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Original Scientific Paper

Crystal Structure Investigations of Amide Sulfate Tetrahydrates with Divalent Cations*

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Single crystals of three amide sulfate tetrahydrate compounds, $Ca(NH_2SO_3)_2 \cdot 4H_2O$, $Mn(NH_2SO_3)_2 \cdot 4H_2O$ and $Ni(NH_2SO_3)_2 \cdot 4H_2O$, were synthesized by controlled evaporation of aqueous solutions. The crystal structures were investigated using single-crystal X-ray diffraction methods. $Ca(NH_2SO_3)_2 \cdot 4H_2O$: space group $C2/c$, $Z = 4$, $a = 11.616(3)$ Å, $b = 7.761(2)$ Å, $c = 11.638(3)$ Å, $\beta = 98.93(1)°$, $V = 1036.47$ Å^3, $R1 = 0.026$; $Mn(NH_2SO_3)_2 \cdot 4H_2O$: space group $P2_1/c$, $Z = 2$, $a = 6.143(2)$ Å, $b = 5.324(2)$ Å, $c = 15.441(5)$ Å, $\beta = 91.72(1)°$, $V = 504.78$ Å^3, $R1 = 0.024$; $Ni(NH_2SO_3)_2 \cdot 4H_2O$: space group $P\bar{1}$, $Z = 1$, $a = 6.331(8)$ Å, $b = 6.731(9)$ Å, $c = 6.784(8)$ Å, $\alpha = 88.93(9)°$, $\beta = 67.87(5)°$, $\gamma = 67.76(6)°$, $V = 245.27$ Å^3, $R1 = 0.030$.

In $Ca(NH_2SO_3)_2 \cdot 4H_2O$ antiprismatic CaO_8 polyhedra share four oxygen atoms with NH_2SO_3 tetrahedra forming sheets parallel (001). In $Mn(NH_2SO_3)_2 \cdot 4H_2O$ and $Ni(NH_2SO_3)_2 \cdot 4H_2O$, MnO_6 octahedra and NiN_2O_4 octahedra, respectively, are linked by common corners with two NH_2SO_3 tetrahedra forming isolated groups. These units are interconnected by hydrogen bonds only to form three-dimensional framework structures. The amide sulfate group has a distorted tetrahedral configuration with mean S–O and S–N bond lengths of 1.449 and 1.654 Å, respectively. The average cation–oxygen distances are 2.456 Å (Ca–O), 2.173 Å (Mn–O), and 2.049 Å (Ni–O), both Ni–N bond lengths are 2.153 Å. Three different types of hydrogen bonds are observed in the title compounds, namely O–H···O bonds ranging from 2.680 to 2.968 Å, N–H···O bonds between 2.966 and 3.339 Å, and one O–H···N bond with

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* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday.

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2.905 Å. Generally, observed interatomic bond lengths and angles comply well with crystal chemical expectations.

Key words: crystal structure, crystal chemistry, amide sulfates, $Ca(NH_2SO_3)_2 \cdot 4H_2O$, $Mn(NH_2SO_3)_2 \cdot 4H_2O$, $Ni(NH_2SO_3)_2 \cdot 4H_2O$.

INTRODUCTION

Sulfamic acid has been first synthesized by Berglund[1] (1878). The procedure of Raschig[2] (1887) made the extensive application of this substance possible. Various review articles on the chemical properties of sulfamic acid and related compounds have been published. The paper by Audrieth *et al.*[3] (1940) gives a comprehensive survey of the older literature, more recent references can be found in Benson and Spillane[4] (1980).

The tetrahedral configuration of the $[NH_2SO_3]^-$ anion was first established by crystal structure investigations of potassium amide sulfate by Brown and Cox[5] (1940), and Ketelaar and Heilmann[6] (1941). Kanda and King[7] (1951) characterized the structure of crystalline sulfamic acid using X-ray diffraction methods. The existence of the $^+NH_3{\cdot}SO_3^-$ zwitterion in sulfamic acid was proven by Sass[8] (1960) from neutron diffraction data. A detailed summary and references on crystal structure investigations of sulfamic acid and amide sulfates performed so far is given by Angerer[9] (1997). Furthermore, several crystalline amide sulfate compounds were investigated in respect to their interesting physical – especially piezoelectric – properties (*cf. e.g.* Haussühl and Haussühl,[10] 1995). These studies initiated experiments aiming at the synthesis and structure determination of new amide sulfate compounds. The present study reports the syntheses and single-crystal X-ray structure investigations of three new amide sulfate tetrahydrate compounds.

