Proton nmr spectra were recorded on a Varian A-60. Attempts were made to obtain Raman spectra on an instrument employing a SPEX 1400-II double monochromator and Ar ion laser excitation. The samples decomposed in the laser beam even when cooled to −100°.

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## Preparation and Properties of Some Rare Earth and Americium Chelates

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Our continuing interest in methods for the separation of actinide elements has been directed to the volatile chelates of the lanthanides.[1-6] The assumption that trivalent lanthanides and actinides have similar properties was justified by the finding, reported herein, that americium chelates are volatile. 2,2,6,6-Tetramethyl-3,5-heptanedione (Hthd) was used to prepare the compound $^{243}Am(thd)_3$ by the method of Eisentraut and Sievers[1] and 1,1,1,5,5,5-heptafluoro-2,4-pentanedione (Hhfa) was used to prepare $Cs^{243}Am(hfa)_4$ by a modification of the method of Lippard.[2] (See Table I.) Likewise a number of these chelates of the lanthanide elements were prepared for a direct comparison of properties. Elemental analyses were made for at least one representative of each crystal structure type. Identification of other members of isomorphous series were made by X-ray diffraction.

TABLE I
ANALYTICAL DATA FOR RARE EARTH AND AMERICIUM CHELATES $CsM(hfa)_4 \cdot nH_2O$

| | | % compn | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C | | H | | $H_2O$ | | Cs | | $M^{3+}$ | | Equiv wt[c] | | |
| M | n | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found | Calcd | Found | Mp, °C |
| Am | 0 | 19.9 | 17.3 | 0.33 | 0.50 | | | 10.9 | 11.6 | 19.9 | 20.2 | | | 193–194 |
| La[a] | 1 | 21.5 | 21.7 | 0.54 | 0.39 | 1.61 | 1.50 | 11.9 | 11.2 | 12.4 | 11.9 | 1118 | 1121 | 186–187 |
| Ce[b] | 1 | | | | | 1.61 | 1.20 | | | | | 1119 | 1135 | 180–182 |
| Pr[b] | 1 | | | | | 1.60 | 1.62 | | | | | 1120 | 1126 | 188–189 |
| Nd | 0 | 21.6 | 21.6 | 0.36 | 0.38 | 0 | 0.07 | | | | | 1105 | 1103 | 191–192 |
| Nd | 1 | 21.3 | 21.5 | 0.53 | 0.43 | 1.6 | 2.2 | | | | | 1123 | 1143 | 189–191 |
| Sm[b] | 0 | | | | | | | | | | | 1111 | 1108 | 206–208 |
| Eu | 0 | 21.6 | 21.3 | 0.36 | 0.33 | 0 | 0.2 | 11.9 | 12.1 | | | 1113 | 1108 | 208–211 |
| Tb[b] | 0 | | | | | | | | | | | 1120 | 1135 | 216–220 |
| Tm[b] | 0 | | | | | | | | | | | 1130 | 1151 | 262–265 |

[a] Per cent F: found, 39.9; calcd, 40.8. [b] Identity established with X-ray powder diagram. [c] Titration in glacial acetic acid with perchloric acid.

All of the compounds except $Nd(thd)_3 \cdot DMF$ and $Am(thd)_3$ were obtained as single crystals suitable for X-ray diffraction study. With these specimens the crystallographic data presented in Table II were obtained. Three of the structure types represented there have been the subject of crystal structure determinations. $CsEu(hfa)_4$ (and anhydrous $CsAm(hfa)_4$) was shown[7] to be composed of chains of $Eu(hfa)_4^-$ and $Cs^+$ ions. Between the chains there are only F···F contacts, which suggests the reason for its volatility. For $Pr(thd)_3$, which is isomorphous with the $Nd(thd)_3$ and $Am(thd)_3$ compounds listed here, a structure analysis by Erasmus and Boeyens[8] has revealed the presence of $Pr_2(thd)_6$ dimers packed together in a molecular crystal. We have carried out a refinement of this structure using X-ray diffractometer data from $Nd(thd)_3$ crystals, providing some additional details of thermal motion.[9] The crystal structure of $CsLa(hfa)_4 \cdot H_2O$ is under investigation by Sands and coworkers.[10]

All of the $CsLn(hfa)_4$ compounds sublimed under vacuum in the temperature range 135–150° with little decomposition. The monohydrate of the lanthanum compound sublimed with little loss of water, as indicated by X-ray powder patterns and Karl Fischer analyses. There was an apparent loss of water on subliming $CsNd(hfa)_4 \cdot H_2O$ with differences in the X-ray powder patterns occurring. Water analyses on the sublimate indicated 0.7% water, less than half that required by the monohydrate (1.59%). Both $Nd(thd)_3 \cdot DMF$ and $Nd(thd)_3 \cdot 2DMF$ lost all of their DMF on heating *in vacuo* and reverted to $Nd(thd)_3$.

