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Synthesis, Powder Data, Infrared and Raman Spectra of $N_2H_5Ln(SO_4)_2 \cdot H_2O$ (Ln = La–Tb, except Pm)

NATAŠA BUKOVEC* and SVETOZAR MILIĆEV

Department of Chemistry, Edvard Kardelj University, Ljubljana, Yugoslavia

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The lanthanides form a variety of double sulphates with formula $M^{I}Ln^{III}(SO_4)_2 \cdot xH_2O$. We have reported recently the synthesis, thermal decomposition [1] and crystal structure [2] of a new compound $N_2H_5Nd(SO_4)_2 \cdot H_2O$. We now report the syntheses, unit cell dimensions (determined from powder data) and assignments of infrared and Raman spectra for the family of eight compounds of the lanthanide elements (from La to Tb, with the exception of Pm) of the same composition.

Experimental

The compounds were prepared as described elsewhere [1]. X-ray powder data were collected by a Philips diffractometer (Cu Kα radiation) using silicon (a = 5.431 065 Å) [3] as an internal standard. Unit cell dimensions were refined by a least-squares program (SOS2) [4].

The infrared spectra were taken as nujol and perfluorobutadiene mulls on a Perkin-Elmer 521 spectrophotometer in the 250–4000 cm^{-1} region. Raman spectra were obtained with a SPEX-1401 double monochromator at the Department for Fluorine Chemistry of the Jožef Stefan Institute. They were excited by the 5145 Å line of a Spectraphysics Ar$^+$ ion laser, model CR-3, in back-scattering geometry.

Results and Discussion

The compounds $N_2H_5Ln(SO_4)_2 \cdot H_2O$ (Ln = La, Ce, Pr, Sm, Eu, Gd, and Tb) are isomorphous with $N_2H_5Nd(SO_4)_2 \cdot H_2O$ [2] (Table I). We may reasonably conclude that in the new compounds the lanthanide atom is likewise nine-coordinated with seven O-atoms of the sulphate ions, one water mole-

TABLE I. Unit Cell Dimensions of $N_2H_5Ln(SO_4)_2 \cdot H_2O$ (Ln = La–Tb except Pm) from X-ray Powder Data

Ln	a (Å)	b (Å)	c (Å)	V (Å^3)
La	11.050(1)	9.585(2)	15.874(4)	1680.0
Ce	11.023(2)	9.568(1)	15.817(2)	1668.2
Pr	10.956(4)	9.567(4)	15.786(3)	1654.6
Nd[a]	10.960(3)	9.561(4)	15.764(6)	1651.9
Sm	10.859(2)	9.510(2)	15.678(2)	1619.1
Eu	10.821(2)	9.509(2)	15.684(3)	1613.8
Gd	10.769(1)	9.505(2)	15.645(2)	1601.4
Tb	10.738(1)	9.538(2)	15.642(3)	1602.0

[a] Cell dimensions from monocrystal data [2].

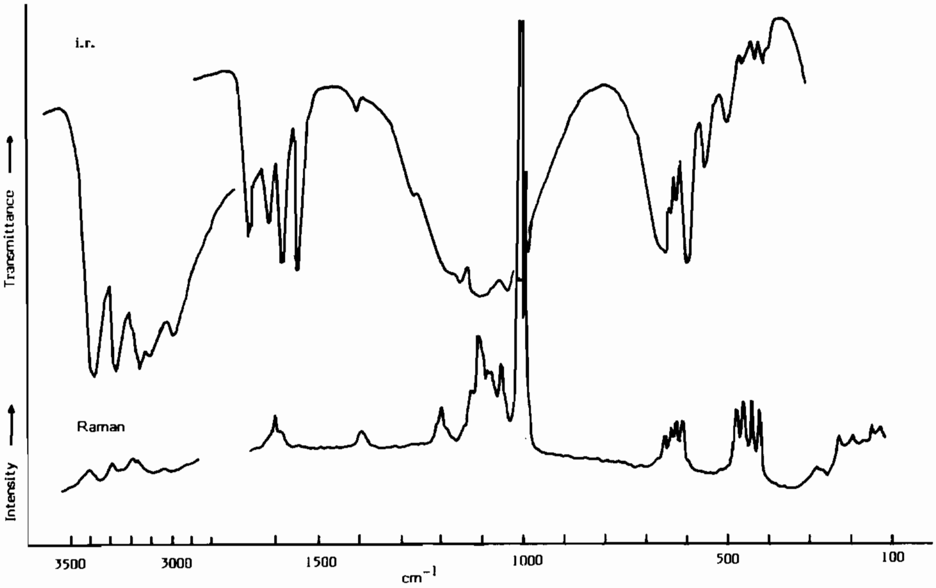

Fig. 1. Representative spectra of the series. Infrared spectra (nujol and perfluorobutadiene mulls) and Raman spectrum of $N_2H_5Ce(SO_4)_2 \cdot H_2O$.

