Hydrazinium as a Ligand: Structural, Thermal, Spectroscopic, and Magnetic Studies of Hydrazinium Lanthanide Di-sulphate Monohydrates; Crystal Structure of the Neodymium Compound[†]

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Hydrazinium lanthanide complexes of formula $N_2H_5Ln(SO_4)_2{\cdot}H_2O$, where Ln = La, Ce, Pr, Nd, or Sm, have been prepared and investigated by means of i.r. and electronic spectroscopy, thermal analysis, and magnetic susceptibility measurements. The crystal structure of the neodymium compound has been determined by conventional Patterson and Fourier methods and refined by full-matrix least squares to an R of 0.059 for 2 427 independent reflections. The two independent neodymium atoms in the asymmetric unit are nine-co-ordinated by seven sulphate oxygen atoms, one water molecule, and one nitrogen atom of the $N_2H_5^+$ ion. The co-ordination polyhedron in both the cases is a distorted tricapped trigonal prism. The sulphate groups are present as bridging ligands among three metal atoms. Powder patterns indicate isomorphism of the above series of compounds.

The chemistry of hydrazine is of interest since the molecule has two free electron pairs, four substitutable H atoms, and an energetic N–N bond. Because of the presence of two free electron pairs it acts as a uni-[1,2] or bi-dentate (bridging)[3–7] ligand. Monoprotonated hydrazine, hydrazinium ($N_2H_5^+$), still retains a basic site and is capable of co-ordination. A number of complexes containing $N_2H_5^+$ cations are known[8–16] of which $(N_2H_5)_2M(SO_4)_2$, where M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, or Mg, have been investigated in detail. Single-crystal X-ray structure studies of $(N_2H_5)_2Zn(SO_4)_2$[8] and $N_2H_5CuCl_3$[16] indicate the co-ordination of $N_2H_5^+$ cation to the metal. Infrared spectra of these complexes show characteristic absorptions in the region 990—1 010 cm^{-1} due to ν(N–N) of co-ordinated[12,16] $N_2H_5^+$.

During the course of our studies on the chemistry of hydrazine derivatives[17–23] we have prepared a number of hydrazinium metal sulphate,[13,20,21] oxalate,[22] and hydrazidocarboxylate[23] complexes. We have been particularly interested in the relationship between the structure and thermal reactivity of these complexes. In continuation of these studies we now report the preparation, characterization, spectral, and thermal studies of $N_2H_5Ln(SO_4)_2{\cdot}H_2O$, where Ln = La, Ce, Pr, Nd, or Sm. The crystal structure of $N_2H_5Nd(SO_4)_2{\cdot}H_2O$ has also been determined. As far as we are aware this is the first reported work on rare-earth-metal complexes of the hydrazinium cation.

Experimental

Preparation.—Hot aqueous solutions of lanthanide sulphate hydrates, $Ln_2(SO_4)_3{\cdot}nH_2O$, where Ln = La, Ce, Pr, Nd, or Sm (3.60 g, 5 mmol, for Nd), in 2 N sulphuric acid (25 cm^3) and $(N_2H_5)_2SO_4$ (0.81 g, 5 mmol) or $N_2H_6SO_4$ (1.30 g, 10 mmol) were mixed and the resulting solution left to stand in air. Small crystals suitable for X-ray studies were obtained in a few days. They exhibited the characteristic colours of the lanthanide ions.

$$(N_2H_5)_2SO_4 + Ln_2(SO_4)_3{\cdot}nH_2O \longrightarrow 2N_2H_5Ln(SO_4)_2{\cdot}H_2O + (n-2)\,H_2O \quad (1)$$

$$2N_2H_6SO_4 + Ln_2(SO_4)_3{\cdot}nH_2O \longrightarrow 2N_2H_5Ln(SO_4)_2{\cdot}H_2O + H_2SO_4 + (n-2)\,H_2O \quad (2)$$

$$n = 9 \text{ for La or Ce, 8 for Pr, Nd, or Sm}$$

The composition of the complexes was determined by chemical analysis (Table 1), the metal content by titration with ethylenediaminetetra-acetate (edta), hydrazine content by titration with 0.025 mol dm^{-3} potassium iodate under Andrew's conditions,[24] and sulphate gravimetrically as $BaSO_4$.

