surements. Within experimental error no deviation from Beer's law was found. Apparently the extent of association is small and can be detected only by the sensitive pmr technique. Attempts to detect association by molecular weight measurements were inconclusive (see Experimental Section).

A qualitative comparison may be made of the relative tendencies of the aminomethylenecamphorates (amcs), salicylaldiminates (sals), β-ketoamineates (ketos), aminotroponeimineates (atis), and pyrrole-2-aldimineates (pyrs) to adopt the tetrahedral stereochemistry in solution at normal temperatures. When the R group is H, complexes of all five series are completely planar. For aromatic R groups the amcs are nearly 100% in the tetrahedral form; the atis vary from 25 to 75% tetrahedral; the ketos are ~10% tetrahedral and show evidence of molecular association; the pyrs are planar; and the sals are strongly associated. Where R is isopropyl the amcs, atis, and the ketos are fully tetrahedral, whereas the sals and pyrs are ~50 and ~10% tetrahedral, respectively. Finally, for R = *n*-alkyl, only the atis are fully tetrahedral. The amc complex having R = ethyl is ~20% tetrahedral (neglecting association) and is comparable to the R = ethyl keto complex which is ~30% tetrahedral. The pyrs are completely planar, and the sals are appreciably associated.

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Volatile Lanthanide Chelates. II. Vapor Pressures, Heats of Vaporization, and Heats of Sublimation[1a]

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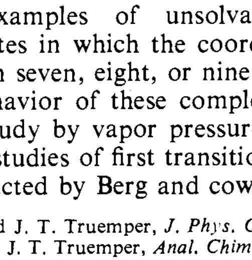
Abstract: Thermodynamic measurements were undertaken on a series of remarkably volatile and thermally stable lanthanide chelates of 2,2,6,6-tetramethyl-3,5-heptanedione. The complexes are unusual examples of unsolvated monomeric lanthanide chelates in which the coordination number is six. Large differences were found in the vapor pressures, heats of vaporization, and heats of sublimation of the tetramethylheptanedionato complexes. The findings corroborate the trend detected by gas chromatography; complexes of the lanthanides with higher atomic number are considerably more volatile than those of the lighter, larger members of the lanthanide series. For example, at 200° vapor pressures range from *ca.* 5 mm for the ytterbium(III) complex down to 0.2 mm for the lanthanum(III) complex. A plot of the heat of vaporization of the chelates *vs.* the atomic number of the metal in general reflects the effects of the lanthanide contraction, but there is an irregularity at gadolinium.

Although it has been known for many years that β-diketonates of metals in the first transition series are volatile, efforts to find similar volatile complexes of the lanthanides were always unsuccessful until very recently.[2-4] Previously known chelates of the lanthanides were invariably either nonvolatile or thermally unstable.

Indeed virtually all other reported lanthanide compounds are either nonvolatile or have very low volatility at temperatures below 700°. In part I[3] we recently described the synthesis and gas chromatographic behavior of the lanthanide complexes of 2,2,6,6-tetramethyl-3,5-heptanedione [H(thd)]. These compounds, $Ln(thd)_3$



are remarkably volatile and thermally stable. They are unusual examples of unsolvated monomeric lanthanide chelates in which the coordination number is six rather than seven, eight, or nine. The gas chromatographic behavior of these complexes suggested a more detailed study by vapor pressure measurements. Vapor pressure studies of first transition series chelates have been conducted by Berg and coworkers[5-7] and by

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(1) (a) Presented in part at the 10th International Conference on Coordination Chemistry, Nikko, Japan, Sept 1967. (b) Ohio State University Research Foundation Visiting Research Associate. (c) Deceased. Dr. Dubois was the victim of a tragic airliner crash on March 9, 1967. (d) Direct correspondence to this author at the Aerospace Research Laboratories, ARC, Wright-Patterson Air Force Base, Ohio 45433.

(2) R. W. Moshier and R. E. Sievers, "Gas Chromatography of Metal Chelates," Pergamon Press, Oxford, 1965, p 36, and references cited therein.

(3) K. J. Eisentraut and R. E. Sievers, *J. Am. Chem. Soc.*, 87, 5254 (1965).

(4) C. S. Springer, Jr., D. W. Meek, and R. E. Sievers, *Inorg. Chem.*, **6**, 1105 (1967).

(5) E. W. Berg and J. T. Truemper, *J. Phys. Chem.*, **64**, 487 (1960).

(6) E. W. Berg and J. T. Truemper, *Anal. Chim. Acta*, **32**, 245 (1965).

(7) E. W. Berg and F. R. Hartlage, Jr., *ibid.*, **33**, 173 (1965); **34**, 46 (1966).