The compound $Cs_2La(hfa)_5$ is an analog of the type reported by Richardson, Wagner, and Sands;[4] $(pyH)_2Ln(hfa)_5$, where py is pyridine and Ln either La, Pr, or Nd. We agree with their speculation that the lanthanide in these compounds may be ten-coordinated.

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TABLE II
CRYSTALLOGRAPHIC DATA FOR SOME CHELATES OF TRIVALENT RARE EARTHS AND AMERICIUM

| Formula | Crystal system | Space group | Unit cell dimensions | | | |
|---|---|---|---|---|---|---|
| | | | *a*, Å | *b*, Å | *c*, Å | $\beta$ |
| $CsLa(hfa)_4 \cdot H_2O$ | Monoclinic | $P2_1/n$ | 12.10 | 20.84 | 13.53 | 94° 11′ |
| $CsCe(hfa)_4 \cdot H_2O$ | Monoclinic | $P2_1/c$ | 20.44 | 21.10 | 17.47 | 102° 35′ |
| $CsPr(hfa)_4 \cdot H_2O$ | Monoclinic | $P2_1/c$ | 23.71 | 18.76 | 16.31 | 111° 50′ |
| $CsNd(hfa)_4 \cdot H_2O$ | Monoclinic | $P2_1/c$ | 23.62 | 18.78 | 16.31 | 111° 42′ |
| $CsAm(hfa)_4 \cdot H_2O$ | Monoclinic | $P2_1/c$ | 23.15 | 18.78 | 16.29 | 109° 59′ |
| $CsNd(hfa)_4$ | Orthorhombic | Pbcn | 8.61 | 21.87 | 17.32 | |
| $CsSm(hfa)_4$ | Orthorhombic | Pbcn | 8.72 | 21.91 | 17.34 | |
| $CsEu(hfa)_4$ | Orthorhombic | Pbcn | 8.66 | 21.75 | 17.43 | |
| $CsTb(hfa)_4$ | Orthorhombic | Pbcn | 8.67 | 21.65 | 17.48 | |
| $CsTm(hfa)_4$ | Orthorhombic | Pbcn | 8.68 | 21.48 | 17.60 | |
| $CsAm(hfa)_4$ | Orthorhombic | Pbcn | 8.62 | 21.93 | 17.45 | |
| $Nd(thd)_3$ | Monoclinic | $P2_1/c$ | 12.40 | 22.38 | 28.03 | 106° 35′ |
| $Am(thd)_3$ | (Powder diagram showed isomorphism with $Nd(thd)_3$) | | | | | |
| $Eu(thd)_2 \cdot 2DMF^a$ | Orthorhombic | Pbca | 24.88 | 22.71 | 17.37 | |
| $Nd(thd)_3 \cdot 2DMF^a$ | (Powder diagram showed isomorphism with $Eu(thd)_3 \cdot 2DMF$) | | | | | |
| $Cs_2La(hfa)_5$ | Triclinic | $P\bar{1}$ or P1 | 9.81 | 10.81 | 17.06 | 106° 42′$^b$ |

$^a$ DMF = dimethylformamide. $^b$ $\alpha = 91° 47'$, $\gamma = 114° 57'$.

$CsAm(hfa)_4$ and $CsAm(hfa)_4 \cdot H_2O$ also sublimed at about 135°, but sublimation had to be carried out within a limited length of time after the compounds were prepared. Otherwise, a distinct chemical change occurred and, after heating, $AmF_3$ was formed as one of the products (identified by an X-ray powder pattern). This minimum time appears to be less than 1 week but may depend on other factors such as particle size and atmosphere. We have observed a gradual degradation of long-range order in the course of obtaining single-crystal data for $CsAm(hfa)_4$. The decrease in intensity of a standard reflection, measured periodically, was approximately linear with time, but there was no striking color change. However, a marked change in color occurred when black $AmF_3$ was formed at higher temperatures during attempts to sublime aged compounds. This decomposition we attribute to self-radiolysis.

## Experimental Section

**Materials.**—The diketones Hhfa and Hthd were commercial products and their high purity was established by gas chromatography. Americium oxide was obtained from the Chemical Technology Division of ORNL. Dimethylformamide (DMF) was treated by first passing the liquid downward through a column that was packed on top with sodium hydroxide pellets and beneath with Drierite. The effluent was then distilled through a Todd column under reduced pressure, the middle 60% being retained.

