

Table V. Values of the Ligand Field Parameters θ and Δ and the Spin-Orbit Coupling Constant ζ for 5f Octahedral Compounds

Compd	Parameters, cm ⁻¹			Compd	Parameters, cm ⁻¹			Compd	Parameters, cm ⁻¹		
	θ	Δ	ζ		θ	Δ	ζ		θ	Δ	ζ
α -(NEt ₄) ₂ PaF ₆	4502	3074	1508	(Ph ₄ As)UF ₆	6882	4479	1885	NpF ₆	17498	5619	2433
(NEt ₄) ₂ PaCl ₆	1873	1634	1523	(NEt ₄)UCl ₆	3371	2936	1913				
(NEt ₄) ₂ PaBr ₆	1268	1707	1535	(NEt ₄)UBr ₆	2375	2935	1925				

complexes (NEt₄)₂PaCl₆ and (NEt₄)₂PaBr₆, and the optical absorption bands are again assigned to transitions from the ground Γ_7 level to the Γ_7' , Γ_8 , and Γ_6 states (Table IV). Not unexpectedly, however, the observed bands have shifted appreciably to lower wavelengths. β -(NEt₄)₂PaF₆ exhibits an identical spectrum.

The spectrum of α -(NEt₄)₂PaF₆ is dominated by vibronic bands as were those recorded¹ for the hexachloro- and hexabromoprotactinate(IV), and the mean values obtained for the vibrational transitions, 147 and 407 cm⁻¹, compare favorably with those observed directly for ν_4 and ν_3 , respectively, in the infrared spectra of both α - and β -(NEt₄)₂PaF₆. A further similarity with the spectra of (NEt₄)₂PaCl₆ and (NEt₄)₂PaBr₆ is the splitting observed for the Γ_8' level in octahedral symmetry. Data available on similar splittings observed for a range of uranium(V) complexes are summarized and discussed elsewhere.¹³ The shifts to lower wavelength observed with decreasing temperature for the bands associated with the Γ_8' and Γ_6 levels are associated with the smaller contribution from vibronic transitions to the low-energy side of the bands at lower temperatures.

The 300 K spectrum shows broad unresolved features for the higher energy transitions which makes their assignment difficult. Therefore, the assignment at 85 K shown in Table III was used to fit the ligand field splittings, θ and Δ , and the spin-orbit coupling constant, ζ . In order to have a check on these parameters the g value for PaF₆²⁻ was estimated as -0.75 (cf. the values available for the UF₆⁻ ion and NpF₆,¹ -0.700 and -0.604, respectively). The experimental and calculated values are compared in Table IV. The values

(13) D. Brown, B. Whittaker, and N. Edelstein, Report AERE-R 7481, Atomic Energy Research Establishment, Harwell, England, 1973.

obtained for θ , Δ , and ζ are compared in Table V with those for other 5f¹ octahedral compounds. It can readily be seen that the PaF₆²⁻ parameters fit the trends observed in the other 5f¹ compounds. The parameter Δ changes less with increasing oxidation state or increasing electronegativity of the halide ion for a fixed oxidation state than does θ .

Qualitatively this trend has been correlated with changes in σ bonding dominating the total ligand field splittings.

Further magnetic and optical measurements in progress on the 5f¹ compounds will enable more quantitative conclusions to be drawn.

Summary

The syntheses of two crystallographic forms of (NEt₄)₂PaF₆ are described and X-ray powder diffraction data for these compounds and (NEt₄)₂UF₆ are reported. (NEt₄)₂PaF₆ exhibits face-centered cubic symmetry and the powder pattern from β -(NEt₄)₂UF₆ was indexed on the basis of an orthorhombic unit cell. Infrared and optical data are reported for α - and β -(NEt₄)₂PaF₆. The spectral data are consistent with an octahedral (or a very slightly distorted octahedral) array of F⁻ ions surrounding the tetrapositive metal ion. The ligand field and spin-orbit parameters obtained fit the trends reported earlier for other octahedral 5f¹ halide compounds.

