid substances that were recovered from the aqueous solutions indicated the presence of an organometallic compound, but the spectra were considerably different from those of the palladium and chromium chelates. All the infrared spectra showed both a strong O–H absorption band and a perturbed carbonyl band. This seemed to indicate that a nonchelate compound or mixture of compounds may have been formed. Efforts to further purify the reaction products were unsuccessful. The NMR spectrum of the rhodium compound, in deuterated water, was almost identical with that of the sodium enolate. The carbon and hydrogen analyses of the products could not be correlated with those of the normal chelate, the enolate, or the *gem*-diol chelate. The aqueous solutions containing the aluminum(III), copper(II), iron(III), and platinum(II) reaction products were extracted with ether, and the ether phase was treated by various chromatographic techniques, but no solid was recovered. The chromotographic data indicated that at least two types of components were present, one that could be eluted with benzene or dichloromethane and another that could be eluted with ethanol.

The chromium(III) chelate sublimed without noticeable decomposition in the same temperature range as the Cr(III) chelates of acetylacetone (AA)[5] and dipivaloylmethane (DPM)[7] but was less volatile than the Cr(III) chelates with trifluoroacetylacetone (TFAA) and hexafluoroacetylacetone (HFAA).[5] The sublimation temperature zones for the various Cr(III) chelates studied were as follows: Cr(HFAA)$_3$, 20–32 °C; Cr(TFAA)$_3$, 50–70 °C; Cr(DPM)$_3$, 62–88 °C; Cr(MDA)$_3$, 65–98 °C; Cr(AA)$_3$, 80–106 °C.

The sublimation temperature zones of the palladium chelates formed with AA,[5] thioacetylacetone (SAA), DPM,[7] TFAA,[5] benzoyltrifluoroacetone (BTFA),[5] thenoyltrifluoroacetone (TTFA),[8] thiothenoyltrifluoroacetone (STTFA),[9] and MDA were as follows: Pd(MDA)$_2$, 40–60 °C; Pd(TFAA)$_2$, 58–76 °C; Pd(DPM)$_2$, 70–100 °C; Pd(AA)$_2$, 72–98 °C; Pd(SAA)$_2$, 92–106 °C; Pd mirror, 110–125 °C; Pd(BTFA)$_2$, 118–140 °C; Pd(STTFA)$_2$, 133–148 °C; Pd(TTFA)$_2$, 162–175 °C.

A comparison of the fractional sublimation temperature zones of various palladium complexes shows that the MDA complex is the most volatile but is unstable.

The palladium(II) chelate sublimed readily, but the sublimation was accompanied by partial decomposition in which a smooth, fine-grained, shiny palladium mirror was deposited on the surface of the sublimation tube at temperatures between 110 and 125 °C. The chelate deposition occurred in the region between 40 and 70 °C, near the condenser-cooled section of the sublimation tube. Ten separate sublimations of the palladium complex under varying conditions of temperature and pressure in the sublimator showed that from 50 to 65% of the palladium was deposited as the metal (mirror), 5 to 15% remained in the sample boat as a decomposition product, and the remainder deposited as the chelate. Deposition of the

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mirror appeared to be relatively independent of the maximum temperature of the sublimator over the range 123–212 °C and a pressure range 0.01–3.8 torr.

It is interesting to note that, of the literally hundreds of metal β-diketone chelates studied for their volatility in this laboratory, only the palladium MDA complex vaporized and then formed a deposit of the free metal under these moderate temperature and pressure conditions. These observations of the behavior of the palladium MDA complex suggested that a sublimation technique could be used to produce palladium (front-surface) mirrors and possibly palladium catalysts by depositing the metal on a catalyst support. Porous plugs 1 cm long of charcoal (activated carbon) and Chromosorb P and W were placed in the fractional sublimator in the temperature range where palladium metal was deposited. Palladium was readily deposited on the carbon and Chromosorb support.

The sublimation-produced palladium was tested for catalytic activity by comparing its activity with a commercial hydrogenation catalyst with 5% palladium on activated carbon. Cyclohexene, benzophenone, *p*-nitrotoluene, and maleic acid were each hydrogenated with the commercial catalyst and the catalyst produced in the sublimation apparatus. Comparable results were obtained with the different catalysts. The hydrogenation of maleic acid was studied in more detail. The average of three runs with each catalyst showed virtually no difference in the yields, which ranged from 92 to 96%. The primary difference noted was that the half-hydrogenation times with the commercial catalysts were significantly less than for the sublimation-produced palladium. The slower catalytic activity of the sublimation-produced catalysts on carbon and Chromosorb P and W is believed due to its lower palladium content, ~2.5% Pd, compared to that of the commercial catalyst, which was 5% Pd.

