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THE SALTS AND DOUBLE SALTS OF RARE EARTHS VIII[1]. CRYSTAL STRUCTURE INVESTIGATIONS OF DIMETHYLAMMONIUM RARE EARTH(III) SULPHATE TETRAHYDRATES*

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The isomorphous compounds $(CH_3)_2NH_2Ln(SO_4)_2.4H_2O$ (Ln=Y,Tb,Dy,Ho,Er and Yb) crystallize in the orthorhombic space group Pnma (No.62) with 4 formula units in the unit cell. The unit cell dimensions were determined for the above compounds and the complete crystal structure determination was done for $(CH_3)_2NH_2Ho(SO_4)_2.4H_2O$ resulting in R and R_w-values of 0.015 and 0.016 for 1941 diffractometrically measured reflexions (MoK$\bar{\alpha}$ radiation).The holmium atom, occupying special position, is coordinated by 8 oxygens (4 from sulphate groups and 4 from water molecules) in the form of bicapped trigonal prism with Ho-O distances ranging from 2.315(2) to 2.401(3) Å. Dimethylammonium cations are linked by bifurcated hydrogen bonds N-H....O only to sulphate groups.

As part of the investigations of rare earth sulphates, a series of sulphates with general formula $CH_3(NH)_2Ln(SO_4)_2.4H_2O$

*Dedicated to Professor Roman Modic on the occasion of his seventieth birthday

(Ln=Y,Tb,Dy,Ho,Er and Yb) was prepared [2]. The compounds proved to be isomorphous because all of them crystallize in the same space group Pnma (No. 62) with 4 formula units in the crystal unit cell. Precise unit cell dimensions (Table 1.) were obtained by the least-squares procedure from the 2θ-values of 75 moderately high order reflexions measured on a CAD-4 diffractometer ($MoK\alpha_1$, λ = 0.70926 Å).

A suitable crystal was obtained for the Ho-compound and was used for the data collection. Diffraction data were collected on the diffractometer using $MoK\bar{\alpha}$ radiation with graphite monochromator. Details of data collection and reduction are given in Table 2.

The data were corrected for variation in reference reflexions and Lorentz-polarization effects. For the linear absorption coefficient μ = 68.72 cm^{-1}, the precise absorption correction was performed (12 faces, grid: 10 x 10 x 10, dimensions of crystal: 0.20 x 0.22 x 0.26 mm). Structure was solved by a heavy atom method for the Ho atom. Successive electron-density map revealed the positions for all the nonhydrogen atoms. The data were refined by the full-matrix least-squares method minimizing $\Sigma w(|F_o| - k|F_c|)^2$ using an empirical weighting function $w = w_F \times w_S$ where

$w_F(|F_o| < 40.0) = (|F_o|/40.0)^2$
$w_F(|F_o| > 50.0) = (50.0/|F_o|)^2$
$w_F(40.0 < |F_o| < 50.0) = 1.0$
$w_S(\sin\theta < 0.44) = (\sin\theta/0.44)^{1.5}$
$w_S(\sin\theta > 0.45) = (0.45/\sin\theta)$
$w_S(0.44 < \sin\theta < 0.45) = 1.0$

to keep $\Sigma w(\Delta F)^2$ uniform over the ranges of $(\sin\theta)/\lambda$ and $|F_o|$.

The positions of hydrogens were deduced from difference electron density map and were included in the refinement with isotropic temperature factors. At the final stage, the refinement converged to $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and

Table 1.

Crystal Data at 293 K

Formula: $CH_3NH_2Ln(SO_4)_2.4H_2O$; Orthorhombic, Space Group Pnma (No.62); Z=4

	Y	Tb	Dy	Ho	Er	Yb
M_r	399.18	469.20	472.78	475.21	477.54	483.32
a(Å)	10.953(2)	10.983(1)	10.967(2)	10.949(1)	10.929(2)	10.907(1)
b(Å)	11.675(2)	11.711(1)	11.690(2)	11.684(2)	11.664(2)	11.623(1)
c(Å)	9.940(2)	9.970(1)	9.925(2)	9.933(1)	9.921(2)	9.892(1)
$V(Å^3)$	1271.1	1282.4	1275.9	1270.7	1264.7	1254.0
$D_x(g/cm^3)$	2.086	2.430	2.461	2.485	2.508	2.560

Table 2.