**Analytical Methods.**—Carbon, hydrogen, and nitrogen analyses of radioactive materials were performed in our own laboratories while many of the nonradioactive lanthanide chelates were submitted to a commercial laboratory. Cesium and lanthanide elements were determined spectrographically after separation by means of ion-exchange chromatography, while americium was determined radiometrically and coulometrically.[11] Water was determined by the Karl Fischer method. The equivalent weights of the $CsM(hfa)_4$ chelates were determined electrometrically by titration with perchloric acid in glacial acetic acid solution. The compounds $CsM(hfa)_4$ react as strong monofunctional bases and $CsClO_4$ is precipitated. Space groups and unit cell dimensions were determined by X-ray precession patterns from single crystals, and, in two instances, complete structural analyses were performed.[7] X-ray powder patterns were used for identification of phases in many instances.

All work with americium was performed inside glove boxes where the air pressure was maintained lower than that in the room, thereby minimizing the diffusion of radioactive materials out into the room. Transfers between boxes were made with the compounds sealed inside plastic bags.

$^{243}Am(thd)_3$ was prepared by a modification of the method of Eisentraut and Sievers.[1] $^{243}AmO_2$ (0.25 mmoles) was dissolved in excess 6 *N* HCl and converted to the sulfate by the addition of 1 ml of 0.75 *N* $H_2SO_4$, evaporated to dryness, redissolved in 1 ml of distilled water, and evaporated again. The cycle of addition of water and evaporation was repeated twice more to remove excess HCl. The residue of americium sulfate, dissolved in 2 ml of water, was transferred to a microfilter beaker containing a stirred solution of 0.876 mmol of H(thd) and 0.75 mmol of NaOH in 2.5 ml of 70% ethanol. The reagents were rinsed in with 1 ml of ethanol and then 0.5 ml of water. The volume was reduced to one-third by a vacuum distillation and filtered, and the filtrate was discarded. The precipitate was then extracted twice with 2-ml portions of ethanol and the resulting mixture was filtered. One milliliter of water was added to the filtrate, and the solution was left overnight with nitrogen flowing over the surface to remove the ethanol. The precipitate was collected by filtration, washed three times with water (3 ml each), dried *in vacuo* at room temperature for 1 hr, and sublimed at 124–135° at $10^{-5}$ Torr for 1.5 hr. The melting point, 216–218° after softening at 205°, was determined in tubes that had been evacuated and sealed. *Anal.* Calcd for $C_{33}H_{57}AmO_6$: C, 50.0; H, 7.2. Found: C, 50.3; H, 7.1.

The neodymium compound was prepared by the method of Eisentraut and Sievers[1] and when recrystallized from dimethylformamide in the absence of air gave the disolvate $Nd(thd)_3 \cdot 2DMF$ (mp 104–133°) which decomposed rapidly in air. *Anal.* Calcd for $C_{39}H_{71}N_2NdO_8$: C, 56.0; H, 8.1; N, 3.4. Found: C, 55.3; H, 8.4; N, 3.0.

The corresponding monosolvate of Schwarberg, *et al.*[3] (mp 136–140°), and the above-mentioned disolvate were both readily converted to the nonsolvated tris chelate *in vacuo*.

$^{243}AmO_2$ (0.36 mmol) was converted to the hydrated chloride by dissolving in twice the calculated volume of 12 *N* HCl and evaporating to dryness. The residue was dissolved in 0.09 ml of 12 *N* HCl and then 40 ml of acetone was added, precipitating the hydrated chloride. The crystals were washed twice with 40-ml portions of acetone, dissolved in 1 ml of water, and filtered through a glass wool plug in a capillary tube. The equipment was rinsed with 1 ml of water and two portions (2.5 ml) of 50% aqueous ethanol. Cs(hfa), 2.9 mmol in 5.5 ml of 50% aqueous ethanol, was added to the solution and was followed by

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two small ethanol rinses. This solution was evaporated overnight to half its original volume and the yellow precipitate was collected on a sintered-glass funnel by suction filtration. The solid was washed five times with 2–3-ml portions of water and then dried by exposure to a stream of air for 15 min. Its melting point was 189–191°.

A portion of this product was immediately sublimed at $10^{-6}$ Torr at a bath temperature of 130–140° for 1 hr. The X-ray powder patter and melting point (193–194°) were taken within 1 hr of the termination of sublimation. Another portion of the crude product was kept in a screw-cap vial for 8 days longer; it then melted at 168–174° and decomposed on attempted sublimation.

Several lanthanide chelates of the basic formula CsM(hfa)$_4$ were prepared by the method of Lippard;[2] however, in some cases the yield of product was raised from 45 to 80% by doubling the concentration of Cs(hfa) added to the reagent solution. The products were purified either by recrystallization from 50% ethanol or by sublimation. Monohydrates for the rare earth ions La$^{+}$ through Nd$^{3+}$ resulted both from the original preparation and on crystallization from 50% aqueous–ethanol solutions. Anhydrous forms were usually obtained by recrystallization from 1-butanol and washing with toluene.

