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Abstract — Complexes between thiourea and lanthanide acetates were prepared of the general composition: $LnAc_3 \cdot tu \cdot xH_2O$, where x = 2 for lanthanum, cerium, and praseodymium complexes, and x = 1 for neodymium through dysprosium complexes (Ac = CH_3COO^-, tu = $SC(NH_2)_2$). Dihydrated thiourea complexes are isomorphous; monohydrates are also isomorphous, but with a different structure from the dihydrates. Infrared spectra of the dihydrates and monohydrates show conspicuous differences in regions of $-CO_2^-$ absorption. The acetate ligand was deduced from infrared spectra to be predominantely bidentate for x = 2 complexes, and monodentate for x = 1 complexes. No definite evidence for metal-sulfur bonding was found.

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INTRODUCTION

Thiourea complexes with some lanthanide acetates were first prepared by Sakharova,(1,2) who characterized them as $LnAc_3 \cdot tu \cdot xH_2O$ ($Ac = CH_3COO^-$, $tu = SC(NH_2)_2$) with $x = 2$ for lanthanum and cerium complexes, $x = 1$ for praseodymium and neodymium complexes, and $x = 0.5$ for the samarium complex.

Previous X-ray and infrared studies have shown that thiourea can form ionic(3-5) or covalently bonded complexes.(6-14)

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(1) N. N. Sakharova, <u>Dokl. Akad. Nauk. SSSR</u> <u>113</u>, 1073 (1957).

(2) V. P. Frontasev, Yu. G. Sakharova, and N. N. Sakharova, <u>Zh. Neorgan. Khim.</u> <u>10</u>, 1816 (1965).

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(11) M. Nardelli, A. Braibanti, and G. Fava, <u>Gazz. Chim. Ital.</u> <u>87</u>, 1209 (1957).

(12) A. Lopez-Castro and M. R. Truter, <u>J. Chem. Soc.</u> 1309 (1963).

(13) R. G. Vranka and E. L. Amma, <u>J. Amer. Chem. Soc.</u> <u>88</u>, 4270 (1966).

(14) E. A. Vizzini and E. L. Amma, <u>J. Amer. Chem. Soc.</u> 88, 2872 (1966).

In this study, compounds of higher lanthanides were prepared, and their properties characterized. A recent study of the lanthanide acetates(15) produced essential background information for the interpretation of infrared data.

EXPERIMENTAL

The reagents and experimental methods used in this work were identical with those previously described.(15) All infrared spectra were measured on KCl pellets to avoid complex formation between thiourea and KBr.(3-5)

The thiourea complexes were prepared by a procedure modeled upon that of Sakharova.(1,2) Lanthanide acetate and thiourea in the mole ratio of 1:2 were dissolved in water and filtered, and the complex was crystallized from solution by evaporating the water at room temperature. The crystalline product was filtered, washed with 95% ethanol, and dried in vacuum for 8-16 hr before analysis. The yield from this procedure depends upon the extent to which evaporation is allowed to proceed before the crystals are separated from solution, and cannot exceed more than 50% of the lanthanide acetate without an unacceptable loss in purity.

RESULTS

The analytical data for the complexes are listed in Table I; for the lanthanum, cerium, and neodymium complexes, the results of this work agree with those of Sakharova.(1) However, the praseodymium complex was found to be a dihydrate, and the samarium complex a monohydrate, whereas Sahkarova found a monohydrate for

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(15) D. G. Karraker, in preparation.

praseodymium and a hemihydrate for samarium. The complexes of lanthanides europium through dysprosium, first prepared in this work, were all monohydrates. Repeated attempts to prepare thiourea complexes of the acetates of heavier lanthanides failed. Despite a number of attempts, the $DyAc_3 \cdot tu \cdot H_2O$ complex could not be prepared better than ~90% pure.

An appreciable deviation (~20%) in water content from the simple monohydrate or dihydrate stoichiometry is noted in the analytical data of Table I, and is attributed to a combination of a hydrated lanthanide acetate (H_2O content ~18%) as an impurity and the occlusion of water in large crystals.

X-ray diffraction data (Table II) show that the thiourea complexes have two different crystal structures; the dihydrated thiourea complexes of lanthanum, cerium, and praseodymium are isomorphous; the monohydrated thiourea complexes of neodymium through dysprosium acetates are also isomorphous but with a different structure than the dihydrates. The X-ray diffraction data could not be computer fitted to a rectilinear cell structure, and it is inferred that the crystals of both complexes have monoclinic or triclinic cells.