Physical Measurements.—Infrared spectra of the samples as Nujol mulls were recorded using a Perkin-Elmer 597 spectrophotometer. Electronic spectra (reflectance) were recorded on a Shimadzu UV-210A double-beam spectrophotometer using MgO as reference. The spectra were obtained in the solid state by dispersing the sample in Nujol. Magnetic susceptibility measurements were carried out on a Gouy balance at room temperature using $Hg[Co(SCN)_4]$ as a calibrant. The values were corrected for diamagnetism with the appropriate Pascal constants.

The X-ray powder diffraction patterns were recorded on a Philips model PW 1050/70 diffractometer with a vertical goniometer and using nickel-filtered Cu-K_α radiation. Thermogravimetric (t.g.) experiments were carried out using a Stanton-Redcroft TG-750 thermobalance employing 6—8 mg samples. Differential thermal analysis (d.t.a.) curves were recorded on an instrument constructed in our laboratory[25] and fitted with an Omniscribe strip-chart recorder; 50—100 mg samples were used. Both t.g. and d.t.a. were carried out in air and the heating rate employed was 10 °C min^{-1}. Platinum cups were used as sample holders.

X-Ray Crystallography.—Crystal data. $N_2H_5Nd(SO_4)_2{\cdot}H_2O$, $M = 387.3$, $a = 10.951(3)$, $b = 9.554(2)$, $c = 15.762(3)$ Å,

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[†] *Supplementary data available* (No. SUP 56362, 17 pp.): i.r. and electronic spectral data, thermal analysis data, thermal parameters, complete bond lengths and angles, hydrogen bonds and non-bonded contacts, mean plane calculations, powder diffraction data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Analytical and magnetic data

		% Metal		% Hydrazine		% Sulphate		
Compound	Colour	Found	Calc.	Found	Calc.	Found	Calc.	$\mu_{eff.}$(25 °C)
$N_2H_5La(SO_4)_2{\cdot}H_2O$	Colourless	36.4	36.4	8.3	8.4	49.5	50.3	Diamagnetic
$N_2H_5Ce(SO_4)_2{\cdot}H_2O$	Colourless	36.5	36.6	8.4	8.4	51.1	50.1	2.30
$N_2H_5Pr(SO_4)_2{\cdot}H_2O$	Green	36.6	36.7	8.2	8.3	48.9	50.0	3.37
$N_2H_5Nd(SO_4)_2{\cdot}H_2O$	Violet	37.6	37.2	8.3	8.3	49.2	49.6	3.43
$N_2H_5Sm(SO_4)_2{\cdot}H_2O$	Light yellow	38.2	38.2	8.1	8.1	49.5	48.8	1.48

U = 1 649.1 Å^3 (by least squares refinement of diffractometer angles for 20 automatically centred reflections, λ = 0.71069 Å), space group *Pca*2$_1$ (attempts to solve the structure in the alternative centrosymmetric space group *Pcam* were unsuccessful), D_m = 3.10 g cm^{-3}, Z = 8, D_c = 3.11, F(000) = 1 480, crystal dimensions (tabular) 0.15 × 0.25 × 0.30 mm, μ = 65.1 cm^{-1}.

Data collection and processing. CAD-4 diffractometer, ω–2θ mode with ω scan width = 0.75 + 0.45 tan θ, graphite-monochromated Mo-K_α radiation; 3 052 reflections measured (2θ up to 60°), 2 427 [$F \geqslant 3\sigma(F)$] of which were considered observed and used in the structure analysis. Two standard reflections monitored every hour of exposure did not show any significant changes in intensity throughout the course of data collection. Data were corrected for Lorentz polarization effects but not for absorption.

Structure analysis and refinement. Conventional heavy-atom and Fourier techniques were employed. Full-matrix least-squares refinement with heavy atoms alone anisotropic. The weighting scheme used was $w = 1/[\sigma^2(F) + 0.023|F|^2]$. Attempts to locate the hydrogen atoms were not successful. During the refinement zero weight was assigned to two (002 and 024) strong low-order reflections, which may be affected by extinction. The final residuals $R (= \Sigma|F_o - |F_c||/\Sigma F_o)$ and R' $\{= [\Sigma(F_o - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$ were 0.059 and 0.074 respectively. Atomic scattering factors and anomalous dispersion corrections were taken from ref. 26. Computations were carried out on a DEC 1090 computer using the programs SHELX 76,[27] ORTEP,[28] and others written locally.