Acknowledgment. Part of this work was done while N. E. was a visitor at the Physical Chemistry Laboratory of Oxford University, whose hospitality is gratefully acknowledged. This work was supported in part by the U. S. Atomic Energy Commission.

Registry No. (NEt₄)₂PaF₆, 49772-07-8; (NEt₄)₂UF₆, 42294-80-4; NEt₄F, 665-46-3; PaF₄, 13842-89-2; UF₄, 10049-14-6.

Contribution from Ames Laboratory—USAEC and the Department of Chemistry, Iowa State University, Ames Iowa 50010

The Detection of Praseodymium, Europium, Gadolinium and Holmium Carbonyls Using Matrix Isolation

J. L. SLATER,* T. C. DeVORE, and V. CALDER

Received September 6, 1973

AIC306558

Carbonyl compounds of the rare earth metals praseodymium, gadolinium, and holmium were prepared by codeposition of the metal atoms with carbon monoxide in argon matrices. Infrared absorptions attributable to the species M(CO)_x, x = 1-6, were observed. The final product upon controlled annealing of the matrix was assigned to the hexacarbonyl. The variation of the carbonyl stretching frequency with coordination number is similar to that observed in other carbonyl complexes, namely, the frequency increases with increasing coordination number; however, the variation of the CO stretching frequency for different metals is very small. The spectra of the carbonyl compounds of europium were measured but the assignments were less certain.

Introduction

On the basis of their chemical and physical properties, the

lanthanide metals can be classified as "typical" or "atypical."¹ A "typical" lanthanide shows a characteristic oxidation number of +3 and possesses a high melting and

* To whom correspondence should be addressed at the Department of Chemistry, University of Virginia, Charlottesville, Va. 28213

(1) K. A. Gschneidner, *J. Less-Common Metals*, 25, 405 (1971).

boiling temperature; the physical and chemical properties across the series show a regular monotonic variation.² The "atypical" lanthanides, europium and ytterbium, on the other hand, show characteristic oxidation numbers of +2 and have melting and boiling points several hundred degrees lower than the "typical" lanthanides; the chemical and physical properties generally differ markedly from the other lanthanides. This difference is due to the presence of filled or half-filled 4f orbitals in the "atypical" metals.

The detection of the first lanthanide carbonyls using matrix isolation infrared spectroscopy was reported previously.³ It was found that neodymium, a "typical" rare earth, formed carbonyls having a stoichiometry $\text{Nd}(\text{CO})_{1-6}$ similar to the results found by Slater, *et al.*,⁴ for uranium carbonyls, the only known 5f carbonyl compounds. In contrast ytterbium formed a complex system of carbonyls that could not be completely analyzed. It was clear, however, that more than one final product was formed upon controlled annealing of the matrix.³

The purpose of this work was to examine the carbonyl compounds formed by several metals spanning the lanthanide series in order to determine whether the hexacoordinated molecule was the final product for all "typical" lanthanides and to observe any regularities in the frequencies of the carbonyl stretching vibrations that might be correlated with models for metal carbonyl bonding. The carbonyl species formed by europium also were examined to determine if it behaved like a "typical" lanthanide or if it behaved like ytterbium, as might be expected from the half-filled 4f shell Eu possesses.

Experimental Section

The apparatus used in this work has been described previously³ so that only a brief resume of the experimental conditions will be given. The metals were vaporized from a tungsten container using resistive heating. The furnace temperature was selected so that the vapor pressure of the metal was about 1×10^{-5} Torr. This corresponded to 1770, 1840, 1430, and 875°K for praseodymium, gadolinium, holmium, and europium, respectively, and ensured that only monatomic metal species were present in the vapor. The metal atoms were codeposited with a mixture of carbon monoxide and argon ranging in concentration from 0.5 to 8 mol % depending on the experiment. The rate of deposition was typically 0.3 mmol of mixture min^{-1} for 30–60 min. All depositions were made on a CsI window at 8–12°K.