Table I. Vapor Pressure, Heats of Sublimation, and Heats of Vaporization of Lanthanide Chelates[a]

Sample	A	B	Error, %	Limits, °K	ΔH_{sub}, kcal mole^{-1}	ΔH_{vap}, kcal mole^{-1}
La(thd)$_3$ (solid)	15.131	7498.3	1.17	450–520	34.31	
Pr(thd)$_3$ (solid)	18.033	8637.2	1.62	450–495	39.52	
Pr(thd)$_3$ (liquid)	12.109	5703.7	3.49	495–530		26.10
Nd(thd)$_3$ (solid)	17.477	8273.3	0.85	430–491	37.86	
Nd(thd)$_3$ (liquid)	11.171	5176.7	0.84	491–510		23.69
Sm(thd)$_3$ (solid)	17.141	7868.0	2.11	430–468	36.00	
Sm(thd)$_3$ (liquid)	10.242	4637.5	0.61	468–500		21.22
Eu(thd)$_3$ (solid)	18.959	8640.1	1.29	430–466	39.54	
Eu(thd)$_3$ (liquid)	10.126	4562.9	0.48	466–490		20.88
Gd(thd)$_3$ (solid)	18.594	8427.0	2.98	420–456	38.55	
Gd(thd)$_3$ (liquid)	10.452	4711.4	1.58	456–500		21.55
Tb(thd)$_3$ (solid)	16.415	7388.6	1.72	420–454	33.81	
Tb(thd)$_3$ (liquid)	10.145	4544.8	1.83	454–500		20.80
Dy(thd)$_3$ (solid)	15.484	6972.1	1.54	410–456	31.90	
Dy(thd)$_3$ (liquid)	10.067	4504.6	0.24	456–500		20.61
Ho(thd)$_3$ (solid)	15.246	6861.7	1.78	420–458	31.40	
Ho(thd)$_3$ (liquid)	9.916	4419.7	0.59	458–500		20.22
Er(thd)$_3$ (solid)	15.526	6955.5	1.79	410–454	31.83	
Er(thd)$_3$ (liquid)	10.065	4478.3	0.58	454–490		20.49
Tm(thd)$_3$ (solid)	15.448	6860.1	0.89	410–446	31.39	
Tm(thd)$_3$ (liquid)	9.910	4390.3	0.85	446–490		20.09
Yb(thd)$_3$ (solid)	15.757	6962.0	0.75	410–444	31.86	
Yb(thd)$_3$ (liquid)	9.825	4328.9	1.72	444–495		19.80
Lu(thd)$_3$ (solid)	15.799	7011.7	2.31	420–448	32.08	
Lu(thd)$_3$ (liquid)	9.894	4368.1	1.10	448–490		19.99

[a] Log P (mm) = $A - [B/T(°\mathrm{K})]$.

Wood and Jones,[8,9] but similar studies of lanthanide chelates have heretofore been impossible. In the present study the vapor pressure was measured as a function of temperature for 13 lanthanide complexes in an effort to determine what trends might exist in the thermodynamics of vaporization as a function of atomic number.

Experimental Section

Preparation of Lanthanide Chelates. The complexes were prepared by the method described in part I[3] from the lanthanide nitrate and 2,2,6,6-tetramethyl-3,5-heptanedione (Pierce Chemical Co., Rockford, Ill.) which had previously been neutralized with sodium hydroxide. Each complex was purified by recrystallization from *n*-hexane and/or by fractional sublimation *in vacuo*. The melting points are the same as reported in part I. Using the preparative procedure we reported earlier, Berg and Chiang[10] have synthesized these same complexes and studied their sublimation characteristics. It should be noted that solvents such as dimethylformamide must be avoided if the correct compound is to be obtained. The preparative method of Hammond, *et al.*,[11] yields a dimethylformamide adduct,[12] rather than the simple tris chelate as was originally claimed.

Vapor Pressure Apparatus. In previous studies in which the isoteniscope method was employed, vapors of the metal chelate came in direct contact with mercury. In the present experiments we were anxious to make the measurements in a more inert system. Therefore a modification of a Bourdon spoon gauge[13] was constructed. In this device the entire system is inert and the metal chelate comes into contact only with borosilicate glass and Teflon. The Pyrex Bourdon gauge shown in Figure 1 has a sensitivity of nearly 3 mm pressure per mm of pointer displacement. This was achieved by constructing a pointer with a length of 30 cm. As seen in the schematic drawing, the reference pointer is fused to the fixed handle of the Pyrex spoon. Both pointers are extremely sharp, the final shaping process being accomplished by chemical erosion with 30% HF. Pointer displacement was measured with a Gaertner micrometer slide comparator. The gauge, heated to 250°, was calibrated by recording pointer displacement corresponding to a given pressure of air, read on a mercury manometer, while the outer jacket of the Pyrex spoon was under high vacuum. Within the pressure range used in this work, such gauges were found to give a linear response with pressure and to be free of hysteresis.