Results and Discussion

The reaction of $Ln_2(SO_4)_3{\cdot}nH_2O$ with $(N_2H_5)_2SO_4$ or $N_2H_6SO_4$ yields hydrazinium lanthanide sulphate monohydrate, $N_2H_5Ln(SO_4)_2{\cdot}H_2O$. It is known[24] that $N_2H_6^{2+}$ ion dissociates in water to give $N_2H_5^+$ ion as in equation (3).

$$N_2H_6^{2+} + H_2O \rightleftharpoons N_2H_5^+ + H_3O^+ \qquad (3)$$

Efforts to prepare the hydrazinium lanthanide sulphate complexes of heavier elements (Eu to Lu) were not successful due to separation of the starting materials.

Infrared Spectra.—The observed i.r. absorption frequencies of $N_2H_5Ln(SO_4)_2{\cdot}H_2O$ are similar to those reported[12] for $(N_2H_5)_2M(SO_4)_2$ complexes. The main features of the spectra are: (*i*) ν(N–N) of $N_2H_5^+$ is seen in the region 995—1 000 cm^{-1} indicating co-ordination of $N_2H_5^+$ to Ln^{3+} [ν(N–N) of free or ionic $N_2H_5^+$ is known to absorb in the region 965—980 cm^{-1}]; (*ii*) the splitting of ν_3 and ν_4 of SO_4^{2-} into three or four bands indicates the presence of bidentate or bridging sulphate groups.[29]

Electronic Spectra.—Electronic spectra of the praseodymium, neodymium, and samarium complexes were recorded and compared with data for the corresponding aquo-ions. The spectral profiles of the complexes show not only shifts in positions but also changes in intensity compared to those of the aquo-ions, *i.e.* the energies at which the various bands appear are lower. This red shift, which is a measure of metal–ligand covalent binding, has been ascribed to the nephelauxetic (cloud expanding) effect.[30,31] The covalency parameter, δ, has been calculated using Sinha's[32] expression (4) where $\beta = n^{-1}$-

$$\delta/\% = [(1 - \beta)/\beta] \times 100 \qquad (4)$$

$\Sigma(\nu^i_{complex}/\nu^i_{aquo})$; β is the average value of the ratio $\nu_{complex}/\nu_{aquo}$ and n the number of transitions considered. The δ and β values are comparable with those of oxygen-donor ligands such as oxalate and phthalate.[32] The small δ values (*ca.* 1.0) indicate relatively little covalent character. Further, the observed changes in the shape and intensity of 'hypersensitive' transitions, *e.g.* for Nd^{III}, $^4I_{\frac{9}{2}} \longrightarrow {}^4G_{\frac{5}{2}}, {}^2G_{\frac{7}{2}}$, indicate a co-ordination number of eight or nine.[33,34]

Magnetic Susceptibility Measurements.—The room-temperature magnetic moments of $N_2H_5Ln(SO_4)_2{\cdot}H_2O$ (Table 1) are similar to those of the respective rare-earth-metal ion and to those reported[35] for $Ln_2(SO_4)_3{\cdot}8H_2O$.

Thermal Analysis.—Both t.g. and d.t.a. show three distinct steps of decomposition and the reaction sequence is as in equations (5)—(7), where Ln = La, Ce, Pr, Nd, or Sm. The

$$N_2H_5Ln(SO_4)_2{\cdot}H_2O \xrightarrow{255-305\,°C} N_2H_5Ln(SO_4)_2 + H_2O \qquad (5)$$

$$2N_2H_5Ln(SO_4)_2 \xrightarrow{300-445\,°C} N_2H_6SO_4{\cdot}Ln_2(SO_4)_3 + NH_3 + \tfrac{1}{2}N_2 + \tfrac{1}{2}H_2 \qquad (6)$$

$$2N_2H_6SO_4{\cdot}Ln_2(SO_4)_3 \xrightarrow{425-560\,°C} 2Ln_2(SO_4)_3 + 2NH_3 + N_2 + 3H_2O + 2SO_2 + \tfrac{1}{2}O_2 \qquad (7)$$

endothermic peak due to dehydration occurs at a fairly high temperature (>250 °C) indicating the presence of co-ordinated water. The second and third steps of decomposition involving dissociation of hydrazine are both exothermic. Because of the close similarity of rare-earth-metal complexes, the observed decomposition temperatures are identical.

