

densation reactions to yield higher nuclearity clusters.^{5,13} This apparently occurred in these solutions also, and 1 mol of **1** combined with 1 mol of Os₃(CO)₁₀(μ₃-S) to yield **2**. This was supported by the results of an independent reaction of **1** with Os₃(CO)₁₀(μ₃-S), which gave **2** in 43% yield.

Acknowledgment. This research was supported by the National

Science Foundation under Grant No. CHE-8416460.

Registry No. 1, 101032-85-3; 2, 101032-86-4; Os₃(CO)₁₀(μ₃-S), 93426-79-0; Me₃NO·2H₂O, 62637-93-8.

Supplementary Material Available: Tables of structure factor amplitudes and general temperature factor expressions for both structures (67 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto di Chimica Farmaceutica e Tossicologica, Università di Milano, 20132 Milano, Italy, Istituto di Chimica e Tecnologia Radioelementi, CNR, 35100 Padova, Italy, and Department of Chemistry, Virginia Commonwealth University, Richmond, Virginia 23284

Synthesis, Characterization, and Crystal Structure of a Hexaaza Macrocyclic Complex of Lutetium(III)

G. Bombieri,*† F. Benetollo,‡ A. Polo,‡ L. De Cola,§ D. L. Smailes,§ and L. M. Vallarino*§

Received March 25, 1985

A compound of formula Lu(C₂₂H₂₆N₆)(CH₃COO)(OH)(ClO₄)(CH₃OH)(H₂O)_{0.5} was obtained by the metal-templated cyclic condensation of 1,2-diaminoethane with 2,6-diacetylpyridine, and its structure was determined by a single-crystal X-ray diffraction analysis. The compound crystallized in the triclinic space group *P*1̄ with *Z* = 2, in a unit cell having *a* = 13.051 (3) Å, *b* = 11.351 (2) Å, *c* = 11.400 (2) Å, α = 108.95 (3)°, β = 104.63 (3)°, and γ = 100.40 (3)°. Its structure was ionic, with the complex cation consisting of 9-coordinate Lu(III) linked to the six N-donor atoms of the C₂₂H₂₆N₆ macrocycle, to a bidentate chelating acetate, and to either a water or methanol molecule. Noncoordinated OH⁻ and ClO₄⁻ balanced the residual cationic charges; clathrated methanol was also present. Thermogravimetric measurements and NMR (¹H and ¹³C) spectra showed the compound to be thermally stable in the solid state as well as inert toward metal release in solution.

Introduction

It was recently established that the trivalent lanthanides can act as templating agents in the formation of polyaza macrocyclic systems of appropriate cavity size. Several series of complexes containing the hexaaza hexadentate, 18-member macrocyclic cations L_A and L_B (Figure 1)¹⁻⁶ were obtained with all elements from lanthanum to lutetium (except radioactive promethium) in the presence of O-donor counterions. Closely related lanthanide derivatives were described for a dioxatetraaza tetradentate analogue of L_A containing two furan rings instead of two pyridines. Complexation of the hexaaza, 14-member macrocycle L_C acting as a tetradentate ligand was reported for the smaller lanthanides, terbium to lutetium.⁷ Compounds of La(III), Ce(III), and Nd(III) nitrates with the rigid, 18-member macrocyclic system obtained from the (2 + 2) Schiff-base condensation of 1,2-diaminoethane and 2,6-diacetylpyridine were also described.^{8,9} Crystal structures were reported for two polyaza macrocyclic lanthanide complexes: A lanthanum(III) species, [LaL_A(NO₃)₂], was found to be 12-coordinate,¹ and a samarium(III) species, [SmL_B(OH)(NO₃)H₂O]NO₃·2CH₃OH, was 10-coordinate;² both contained bidentate chelating NO₃⁻ groups. However limited, this evidence suggested that the decrease in ionic radii along the 4fⁿ series, while not drastically affecting the ability of the metal ions to function as templating agents and to complex with the resulting macrocyclic ligands, may tend to lower their total coordination number.

The structural data for La(III) and Sm(III)—two of the larger lanthanides—did not, however, permit one to assess how a decrease in the ionic radius of the metal might influence the structural features and spatial arrangement of the macrocyclic entity itself. This question was particularly relevant to an understanding of the striking inertness of these complexes toward transmetalation^{1,2} and metal release⁴ in solution. To provide some insight on this question, we have synthesized a complex of the smallest lanthanide, lutetium(III), with the six-nitrogen macrocyclic ligand L and report here its properties and crystal structure.

Experimental Section

Synthesis and Characterization of the Complex. Lutetium(III) acetate (Alfa Products, 1 mmol, 0.389 g dissolved in 45 mL of anhydrous methanol), 2,6-diacetylpyridine (Aldrich Chemical Co., 2 mmol, 0.3265 g dissolved in 10 mL of methanol) and 1,2-diaminoethane (2 mmol, 5.0 mL of an 0.40 M methanol solution⁴) were refluxed together with 6 h. The pale yellow solution was allowed to cool, filtered over cotton, evaporated to 30 mL over mild heat and treated with LiClO₄ (10 mmol, 0.904 g dissolved in 10 mL of methanol). The mixture was heated at 50 °C for 1 h and then kept at room temperature overnight. A minute amount of a pale lavender crystalline precipitate formed and was filtered off. (Its infrared spectrum showed it to be nearly anhydrous lutetium(III) perchlorate). After the filtered solution was allowed to stand loosely covered for several days, well-formed light amber crystals were deposited, which were filtered, washed with methanol and diethyl ether, and dried in an oven at 70 °C. Yields: 30–40%.

Anal. Calcd for Lu(C₂₂H₂₆N₆)(CH₃COO)(OH)(ClO₄)-(CH₃OH)(H₂O)_{0.5}: C, 39.18; H, 4.60; N, 11.22; O, 17.75. Found: C, 38.00; H, 4.05; N, 10.65; O, 17.57. The compound was moderately soluble in dimethyl sulfoxide, sparingly soluble in chloroform, and very nearly insoluble in other common solvents. The IR spectrum (4000–200 cm⁻¹) was taken in a combination of Nujol and hexachlorobutadiene mulls. The ¹H and ¹³C NMR spectra were recorded in Me₂SO solution. Thermogravimetric measurements were carried out under a dry He flow of 50 mL/min. The PYR-GC-mass spectrum was recorded with the pyrolysis furnace set at 195 °C. Relevant results from these measurements are reported in the Results and Discussion section.