The adequacy of this system for the measurements undertaken was checked with benzoic acid as a standard. The following procedure was adopted: the Bourdon gauge B, connecting tubes, and Teflon stopcock TS were heated to 250°. The chelate samples C heated in the furnace F were subjected to repeated cycles of evaporation, condensation, and pumping to remove traces of air and other occluded vapors, and subsequently the vapor pressures were measured with ascending temperature. Occasionally measurements were made during the cooling cycle to check against systematic errors and potential sample decomposition. All temperatures were measured with iron–constantan thermocouples and a Leeds and Northrup precision portable potentiometer.

Infrared Spectra. The infrared spectra of all of the complexes dissolved in carbon tetrachloride were obtained with a Perkin-Elmer Model 521 recording grating spectrophotometer using potassium bromide liquid cells in the region from 4000 to 360 cm^{-1}.

Results

Vapor pressure measurements were made for each of the complexes over as wide a temperature range as possible. The data were processed using a program[14] written for the IBM 7094 computer. In this program the squares of the pressure residuals were minimized. The vapor pressure results are shown in Table I. Measurements were made at least at 14 different temperatures for each compound, and as many as 35 measurements were made in some cases. The A and B values in Table I were calculated to fit the equation log P (mm) = $A - [B/T(°\mathrm{K})]$. The raw data were first plotted to determine the temperature limits valid for the computation of the heats of vaporization and to separate

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[8] J. L. Wood and M. M. Jones, *Inorg. Chem.*, 3, 1553 (1964).

[9] J. L. Wood and M. M. Jones, *J. Inorg. Nucl. Chem.*, 29, 113 (1967).

[10] E. W. Berg and J. J. Chiang, *Anal. Chim. Acta*, 40, 101 (1968).

[11] G. S. Hammond, D. C. Nonhebel, and C. S. Wu, *Inorg. Chem.*, 2, 73 (1963).

[12] J. E. Schwarberg, D. R. Gere, R. E. Sievers, and K. J. Eisentraut, *ibid.*, 6, 1933 (1967).

[13] G. W. Thomson, "Physical Methods of Organic Chemistry," Vol. 1, Part I, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1959, p 427, and references cited therein.

[14] J. G. Becsey, L. Berke, and J. R. Callan, *J. Chem. Educ.*, 45, 728 (1968); A. C. Worthing and J. Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1960, pp 198–261.

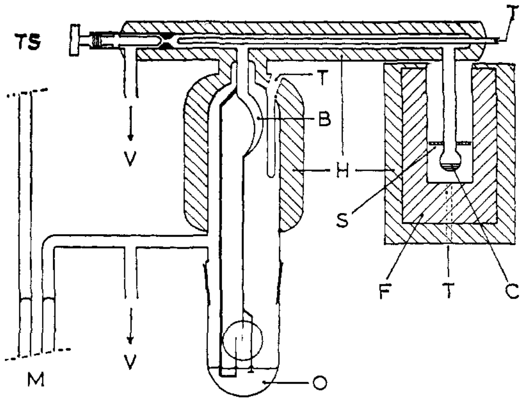

Figure 1. Vapor pressure apparatus: (B) Pyrex spoon Bourdon gauge, (O) high-vacuum pump oil for damping fixed and measuring pointers, (H) nichrome heating wire and asbestos paper insulation, (T) thermocouple well, (F) furnace, (C) sample of metal chelate, (TS) Fischer and Porter No. 795-005 90° Pyrex glass stopcock with Teflon valve, (V) vacuum system, (M) mercury manometer, (S) spacer.