Co-ordination around the Metal.—Infrared data coupled with the thermal analysis results suggest that the lanthanide atoms are surrounded by two bidentate or bridging sulphate groups, one $N_2H_5^+$ ion, and one water molecule forming octahedra (six co-ordination). However, the electronic spectral results suggest a co-ordination number of eight or nine for the lanthanides. Unequivocal proof of the co-ordination comes from a single-crystal *X*-ray study.

Description of the Structure of $N_2H_5Nd(SO_4)_2{\cdot}H_2O$.—Final atomic co-ordinates and bond lengths are given in Tables 2 and

Table 2. Fractional atomic co-ordinates (× 10^5 for Nd, × 10^4 for the rest)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Nd(1)	54 534(5)	46 521(4)	0	O(9)	7 033(7)	6 165(9)	−335(6)
Nd(2)	70 420(5)	3 302(5)	4 040(5)	O(10)	4 156(7)	3 056(9)	−638(6)
S(1)	4 389(3)	2 307(3)	1 353(2)	O(11)	7 441(9)	−1 382(7)	−662(5)
S(2)	8 111(2)	2 734(3)	−903(2)	O(12)	7 596(10)	6 809(9)	−1 773(6)
S(3)	7 800(2)	7 164(3)	−866(2)	O(13)	5 359(7)	−1 160(9)	822(6)
S(4)	4 699(2)	−2 145(3)	1 324(2)	O(14)	8 406(6)	1 190(8)	1 136(5)
O(1)	5 508(6)	2 052(8)	840(5)	O(15)	5 060(9)	6 395(7)	1 137(6)
O(2)	4 048(7)	3 808(8)	1 205(5)	O(16)	4 889(8)	−1 930(8)	2 223(5)
O(3)	8 437(7)	−1 309(9)	1 065(6)	OW(1)	6 966(6)	4 480(8)	1 230(7)
O(4)	4 657(7)	2 097(10)	2 244(6)	OW(2)	5 527(7)	464(8)	−797(8)
O(5)	6 933(7)	2 923(9)	−396(6)	N(1)	5 731(7)	4 829(10)	−1 754(6)
O(6)	8 457(7)	1 267(8)	−722(5)	N(2)	6 800(12)	304(11)	2 194(13)
O(7)	4 123(9)	6 379(11)	−577(7)	N(3)	4 545(8)	4 849(12)	−2 243(8)
O(8)	7 896(7)	2 993(9)	−1 800(6)	N(4)	7 825(7)	37(14)	2 715(6)

Table 3. Bond lengths (Å); primes refer to the equivalent positions: $\frac{1}{2}$ + *x*, −*y*, *z*

Nd(1)–O(1)	2.819(8)	Nd(2)–O(1)	2.452(7)
Nd(1)–O(2)	2.576(8)	Nd(2)–O(3)	2.426(9)
Nd(1)–O(5)	2.399(8)	Nd(2)–O(5)	2.786(8)
Nd(1)–O(7)	2.384(10)	Nd(2)–O(6)	2.523(8)
Nd(1)–O(9)	2.317(8)	Nd(2)–O(11)	2.388(8)
Nd(1)–O(10)	2.316(8)	Nd(2)–O(13)	2.422(8)
Nd(1)–O(15)	2.486(8)	Nd(2)–O(14)	2.467(7)
Nd(1)–O(W1)	2.557(9)	Nd(2)–O(W2)	2.523(11)
Nd(1)–N(1)	2.789(10)	Nd(2)–N(2)	2.837(20)
S(1)–O(1)	1.489(7)	S(3)–O(9)	1.523(9)
S(1)–O(2)	1.502(8)	S(3)–O(10′)	1.544(9)
S(1)–O(3′)	1.485(8)	S(3)–O(11)	1.480(7)
S(1)–O(4)	1.451(9)	S(3)–O(12)	1.489(10)
S(2)–O(5)	1.530(8)	S(4)–O(13)	1.428(9)
S(2)–O(6)	1.481(8)	S(4)–O(14′)	1.455(9)
S(2)–O(7′)	1.488(8)	S(4)–O(15)	1.482(8)
S(2)–O(8)	1.456(9)	S(4)–O(16)	1.449(8)
N(1)–N(3)	1.512(12)	N(2)–N(4)	1.415(17)

3 respectively. The structure is polymeric with two crystallographically independent neodymium atoms in the asymmetric unit having similar co-ordination. The asymmetric part of the structure shown in Figure 1 has an amazingly accurate local centre of inversion at $\frac{1}{8}$, $\frac{1}{4}$, 0.02 which is repeated at $\frac{3}{8}$, $\frac{1}{4}$, 0.52, $\frac{5}{8}$, $\frac{3}{4}$, 0.02, and $\frac{7}{8}$, $\frac{3}{4}$, 0.52. This is a fascinating feature of the structure.