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*Author to whom correspondence should be addressed.

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TABLE II. Infrared and Raman Spectra[a] of the $N_2H_5Ln(SO_4)_2 \cdot H_2O$ Compounds (cm^{-1})

La		Ce		Pr		Nd		Sm	Eu	Gd	Tb	Assignment[b]
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	IR	IR	IR	
3375s, br		3375s, br	3380(2)	3375s, br		3375s, br	3380(3)	3385s, br	3390s, br	3390s, br	3395s, br	$(H_2O)_s$
3275s		3275s	3275(2)	3275s		3270s	3270(3)	3275s	3275s	3275s	3275s	$(NH)_s$
			3175(2)				3180(3)					
3150s, br		3150s	3155(1)	3150s		3160m, br		3160s	3160s	3160s	3160s	
3110s, br		3110s, br		3105s, br		3110m, br		3110s, br	3115s, br	3115s, br	3110s, br	
3000m, br		3000m, br	3015(?)	2995m, br		2995m, br		3000m, br	3000m, br	2995m, br	2995m, br	
1655 w–m		1655w–m		1655w–m		1650w–m		1655w–m	1655w–m	1650w–m	1650sh	$(NH_2)_d$ + $(H_2O)_d$ (?)
1640sh		1640sh		1640sh		1638sh		1640sh	1640sh	1640sh	1645w–m	
1610w–m		1610w–m	1610(2)	1610w–m		1610w–m		1610w–m	1615w–m	1615w–m	1615w–m	$(NH_3^+)_d$
	1603(4)		1600(4)		1601(4)		1605(5)					
1580m		1580m	1585(2)	1580m		1580m		1580m	1580m	1585m	1585m	
1535m		1540m	1540(1)	1535m		1540m		1540m	1540m	1545m	1545m	
1393vw	1395(3)	1393vw	1392(2)	1390vw	1393(2)	1395vw	1398(3)	1394vw	1395vw	1396vw	1396vw	$(NH_2)_r$
1260sh	1265(1)	1260sh		1265sh		1265sh		1265sh	1270sh	1270sh	1270sh	
	1204(4)		1202(5)		1202(5)		1205(4)					$(NH_3^+)_r$
1180sh		1180sh		1180sh		1180sh		1180sh	1180sh	1180sh	1175sh	$\nu_3(SO_4^{2-})$
1145vs		1145vs	1146(2)	1145vs	1147(3)	1150vs		1150vs	1150vs	1150vs	1150vs	
	1130(6)		1125(7)		1126(6)	1120sh	1126(sh)					
	1110(11)		1105(14)		1107(13)		1110(17)					
1090vs	1100(6)	1095vs	1095(sh)	1095vs	1097(sh)	1100vs		1100vs	1105vs		1100vs	
	1080(8)		1085(4)		1085(5)	1085vs	1092(8)	1080vs		1085vs		
			1073(4)	1075vs	1074(sh)		1078(8)					
	1053(7)		1052(10)		1053(10)	1060sh	1060(13)		1050vs	1065vs	1065vs	
1025vs		1030vs		1030vs		1032vs		1035vs		1040vs	1045vs	
1005vw	1015(100)	1010vw	1012(100)	1010vw	1011(100)	1012w	1015(100)	1010vw	1020vw	1015vw	1015w	$\nu_1(SO_4^{2-})$
990w	1002(34)	990w	999(35)	990w	999(39)	995w–m	1002(40)	995vw	1005vw	1000sh	1000vw	$(NN)_s$
665sh		665sh	666(1)	660sh		670m, br	674(1)	670m, br	680m, br	670m	665sh	$\nu_4(SO_4^{2-})$
650m	653(5)	650m	650(4)	650m	652(5)	650m	650(3)	650m	650m	650m	650m	
	640(5)		635(5)		636(6)	635w	636(4)	635w–m	640w–m	635w–m	640w–m	
630sh	627(6)	630w–m		630w–m								
620w–m		620w	622(6)	620w	623(7)	620w–m	624(3)	620w–m	615w–m	615w–m	620w–m	
	612(6)		608(6)		609(8)		610(3)					
595m		595m		595m		595s		595m	595m	595m	595m	