Data-collection Summary

Temperature (K)	293(1)
Diffractometer	CAD-4-automatic, fourcircle
Scan method	$\omega-2\theta$
2θ scan width (^{o})	0.7 + 0.3 x tanθ
Aperture (mm)	2.4 + 0.9 x tanθ
Reference reflexions	$\bar{4}$ 4 2; $\bar{5}$ $\bar{2}$ 1; 2 5 2
Radiation (Å)	MoK$\bar{\alpha}$ (λ = 0.7107)
Size of crystal (mm)	0.20 x 0.22 x 0.26
Scan rate (^{o}min^{-1})	min.: 1.7 max.: 20.1
Maximum scan time (s)	40
$2\theta_{max}$ (^{o})	60
Intensity decrease (%)	6
Measured reflexions	7242 ($\pm$h, $\pm$k, $\pm$l)
Unique reflexions	1941
Mean discrepancy on I(%)	2.2
Observed reflexions [I>3σ(I)]	1574
Unobserved reflexions	367
σ(I) based on	Counting statistics
μ(cm^{-1})	68.27
Transmittance	min.: 0.260 max.: 0.326

Table 3.

Refinement summary

Final refinement cycle

Scale factor (k)	0.99952_{-3}
Extinction coefficient	$3.76.10^{-3}$
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.015
$R_w = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}$	0.016
Average shift/error	0.0494
Maximum shift/error	0.4614
Data (m) - to - variable (n) ratio	14.63
$[\Sigma w(\Delta F)^2/(m-n)]^{1/2}$	0.643
Number of reflexions	1799

$R_w = [\Sigma w(F_o-F_c)^2/\Sigma wF_o^2]^{1/2}$ of 0.015 and 0.016 respectively for 1799 contributing reflexions. An average value for shift/error was 0.05, with a maximum value of 0.46 for y of H(5) in the last cycle of the refinement. Final refinement parameters are given in Table 3. Scattering factors for Ho, S, O, N and C were given in reference [3] and for H in reference [4]. Anomalous dispersion coefficients $\Delta f'$ and $\Delta f'$ for Ho and S [5] were used in the calculation together with an isotropic extinction correction [6]. Lists of structure factors and anisotropic thermal parameters are available on request.

All calculations were caried out on the CDC-Cyber 72 computer at RRC Ljubljana using the X-Ray 72 system of crystallographic programs [7].

Final fractional atomic coordinates are given in Table 4. Some important interatomic distances and angles are summarized in Table 5. A view of the asymmetric unit of the crystal structure along [010] direction is presented in Figure 1.

The crystal structure of $(CH_3)_2NH_2Ho(SO_4)_2.4H_2O$ consists of holmium, dimethylammonium cations, sulphate anions and water molecules.

Ho atom, lying in the mirror plane [x,1/4,z], is surrounded by 8 oxygen atoms in the form of bicapped trigonal prism. Trigonal prism is formed by 4 oxygens belonged to two symmetrically related sulphate groups and 2 water molecules: O(1), $O(1^V)$, O(2), $O(2^V)$, O(22), $O(22^V)$. Two caps of the prism are formed by O(11) and O(33) of water molecules, both lying on the mirror plane [x,1/4,z]. The average Ho-O distance is 2.358 Å, with the range from 2.315(2) to 2.401(3) Å.

Sulphate group has a usual, nearly perfect, tetrahedral arrangement of oxygen atoms with an average value of S-O distance 1.476 Å, and the average angle O-S-O of 109.47°.

Table 4.