Both Nd atoms have similar nine-co-ordination. There are two idealized ground-state polyhedra for this co-ordination geometry,[36,37] *viz.* the tricapped trigonal prism of $\bar{6}m$ (D_{3h}) symmetry and the monocapped square antiprism of 4 *mm* (C_{4v}) symmetry. In the present structure the co-ordination polyhedron is deduced to be the former (see SUP 56362 for details). Each neodymium atom is co-ordinated to seven oxygens from six sulphate groups, one water oxygen, and one nitrogen atom of N_2H_5 (Figure 1). In the co-ordination sphere of Nd(1), the seven Nd–O distances vary from 2.316(8) to 2.576(8) Å, except for one long Nd(1)–O(1) distance of 2.819(8) Å. The average value is 2.48 Å, in agreement with those found in earlier work.[38] The Nd(1)–N(1) distance of 2.789(10) Å is longer than the commonly observed[39–41] Ln–N distances (2.50—2.68 Å) for some nitrogen donor ligands with the lighter rare-earth metals, indicating a weak interaction in the present case. A similar situation also exists in the Nd(2) co-ordination sphere. The Nd(1) ••• Nd(2) distance of 4.53 Å confirms the absence of metal–metal interaction, a conclusion which is supported by the magnetic data (see above).

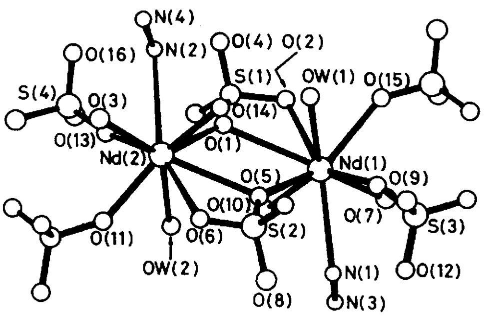

Figure 1. Molecular structure of $N_2H_5Nd(SO_4)_2{\cdot}H_2O$

There are four crystallographically non-equivalent sulphate groups present in the structure, all of them acting as bridging ligands. In all the sulphates, three oxygen atoms take part in metal co-ordination, the fourth being free. The bridging mode for the S(1) and S(2) sulphate groups is different from the other two, in that while the former link two dimers, the latter link three. It is interesting that O(1) and O(5) of the S(1) and S(2) sulphate groups, respectively, are co-ordinated to both Nd(1) and Nd(2) atoms. This type of bonding with two bridging oxygens has not been previously observed in lanthanide sulphate complexes, except in $CsLa(SO_4)_2$,[42] where one of the oxygen atoms is co-ordinated to two lanthanum atoms of adjacent molecules. Unlike in the case of $CsLa(SO_4)_2$, where the lanthanum–bridging oxygen distances are nearly equal [La–O(7) 2.739(8) and La′–O(7) 2.801(8) Å], in the present structure the bridging interactions are asymmetric [Nd(1)–O(1) 2.819(8) and Nd(2)–O(1) 2.452(7); Nd(1)–O(5) 2.399(8) and Nd(2)–O(5) 2.786(8) Å]. The dimensions of the sulphate groups are normal.

The two crystallographically independent $N_2H_5^+$ ions in the asymmetric unit are both co-ordinated to the metal, as in the case of transition-metal double sulphates[10] and $N_2H_5CuCl_3$.[16] The N–N distances are 1.512(12) and 1.415(17) Å. The reason for the significant difference in these distances for chemically equivalent $N_2H_5^+$ ions is not clear. It may, however, be noted that the longer N(1)–N(3) bond length is related to the stronger interaction of N(1) with Nd(1), while the shorter distance N(2)–N(4) is accompanied by the longer Nd(2)–N(2) distance. A similar correlation may be noted in the metal–oxygen and corresponding S–O distances. The above N–N values can be