EXPERIMENTAL

Synthesis

Crystals of the title compounds were synthesized by slow controlled evaporation at room temperature of aqueous solutions of the respective amide sulfates. These aqueous solutions were obtained either by reaction of the particular carbonate with sulfamic acid (1)

$$M^{2+}CO_3 + 2(NH_2SO_3)H \Rightarrow M^{2+}(NH_2SO_3)_2 + CO_2\uparrow + H_2O \qquad (1)$$

or by reaction of a solution of barium amide sulfate, obtained according to (1), with the respective sulfate and subsequent precipitation of barium sulfate (2).

$$Ba(NH_2SO_3)_2 + M^{2+}SO_4 \Rightarrow M^{2+}(NH_2SO_3)_2 + BaSO_4\downarrow \qquad (2)$$

Using one or both of these methods single crystals of the title compounds up to 5 mm were obtained. $Ca(NH_2SO_3)_2 \cdot 4H_2O$ and $Ni(NH_2SO_3)_2 \cdot 4H_2O$ form colourless (Ca) and green (Ni) platelike crystals, $Mn(NH_2SO_3)_2 \cdot 4H_2O$ elongated pink crystals.

Structure Investigations

X-ray diffraction data of selected single crystals were measured at room temperature with graphite-monochromatized Mo-Kα radiation on a Stoe AED2 four-circle diffractometer (2θ-ω scans, 38 steps/reflection, increased for α_1–α_2 splitting, 2×5 steps for background correction, 0.03° and 0.5–2 sec/step; 3 standard reflections every 120 min). The intensities were corrected for Lorentz- and polarization effects as well as for absorption by ψ-scans ($\Delta\psi = 10°$). Lattice parameters were refined from a set of accurate 2θ values in the range $30 < 2\theta < 42°$. The crystal structures of $Ca(NH_2SO_3)_2 \cdot 4H_2O$ and $Mn(NH_2SO_3)_2 \cdot 4H_2O$ were determined by the interpretation of the respective Patterson maps and subsequent difference Fourier syntheses. The structure of $Ni(NH_2SO_3)_2 \cdot 4H_2O$ was solved by direct methods with SHELXS-86 (Sheldrick,[11] 1986). All hydrogen atoms could be located in final difference Fourier maps. The least-squares refinements on F^2 were done with the program SHELXL-93 (Sheldrick,[12] 1993) including anisotropic displacement parameters for all non-hydrogen atoms and isotropic displacement parameters for the H atoms. For a compilation of crystal data and details of the data collections and structure refinements see Table I. Final atomic parameters are summarized in Tables II – IV.*

RESULTS AND DISCUSSION

The crystal structures of $Ca(NH_2SO_3)_2 \cdot 4H_2O$, $Mn(NH_2SO_3)_2 \cdot 4H_2O$ and $Ni(NH_2SO_3)_2 \cdot 4H_2O$ are illustrated in Figures 1–3, selected interatomic bond lengths and angles are listed in Tables V to VII, respectively.

The characteristic common structural element in $Ca(NH_2SO_3)_2 \cdot 4H_2O$, $Mn(NH_2SO_3)_2 \cdot 4H_2O$, and $Ni(NH_2SO_3)_2 \cdot 4H_2O$ is the $[NH_2SO_3]^-$ group, which exhibits a very similar distorted tetrahedral geometry in all three compounds. Ignoring the two hydrogen atoms, the $[NH_2SO_3]^-$ group shows pseudotrigonal symmetry parallel with the S–N bond axis. The displacement ellipsoids of the three oxygen atoms also approximately obey this threefold symmetry. Including the hydrogen atoms, a pronounced pseudo-mirror symmetry of the $[NH_2SO_3]^-$ group is observed parallel to the N–S–O plane bisecting the NH_2 group. A typical example is illustrated in Figure 4.

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* Additional material to this paper can be ordered referring to the no. CSD 410198 (Ni), CSD 410199 (Ca), CSD 410200 (Mn), names of the authors and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft fuer wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Lists of F_o/F_c-data are available from the authors up to one year after the publication has appeared.