The infrared spectra for these complexes showed different patterns for the two isomorphous series of complexes. The infrared spectra of thiourea, $LaAc_3 \cdot tu \cdot 2H_2O$, and $SmAc_3 \cdot tu \cdot H_2O$ are shown in Fig. 1, and the absorption bands are tabulated in Table III. The lanthanum and samarium complexes are representative of the essentially identical spectra of lanthanum, cerium, praseodymium, and neodymium through dysprosium complexes, respectively.

Assignments for the absorption bands in Table III are based upon previous infrared studies of thiourea,(3,16) the KBr·4tu complex,(3) and lanthanide acetates.(15)

Most of the bands were assigned from the correspondence in frequency with the infrared bands in lanthanide acetates or thiourea. These assignments are considered the most probable, but bands that shift considerably in frequency could be erroneously assigned.

The formation of a definite complex between thiourea and the lanthanide acetate is indicated by the splitting of the 1617 cm^{-1} band due to NH_2 deformation vibrations. A similar splitting has been observed(3-5) for the KBr·4tu complex. Characteristic differences in the infrared spectra of the lanthanum group and the neodymium group of complexes are observed in the 3200-3500 cm^{-1} region (OH, CH, and NH stretching frequencies) and in the 1560-1400 cm^{-1} region (CO_2^- asym. and sym. stretch, CN asym. stretch, C = S sym. stretch, and CH_3 asym. bend); but because multiple bands occur in both regions, maxima cannot be specifically assigned.

The shape of the absorption band differed for the $^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$ transition of Nd^{3+} in solid $NdAc_3 \cdot 3/2H_2O$ and $NdAc_3 \cdot tu \cdot H_2O$ (Fig. 2); this difference indicated that the environment of the Nd^{3+} ion is different in the two solids. The absorption spectra of aqueous solutions of these compounds were identical in shape and agreed within 5% in oscillator strengths.

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(16) R. M. Badger and R. D. Waldron, J. Chem. Phys. 26, 255 (1957).

DISCUSSION

Chemical analyses, X-ray diffraction patterns, and infrared spectra demonstrate the formation of two types of thiourea-lanthanide acetate complexes, $LnAc_3 \cdot tu \cdot xH_2O$ where $x = 2$ for lanthanum, cerium, and praseodymium, and $x = 1$ for neodymium through dysprosium complexes. Thiourea complexes could not be prepared for acetates of holmium through lutetium; the formation of the complexes is apparently determined by the size of the lanthanide ion. In a series of homologous lanthanide complexes, the decrease in the ionic radius of lanthanide ions with increasing atomic number results in increasing ligand repulsion. When ligand-ligand repulsion becomes sufficiently strong, the coordination sphere changes in either geometry and/or composition. This model of lanthanide ion coordination is consistent with the composition and structure changes observed between the two types of thiourea-lanthanide acetate complexes, and with the inability to prepare complexes of the heaviest lanthanides.

Lanthanide ion-ligand bonding is normally ionic; although previous infrared studies have identified ionic(3) and covalently coordinated thiourea,(6-9) no definite evidence for coordinated thiourea with the lanthanide ion was deduced in this study. Splitting and shifting of the NH_2 bending vibrations (~1617 cm^{-1}) observed in the complexes were similar to that found in the ionic(5) KBr·4tu complex. While suggestive of a similarity in bonding, the splitting of NH_2 bending vibrations could result from a constraint placed on these vibrations by the crystal lattice.

Splitting of the C=S and N-C-N stretching vibrations also occurs in ionic thiourea complexes. Unfortunately, the coincidence of strong acetate bands in the same frequency region as the C=S vibration prevents positive observation of the C=S vibration. No splitting of the N-C-N vibration was observed. Thiourea-lanthanide acetate complexes probably involve sulfur-lanthanide ion coordination, but without observation of an effect on the C=S or N-C-N vibrations, such coordination cannot be deduced from infrared spectra.

The infrared spectra of the $LnAc_3 \cdot tu \cdot 2H_2O$ complexes for the CO_2^- symmetric stretching vibrations (~1445-1410 cm^{-1}), though subject to an unknown interference from the thiourea C=S vibration, conforms to the pattern previously deduced for a bidentate acetate coordination.(15) The pattern found for $LnAc_3 \cdot tu \cdot H_2O$ complexes is similar to that observed for monodentate acetate ligands, though either complex might have an acetate ligand of a different ccoordination.

Acknowledgement — The author is grateful to Christine B. Hall for analytical support work.