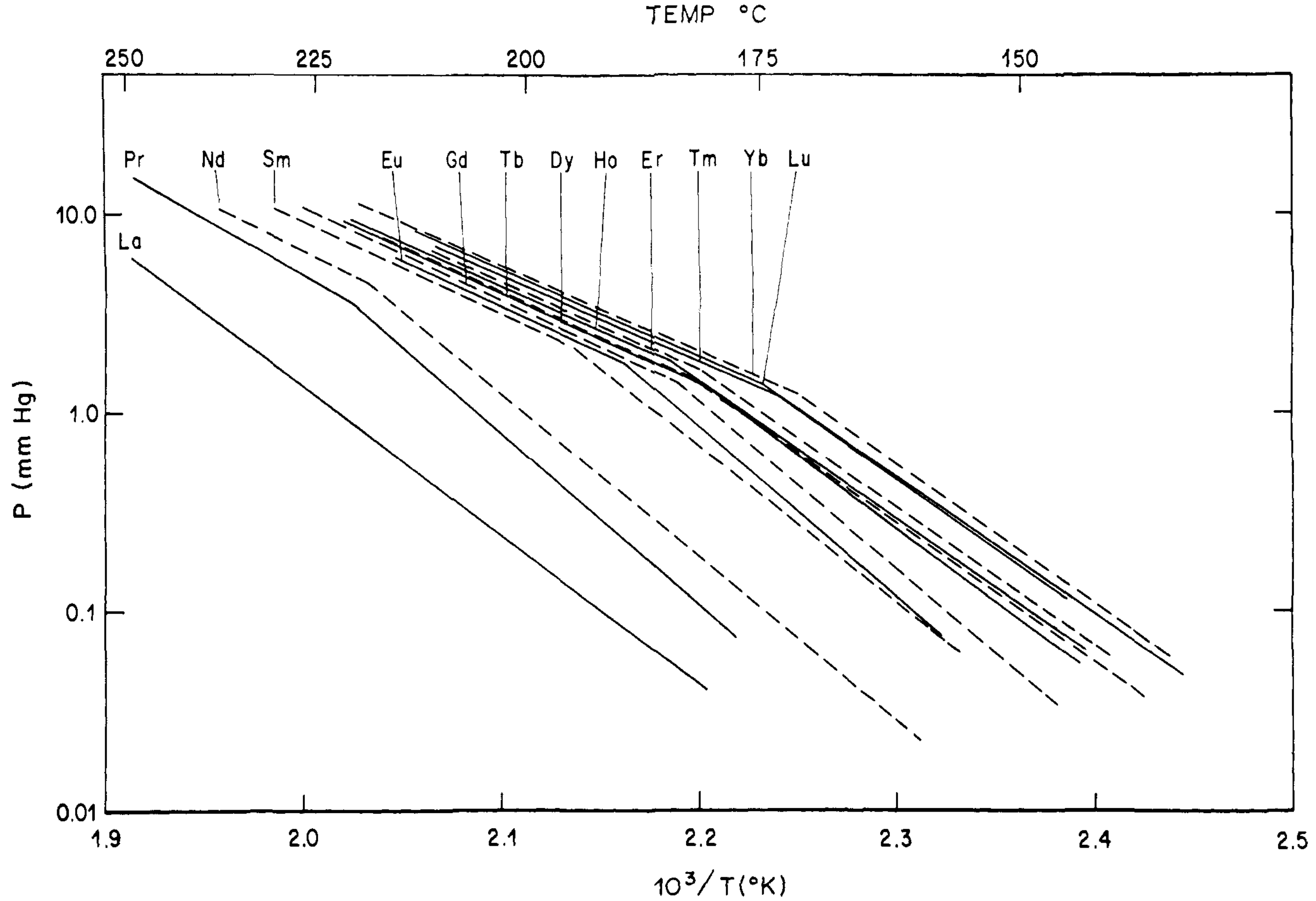

Figure 2. Clausius-Clapeyron plots for Ln(thd)$_3$ complexes.

the data points to be used in calculating the heats of sublimation. Selection of limits presented no problem because a sharp break was seen at the experimentally observed melting point for every compound except the lanthanum complex. The lanthanum complex melted at too high a temperature to enable ready measurement of the heat of vaporization. There was no curvature in any of the plots of reciprocal temperature *vs.* the logarithm of the pressure throughout the ranges examined. The heats of vaporization and sublimation were calculated from the Clausius-Clapeyron equation at the mean temperatures of the ranges indicated. The error column shows the average per cent deviation of the observed vapor pressure points from the computed least-squares plot.

Figure 2 shows the Clausius-Clapeyron plots. To improve clarity of presentation the plots for lanthanides with odd atomic number are shown in solid lines while those of even atomic number are given in dotted lines. No other significance is intended. It is seen that quite pronounced breaks appear in each of the plots. Since theory requires a discontinuity at the melting point, it was considered a useful independent check on the accuracy of the measurements to compare the temperature at which the break occurs in the plots with the experimentally determined melting points. This agreement lent further confidence to the accuracy of the vapor pressure measurements. In the subsequent list the values obtained from the Clausius-Clapeyron plot are followed by the experimentally observed[3] melting point range (in °C) in parentheses: Lu(thd)$_3$, 175 (172–174); Yb(thd)$_3$, 171 (166–169); Tm(thd)$_3$, 173 (171.5–173.5); Er(thd)$_3$, 181 (179–181); Ho(thd)$_3$, 185 (180–182.5); Dy(thd)$_3$, 183 (180–183.5); Tb(thd)$_3$, 181 (177–180); Gd(thd)$_3$, 183 (182–184); Eu(thd)$_3$, 193 (187–189); Sm(thd)$_3$, 195 (195.5–198.5); Nd(thd)$_3$, 218 (215–218); Pr(thd)$_3$, 222 (222–224).