The rare earth metals were obtained from the Ames Laboratory. The purity of the praseodymium, gadolinium, holmium, and europium was 99.91, 99.96, 99.98, and 99.95 wt %, respectively. Research grade CO and Ar, obtained from Matheson, Inc., were used. All spectra were recorded at 8°K on a Beckman IR 7. The band positions were calibrated using atmospheric water bands and were estimated to be accurate to $\pm 2 \text{ cm}^{-1}$.

After deposition, further reaction between the metal atoms and CO was accomplished by controlled annealing of the matrix. Using this procedure it was possible to observe the growth and disappearance of various absorption bands which aided in the assignment of the spectra.

Results

Praseodymium Carbonyls. The carbonyl absorptions of Pr atoms isolated in a 2 mol % CO-Ar matrix observed at four stages of annealing are shown in Figure 1. Strong bands at 2138 and 2092 cm^{-1} due to diatomic ^{12}CO and ^{13}CO were present in all spectra but are deleted from the figures. Spectrum 1a, which was recorded prior to any annealing, shows only one absorption at 1858 cm^{-1} . Annealing resulted in

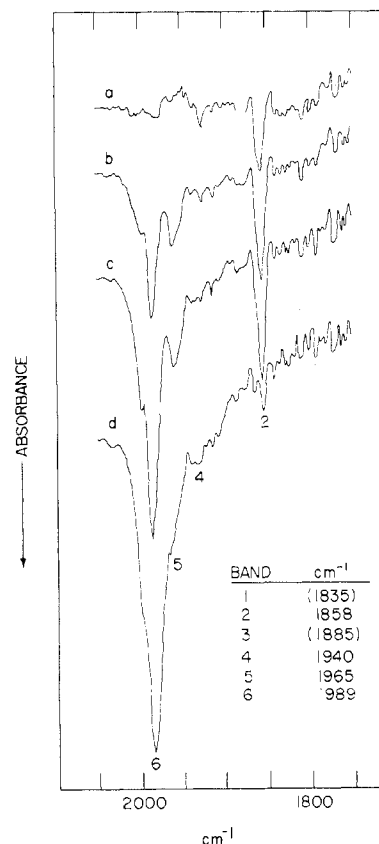


Figure 1. The infrared spectra of praseodymium carbonyl species in argon matrices during annealing—2 mol % CO-Ar.

the appearance of new features at 1965 and 1989 cm^{-1} , spectrum 1b, as well as an increase in the original feature at 1858 cm^{-1} . As shown in traces 1c and 1d, further annealing resulted in the continued growth of the high-frequency features, but the 1858- cm^{-1} absorption reached a maximum and then began to decrease in intensity. Ultimately, the feature at 1889 cm^{-1} dominated the spectra. In matrices containing smaller concentrations of CO, other weak but reproducible features at 1835 and 1885 cm^{-1} were observed which are not apparent in Figure 1. The relatively high concentration of CO used in the experiment shown in Figure 1 was selected to illustrate the dramatic effect of annealing and not to maximize the intensity of the absorptions of intermediate species.

Gadolinium Carbonyls. The infrared spectra from one annealing experiment of gadolinium atoms in a 1 mol % CO-Ar matrix are presented in Figure 2. Prior to annealing, absorptions at 1841, 1864, 1967, 1986 cm^{-1} and a broad feature at about 1945 cm^{-1} were observed (trace 2a). After annealing, the high-frequency absorptions increased in intensity and the feature at 1945 cm^{-1} sharpened (traces 2b, 2c). Continued annealing, trace 2d, resulted in the decrease in intensity of all absorptions except the one at 1986 cm^{-1} . Although the ratio of the intensities of the 1967 and 1864 cm^{-1} bands appears constant throughout the annealing experiment shown in Figure 2, the relative intensity of the lower band could be increased in a matrix having a lower CO concentration. It was generally true that the intensities of the bands varied independently and no two bands could be assigned to the same molecular species from the intensity data.

Holmium Carbonyls. The infrared spectra of Ho atoms isolated in a 2 mol % CO-Ar matrix, recorded during a

(2) L. Brewer, *J. Opt. Soc. Amer.*, **61**, 1101 (1971).