X-ray Measurements and Structure Determination. The crystal and refinement data for LuL(CH₃COO)(OH)(ClO₄)-CH₃OH·0.5H₂O (pale yellow transparent regular prisms) are summarized in Table I. A prismatic single crystal of 0.32 × 0.20 × 0.12 mm was lodged in a Lindeman glass capillary and centered on a four-circle Philips PW1100

- (1) Backer-Dirks, J. D. J.; Gray, C. J.; Hart, F. A.; Hursthouse, M. B.; Schoop, B. C. *J. Chem. Soc., Chem. Commun.* **1979**, 774.
- (2) Abid, K. K.; Fenton, D. E.; Casellato, U.; Vigato, P. A.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1984**, 351.
- (3) Radecka-Paryzek, W. *Inorg. Chim. Acta* **1980**, *45*, L147.
- (4) De Cola, L.; Smailes, D. L.; Vallarino, L. M. *Inorg. Chem.*, in press.
- (5) Abid, K. K. M.Sc. Thesis, University of Sheffield, 1982.
- (6) Abid, K. K.; Fenton, D. E. *Inorg. Chim. Acta* **1984**, *95*, 119.
- (7) Radecka-Paryzek, W. *Inorg. Chim. Acta* **1981**, *52*, 261.
- (8) Radecka-Paryzek, W. *Inorg. Chim. Acta* **1981**, *54*, L251.
- (9) Radecka-Paryzek, W. *Inorg. Chim. Acta* **1985**, *109*, L21.

* Università di Milano.

† CNR.

§ Virginia Commonwealth University.

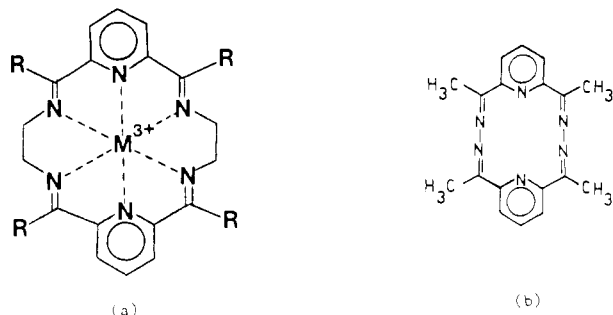


Figure 1. (a) Schematic formula of the hexaaza macrocyclic-lanthanide moiety: L_A , $R = CH_3$; L_B , $R = H$.² (b) Schematic formula of the tetraaza macrocycle-lanthanide moiety, L_C .

Table I. Crystal Data

formula	$LuClO_{8.5}N_6C_{25}H_{35}$
M_r	766.0
space group	$P\bar{1}$
cryst syst	triclinic
$a/\text{\AA}$	13.051 (3)
$b/\text{\AA}$	11.351 (2)
$c/\text{\AA}$	11.400 (2)
α/deg	108.95 (3)
β/deg	104.63 (3)
γ/deg	100.40 (3)
$V/\text{\AA}^3$	1481
Z	2
$D_c/(\text{mg m}^{-3})$	1.72
$F(000)$	766
radiation ($\lambda/\text{\AA}$)	Mo $K\alpha$ (0.71069)
temp/ $^{\circ}\text{C}$	22
reflcs measd	6091
scan method	$\theta/2\theta$
scan speed/(deg min^{-1})	1.8
scan width/deg	1.2
bkgd counts/s of counting time	20
$2\theta_{\text{max}}/\text{deg}$	52
data collcd	$\pm h, \pm k, +l$
σ limit [$I \geq n\sigma(I)$]	$n = 3$
no. of unique obsd reflcs	5042
[$I \geq 3\sigma(I)$]	
weighting scheme w	$2.8940 [\sigma^2(F_o) + 0.000738(F_o)^2]^{-1}$
$R = \sum[F_o - F_c] / \sum F_o $	0.043
$R_w = \left[\frac{\sum w(F_o - F_c)^2}{\sum w F_o ^2} \right]^{1/2}$	0.049
$\mu(\text{Mo } K\alpha)/\text{cm}^{-1}$	33.1
R_{int} (hkl reflcs only)	0.01
transmissn coeff	0.713–0.788

diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The orientation matrix and preliminary unit cell dimensions were determined from 25 reflections found by mounting the crystal at random and varying each of the orientation angles χ and ϕ over a range of 120° , with $6 \leq \theta \leq 9^\circ$. For the determination of precise lattice parameters, 25 strong reflections with $9 \leq \theta \leq 18^\circ$ were considered. Integrated intensities for hkl reflections with $l > 0$ were measured, and two standard reflections, $-3, -2, 4$ and $6, -1, -1$, were monitored every 180 min. There was no significant fluctuation of intensities other than those expected from Poisson statistics.

The intensity data were corrected for Lorentz-polarization effects and for absorption, following the method of North et al.;¹⁰ no correction was made for extinction. The structure was solved by using three-dimensional Patterson and Fourier techniques and refined by full-matrix least-squares techniques, with anisotropic thermal parameters for Lu, N(1–6), O(31), O(32), O(51) and isotropic thermal parameters for the remaining non-hydrogen atoms. Hydrogen atoms were in calculated positions and were allowed to ride on associated carbon atoms during the least-squares refinement ($d_{C-H} = 0.95 \text{ \AA}$ and $U_{\text{iso}} = 0.06 \text{ \AA}^2$). The function minimized was $\sum w\Delta^2$ with $\Delta = (|F_o| - |F_c|)$. The anomalous dispersion terms¹¹ for

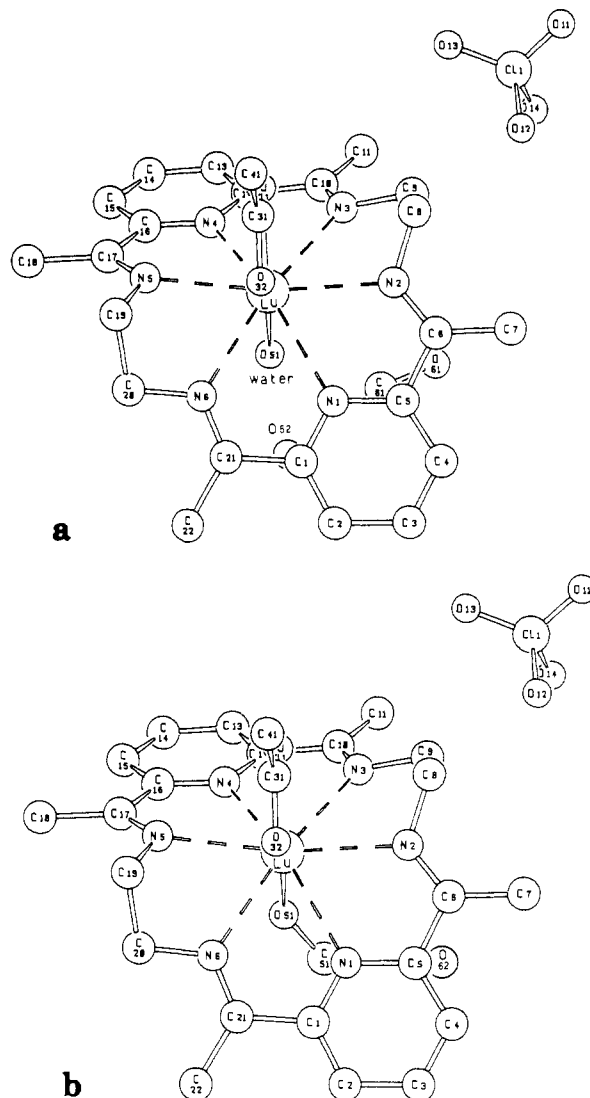


Figure 2. Perspective views: (a) $[LuL(CH_3COO)(H_2O)](CH_3OH)(O-H)(ClO_4)$; (b) $[LuL(CH_3COO)(CH_3OH)](OH)(ClO_4)$.