TABLE I

Analytical Data for $LnAc_3 \cdot tu \cdot xH_2O$ Complexes

Lanthanide	x Value	Metal, %		Carbon, %		H, %		N, %		H_2O, %	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
La	2	32.48	32.44	19.63	19.50	3.97	3.89	6.54	6.58	8.41	9.04
Ce	2	32.63	32.11	19.58	19.58	3.96	3.91	6.53	6.82	8.39	7.86
Pr	2	32.79	32.95	19.53	19.66	3.95	3.81	6.51	6.65	8.37	9.22
Nd	1	34.69	34.24	20.24	20.32	3.61	3.60	6.75	7.07	4.34	5.07
Sm	1	35.69	35.38	19.93	19.96	3.56	3.55	6.64	6.69	4.27	5.31
Eu	1	35.93	35.91	19.86	19.92	3.54	3.53	6.62	6.66	4.26	5.38
Gd	1	36.75	36.50	19.63	19.66	3.50	3.42	6.54	6.74	4.21	5.31
Th	1	36.96	35.75	19.53	19.50	3.49	3.42	6.51	6.39	4.18	5.47
Dy[a]	1	37.20	37.21	19.38	19.69	3.46	3.35	6.46	5.74	4.15	-

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[a] ~90% pure compound

TABLE II

X-ray Diffraction Data for Thiourea-Lanthanide Acetate Complexes

$LnAc_3\cdot tu\cdot 2H_2O$						$LnAc_3\cdot tu\cdot H_2O$											
Lanthanum		Cerium		Praseodymium		Neodymium		Samarium		Europium		Gadolinium		Terbium		Dysprosium	
d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o
9.41	100	9.39	100	9.37	100	11.48	19	11.48	29	11.56	19	11.48	34	11.57	10	11.52	7
8.62	50	8.63	52	8.64	42	7.55	10	7.50	7	7.52	14	7.47	9	7.49	8	7.47	23
5.26	27	5.26	27	5.25	26	7.03	100	7.03	100	7.04	100	7.00	100	7.03	100	7.01	100
4.85	5	4.85	3	4.85	5	5.74	63	5.74	57	5.76	90	5.75	100	5.77	70	5.77	80
4.71	36	4.70	32	4.68	38	4.31	2	4.28	2	4.28	3	4.27	2	4.27	2	4.26	9
4.21	4	4.20	4	4.20	3	3.89	6	3.87	5	3.87	10						
3.95	4	3.94	4	3.93	3	3.82	7	3.82	8	3.83	12	3.83	15	3.84	10	3.85	29
3.83	3	3.83	3	3.83	3	3.76	18	3.76	21	3.77	31	3.76	14	3.76	18	3.76	31
3.55	3	3.54	3	3.54	3	3.44	2	3.43	3	3.43	4	3.42	2	3.42	2	3.42	9
3.51	7	3.50	8	3.49	6	2.90	5	2.90	6	2.90	6	2.90	4	2.90	6	2.91	8
3.13	18	3.13	13	3.11	12	2.57	3	2.56	5	2.56	6	2.56	3	2.56	2	2.56	9
2.63	3	2.63	4	2.62	3	2.34	4	2.34	5	2.34	5	2.34	4	2.34	3	2.34	8
2.59	12	2.58	13	2.57	11												
2.33	20	2.34	12	2.34	12												

TABLE III

Infrared Absorption Frequencies

cm^{-1}

Thiourea[a,b]	$KBr\cdot 4tu$[a]	$LaAc_3\cdot tu\cdot 2H_2O$	$SmAc_3\cdot tu\cdot H_2O$	Assignment
		3450 sh		-OH, -CH
3365 s		3380 sh	3380 S	-NH stretching vibrations
		3320 vs	3320 sh	
3260 s			3280 sh	
		3200 s		
3156 s		3160 sh	3160 s	
2670 w		2700 w		
			2360 w	Combination bands
		2240 m	2240 w	
2120 w		2130 sh	2100 w	
		1655 sh	1680 sh	HOH bend
1617 s	1634 w	1638 m	1650 w	$-NH_2$ deformation
	1592 s	1615 w	1628 m	
		1560 s		$-CO_2^-$ asym. stretch
		1525 s	1533 s	
				-C-N-asym. stretch
1473 s	1470 s			
		1445 s	1448 s	$-CO_2^-$ sym. stretch
	1433 s		1425 sh	-C=S sym. stretch
1413 s			1412 sh	$-CH_3$ asym. bend
	1389 m	1398 s	1395 sh	-C=S sym. stretch
		1337 w	1342 m	$-CH_3$ sym. bend
1086 m	1093 m	1085 sh	1085 sh	$-NH_2$ rock
		1060 w		
		1045 sh	1045 sh	$-CH_3$ rock
		1010 m	1007 w	
			960 sh	-C-C stretch
		938 s	946 m	
730 s	739 m	732 m	735 m	-C-N-sym. stretch
	725 m		725 sh ?	
		660 m	668 s	O-C-O bend
629 s	636 m	635 sh	635 w	tu out-of-plane skeletal vibration
	621 m	610 w	610 w	$-CO_2$ rock
		575 sh	570 sh	$-NH_2$ wag
486 s,b	483 s,b	485 m	495 w	tu skeletal deformation ?
463 sh		465 sh	470 w	$-CO_2^-$ rock
411 m	408 w	412 w	412 sh	$-NH_2$ torsional ?