(3) J. L. Slater, T. C. DeVore, and V. Calder, *Inorg. Chem.*, **12**, 1918 (1973).

(4) J. L. Slater, R. K. Sheline, K. C. Lin, and W. Weltner, Jr., *J. Chem. Phys.*, **55**, 5129 (1971).

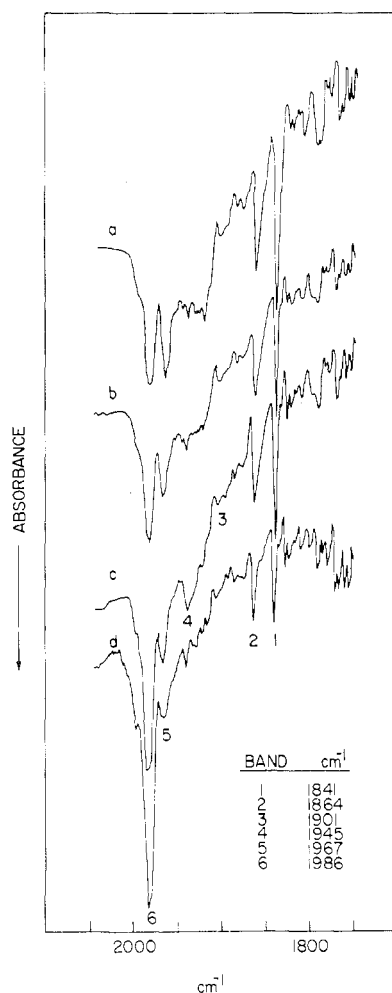


Figure 2. The infrared spectra of gadolinium carbonyl species in argon matrices during annealing—1 mol % CO-Ar.

sequence of annealing steps, are shown in Figure 3. Prior to annealing, the spectrum is essentially blank. During various stages of annealing, features appear at 1830, 1859, 1902, 1929, 1961, and 1982 cm^{-1} . Ultimately, the spectrum is dominated by the highest frequency feature.

Europium Carbonyls. The infrared spectra of Eu atoms in a 2 mol % CO-Ar matrix during an annealing sequence are shown in Figure 4. Initially the spectrum was blank. During the various stages of annealing, features appeared at 1873, 1968, 1974, and 2000 cm^{-1} with the feature at 2000 cm^{-1} dominating the spectrum.

Discussion

The assignment of the observed frequencies for the Pr, Gd, and Ho carbonyls is based on arguments similar to those used for the assignment of the Nd species,³ which are summarized as follows.

(1) Since only metal atoms, CO, and Ar are present in the matrix, the absorptions must be due to the formation of some metal carbonyl species.

(2) Because the intensity of lower frequency features is always greater relative to higher frequency features in matrices containing less CO and because the low-frequency features always increase and then decrease in intensity during annealing, these features must be due to partially coordinated metal carbonyls.

(3) The high-frequency absorption which persists after annealing must be attributed to the fully coordinated metal

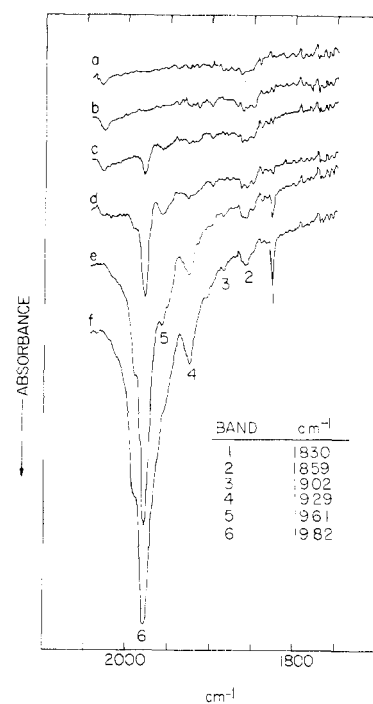


Figure 3. The infrared spectra of holmium carbonyl species in argon matrices during annealing—2 mol % CO-Ar.