Lu were taken into account in the refinement. Atomic scattering factors were taken from ref 11. Data processing and computation were carried out by using the SHELX 76 program package.¹²

In the last stage of the refinement, difficulties were encountered in identifying the species in the ninth coordination position, as well as the positions of solvent atoms. After the clearly indicated position of O(51) was accounted for, there remained in the final difference Fourier map five residuals on the order of $3\text{--}4 \text{ e}/\text{\AA}^3$. If chemically impossible contacts are avoided, these could be interpreted as a statistical distribution of methanol, water, and a hydroxyl group, as indicated in Figure 2 (see Discussion), with contacts $O(51)_{\text{water}} \cdots O(52)_{\text{OH}} = 2.20 \text{ \AA}$, $O(52)_{\text{OH}} \cdots C(61)_{\text{Me}} = 2.26 \text{ \AA}$ and $C(51)_{\text{Me}} \cdots O(62)_{\text{OH}} = 2.49 \text{ \AA}$. Some other minor residuals ($1 \text{ e}/\text{\AA}^3$) suggested that an even more complicated statistical distribution of solvent may be possible. The solution indicated here was in agreement with the analytical elemental composition and other chemical evidence. Listings of anisotropic and isotropic thermal parameters, selected least-squares planes with deviations therefrom, and observed and calculated structure factors ($\times 10$) are available as supplementary material.

Results and Discussion

The Schiff-base condensation of 2,6-diacetylpyridine and 1,2-diaminoethane in the presence of lutetium(III) acetate, followed by precipitation with perchlorate ions, yielded as the only product a light amber crystalline complex having an elemental composition corresponding to $Lu(C_{22}H_{26}N_6)(CH_3COO)(OH)(ClO_4)(CH_3OH)(H_2O)_n$, where n varied between 1.5 and 0.5 depending

(10) North, A. C. T.; Philips, D. C.; Mathews, F. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **1968**, *A24*, 351.
 (11) "International Tables for X-Ray Crystallography", 2nd ed.; Kynoch Press: Birmingham, England 1974; Vol. 4, p 101.

(12) Sheldrick, G. M. "SHELX 76", University of Cambridge, 1976.

Table II. Atomic Coordinates ($\times 10^4$) with Esd's in Parentheses

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	pp ^a
Lu	1794.9 (2)	2804.6 (2)	3865.1 (2)	
N(1)	-146 (4)	1836 (5)	2158 (5)	
N(2)	1617 (5)	2014 (6)	1484 (5)	
N(3)	3124 (5)	4246 (6)	3177 (6)	
N(4)	3210 (4)	4878 (5)	5651 (5)	
N(5)	2248 (5)	3006 (5)	6174 (5)	
N(6)	170 (5)	1939 (5)	4552 (5)	
C(1)	-1042 (6)	1703 (6)	2529 (7)	
C(2)	-2089 (7)	1417 (8)	1671 (8)	
C(3)	-2223 (8)	1269 (9)	370 (10)	
C(4)	-1320 (7)	1377 (8)	-21 (8)	
C(5)	-287 (5)	1628 (6)	894 (6)	
C(6)	725 (6)	1716 (7)	523 (7)	
C(7)	632 (8)	1470 (9)	-858 (8)	
C(8)	2702 (7)	2283 (7)	1303 (8)	
C(9)	3137 (7)	3754 (8)	1834 (8)	
C(10)	3643 (6)	5427 (7)	3918 (7)	
C(11)	4214 (8)	6372 (10)	3530 (10)	
C(12)	3705 (6)	5830 (6)	5307 (6)	
C(13)	4282 (7)	7083 (8)	6261 (8)	
C(14)	4353 (7)	7379 (8)	7540 (8)	
C(15)	3871 (6)	6396 (7)	7907 (8)	
C(16)	3310 (6)	5161 (6)	6902 (7)	
C(17)	2776 (6)	4062 (7)	7192 (7)	
C(18)	2866 (9)	4326 (11)	8622 (10)	
C(19)	1603 (6)	1882 (7)	6314 (7)	
C(20)	412 (6)	1878 (7)	5873 (7)	
C(21)	-838 (6)	1782 (7)	3903 (7)	
C(22)	-1793 (7)	1719 (9)	4414 (9)	
O(31)	3320 (4)	2002 (5)	4053 (5)	
O(32)	1710 (4)	597 (4)	3436 (5)	
C(31)	2753 (5)	847 (6)	3729 (6)	
C(41)	3308 (8)	-181 (8)	3722 (9)	
Cl(1)	5469 (2)	8552 (2)	1672 (2)	
O(11)	6069 (16)	8371 (17)	855 (19)	0.6
O(12)	4367 (11)	7608 (12)	1134 (12)	0.6
O(13)	5977 (12)	8549 (15)	2936 (15)	0.6
O(14)	5088 (20)	9763 (25)	1867 (27)	0.6
O(111)	6548 (18)	8769 (21)	1484 (22)	0.4
O(121)	4972 (22)	7175 (26)	1194 (24)	0.4
O(131)	5743 (23)	9369 (27)	3023 (27)	0.4
O(141)	5001 (18)	9191 (22)	886 (24)	0.4
O(51)	998 (4)	4410 (5)	4090 (6)	
C(51)	336 (12)	4822 (13)	3372 (14)	0.5
O(52)	-508 (10)	5037 (12)	3657 (12)	0.5
C(61)	388 (19)	4988 (22)	2191 (23)	0.5
O(61)	686 (8)	5610 (8)	1456 (8)	0.5
O(62)	115 (9)	5302 (10)	1357 (10)	0.5

^a Population parameters (pp) are reported when different from 1.

on the treatment of the sample. The structural elucidation, spectral properties, and thermal behavior of the compound follow.