Attempts were also made to measure the vapor pressure of another class of lanthanide chelates, but these were not very successful owing to the thermal instability of such compounds. An example is triethylammonium tetrakis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)europate(III) which was described by Melby, Rose, Abramson, and Caris.[15] This complex undergoes sublimation *in vacuo* apparently as an ion pair. At 146° the complex exhibited an apparent vapor pressure of 0.07 mm, while at 185° thermal decomposition was quite noticeable and further measurements could not be made. By contrast, all of the tris thd complexes showed surprising thermal stability. This method of measurement is very sensitive to thermal decomposition because some decomposition products are inevitably much more volatile than the chelates, and degradation is detected very readily by a pressure buildup at constant temperature. As an illustration of the excellent thermal stability of the thd complexes, $Pr(thd)_3$ was held at 250° for 6 hr and no evidence of decomposition was observed.

In solution the thd complexes of terbium, dysprosium, europium, and samarium exhibit fluorescence when irradiated in the ultraviolet at 3660 Å. It was also established that $Tb(thd)_3$ exhibits fluorescence in the gas phase, offering some hope that gas-phase optical maser devices based on long sought volatile lanthanide complexes may be feasible if the compounds can be made to lase and are sufficiently stable to radiative damage.

Discussion

Figure 2 shows that the $Ln(thd)_3$ complexes exhibit a vapor pressure of 1 mm at temperatures from *ca.* 170° for Lu to 225° for La. It is interesting to compare the vapor pressures of the complexes with more common compounds. For example, the vapor pressure of the saturated hydrocarbon, *n*-tetracosane, is 1 mm at 183.8°,[16] which means that more than half of the complexes have higher vapor pressures than this compound. This was entirely unexpected, particularly when it is recalled that the empirical formula of the complexes is $Ln(C_{33}H_{57}O_6)$ (compare with $C_{24}H_{50}$ for tetracosane) and bonding in the lanthanide complexes has always been thought to have large ionic contributions with the resulting dipoles rendering the compounds nonvolatile. Undoubtedly, stereochemical factors are playing an important role in altering the physicochemical properties of the complexes. Perhaps the bulky ligands can be envisioned as forming a hydrocarbon shell at the periphery which partially shields the polar groups from interactions with neighboring molecules.

A striking trend is immediately obvious from examination of Figure 2. The complexes of the lanthanides with higher atomic number are much more volatile than those of lower atomic number. This confirms in a quantitative manner our qualitative observations by gas chromatography[3] and thermogravimetric studies.[17] This is a quite general phenomenon that we now know to exist for other classes of lanthanide complexes as well.[4,18] The source of this phenomenon, which can now be considered virtually a rule, is not entirely clear but possible explanations can be advanced. One would expect the magnitude of local dipole and induced dipole forces to become smaller as the metal ion becomes smaller toward the lutetium end of the series, a consequence of the lanthanide contraction. According to a related explanation, the polar groups in the interior of the molecule become progressively better shielded from the attractive forces of neighbors as the molecule becomes more compact.

Significant mass effects were ruled out on the basis of gas chromatographic[3] and thermogravimetric[17] data that indicated that $Y(thd)_3$ behaved essentially the same as complexes of metal ions with similar size but much higher mass (*e.g.*, $Ho(thd)_3$ and $Er(thd)_3$). Muetterties, Roesky, and Wright[19] found in their studies of lanthanide chelates of γ-isopropyltropolone that there was a change in the extent of polymerization of the complexes as one progressed through the lanthanide series. If a similar change were to occur in the thd complexes, this could easily give rise to the large differences in volatility observed. Molecular weight measurements have been made in a variety of media, including nonpolar and highly inert solvents such as *n*-hexane, and the complexes are monomeric in solution in every case. However, even though the complexes are apparently monomeric in solution and in the gas phase, they may exhibit some association in the melt or in the solid state. It should be noted that the vapor pressure plots are linear over the entire measurable temperature range.

The effects are large enough to permit novel separation of mixtures of the rare earth complexes by fractional distillation.[20] This has been effected in the presence of codistilling agents that act as solvents for the chelates with concomitant alterations in the partial pressures that the complexes exhibit.