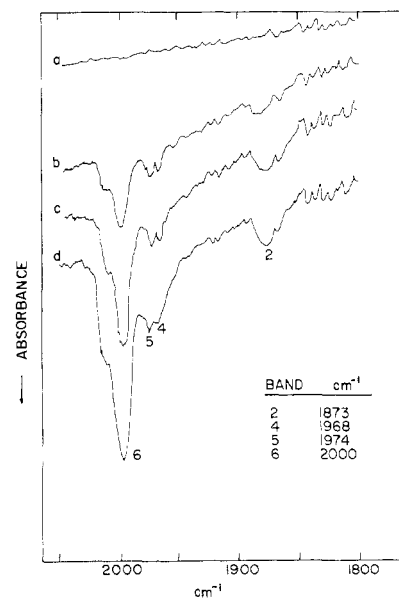


Figure 4. The infrared spectra of europium carbonyl species in argon matrices during annealing—2 mol % CO-Ar.

carbonyl. The observation of only a single feature suggests that the final product has high symmetry.

(4) There is a striking consistency in the carbonyl stretching frequency as a function of coordination number. This correlation is shown in Figure 5. In the upper half of the figure the coordination number of various metal carbonyls³⁻⁵ was plotted *vs.* the carbonyl stretching frequency. In general hexacoordinated molecules show the highest frequencies, the pentacoordinated molecules show the next highest frequencies, etc. The correlation also can be illustrated by plotting coordination number *vs.* frequency. The linear relation between these two quantities is shown in the lower half of the figure. For clarity only the "typical" lanthanide car-

(5) M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. A*, 2939 (1971).

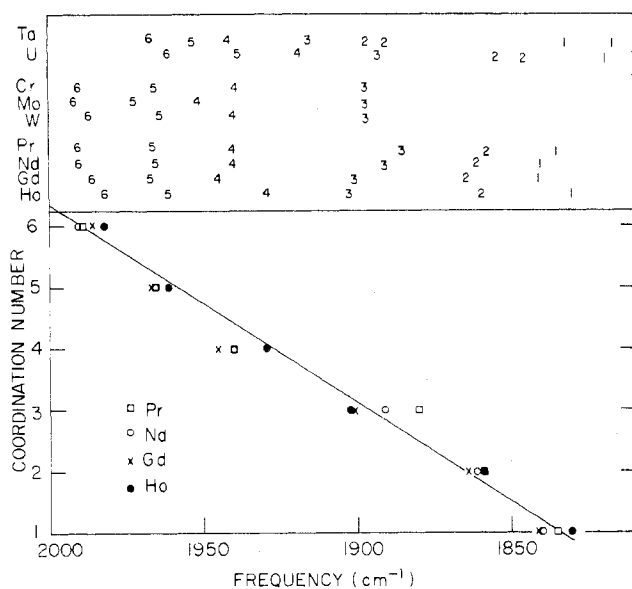


Figure 5. The correlation of the coordination number and the carbonyl stretching frequency for a number of metal carbonyls having a maximum coordination number of 6.

bonyls have been included in the lower part of the figure, although the frequencies of the other transition metal carbonyls also fall close to the line.