Single-Crystal X-ray Diffraction Analysis. Final atomic position parameters are given in Table II, bond distances and angles are given in Table III, and torsion angles are given in Table IV. Views of the compound are reported in Figures 2 and 3, which also show the atom-numbering scheme. A noteworthy feature of this structure is that the crystals may be considered to consist of the two species shown in parts a and b of Figure 2, present in a 1:1 ratio. The species illustrated in Figure 2a has the structural formula $[\text{LuL}(\text{CH}_3\text{COO})(\text{H}_2\text{O})](\text{ClO}_4)(\text{OH})(\text{CH}_3\text{OH})$. The organic macrocycle surrounds the lutetium ion with all nitrogen atoms bound to it, the acetate ion is bidentate and chelated to the metal on one side of the macrocycle, and a water molecule on the opposite side completes the coordination sphere. A hydroxide ion group and a disordered perchlorate ion balance the two positive charges of the complex cation, with a methanol molecule clathrated in the structure. The species illustrated in Figure 2b has the structural formula $[\text{LuL}(\text{CH}_3\text{COO})(\text{CH}_3\text{O}-\text{H})](\text{ClO}_4)(\text{OH})$, and therefore differs from the first species only by having a methanol molecule coordinated to the metal instead of a water molecule. A hydroxide ion, occupying a position different from that of the first species, and a disordered perchlorate

Table III. Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses

(a) Lutetium Environment			
Lu-N(1)	2.555 (5)	N(1)-Lu-N(2)	61.8 (2)
Lu-N(2)	2.501 (6)	N(1)-Lu-N(6)	61.2 (2)
Lu-N(3)	2.608 (7)	N(2)-Lu-N(3)	63.0 (2)
Lu-N(4)	2.552 (4)	N(3)-Lu-N(4)	61.6 (2)
Lu-N(5)	2.471 (6)	N(4)-Lu-N(5)	61.9 (2)
Lu-N(6)	2.581 (7)	N(5)-Lu-N(6)	63.5 (2)
Lu-O(31)	2.325 (6)	O(31)-Lu-O(32)	55.4 (2)
Lu-O(32)	2.368 (5)		
Lu-O(51)	2.232 (6)		
(b) Ligands			
N-C(py) _{av}	1.33 (1)	C-C(phen) _{av}	1.39 (1)
Cl-O _{av}	1.44 (2)	C-C(aliphatic) _{av}	1.49 (1)
C(31)-O(31)	1.264 (8)	O(51)-C(51)	1.29 (2)
C(31)-O(32)	1.270 (8)	C(61)-O(61)	1.34 (3)
C(31)-C(41)	1.48 (1)		
Lu-N(1)-C(1)	120.8 (4)	C(10)-C(12)-C(13)	123.3 (7)
Lu-N(1)-C(5)	119.9 (5)	C(13)-C(12)-N(4)	120.5 (6)
N(1)-C(1)-C(2)	122.1 (7)	C(12)-C(13)-C(14)	120.6 (8)
C(2)-C(1)-C(21)	122.1 (7)	C(13)-C(14)-C(15)	119.2 (8)
C(1)-C(2)-C(3)	118.9 (9)	C(14)-C(15)-C(16)	117.2 (7)
C(2)-C(3)-C(4)	119.2 (9)	C(15)-C(16)-C(17)	121.2 (6)
C(3)-C(4)-C(5)	118.6 (8)	C(15)-C(16)-N(4)	123.9 (7)
N(1)-C(5)-C(4)	122.3 (7)	Lu-N(4)-C(16)	120.4 (5)
C(4)-C(5)-C(6)	121.4 (6)	Lu-N(4)-C(12)	119.7 (4)
C(5)-C(6)-C(7)	119.3 (7)	C(16)-C(17)-C(18)	117.5 (7)
C(7)-C(6)-N(2)	126.5 (8)	C(18)-C(17)-N(5)	127.8 (8)
Lu-N(2)-C(6)	125.6 (5)	Lu-N(5)-C(17)	125.3 (5)
Lu-N(2)-C(8)	111.8 (4)	Lu-N(5)-C(19)	112.9 (4)
Lu-N(3)-C(9)	118.9 (5)	Lu-N(6)-C(20)	118.8 (5)
Lu-N(3)-C(10)	121.7 (5)	Lu-N(6)-C(21)	122.0 (5)
N(3)-C(10)-C(11)	125.7 (8)	N(6)-C(21)-C(22)	126.3 (7)
C(11)-C(10)-C(12)	118.0 (8)	C(1)-C(21)-C(22)	118.5 (7)
Lu-O(31)-C(31)	93.9 (5)	O(31)-C(31)-O(32)	118.9 (7)
Lu-O(32)-C(31)	91.7 (4)	O(31)-C(31)-C(41)	120.0 (7)
		O(32)-C(31)-C(41)	121.1 (7)
O-Cl-O _{av}	109 (1)		

Table IV. Torsion Angles

atoms	dist 2-3, Å	angles 1-2-3, deg	torsion angles 1-2-3-4, deg
C(1)-N(1)-C(5)-C(6)	1.340 (9)	118.6 (6)	-176.6 (7)
N(1)-C(5)-C(6)-N(2)	1.482 (11)	116.3 (6)	-2 (1)
C(5)-C(6)-N(2)-C(8)	1.281 (8)	114.1 (6)	-173.0 (7)
C(6)-N(2)-C(8)-C(9)	1.474 (11)	120.5 (6)	98.8 (8)
N(2)-C(8)-C(9)-N(3)	1.518 (11)	105.4 (7)	54.9 (8)
C(8)-C(9)-N(3)-C(10)	1.454 (11)	106.9 (7)	166.8 (7)
C(9)-N(3)-C(10)-C(12)	1.272 (8)	118.8 (7)	-173.4 (7)
N(3)-C(10)-C(12)-N(4)	1.474 (11)	116.2 (7)	1 (1)
C(10)-C(12)-N(4)-C(16)	1.375 (10)	116.1 (6)	175.1 (7)
C(12)-N(4)-C(16)-C(17)	1.322 (10)	118.6 (6)	-178.3 (6)
N(4)-C(16)-C(17)-N(5)	1.490 (12)	115.0 (6)	-3 (1)
C(16)-C(17)-N(5)-C(19)	1.285 (7)	114.6 (7)	-174.7 (6)
C(17)-N(5)-C(19)-C(20)	1.475 (10)	120.0 (6)	101.2 (8)
N(5)-C(19)-C(20)-N(6)	1.507 (11)	106.3 (7)	52.1 (8)
C(19)-C(20)-N(6)-C(21)	1.486 (11)	106.7 (6)	171.4 (7)
C(20)-N(6)-C(21)-C(1)	1.283 (9)	117.9 (6)	-173.3 (6)
N(6)-C(21)-C(1)-N(1)	1.490 (11)	115.2 (7)	-1 (1)
C(21)-C(1)-N(1)-C(5)	1.340 (10)	115.6 (7)	172.5 (6)

ion balance the cationic charges. (It was concluded that the oxygen O(51) of the monodentate ligand must belong to an uncharged atom because the anisotropic thermal parameters associated with this position do not show anomalous features arising from different types of oxygens in very close proximity, as would occur if the hydroxide or methanolic oxygens occupied alternatively close positions).