The plots in Figure 2 are so regular that one can predict with a high level of confidence the vapor pressure of the as yet unstudied radioactive $Pm(thd)_3$. It is expected that this complex will have a vapor pressure of *ca.* 1.0 mm at 193° and exhibit a heat of vaporization of *ca.* 22.5 kcal/mole. Since the volatilities of the lanthanide and yttrium thd complexes have been shown to be relatively unaffected by mass changes, these compounds may prove to be reliable models for the corresponding trivalent actinide complexes.

In Table I, the heats of sublimation appear to fall into two groups. The heats of fusion obtained by difference show a similar pattern with a general increase from 13.4 to 18.6 kcal/mole for praseodymium through gadolinium, while for dysprosium through lutetium they are essentially constant at 11–12 kcal/mole. A calculation of the entropies of fusion produced values that mirrored the fluctuations in the heats of fusion. All of this indicates a change in the crystal structure in the vicinity of terbium or dysprosium. Very recent X-ray studies have shown that the complexes exist in two different crystallographic modifications, with the change occurring at dysprosium.[21]

Because of the change in crystallographic structure, it is difficult to draw further conclusions about the trends in heats of sublimation. On the other hand, by

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(15) L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, *J. Am. Chem. Soc.*, **86**, 5117 (1964).

(16) T. E. Jordan, "Vapor Pressure of Organic Compounds," Interscience Publishers, New York, N. Y., 1954, p 26, and references cited therein.

(17) K. J. Eisentraut and R. E. Sievers, *J. Inorg. Nucl. Chem.*, **29**, 1931 (1967).

(18) M. F. Richardson and R. E. Sievers, unpublished data.

(19) E. L. Muetterties, H. Roesky, and C. M. Wright, *J. Am. Chem. Soc.*, 88, 4856 (1966).

(20) C. W. Harris, R. E. Sievers, and K. J. Eisentraut, U. S. Patent, pending.

(21) A. Mode and G. Smith, private communication, Aug 1968; A. Mode and G. Smith, *J. Inorg. Nucl. Chem.*, in press; E. A. Boudreaux, private communication, Nov 1967.

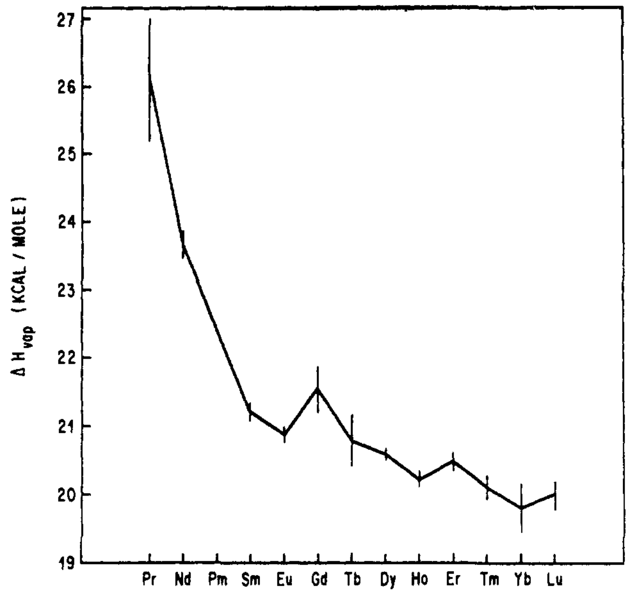

Figure 3. Heats of vaporization of $Ln(thd)_3$ as a function of atomic number of the metal ion.

definition the heats of vaporization should be unaffected because the data are all obtained on equilibria above the melting point. The gross features of Figure 3 are in accord with the rule stated above; as the ionic radii of the metal ions grow progressively smaller, the heats of vaporization also become smaller. However, it will be noticed that there is a small but distinct discontinuity at gadolinium. The heat of vaporization for the praseodymium complex is 26.1 kcal/mole, falling to 23.7 for neodymium, then to 21.2 for samarium and 20.9 for europium, but then rising to 21.5 for gadolinium before becoming progressively smaller again.