TABLE I

Compilation of crystal data and details of the X-ray measurements and structure refinements of the amide sulfate tetrahydrates $M^{2+}(NH_2SO_3)_2 \cdot 4H_2O$ (M^{2+} = Ca, Mn, Ni)

$M^{2+}(NH_2SO_3)_2 \cdot 4H_2O$	M^{2+} = Ca	M^{2+} = Mn	M^{2+} = Ni
M_r / g mol^{-1}	304.30	319.16	322.95
space group	$C2/c$	$P2_1/c$	$P\bar{1}$
a / Å	11.616(3)	6.143(2)	6.331(8)
b / Å	7.761(2)	5.324(2)	6.731(9)
c / Å	11.638(3)	15.441(5)	6.784(8)
α / °			88.93(9)
β / °	98.93(1)	91.72(1)	67.87(5)
γ / °			67.76(6)
V / Å^3	1036.5	504.8	245.3
Z	4	2	1
ρ_{calc} / g cm^{-3}	1.95	2.10	2.19
μ(Mo-Kα) / cm^{-1}	10.5	17.7	24.5
extinction coefficient	0.015(1)	0.003(1)	0.084(6)
$2\theta_{max}$ / °	60	70	75
h,k,l-range	$-16 \leq h \leq 16$	$-9 \leq h \leq 9$	$-10 \leq h \leq 10$
	$-10 \leq k \leq 10$	$-8 \leq k \leq 8$	$-11 \leq k \leq 11$
	$0 \leq l \leq 10$	$0 \leq l \leq 24$	$-11 \leq l \leq 11$
number of ψ-scans	2	4	4
transmission factors	0.85 – 0.99	0.64 – 0.75	0.58 – 0.69
measured reflections	3243	4793	5179
R_i	0.035	0.031	0.047
unique data set	1524	2237	2610
data with $F_o > 4\sigma(F_o)$	1101	1622	1948
variables	93	95	95
$R1$ [for $F_o > 4\sigma(F_o)$]	0.026	0.024	0.030
$R1$ [for all reflections]	0.048	0.043	0.044
$wR2$	0.065	0.059	0.081

$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$,
$wR2 = [\sigma^2 (F_o^2 - F_c^2)^2 / \Sigma\, wF_o^4]^{1/2}$,
$w = 1/[\sigma^2 (F_o^2) + 0.045P^2]$,
$P = ([\max \text{ of } (F_o^2,0)] + 2F_c^2)/3$.

The mean S–O distances in the title compounds vary between 1.446 Å in $Ni(NH_2SO_3)_2 \cdot 4H_2O$ and 1.453 Å in $Ca(NH_2SO_3)_2 \cdot 4H_2O$. As is to be expected for $[NH_2SO_3]^-$ groups, these values are significantly below the statistical S–O mean value for $[SO_4]^{2-}$ tetrahedra of 1.473 Å, given by Baur[13] (1981). The S–N bond lengths range from 1.624(2) Å in the Ca to 1.690(1) Å in the Ni compound, the average S–N distance is 1.654 Å. This is between

TABLE II

Structure parameters for $Ca(NH_2SO_3)_2 \cdot 4H_2O$[a]

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}/U_{iso}
Ca	0	0.07572(5)	0.25	0.0175(2)	0.0235(2)	0.0265(2)	0	0.0034(2)	0	0.0225(1)
S	0.81712(3)	0.70341(5)	0.31400(4)	0.0172(2)	0.0236(2)	0.0336(2)	0.0026(2)	0.0005(1)	–0.0023(1)	0.0252(1)
O1	0.6921(1)	0.7269(2)	0.2851(1)	0.0180(5)	0.0348(7)	0.0461(7)	0.0053(6)	–0.0008(5)	–0.0006(4)	0.0336(3)
O2	0.8783(1)	0.8664(2)	0.3289(1)	0.0308(6)	0.0287(6)	0.0439(8)	–0.0004(6)	0.0034(5)	–0.0106(5)	0.0347(3)
O3	0.8461(1)	0.5903(2)	0.4148(1)	0.0311(6)	0.0343(6)	0.0401(7)	0.0105(6)	–0.0035(5)	–0.0003(5)	0.0361(3)
O4	0.0200(1)	0.2755(2)	0.0935(1)	0.0297(7)	0.0396(7)	0.0380(7)	0.0086(6)	–0.0052(5)	–0.0088(6)	0.0369(3)
O5	0.8840(1)	0.9497(2)	0.0743(1)	0.0356(8)	0.0570(9)	0.0346(8)	–0.0094(7)	0.0013(6)	0.0120(6)	0.0429(4)
N	0.8646(2)	0.6096(2)	0.2057(2)	0.0502(9)	0.0297(8)	0.0523(12)	–0.0020(8)	0.0196(9)	–0.0017(7)	0.0428(4)
H1	0.060(2)	0.352(4)	0.094(2)							0.055(8)
H2	–0.037(3)	0.314(4)	0.044(3)							0.077(9)
H3	0.822(3)	0.978(4)	0.059(2)							0.066(9)
H4	0.903(3)	0.909(4)	0.025(2)							0.070(9)
H5	0.832(2)	0.508(4)	0.190(2)							0.068(8)
H6	0.859(3)	0.668(4)	0.158(2)							0.07[b]