In both species the coordination number of Lu(III) is nine. The conformation of the macrocycle is characterized by two approximately planar sections, (C(8)-N(2)...N(6)-C(20) and C(19)-N(5)...N(3)-C(9)), with the deviations from planarity ranging from -0.17 to +0.23 Å. The two sections are hinged along an

Table V. Selected Structural Parameters for Lanthanide Complexes with Hexaaza and Hexaoxa Hexadentate Macrocyclic Ligands

(a) Complexes with Hexaaza Hexadentate Macrocycles						
complex	CN	Ln-N(py), Å	Ln-N(imine), Å	Ln-O(anionic), Å	ionic radii, ^a Å	
[La(C ₂₂ H ₂₆ N ₆)(NO ₃) ₃] ¹	12	2.746 2.764	2.672–2.729 ^a	2.689–2.767 ^a	1.061	
[Sm(C ₁₈ H ₁₈ N ₆)(NO ₃)(OH)(H ₂ O)]NO ₃ ·2CH ₃ OH ²	10	2.65 (1) 2.66 (1)	2.60 (1)–2.64 (1)	2.51 (1) 2.52 (1)	0.964	
[Lu(C ₂₂ H ₂₆ N ₆)(CH ₃ COO)(CH ₃ OH) _{0.5} (H ₂ O) _{0.5} -(OH)(ClO ₄)(CH ₃ OH) _{0.5}]	9	2.556 (7) 2.556 (9)	2.471 (7)–2.620 (9)	2.326 (6) 2.365 (7)	0.848	
(b) Complexes with Hexaoxa Hexadentate Macrocycles						
complex	CN	Ln-O(ether), Å	Ln-O(anionic), Å	ionic radii, Å		
La(NO ₃) ₃ (18-crown-6) ¹⁰	12	2.627–2.772 (6)	2.644–2.675 (6)	1.061		
La(NO ₃) ₃ (dicyclohexyl-18-crown-6) ¹¹	12	2.61–2.92 ^a	2.63–2.71 ^a			
Nd(NO ₃) ₃ (18-crown-6) ^{12,13}	12	2.598 (5)–2.788 (4) ¹²	2.580 (4)–2.615 (4) ¹²	0.995		
[Nd(NO ₃) ₂ (18-crown-6)] ₃ [Nd(NO ₃) ₆] ¹⁴		2.576 (6)–2.770 (6) ¹³	2.566 (6)–2.598 (7) ¹³			
complex cation	10	2.54 (2)–2.71 (2)	2.42 (2)–2.57 (2)	0.995		
complex anion	12		2.67 (1)–2.66 (2)			
[GdCl ₂ (EtOH)(18-crown-6)]Cl ¹⁵	9	2.497 (6)–2.608 (5) 2.414 (6) ^b		0.938		
[Gd(NO ₃) ₃ (OH) ₂] ₃ ·(18-crown-6) ¹⁰	9	2.422 (4)–2.454 (6) ^b	2.411 (11)–2.533 (13)			

^a Esd's were not given in reference. ^b The distances are Gd-O(H₂O).

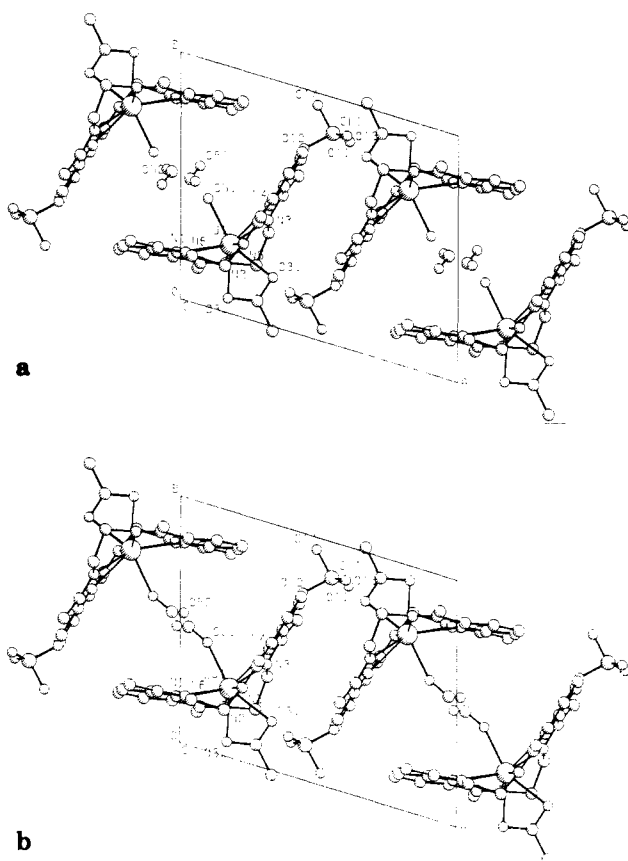


Figure 3. Packing of the molecule viewed down the *c* axis: (a) [LuL(CH₃COO)(H₂O)](CH₃OH)(OH)(ClO₄); (b) [LuL(CH₃COO)](CH₃OH)(OH)(ClO₄).

axis passing midway between C(8)–C(9) and C(19)–C(20) and are folded toward the singly coordinated ligand (water or methanol); the dihedral angle between the two planes is 114.4 (1)°. The torsion angles N(2)–C(8)–C(9)–N(3) and N(5)–C(19)–C(20)–N(6) are quite similar, 55 (1) and 52 (1)°, respectively, resulting in a synclinal conformation.

The bond distances and angles in the macrocycle are as expected: C=N = 1.27 (1)–1.29 (1) Å, C–N(py) = 1.32 (1)–1.34 (1) Å, and C–C(py) = 1.39 (1) Å (average). Significant contacts in the structure are O(51)_{water}...O(52)_{hydroxyl} = 2.20 (1) Å, O(51)...O(52)^I (at $-x, 1-y, 1-z$) = 2.71 (2) Å, O(52)...O(52)^I = 3.05 Å, and O(62)_{hydroxyl}...O(62)^{II} (at $-x, 1-y, -z$) = 2.87 (2) Å; these could be considered as hydrogen bonding.

It appears that in the [LuL(CH₃COO)(H₂O)](CH₃COO)(OH)(ClO₄) species the complex cations are linked two by two through hydrogen bonds involving the coordinated water (O(51)) and the hydroxyl anion (O(52)), whereas in [LuL(CH₃COO)(CH₃OH)](OH)(ClO₄) only the O(62) hydroxyl anions are hydrogen bonded.