Any purely electrostatic model requires a monotonic decrease throughout the series. Discontinuities or so-called "gadolinium breaks" have been observed by many previous workers.[22–30] Attempts have been made to relate several different properties to atomic number. Formation constants, heats of hydration, unit cell volumes, separation factors, and other experimentally derived quantities have been plotted against atomic number to see what deviations from a simple electrostatic model exist. Many cases showed one or more discontinuities, but often the complexity of the property being examined obscured the source of the discontinuities. For example, the polyaminocarboxylic acid complexes of the lanthanides show interesting irregularities that can be caused in a number of ways. The lanthanides have recently been shown to exhibit a wealth of coordination numbers.[15,31–34] For many years it was assumed that the common coordination number was six. Now it is clear that relatively few lanthanide complexes exhibit this coordination number, most complexes having seven, eight, nine, or more donors. This causes problems when considering formation constant or other data as one can never be sure that the coordination number remains the same throughout the series. There is the further complication that the effective hydration number probably also changes from approximately nine for lanthanum to eight for lutetium.[32] Still another possible change is in the dentate number of the ligand. Multidentate ligands such as ethylenediaminetetraacetic acid are able to function with all or only part of the potential donors bonded to the metal, depending on the precise stereochemical factors operative. In such series of compounds one is discouraged by the multiplicity of changes that can occur randomly or simultaneously.

By contrast, one might expect the system under present study to be less complicated. Changes in hydration number which have plagued earlier workers obviously are not relevant when discussing heats of vaporization. We must next ask what causes the discontinuity at gadolinium in Figure 3.

Staveley, Markham, and Jones[22,23] in their studies of the heats of formation of dipicolinate complexes found a relationship to atomic number very similar to that in Figure 3. All of the remaining complexes relative to lanthanum, gadolinium, and lutetium are more stable by amounts of the order of a few tenths of a kilocalorie. The Oxford workers attributed the extra stability to 4f electron crystal field stabilization effects on a scale between one and two orders of magnitude smaller than the better known effects in the 3d transition series. Since no 4f shell crystal field stabilization can occur for the unfilled La(III), the half-filled Gd(III), and the completely filled Lu(III), the heats of formation for these complexes represented maxima in the plot. Other workers have also offered arguments for the occurrence of crystal field stabilization effects in the lanthanide series.[24,35–37]

It is possible that the irregularity discovered in the present study also arises from small crystal field stabilization effects. The focal point of phenomena resulting in intermolecular interactions in the melt is undoubtedly in the Ln–O–C moieties. Any factor which acts to decrease the local dipoles in these groups, *e.g.*, to reduce bond lengths or the magnitudes of charge separation will produce a concomitant reduction in intermolecular forces and lower the heat of vaporization. In this model the heats of vaporization of the lanthanum, gadolinium, and lutetium complexes are considered norms with no crystal field stabilization. The heat of vaporization for the lanthanum chelate could not be

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(22) L. A. K. Staveley, D. R. Markham, and M. R. Jones, *J. Inorg. Nucl. Chem.*, **30**, 231 (1968).

(23) L. A. K. Staveley, D. R. Markham, and M. R. Jones, *Nature*, **211**, 1172 (1966).

(24) K. B. Yatsimirskii and N. A. Kostromina, *Russ. J. Inorg. Chem.*, **9**, 971 (1964).

(25) D. H. Templeton and C. H. Dauben, *J. Am. Chem. Soc.*, **75**, 6069 (1953).

(26) E. J. Wheelwright, F. H. Spedding, and G. Schwarzenbach, *ibid.*, **75**, 4196 (1953).

(27) R. H. Betts and O. F. Dahlinger, *Can. J. Chem.*, **37**, 91 (1959).

(28) I. Grenthe and W. C. Fernelius, *J. Am. Chem. Soc.*, **82**, 6258 (1960).

(29) G. R. Choppin and T. A. Chopoorian, *J. Inorg. Nucl. Chem.*, **22**, 97 (1961).

(30) T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel, and W. J. Randall, *Chem. Rev.*, **65**, 1 (1965).

(31) L. C. Thompson, *J. Inorg. Nucl. Chem.*, **24**, 1083 (1962).

(32) J. L. Hoard, B. Lee, and M. D. Lind, *J. Am. Chem. Soc.*, **87**, 1611, 1612 (1965).

(33) E. D. Watkins, II, J. A. Cunningham, T. Phillips, II, D. E. Sands, and W. F. Wagner, *Inorg. Chem.*, **8**, 29 (1969).

(34) R. A. Lalancette, M. Cefola, W. C. Hamilton, and S. J. La Placa, *ibid.*, **6**, 2127 (1967).

(35) N. S. Hush, *Discussions Faraday Soc.*, **26**, 145 (1958).

(36) P. George, D. S. McClure, J. S. Griffith, and L. E. Orgel, *J. Chem. Phys.*, **24**, 1269 (1956).