Registry No. $Pd(MDA)_2$, 74577-84-7; $Cr(MDA)_3$, 15636-02-9; tetramethoxypropane, 102-52-3; palladium, 7440-05-3; maleic acid, 110-16-7.

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Enthalpy of Formation and Magnetic Susceptibility of Curium Sesquioxide, Cm_2O_3

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Monoclinic Cm_2O_3 has been prepared from the long-lived isotope ^{248}Cm ($t_{1/2} = 3.4 \times 10^5$ y), and its enthalpy of formation has been determined at 298 K to be −1682 ± 12 kJ mol^{-1} from solution calorimetry measurements on four different samples. The magnetic susceptibility of three of these samples has been measured on a Faraday balance between 2 and 298 K. Cm_2O_3 exhibits Curie–Weiss behavior from 100 to 300 K with $\mu_{eff} = 7.89 \pm 0.04\ \mu_B$ and $\Theta = -130 \pm 2$ K. The compound appears to order magnetically as the temperature decreases and has an antiferromagnetic transition at 13 ± 2 K. The results are interpreted by comparison with similar properties of related lanthanide and actinide compounds.

Introduction

Curium sesquioxide was first reported in 1955[1] and has been prepared many times since then. Although many compounds of curium are now known, very few properties other than their crystal structures have been determined because of the high α specific activities of the most common isotopes (^{242}Cm, $t_{1/2} = 163$ d, specific activity 7.36×10^9 disintegrations min^{-1} μg^{-1}; ^{244}Cm, $t_{1/2} = 18.1$ y, specific activity 1.80×10^8 disintegrations min^{-1} μg^{-1}).[2] The recent availability of the very long-lived isotope ^{248}Cm ($t_{1/2} = 3.39 \times 10^5$ y, specific activity 9.44×10^3 disintegrations min^{-1} μg^{-1})[2] has made possible many chemical measurements that would be severely hindered by the more radioactive isotopes.

The metal is the only Cm species for which both thermodynamic and magnetic properties have been measured. Because of the importance of Cm_2O_3 as a key Cm(III) compound and as a pivotal member of the actinide sesquioxides (all three common M_2O_3 structure types are easily prepared), we have determined the enthalpy of formation and magnetic susceptibility of monoclinic Cm_2O_3 using ^{248}Cm. These two properties are essential for a complete understanding of Cm^{3+} ($5f^7$ configuration, half-filled 5f subshell).

The body-centered cubic form of Cm_2O_3 exists below 800 °C, the monoclinic form between 800 and 1615 °C, and the hexagonal form above 1615 °C.[3] Two higher temperature polymorphs have also been found.[3] We chose to study monoclinic Cm_2O_3 for several reasons: It can be prepared by H_2 reduction of CmO_{2-x} at 825 °C,[4] it does not oxidize readily,[5] it is stoichiometric,[6] and it does not suffer lattice distortion from α self-irradiation.[4,7,8] There have been no

Table I. Composition of Curium Samples (Atom Percent Referred to Total Cm)

	samples			samples	
	A, B, E	C, D		A, B, E	C, D
Na[a]	0.1	*a*	^{245}Cm[b]	0.05	0.03
Si[a]	0.3	*a*	^{246}Cm[b]	2.56	2.76
Cl[a]	0.2	*a*	^{247}Cm[b]	0.018	0.02
K[a]	0.02	*a*	^{248}Cm[b]	97.37	97.19
Pm[a]	0.1	*a*	^{249}Bk[c]	0.01	0.01
^{244}Cm[b]	0.0003	0.0002	^{252}Cf[b]	0.00002	0.000001

[a] By spark-source mass spectrometry on sample A only. Other elements not detected or detected at levels ≤0.01 atom %: Mg, Al, S, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Rb, Sr, Y, Zr, Sb, I, Ba, Sm, Ta, Hg, Pb, U. [b] By mass spectrometry and α-energy spectrum. [c] By β counting.

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