Table V summarizes some significant structural parameters of our compound and of the two other hexaaza macrocyclic lanthanide complexes for which structures have been reported.^{1,2} Structural data published to date^{13–18} for lanthanide complexes of flexible macrocyclic ligands of the crown ether type are included for comparison. Such complexes have been extensively investigated and were recently reviewed.¹⁹

For the hexaaza derivatives, the trend in Lu–N(py) internuclear distances is in agreement with the decrease in the ionic radii from La to Lu, despite the differences in the coordination numbers of the complexes—12 for La, 10 for Sm, and 9 for Lu. However, the Ln–N(imine) distances are shorter than the Ln–N(py) distance in the La and Sm complexes, whereas in the Lu complex the average Lu–N(py) distance (2.556 (8) Å) is comparable with the average Lu–N(imine) distance (2.541 (7) Å). It may be noted that the Lu–O(acetate) distances (2.368 (5) and 2.326 (6) Å) are significantly longer than the Lu–O(51) distance (2.232 (6) Å) ascribed to either Lu–O(water) or Lu–O(methanol).

Comparison with the crown ether macrocycles shows that for La(III) the bidentate chelating nitrate groups are more strongly bound to the metal in the oxa complex than in the aza complex. In the crown ether series, the competition between the strongly ligating NO₃[−] and the O-donor organic ligand is actually reflected in the stoichiometry of the complexes. For example, species with Ln to crown ether ratios higher than 1 are stabilized by the presence of the [Ln(NO₃)₆]^{3−} moiety.¹³ Also, coordination of the crown ether does not take place with gadolinium(III) nitrate, even though it readily occurs with the chloride. It should be noted that a similar competitive effect is not observed for the nitrogen-containing, flexible crown ether type ligand L = C₂₂H₂₆N₂O₄,

- (13) Backer-Dirks, J. D. J.; Cooke, J. E.; Galas, A. M. R.; Ghotra, J. S.; Gray, C. J.; Hart, F. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1980**, 2191.
- (14) Harman, M. E.; Hart, F. A.; Hursthouse, M. B.; Moss, G. P.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1976**, 396.
- (15) Bunzli, J. C. G.; Klein, B.; Wessner, D. *Inorg. Chim. Acta* **1980**, *44*, L147.
- (16) Bombieri, G.; De Paoli, G.; Benetollo, F.; Cassol, A. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1417.
- (17) Bunzli, J. C. G.; Klein, B.; Wessner, D.; Schenk, K. J.; Chapuis, G.; Bombieri, G.; De Paoli, G. *Inorg. Chim. Acta* **1981**, *54*, L43.
- (18) Forsellini, E.; Benetollo, F.; Bombieri, G.; Cassol, A.; De Paoli, G. *Inorg. Chim. Acta* **1985**, *109*, 167.
- (19) Bunzli, J. C. G.; Wessner, D. *Coord. Chem. Rev.* **1984**, *60*, 191.

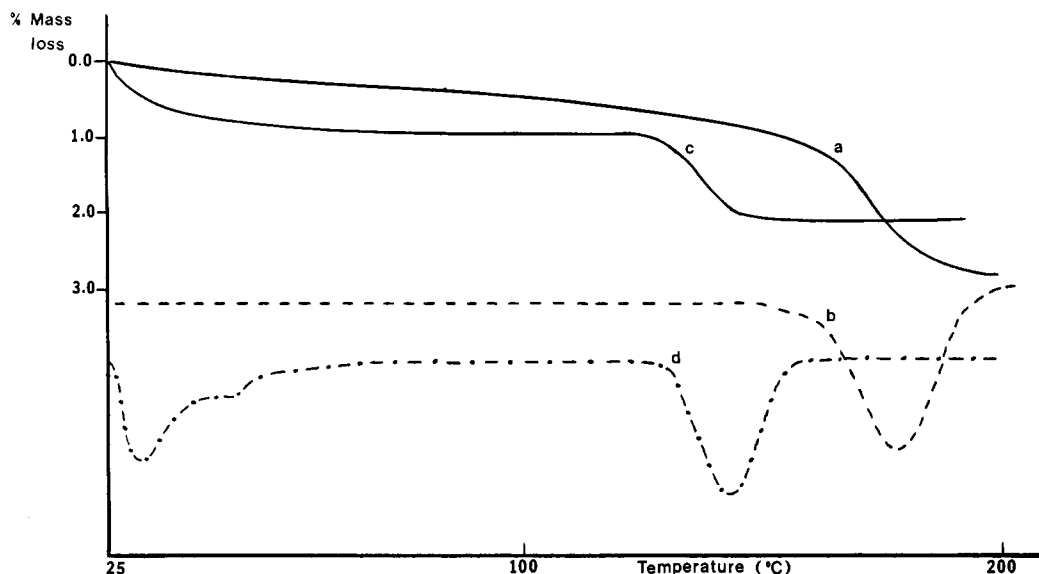


Figure 4. Thermal stability: (a) mass-loss and (b) first-derivative curves of $[\text{LuL}(\text{CH}_3\text{COO})(\text{CH}_3\text{OH})_{0.5}(\text{H}_2\text{O})_{0.5}](\text{OH})(\text{ClO}_4)(\text{CH}_3\text{OH})_{0.5}$; (c) mass-loss and (d) first-derivative curves of the complex after rehydration by exposure to atmosphere.

which forms $\text{ML}(\text{NO}_3)_3$ complexes with all elements of the lanthanide series.²⁰

Infrared Spectra. The infrared spectrum of the compound showed the following diagnostic features: (a) The typical absorptions of ionic ClO_4^- appeared at 1090 (s, br) and 620 (s) cm^{-1} . (b) The acetate ligand gave rise to two strong and fairly sharp carboxylate stretching absorptions, $\nu(\text{COO})$ at 1535 cm^{-1} and $\nu(\text{COO})$ at 1465 cm^{-1} . Their frequency separation, $\Delta\nu = 70 \text{ cm}^{-1}$, was in the range observed for other complexes containing bidentate chelating acetate.²¹ For comparison, the $\Delta\nu$ values for other types of acetates are:²² 144 (ionic), 160–180 (bidentate bridging), and 250–320 (monodentate) cm^{-1} . (c) The absorption pattern of the organic macrocycle was essentially identical with that observed in related complexes of other metal ions;²⁴ the two strong $\nu(\text{C}=\text{N})$ absorptions appeared at 1650 (Schiff-base) and 1595 (pyridine) cm^{-1} . (d) The OH stretching vibration of the hydroxyl-containing species gave rise to a medium-intensity, broad absorption centered at 3370 cm^{-1} , with a shoulder at 3290 cm^{-1} . A very broad, medium-weak absorption extending from 3000 to 2200 cm^{-1} , with ill-resolved peaks at 2750, 2480, and 2400 cm^{-1} , was also observed as a background of the sharp CH stretching absorptions. These features are consistent with the presence of methanol, coordinated water, and uncoordinated hydroxide. In contrast, hydroxide coordinated to trivalent lanthanides has been observed⁴ to produce an extremely sharp, strong OH stretching absorption at ca. 3600 cm^{-1} , together with a strong band at 450 cm^{-1} and a weak one at 355 cm^{-1} ; both of these lower energy bands were missing in the lutetium complex considered here.