In view of the behavior of the observed infrared absorptions upon annealing and upon variation of the concentration of CO and in view of the close analogy of the vibrational spectra with those of other metal carbonyls illustrated in Figure 5, it is reasonable to assign the highest frequency absorption in each metal carbonyl spectrum to the hexacarbonyl molecule. The other observed frequencies were assigned to be consistent with the observed concentration and diffusion effects. The assignments are tabulated in Table I. The assignment of one CO stretching fundamental per species would be consistent with a linear or bent monocarbonyl, a linear dicarbonyl, a trigonal-planar tricarbonyl, either a tetrahedral or a planar tetracarbonyl, and an octahedral hexacarbonyl. The pentacarbonyl species should have two infrared-active modes if the molecule has D_{3h} symmetry ($A_2'' + E'$) and three infrared-active modes if the molecule has C_{4v} symmetry ($2A_1 + E$). $M(CO)_5$ ($M = Cr, Mo, W$) has been found to have C_{4v} symmetry in an isopentane-methylcyclohexane glass at $77^\circ K$ ⁶ and in inert gas matrices at $20^\circ K$.⁵ If the C_{4v} symmetry for $M(CO)_5$ is assumed, the one band would be the more intense doubly degenerate mode. No assignment was made for the shoulder found on the high-frequency side of the strongest feature assigned to the vibration of the octahedral hexacarbonyl. Graham and coworkers⁵ have recorded a reproducible 5-cm^{-1} splitting of the T_{1u} mode in $M(CO)_6$ ($M = Cr, Mo, W$) in argon matrices at $20^\circ K$. The detection of a high-frequency shoulder would not be inconsistent with the known behavior of hexacarbonyls in argon matrices; however such detailed assignments could not be justified with these data.

The most probable alternate assignments for these data would be an octacarbonyl or a tetracarbonyl system. No octacarbonyls are yet known at either ambient or matrix temperatures. For the $M(CO)_{1-8}$ system, a minimum of ten infrared-active stretching modes would be expected.³ Ten bands are definitely not observed in these experiments.

Table I. Stretching Frequencies of Rare Earth Carbonyls (cm^{-1})

Pr	Nd	Gd	Ho	Eu	Assignment
1989	1990	1986	1982	2000	$M(CO)_6$
1965	1965	1967	1961	1974	$M(CO)_5$
1940	1940	1945	1929	1968	$M(CO)_4$
1885	1891	1901	1902		$M(CO)_3$
1858	1861	1864	1859	1873	$M(CO)_2$
1835	1840	1841	1830		$M(CO)$

However, accidental degeneracies or low intensities might be expected to obscure some features in the spectrum and simple "band counting" should not be taken as proof of structure. A tetracarbonyl would be expected to have four infrared-active stretching modes as found for $Ni(CO)_{1-4}$ ⁷ and $Pd(CO)_{1-4}$.⁸ The primary features of the annealing spectra for the rare earth carbonyls were considerably different from those of $Ni(CO)_{1-4}$ ⁷ and no simple correlation (such as that shown for the hexacarbonyl data in Figure 5) could be made for the tetracarbonyl data. The hexacarbonyl assignment is thought to be best due to the general behavior of the rare earth carbonyls during the annealing cycles, the strong correlation of the recorded frequencies with those of other known hexacarbonyl systems, as shown in Figure 5, and the detection of the correct number of bands. It should be emphasized that the assignment of these data to the other symmetrical molecules has not been completely ruled out.

The results of the "atypical" lanthanide, europium, experiments are more difficult to interpret. At first glance, the results of the europium annealing experiment in Figure 4 look very much like those of the other rare earth metals, especially praseodymium in Figure 1. However, there are some differences. The relative intensity of bands due to partially coordinated species of the "typical" lanthanides was very sensitive to changes in concentration of CO in the matrix. Such a mass action effect was much less marked for Eu. For example, the bands assigned to $PrCO$ and $Pr(CO)_3$ were not detected in the 2 mol % CO-Ar matrix shown in Figure 1 but were present in a 0.5 mol % CO-Ar matrix. No other bands were observed for europium in matrices of lower carbon monoxide concentration. Also the strongest high-frequency band of europium carbonyl is 10–20 wave numbers higher in frequency than the hexacarbonyl absorptions of the other rare earth carbonyls. Despite these difficulties, the overall features of Figure 4 are so similar to those of Figure 1 that the assignment of the strongest band to $Eu(CO)_6$ and the other features to $Eu(CO)_5$, $Eu(CO)_4$, and $Eu(CO)_2$ was made, as shown in Table I. The failure to observe the mono- and tricarbonyls is not too surprising since these species have weaker absorptions for most of the "typical" lanthanides.