(very weak bands are omitted)

s, strong; m, medium; w, weak; v, very ; b, broad; sh, shoulder

[a] J. E. Stewart, J. Chem. Phys. 26, 248 (1957).

[b] R. M. Badger and R. D. Waldron, J. Chem. Phys. 26, 255 (1957).

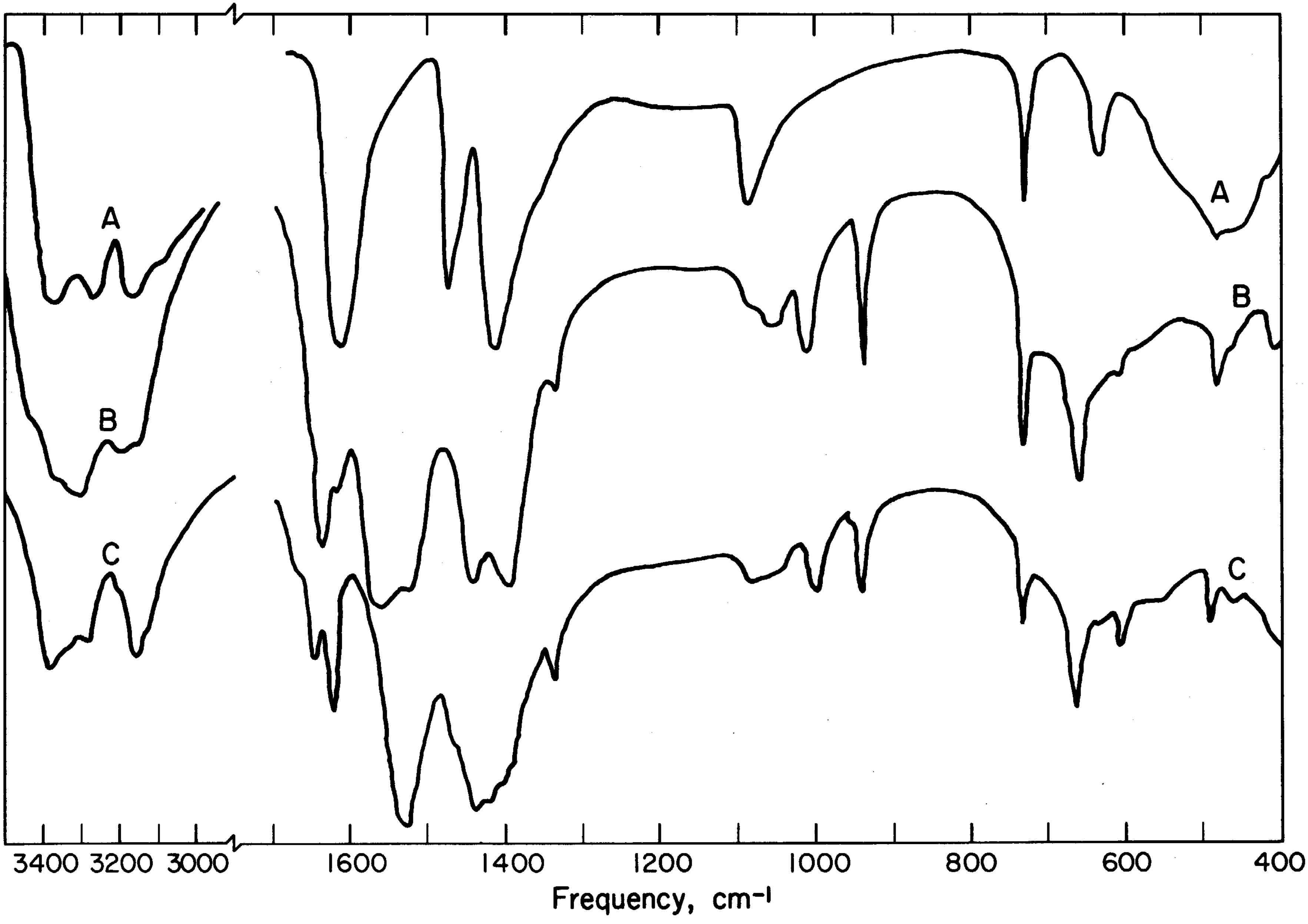

FIG. 1 INFRARED SPECTRA OF THIOUREA-LANTHANIDE ACETATE COMPLEXES
(A) Thiourea (B) $LaAc_3 \cdot tu \cdot 2H_2O$ (C) $SmAc_3 \cdot tu \cdot H_2O$