Nuclear Magnetic Resonance Spectra. Both the ^{13}C and the ^1H NMR spectra (of $\text{LuL}(\text{CH}_3\text{COO})(\text{OH})(\text{ClO}_4)(\text{CH}_3\text{OH})(\text{H}_2\text{O})_{0.5}$) closely resembled those of the La and Lu species of formula $\text{LnL}(\text{CH}_3\text{COO})_2\text{Cl}\cdot n\text{H}_2\text{O}$ ($n = 3\text{--}5$);⁵ the proton-decoupled ^{13}C NMR spectrum of the Lu compound in dimethyl sulfoxide solution gave the following chemical shifts: δ (relative to Me_4Si , at 32.8 KHz) 183.3 (COO⁻ of acetate), 168.4 (C=N of Schiff base), 152.4 ($\alpha\text{-C}$ of pyridine), 141.7 ($\gamma\text{-C}$), 125.4 ($\beta\text{-C}$), 51.6 (C—N), 23.3 (CH_3 of acetate), 15.6 (CH_3 of macrocycle); no resonance was observed for the C atom of methanol because of masking by the Me_2SO multiplet. In the same solvent, the ^1H chemical shifts were as follows: δ (relative to Me Si, at 44.8 KHz)

8.32 (apparent singlet, 6 H, pyridine H), 3.97 (8 H, CH_2), 3.31–3.17 (H_2O and CH_3 of methanol), 2.56 (12 H, CH_3 of macrocycle), 1.34 (3 H, CH_3 of acetate). Both the carbon-13 and the proton spectra remained unchanged for several weeks.

Thermogravimetric Behavior. The thermal stability of the compound in the solid state was quite exceptional for a species containing both water and methanol. Up to 150 °C, only a small gradual mass loss was observed, followed by a well-defined decomposition step between 185 and 195 °C (Figure 4). The observed total mass loss (2.6%) corresponded to the release of the clathrated methanol and coordinated water (calculated loss, 2.6%); the identity of the species released was confirmed by a gas chromatography mass spectrum, utilizing a pyrolysis furnace set at 195 °C.

The product isolated at the end of this decomposition step (200 °C) was uncharred and maintained a crystalline aspect, although the crystals had acquired a cloudy appearance. The sample absorbed moisture very rapidly upon exposure to the atmosphere, returning almost exactly to its original mass. This showed that two H_2O molecules must have taken the place of the one lost methanol. The infrared spectrum of the rehydrated sample was very similar to that of the original compound, but its thermogram was considerably different, with the mass-loss step occurring at 155–160 °C. Successive rehydration–dehydration cycles gave identical results.

Conclusions

The general features of the macrocyclic lutetium(III) complex described in this paper—namely its metal-templated synthesis, its infrared and nuclear magnetic resonance spectra, its thermal stability, and its inertness in solution—did fit in very well with the properties reported for other complexes of the same ligand with the earlier members of the lanthanide series.⁴ However, the crystalline Lu complex presented an unexpected structural feature, in that the Lu–macrocyclic moiety had a “folded butterfly” structure, with the dihedral angle between the wings being 114°. In contrast, only a minor departure from planarity was observed in the complexes $[\text{LaL}(\text{NO}_3)_3]_1$ and $[\text{SmL}(\text{OH})(\text{NO}_3)(\text{H}_2\text{O})]\text{N-O}_3\cdot 2\text{CH}_3\text{OH}$.² Clearly, the hinging of the macrocycle at the two flexible $-\text{CH}_2-\text{CH}_2-$ side chains not only relieves steric strain within the cycle itself but also minimizes repulsion among the hetero ligands, thus allowing the central metal to attain its highest possible coordination number. (The presence in the Lu complex of noncoordinated potential O-donor ligands, such as hydroxide and methanol, suggests nine as the limit for the coordination number of Lu in compounds of this type.) The question still remains, whether the folding of the macrocycle in lanthanide complexes is determined by the ionic size of the metal or rather

(20) Desreux, J. F.; Renard, A.; Duyckaerts, G. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1587.

(21) Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 1912.

(22) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley: New York, 1978.

(23) Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *A32*, 751.

by the steric requirements of the hetero ligands. To answer this question, it will be necessary to establish the structures of selected macrocyclic complexes having the same formula but containing lanthanides of appreciably different sizes; efforts to obtain suitable crystals for this purpose are in progress.

Acknowledgment. This work was supported in part by the U.S. National Institutes of Health (Grant No. RO1-CA30148). The cooperative project was carried out under the sponsorship of

NATO (Research Grant 184/84).

Registry No. Lu(C₂₂H₂₆N₆)(CH₃COO)(OH)(ClO₄)(CH₃OH)(H₂O)_{0.5}, 100447-95-8; 2,6-diacetylpyridine, 1129-30-2; 1,2-diaminoethane, 107-15-3.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms, calculated hydrogen positions, least-squares planes, and structure factors (23 pages). Ordering information is given on any current masthead page.

Contribution from Laboratoire de Dynamique et Thermophysique des Fluides, Associe au CNRS, Université de Provence, Centre de St. Jérôme, F-13397 Marseille Cedex 4, France, and Chemistry Department A, Technical University of Denmark, DK-2800 Lyngby, Denmark

Complex Formation in Pyrosulfate Melts. 2. Calorimetric Investigations of the Systems V₂O₅-K₂S₂O₇, V₂O₅-K₂S₂O₇-K₂SO₄, V₂O₅-2K₂S₂O₇-K₂SO₄, and V₂O₅-3K₂S₂O₇-K₂SO₄ at 430 °C