Final Fractional Coordinates with U_{eq} [Å] for Heavy Atoms and U for Hydrogens Coordinates are multiplied by 10^5 for Ho and S; by 10^4 for O,N and C; and by 10^3 for H atoms. Thermal parameters are multiplied by 10^4 for Ho and S; and by 10^3 for O,N,C,H.

	x	y	z	U_{eq}/U
Ho	37672(1)	25000	53092(1)	129(1)
S	28154(5)	44181(4)	70127(6)	190(2)
O(1)	3963(2)	3748(2)	7195(2)	26(1)
O(2)	2242(2)	3874(2)	5811(2)	27(1)
O(3)	2020(2)	4327(2)	8185(3)	36(1)
O(4)	3109(2)	5620(2)	6761(2)	28(1)
O(11)	2371(3)	2500	3445(3)	27(1)
O(22)	4515(2)	3970(2)	3983(2)	27(1)
O(33)	5865(3)	2500	5706(4)	26(1)
N	0146(4)	7500	4641(4)	40(2)
C	0465(10)	6419(9)	5289(8)	85(5)
H(1)	040(8)	750	376(8)	46(18)
H(2)	-068(7)	750	468(7)	30(15)
H(3)	010(5)	640(5)	606(7)	50(14)
H(4)	106(3)	675(3)	535(3)	3(6)
H(5)	116(12)	590(15)	531(12)	115(44)
H(11)	232(5)	305(4)	303(5)	38(11)
H(21)	406(4)	453(5)	375(5)	33(11)
H(22)	527(5)	408(5)	381(6)	42(12)
H(31)	618(5)	302(5)	608(6)	43(13)

Table 5.

Interatomic Distances (Å) and Angles (°) for

$(CH_3)_2NH_2Ho(SO_4)_2.4H_2O$

a) Ho Environment

Ho - O(1)	2.383(2)
Ho - O(2)	2.369(2)
Ho - O(11)	2.401(3)
Ho - O(22)	2.315(2)
Ho - O(33)	2.330(3)

b) Sulphate Group SO_4^{2-}

S - O(1)	1.491(2)	O(1) - S - O(2)	103.2(1)
S - O(2)	1.491(2)	O(1) - S - O(3)	111.6(1)
S - O(3)	1.458(3)	O(1) - S - O(4)	109.9(1)
S - O(4)	1.462(2)	O(2) - S - O(3)	110.9(1)
		O(2) - S - O(4)	111.4(1)
		O(3) - S - O(4)	109.8(1)

c) Dimethylammonium Cation $(CH_3)_2NH_2^+$

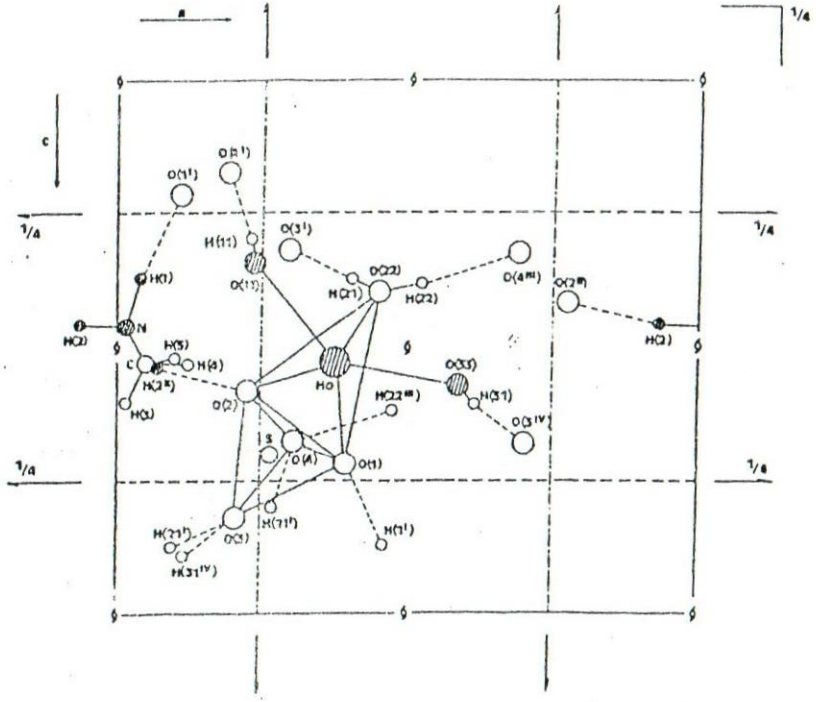
N - C	1.460(10)	C - N - C(v)	119.8(6)
N - H(1)	0.91(8)	H(1) - N - H(2)	110(7)
N - H(2)	0.91(8)	H(1) - N - C	110(2)
C - H(3)	0.86(7)	H(2) - N - C	103(2)
C - H(4)	0.76(4)	H(3) - C - H(4)	110(5)
C - H(5)	0.97(15)	H(3) - C - H(5)	109(8)
		H(4) - C - H(5)	70(10)
		H(3) - C - N	108(4)
		H(4) - C - N	78(3)
		H(5) - C - N	138(8)