545w–m		550w–m		545w–m		550w–m		550w–m	560w–m	560w–m	565w–m	$(H_2O)_w$
495w–m		500w–m		495w–m		495w–m		490w–m	495w–m	495w–m	490w	$(N_2H_5^+)_t$
	479(9)		474(9)		476(10)		476(5)					$\nu_2(SO_4^{2-})$
	460(10)	457vw	457(10)		458(12)	450vw	457(4)	450vw	452vw			
	441(10)	433vw	438(10)		440(11)	430vw	440(4)	428vw	430vw	432vw	425vw	
	423(10)	413vw	419(9)	409vw	420(11)		420(4)	410vw	410vw	414vw	409vw	
	297(2)		283(2)		286(2)		286(5)					Coordinated sulphate, $(Ln–O)_s$, vibrations and lattice vibrations
	267(2)		266(1)				270(12)					
	231(4)		230(3)		232(6)		229(3)					
							213(9)					
	196(2)		196(1)		199(3)		190(1)					
			170(1)		173(1)		164(6)					
	149(2)		148(2)		150(3)		152(3)					
	135(1)		133(2)		135(1)		137(1)					

[a] Raman intensities are given in parentheses. Infrared intensities: s = strong, m = medium, w = weak, sh = shoulder, and v = very. [b] d = deformation, r = rocking, s = stretching, t = torsion, w = wagging.

cule and one nitrogen atom of the $N_2H_5^+$ ion. The SO_4^{2-} ions, $N_2H_5^+$ ions and H_2O molecules are linked by a system of O–H···O and N–H···O hydrogen bonds. We ascribe the continuous decrease of the cell dimensions from the lanthanum to terbium compound to the lanthanide contraction. The compounds have almost identical vibrational spectra (Table II, Fig. 1). All the components are coordinated to the lanthanide ion, so the slight increase (5–10 cm^{-1}) in almost all the bands should also be assigned to the contraction. There are eight formula units in the orthorhombic primitive cell (space group $Pca2_1$, C_{2v}, No 29, with all atoms in general positions [2]). Factor group analysis predicts 288 internal modes uniformly divided into 72 A_1, 72 A_2, 72 B_1 and 72 B_2 symmetry species. A_2 vibrations are inactive in the infrared spectra, and all of them are active in the Raman spectra.

Bands assigned to the vibrations of the SO_4^{2-} ions are easily identified by comparison with the literature data (see for instance ref. 5). The ν_2 vibration is observed as a very weak absorption in the infrared, although it should gain activity because of the lower site symmetry [6]. The explanation might be a weak static field, which is in accord with the crystallographically observed insignificant deformation of the SO_4^{2-} ion [2]. Numerous split bands are obviously caused by the correlation field. Weak hydrogen bonding demonstrated by the spectra both in the OH and NH stretching regions is also in accord with the suggested weak static field. Correlation between O–H or N–H stretching frequencies and O–O [7] or N–O [8] distances almost exactly reproduce the X-ray data (O–O distances from the spectra are about 2.79 Å and N–O distances between 2.77 and 2.97 Å). These values are just under the van der Waals distances [9], confirming the very weak interactions.

Of the two strong bands in the Raman spectra (1015 cm^{-1} and 1002 cm^{-1}), which appear on the slope of the $\nu_3(SO_4^{2-})$ absorption in the infrared spectra as weak to very weak bands, we assign the stronger one to the symmetric breathing of the isotropic sulphate ion, and the weaker one to the N–N stretching of the asymmetric $N_2H_5^+$ ion. The frequency of the N–N mode is unusually high, indicating coordinated $N_2H_5^+$ ions [10]. This is confirmed by X-ray data [2], which give the Nd–N distance as 2.79 Å (the van der Waals radius of N is 1.55 Å and that of Nd should be larger than its Bragg–Slater radius, which is 1.85 Å [11]). Deformation and rocking modes of the $N_2H_5^+$ ion are assigned in accordance with the literature [12] and the references cited therein. Rocking bands of the NH_3^+ group, except the one in the Raman spectra, are hidden by the split ν_3 mode of the SO_4^{2-} ion. The torsion frequency of the $N_2H_5^+$ ion (495 cm^{-1}) is in accord with the weak hydrogen bond (compare the corresponding bands in N_2H_5F at 568 and 638 cm^{-1}, with stronger hydrogen bonding [13]). We could not identify any Nd–N stretching band. Some of the bands of coordinated water are tentatively assigned, mostly in accordance with ref. 14.

Conclusion

Powder diffraction data and vibrational spectra demonstrate the isomorphism of a series of orthorhombic hydrazinium(1+) lanthanide sulphates. Vibrational spectra, which are characteristic of the coordinated hydrazinium(1+) ion, manifest very weak hydrogen bonding. They indicate negligible deformations of the sulphate ions and also coupling of vibrations within the unit cell.

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