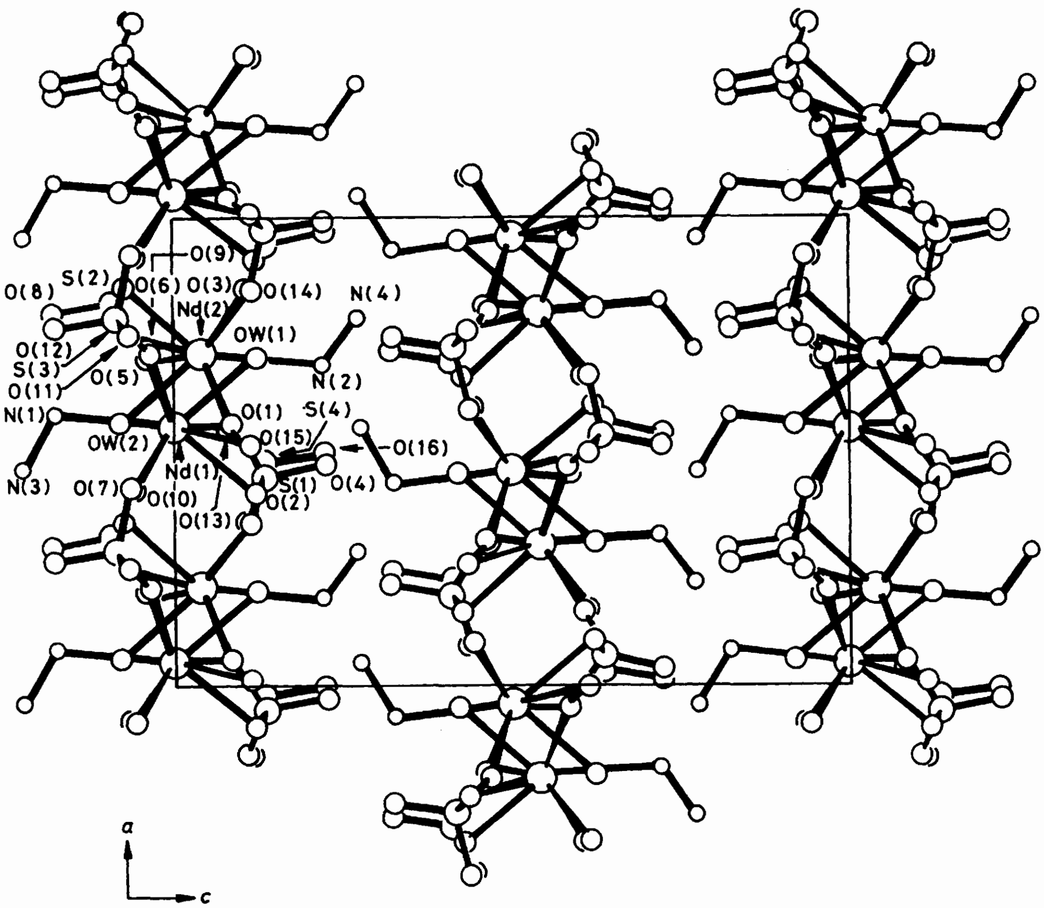

Figure 2. Structure of $N_2H_5Nd(SO_4)_2{\cdot}H_2O$ viewed down *b*. Hydrogen bonds are not indicated

Table 4. Unit-cell dimensions for the isomorphous hydrazinium lanthanide sulphate monohydrates $N_2H_5Ln(SO_4)_2{\cdot}H_2O$

Ln	*a*/Å	*b*/Å	*c*/Å	*U*/Å^3
La	11.05(3)	9.63(3)	15.93(4)	1 695.4
Ce	11.02(3)	9.60(3)	15.87(5)	1 680.0
Pr	10.98(3)	9.57(2)	15.82(4)	1 662.3
Nd*	10.951(3)	9.554(3)	15.762(3)	1 649.1
Sm	10.90(3)	9.50(2)	15.71(4)	1 628.1

* From single-crystal measurements.

compared with the distances of 1.55 and 1.457 Å in $(N_2H_5)_2Zn(SO_4)_2$[10] and $N_2H_5CuCl_3$,[16] respectively.

The structure is built up of neodymium atoms linked by sulphate groups forming sheets parallel to (001) (Figure 2). The sheets are held together by N–H ··· O(sulphate) type hydrogen bonds. Water molecules are also involved in hydrogen bonding with the sulphate oxygens. Further, van der Waals interactions between sheets appear to stabilize the structure.

Unit-cell dimensions for the series lanthanum to samarium (Table 4) were obtained from the powder patterns. These values and the observed intensities of the diffraction lines confirm the expected isomorphism.

A paper on the synthesis and thermal decomposition of hydrazinium(1+) neodymium sulphate monohydrate[43] appeared after the submission of this paper.

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