Rasmus Fehrmann,^{1a} Marcelle Gaune-Escard,^{*1b} and Niels J. Bjerrum^{*1a}

Received July 11, 1985

The enthalpies of mixing of solid V₂O₅ and liquid K₂S₂O₇ have been measured in the whole liquidus range at 430 °C. The maximum concentration of V₂O₅ was found to be in the mole fraction range $X_{V_2O_5} = 0.502-0.509$. On the basis of the results the liquid-liquid enthalpies of mixing of liquid V₂O₅ and K₂S₂O₇ could be calculated. ΔH_{mix} was found to be strongly exothermic, and the data may indicate the formation of dimeric and polymeric complexes such as (VO₂)₂(SO₄)₂S₂O₇⁴⁻ and (VO₂SO₄)_nⁿ⁻, respectively. Also, the enthalpies of mixing of solid K₂SO₄ and the liquid mixtures V₂O₅-K₂S₂O₇, V₂O₅-2K₂S₂O₇, or V₂O₅-3K₂S₂O₇, contained in a calorimeter at 430 °C, were measured. The liquid-liquid enthalpies of mixing could be calculated on the basis of data obtained for the V₂O₅-K₂S₂O₇ system and the calculated heat of fusion of K₂SO₄ at 430 °C. Also in this case dimeric and polymeric complexes seem to be formed (possibly (VO₂)₂(SO₄)₃⁴⁻ and (VO₂(SO₄)₂)_n³ⁿ⁻). Structures for all the complexes are proposed. The importance of the results in relation to the catalytic oxidation of SO₂ to SO₃ is discussed.

Introduction

This paper concerning K₂S₂O₇-K₂SO₄-V₂O₅ molten mixtures is one of a series describing our attempts to explore the chemistry of the catalyst used for the oxidation of sulfur dioxide (i.e. the contact process utilized for the production of sulfuric acid). Earlier papers^{2,3} describe the equilibria in the pure solvent melts K₂S₂O₇-KHSO₄-K₂SO₄ and also the complex formation of V(V) in dilute solutions obtained by addition of V₂O₅ to these melts. The methods of investigation, which are all useful for the study of dilute and transparent systems, were spectrophotometry, Raman spectroscopy, cryoscopy, and potentiometry. In order to study the dark and very viscous melts with a high concentration of V₂O₅ analogous to the concentration in the catalytic melts, other methods must be applied. This work involves the first calorimetric study of the complex formation of V(V) in the binary system K₂S₂O₇-V₂O₅ at 430 °C and in the ternary system K₂S₂O₇-K₂SO₄-V₂O₅ also.

The phase diagram of the K₂S₂O₇-V₂O₅ system has been studied by several authors in the past,⁴⁻⁷ giving rise to rather different diagrams. Discrepancies also arise in the number of different compounds it has been claimed possible to isolate from the melts. These compounds, the so-called pyrosulfovanadates, are often distinguished only by the adduct formula V₂O₅·nK₂S₂O₇, and the existence of different compounds corresponding to the *n* values 1, 1.25, 1.5, 2, 3, and 6 has been reported.⁴⁻⁹ Some

further characterization has been carried out⁶⁻⁸ on the compounds with the *n* values 1, 2, and 3, i.e. V₂O₅·K₂S₂O₇, V₂O₅·2K₂S₂O₇, and V₂O₅·3K₂S₂O₇, which seem to have incongruent melting points at 400, 380, and 330 °C, respectively. On the basis of the IR spectra⁷ of the solids, bidentate (bridging or chelating) coordinate SO₄²⁻ groups appear to be present in all of these compounds, and furthermore, the compounds with *n* = 2 and 3 seem to contain the S₂O₇²⁻ group also. The formulas KVO₂SO₄, K₄(VO₂)₂(SO₄)₂S₂O₇, and K₃VO₂SO₄S₂O₇ have been suggested for the compounds.

In the dilute solutions of V₂O₅ in K₂S₂O₇ in the range 410-450 °C the investigation³ mentioned above has shown that the monomeric complex VO₂SO₄⁻ and its solvated form (VO₂SO₄S₂O₇)⁻ are most probably present in the melt; the existence of the unsolvated complex is also confirmed by others.¹⁰

The published phase diagrams of the binary system V₂O₅-K₂SO₄ show discrepancies.^{8,11} These inconsistencies are illustrated by the different formulas, V₂O₅·K₂SO₄, 5V₂O₅·3K₂SO₄, and 2V₂O₅·K₂SO₄, that have been claimed.^{8,11,12} When the compounds are heated, SO₃ is liberated. When the mixture is cooled, K₂O·4V₂O₅ has been posulated to be formed.¹³

No systematic investigation has been performed on the ternary system K₂S₂O₇-K₂SO₄-V₂O₅. One paper¹³ deals with a system, K₂O·4V₂O₅-K₂S₂O₇, that can be looked upon as the above-mentioned ternary system since K₂O and K₂S₂O₇ can combine to form K₂SO₄. However, in this investigation only one melt composition of the ternary system having the molar ratio

- (1) (a) Technical University of Denmark. (b) Université de Provence.
- (2) Fehrmann, R.; Hansen, N. H.; Bjerrum, N. J. *Inorg. Chem.* **1983**, *22*, 4009.
- (3) Hansen, N. H.; Fehrmann, R.; Bjerrum, N. J. *Inorg. Chem.* **1982**, *21*, 744.
- (4) Bazarova, Zh. G.; Borekov, G. K.; Kefeli, L. M.; Karakchiev, L. G.; Ostankovich, A. A. *Dokl. Akad. Nauk. SSSR* **1968**, *180*, 1132.
- (5) Hähle, S.; Meisel, A. *Kinet. Katal.* **1971**, *12*, 1276.
- (6) Maslennikov, B. M.; Illarionov, V. V.; Gubareva, V. N.; Bushuev, N. N.; Tavrovskaya, A. Ya.; Leneva, Z. L. *Dokl. Akad. Nauk. SSSR* **1978**, *238*, 1411.
- (7) Glazyrin, M. P.; Krasil'nikov, V. N.; Ivakin, A. A. *Zh. Neorg. Khim.* **1980**, *25*, 3368.
- (8) Borekov, G. K.; Illarionov, V. V.; Ozerov, R. G.; Kil'disheva, E. V. *Zh. Obshch. Khim.* **1954**, *24*, 23.

- (9) Gubareva, V. N.; Illarionov, V. V.; Maslennikov, B. M.; Bushuev, N. N.; Leneva, Z. L.; Mikhailova, I. M.; Vilina, V. Yu.; Krasil'nikova, I. G. *Tr. NIUIFa* **1977**, *230*, 23.
- (10) Durand, A.; Picard, G.; Vedel, J. J. *Electroanal. Chem. Interfacial Electrochem.* **1981**, *127*, 169.
- (11) Hähle, S.; Meisel, A. *Z. Anorg. Allg. Chem.* **1970**, *375*, 24.
- (12) Tarama, K.; Teranishi, S.; Yoshida, S.; Tamura, N. "Proceedings of the 3rd International Congress on Catalysis"; North-Holland: Amsterdam, 1965; p 283.
- (13) Bazarova, Zh. G.; Karakchiev, L. G.; Kefeli, L. M. *Kinet. Katal.* **1969**, *10*, 1152.