The bonding in the metal carbonyls is traditionally formulated as σ donation primarily from the lone pair on the carbon atom to an empty metal orbital, coupled with a π donation from a filled d orbital on the metal to an empty CO antibonding orbital. This additional electron density in the CO antibonding orbital causes a weakening of the CO bond and a lower stretching frequency for the complexed carbonyl vs. free carbon monoxide. Since the basicity of CO is so low that it is unlikely that σ donation alone would provide an adequate driving force for the formation of the chemical bond, the bonding in the lanthanide carbonyls might be best formulated as a σ donation into an empty metal orbital,

(6) I. W. Stoltz, G. R. Dobson, and R. K. Sheline, *J. Amer. Chem. Soc.*, **84**, 3539 (1962); **85**, 1013 (1963).

(7) R. K. DeKock, *Inorg. Chem.*, **10**, 1205 (1971).

(8) J. H. Darling and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1079 (1973).

such as an empty d^2sp^3 or sf^3d^2 hybrid orbital,³ coupled with back-bonding from the filled metal 4f orbitals into the CO antibonding orbitals. The direct relationship between frequency and coordination can then be explained by the back-bonding. The back-bonding would be more effective with fewer ligands attached to the metal since there are fewer orbitals competing for the available electrons. The metal carbonyl with the lower coordination number would then have the greater back-bonding causing a lower stretching frequency.

In contrast to the variation of the frequencies with coordination, these quantities are almost independent of the nature of the metal for a given coordination. This point is evident from Figure 5. This result is rather surprising in view of the fact that the number of electrons potentially available for back-bonding varies across the lanthanide series. One might conclude either that the 4f electrons play no part in the π bonding of the ligands and the compounds are formed solely by σ donation of lone pairs on the CO or that the 4f electrons make a relatively constant contribution across the series. The former conclusion seems implausible as mentioned above. On the other hand, the contraction of the f orbitals with increasing atomic number across the lanthanide series, which forces these electrons to remain on the metal rather than being delocalized to the ligands, provides a mechanism for understanding the relatively constant net contribution of these electrons to the bonding. The increased number of available back-bonding electrons across the series is almost exactly offset by a decreased capability

of the electrons to participate in such bonding. There is evidence that this compensation effect occurs in other transition metal carbonyls. For example, Ta with five 5d electrons would be expected to form a weaker hexacarbonyl with CO than W, which has six 5d electrons. In fact, the CO stretching frequencies, shown in Figure 5, suggest that the opposite is the case. The stretching frequency of $Ta(CO)_6$ is 20 cm^{-1} lower than $W(CO)_6$, indicating that Ta forms the stronger bond.

If the assignment of the europium carbonyl data is correct, the higher frequency for $Eu(CO)_6$ indicates a lower capacity for back-bonding by the half-filled 4f electron shell.

In summary, all of the spectra of the carbonyl compounds of the lanthanides Pr, Gd, Ho, Nd, and Eu can be interpreted as arising from species of the type $M(CO)_x$, $x = 1-6$. The regularities and trends observed in the spectra can be correlated with the classical π -back-bonding model for metal carbonyls provided that consideration is given to the effect of the lanthanide contraction on the 4f electrons.

Registry No. Pr(CO)₆, 51540-22-8; Pr(CO)₅, 51540-23-9; Pr(CO)₄, 51567-35-2; Pr(CO)₃, 51540-24-0; Pr(CO)₂, 51540-25-1; Pr(CO), 51540-26-2; Nd(CO)₆, 51540-27-3; Nd(CO)₅, 42494-80-4; Nd(CO)₄, 51540-28-4; Nd(CO)₃, 42494-82-6; Nd(CO)₂, 51540-29-5; Nd(CO), 51540-30-8; Gd(CO)₆, 51540-31-9; Gd(CO)₅, 51540-32-0; Gd(CO)₄, 51540-33-1; Gd(CO)₃, 51540-34-2; Gd(CO)₂, 51540-35-3; Gd(CO), 51540-36-4; Ho(CO)₆, 51540-37-5; Ho(CO)₅, 51540-38-6; Ho(CO)₄, 51540-39-7; Ho(CO)₃, 51540-40-0; Ho(CO)₂, 51540-41-1; Ho(CO), 51540-42-2; Eu(CO)₆, 51540-43-3; Eu(CO)₅, 51540-44-4; Eu(CO)₄, 51540-45-5; Eu(CO)₃, 51540-46-6.