(37) C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Vol. II, Oxford University Press, Oxford, 1966, Chapter 21.

experimentally obtained for the reason mentioned above, but it is assumed to be at least as large as that of praseodymium and probably higher. If one imagines a smooth curve running through lanthanum, gadolinium, and lutetium, the actual values for all of the remaining complexes fall below the "normal" values and lie on a curve with two principal nodes. The effect is perhaps most apparent in the section from samarium to europium to gadolinium. The heat for the europium complex is actually smaller than that for gadolinium even though it is expected to be larger.

One must also consider a different possibility, *i.e.*, a discontinuous change in the structure or ordering of the liquid melt. Admittedly, it is curious that of the 14 metal ions such a change should occur fortuitously at the complex with the half-filled f shell. Nevertheless, support for this explanation is given by trends in the changes of entropies of vaporization. The entropy changes were calculated and compared in two ways, in one case using an arbitrary constant temperature (225°) and in the other an arbitrary constant pressure (0.01 atm). When the entropy changes were plotted against atomic number, the plots had essentially the same shape as for the heats of vaporization, suggesting that a change in ordering in the liquid melt does occur. The question arises as to whether this is only an accidental function of packing or reflects a basic change in the molecular structure, for example, from octahedral to distorted octahedral or trigonal prismatic.

In an effort to see whether any fundamental changes in structure occur at the molecular level, the infrared spectra of all the complexes were examined. The spectra of all of the complexes in both halves of the series were remarkably similar both in band positions and intensities. Therefore if a change does occur, it is not detectable by infrared spectroscopy. The peak maxima (in $\mathrm{cm^{-1}}$) assigned[38] to $\mathrm{C\overset{\cdots}{-}O}$ and $\mathrm{C\overset{\cdots}{-}C}$, respectively, occur at: La, 1592, 1571; Pr, 1592, 1572; Nd, 1592, 1571; Sm, 1593, 1572; Eu, 1594, 1571; Gd, 1593, 1572; Tb, 1596, 1572; Dy, 1597, 1571; Ho, 1598, 1571; Er, 1597, 1571; Tm, 1598, 1571; Yb, 1598, 1571; and Lu, 1599, 1571. Clearly the changes are very small compared with variations in the spectra of other rare earth complexes known to exist in different forms.[39-41] It should be noted that the two explanations offered as possible causes of the discontinuity at gadolinium are not mutually exclusive and may indeed be interrelated.

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(38) G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, **6**, 433 (1967).

(39) A. I. Byrke, N. N. Magdesieva, L. I. Martynenko, and V. I. Spitsyn, *Russ. J. Inorg. Chem.*, **12**, 348 (1967).

(40) M. F. Richardson, W. F. Wagner, and D. E. Sands, *J. Inorg. Nucl. Chem.*, **30**, 1275 (1968).

(41) M. F. Richardson, W. F. Wagner, and D. E. Sands, *Inorg. Chem.*, **7**, 2495 (1968).

Polarographic Kinetic Study of the Oxidation of Metal Complexes by Chlorite Ion. I. Oxidation of Ferrous Citrate, Tartrate, and Ethylenediaminetetraacetate and Cuprous Ammine Complexes

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Abstract: The kinetics of the oxidation of ferrous citrate, ferrous tartrate, ferrous EDTA, and cuprous ammine by chlorite ion, $\mathrm{ClO_2^-}$, have been studied in 1 F $\mathrm{NH_3}$–1 F $\mathrm{NH_4Cl}$ by the catalytic current technique of dc polarography. The reaction orders appear to be first order in both complex and chlorite. The oxidation rates of the citrate and tartrate complexes are not reproducible and are probably complicated by the presence of polymeric species in slow equilibrium with monomeric forms. The rate constants for the oxidation of the ferrous complexes are between 10^3 and 10^4 l./(mole sec). This value for $\mathrm{FeEDTA^{2-}}$ is $3.0 \times 10^4 \pm 0.3 \times 10^4$ l./(mole sec) as compared with 44 ± 3.7 l./(mole sec) for cuprous ammine. The difference in rate constants is attributed to the slowing effect of ligand rearrangement in the oxidation of $\mathrm{Cu(NH_3)_2^+}$ to $\mathrm{Cu(NH_3)_4^{2+}}$. Several types of mechanisms which are possible for the redox reactions considered are discussed.

Under usual conditions, the limiting current through a polarographic cell is controlled by the diffusion of electroactive species and does not contain kinetic information; however, there are the so-called kinetic and catalytic current cases where the limiting current is controlled by the rate of a chemical reaction. Recently Gierst, *et al.*,[2] found that chlorite ion, $\mathrm{ClO_2^-}$, in 1 M

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(2) L. Gierst, L. Vandenberghen, and E. Nicolas, *J. Electroanal. Chem.*, **12**, 462 (1966).