d) Hydrogen Bonds

X - H ... Y	X - H	H....Y	X - H...Y	Y...H...Y(v)
N - H(1)...O(1i)	0.91(8)	2.25(6)	139(2)	81(3)
N - H(2)...O(2ii)	0.91(8)	2.39(6)	135(2)	84(2)
O(11)-H(11)..O(4i)	0.76(5)	2.06(5)	169(5)	
O(22)-H(21)..O(3i)	0.85(5)	1.87(5)	176(5)	
O(22)-H(22)..O(4iii)	0.85(6)	1.90(6)	173(5)	
O(33)-H(31)..O(3iv)	0.79(5)	1.93(6)	174(6)	

Symmetry code: (i) 1/2-x,-y,1/2+z (iv) 1/2+x,y,1/2-z
(ii) -x,1/2+y,-z (v) x,1/2-y,z
(iii) -x,-y,-z

Figure 1.



(Atoms, occupying special positions, are shaded)

The dimethylammonium cation $(CH_3)_2NH_2^+$, also lying in the mirror plane [x,3/4,z], has a distorted arrangement of C and H atoms. The N-C distance is 1.460(11) Å with the angle C-N-C of 119.8(6)°.

There is an extensive hydrogen bonding network of the type O-H...O and N-H...O, interlinking dimethylammonium cations, sulphate and water molecules. The hydrogen bonds from $(CH_3)_2NH_2^+$ were found to be bifurcated, only directed to O(1) and O(2) of sulphate groups, whereas hydrogen bonds O-H...O are nearly linear, interconnecting water molecules and the remaining oxygens O(3) and O(4) of sulphate groups. Details are given in Table 5c and Figure 1.

Acknowledgement

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Povzetek

Izomorfne spojine $(CH_3)_2NH_2Ln(SO_4)_2.4H_2O$ (Ln=Y, Tb, Dy, Ho, Er in Yb) kristalizirajo v rombični prostorski skupini Pnma (No.62) s 4 stehiometrijskimi enotami v osnovni celici. Določene so bile konstante osnovnih celic, popolna kristalna struktura je bila rešena za $(CH_3)_2NH_2Ho(SO_4)_2 \cdot 4H_2O$. Končni R in R_w vrednosti sta bili 0.015 in 0.016 za 1941 uklonov, ki so bili izmerjeni na difraktometru z MoK$\bar{\alpha}$ svetlobo. Holmijev atom je na posebni legi, koordiniran z osmimi atomi kisika (4 od sulfatnih skupin in 4 od molekul vode) v obliki trigonalne prizme z dodatnima dvema molekulama vode. Razdalje Ho-O so v območju od 2.315(2) do 2.401(3) Å. Dimetilamonijevi kationi so vezani z bifurkiranimi vodikovimi vezmi N-H....O le na sulfatne skupine.

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