The lanthanum monohydrate, CsLa(hfa)$_4\cdot$H$_2$O, was dissolved in butanol and part of the solvent was evaporated. The compound that separated, Cs$_2$La(hfa)$_5$, melted at 226–227° and the melting point was unchanged by sublimation at 135°, $10^{-2}$ Torr. *Anal.* Calcd for $C_{22}H_5F_{30}Cs_2LaO_{10}$: C, 20.9; H, 0.35; H$_2$O, 0; Cs, 18.5; La, 9.7; equiv wt 720. Found: C, 20.7; H, 0.4; H$_2$O, 0.3; Cs, 17.6; La, 9.4; equiv wt 732.

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## Magnetic Circular Dichroism and Electronic Structure of Square-Planar Nickel(II) Complexes

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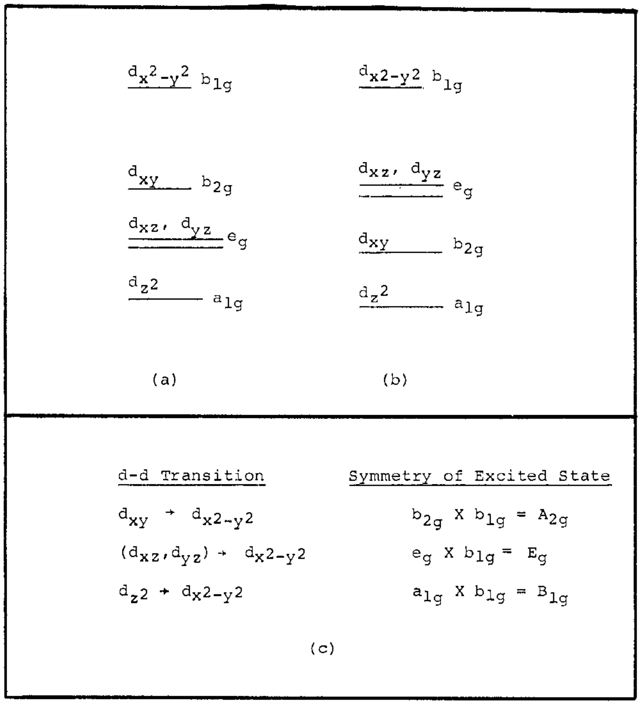
Although it has been established that the splitting of the d orbitals by a square-planar ligand field results in one high-energy ($d_{x^2-y^2}$) and four lower energy [($d_{z^2}$, $d_{xy}$, and the degenerate pair, $d_{xz}$ and $d_{yz}$)] orbitals, the exact ordering of these lower energy orbitals is not certain.[1–3] The work of Martin, *et al.*,[4] and McCaffery, Schatz, and Stephens[5,6] has demonstrated the usefulness of magnetic circular dichroism (MCD) studies in obtaining spectroscopic information about d$^8$ square-planar complexes. This communication reports the MCD spectra of three complexes of Ni(II) (two with sulfur and one with nitrogen as the donor atoms) having square-planar microsymmetry.

The characteristics of MCD spectra have been described elsewhere.[7–9] Since the ground state of a Ni(II) complex in a square-planar ligand field is orbitally nondegenerate, only A and B terms are expected to be present in the MCD spectrum. A B term peaks near the corresponding absorption maximum and is brought about through the mixing of different states by the magnetic field, whereas an A term changes sign near the absorption maximum and is observed only when either the ground or excited state is degenerate. Thus, in the case of a square-planar, d$^8$ complex an A term indicates that the excited state is degenerate.

Of all the square-planar, d$^8$ complexes, PtCl$_4^{2-}$ is probably the most extensively studied. Chatt, *et al.*,[10] proposed that the d orbitals increase in energy as shown in Figure 1a. Thus the excited-state symmetries of



| d-d Transition | Symmetry of Excited State |
|---|---|
| $d_{xy} \rightarrow d_{x^2-y^2}$ | $b_{2g} \times b_{1g} = A_{2g}$ |
| $(d_{xz}, d_{yz}) \rightarrow d_{x^2-y^2}$ | $e_g \times b_{1g} = E_g$ |
| $d_{z^2} \rightarrow d_{x^2-y^2}$ | $a_{1g} \times b_{1g} = B_{1g}$ |

Figure 1.—Alternative orderings of the d-orbital energy levels: (a) after Chatt, *et al.*,[10] and (b) after Leussing.[11] Representations are given for the various excited states arising from d–d transitions, assuming D$_{4h}$ symmetry.

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