Contribution from the Department of Chemistry,
University of Michigan, Ann Arbor, Michigan 48104

Preparation, Phase Equilibria, Crystal Chemistry, and Some Properties of Lanthanide Hydroxide Nitrates

JOHN M. HASCHKE

Received January 14, 1974

AIC400231

The preparative reactions and phase equilibria of solid lanthanide hydroxide nitrates in aqueous media at 400° and 1200 atm have been investigated. Stable members of an anionic substitution series, $Ln_2(OH)_{6-x}(NO_3)_x$ ($Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Yb, Y$), which include the $x = 2$ ($Ln = La-Dy$ and Y), $x = 0.85 \pm 0.05$ ($Ln = La-Nd$), $x = 0.6 \pm 0.1$ ($Ln = Sm-Yb$), and $x = 0$ compositions, have been characterized. For the smaller ions, the hydrated phases $Ln(OH)_2NO_3 \cdot 2H_2O$ ($Ln = Yb$) and $Ln_2(OH)_5NO_3 \cdot 2H_2O$ ($Ln = Y, Yb$) are observed. X-Ray crystallographic and thermal decomposition data are reported for the polymorphic hydroxide nitrates. Decomposition intermediates include $Ln_2O_2(OH)NO_3$ ($Ln = La-Nd$), $LnONO_3$ ($Ln = La-Gd$), $Ln_3O_4NO_3$ ($Ln = La-Gd$), and $Ln_4O_5(NO_3)_2$ ($Ln = Dy-Yb$); $GdONO_3$ exists in the $PbFCl$ -type structure. The crystal chemistry of the anhydrous hydroxide nitrate phases is discussed and employed in interpreting their structural similarities, phase equilibria, and crystal growth habits.

Introduction

Hydrothermal conditions have been extensively employed in studies of geological systems and in crystal growth procedures,¹ but the investigation of chemical systems in aqueous media at high temperatures and pressures has been limited. A review of the literature shows that neither the preparative inorganic chemistry nor the phase equilibria of simple metal-anion systems have been extensively or systematically investigated. In this respect the lanthanide elements are typical. The hydrothermal phase equilibria of lanthanide oxides were first examined by Roy and coworkers,^{2,3} the preparation

and crystallographic data for the trihydroxides and oxide hydroxides have been reported by Christensen.^{4,5} More recent hydrothermal investigations have been extended to the lanthanide hydroxide anion phases. These anionic systems include fluoride,⁶ chloride,⁷ nitrate,⁸ and carbonate.⁸⁻¹⁰

(1) R. A. Laudise and E. D. Klob, *Endeavour*, **28**, 114 (1969).
(2) M. W. Shafer and R. Roy, *J. Amer. Ceram. Soc.*, **42**, 563 (1959).

(3) I. Warshaw and R. Roy, *J. Phys. Chem.*, **65** 2048 (1961).
(4) A. N. Christensen, *Acta Chem. Scand.*, **19**, 1391 (1965).
(5) A. N. Christensen, *Acta Chem. Scand.*, **20**, 896 (1966).
(6) A. Marbuef, G. Demazeau, S. Turrell, P. Hagenmuller, J. Derouet, and P. Caro, *J. Solid State Chem.*, **3**, 637 (1971).
(7) F. L. Carter and S. Levinson, *Inorg. Chem.*, **8**, 2788 (1969).
(8) J. M. Haschke and L. Eyring, *Inorg. Chem.*, **10**, 226 (1971).
(9) P. Caro, M. Lemaitre-Blaise, H. Dexpert, and J. Sawyer, *C. R. Acad. Sci., Ser. C*, **272**, 57 (1971).
(10) R. Aumont, F. Genet., M. Passaret, and Y. Toudic, *C. R. Acad. Sci., Ser. C*, **272**, 314 (1971).