[a] U_{ij} in Å^2.
ADP = $\exp(-2\pi^2 \Sigma_i \Sigma_j U_{ij}\, h_i\, h_j\, \mathbf{a}^*_i\, \mathbf{a}^*_j)$;
$U_{eq} = \frac{1}{3} \Sigma_i \Sigma_j U_{ij}\, \mathbf{a}^*_i\, \mathbf{a}^*_j\, \mathbf{a}_i\, \mathbf{a}_j$ (Fischer and Tillmanns, 1988).[17]

[b] Fixed during refinement.

TABLE III

Structure parameters for $Mn(NH_2SO_3)_2 \cdot 4H_2O$[a]

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}/U_{iso}
Mn	0	0	0	0.0209(1)	0.0171(1)	0.0166(1)	0.0016(1)	0.0024(1)	–0.0001(1)	0.0182(1)
S	0.25471(4)	0.23724(5)	0.82578(2)	0.0213(1)	0.0211(1)	0.0148(1)	0.0013(1)	0.0025(1)	–0.0011(1)	0.0191(1)
O1	0.0712(2)	0.1957(2)	0.8814(1)	0.0277(4)	0.0381(5)	0.0244(4)	0.0119(4)	0.0081(3)	–0.0020(4)	0.0299(2)
O2	0.2159(2)	0.1261(2)	0.7411(1)	0.0660(7)	0.0342(5)	0.0171(4)	–0.0045(4)	0.0024(4)	–0.0053(5)	0.0390(3)
O3	0.4603(2)	0.1593(3)	0.8640(1)	0.0258(5)	0.0474(7)	0.0487(6)	0.0077(5)	–0.0049(4)	0.0074(4)	0.0408(3)
O4	0.7228(2)	0.2396(2)	0.5071(1)	0.0265(4)	0.0259(4)	0.0337(5)	–0.0017(4)	0.0037(4)	–0.0034(4)	0.0286(2)
O5	0.2069(2)	0.2670(2)	0.0676(1)	0.0408(5)	0.0245(4)	0.0202(4)	0.0009(3)	–0.0043(4)	–0.0060(4)	0.0286(2)
N	0.2696(2)	0.5453(2)	0.8170(1)	0.0369(6)	0.0219(5)	0.0337(6)	0.0008(4)	0.0105(5)	–0.0034(4)	0.0306(2)
H1	0.626(3)	0.275(4)	0.484(1)							0.036(5)
H2	0.682(4)	0.218(5)	0.558(2)							0.069(8)
H3	0.218(4)	0.425(5)	0.047(1)							0.058(6)
H4	0.181(5)	0.271(5)	0.109(2)							0.084(5)
H5	0.372(4)	0.567(5)	0.789(2)							0.068(7)
H6	0.164(5)	0.601(7)	0.789(2)							0.098(9)

[a] U_{ij} in Å^2.
ADP = $\exp(-2\pi^2 \Sigma_i \Sigma_j U_{ij}\, h_i\, h_j\, \mathbf{a}^*_{\boldsymbol{i}}\, \mathbf{a}^*_{\boldsymbol{j}})$;
$U_{eq} = \frac{1}{3}\, \Sigma_i \Sigma_j U_{ij}\, \mathbf{a}^*_{\boldsymbol{i}}\, \mathbf{a}^*_{\boldsymbol{j}}\, \mathbf{a}_{\boldsymbol{i}}\, \mathbf{a}_{\boldsymbol{j}}$ (Fischer and Tillmanns, 1988).[17]

TABLE IV

Structure parameters for $Ni(NH_2SO_3)_2 \cdot 4H_2O$[a]

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}/U_{iso}
Ni	0	0	0	0.0263(1)	0.0176(1)	0.0173(1)	0.0023(1)	–0.0091(1)	–0.0086(1)	0.0204(1)
S	0.60404(6)	0.63761(5)	0.71666(4)	0.0278(2)	0.0206(2)	0.0201(1)	0.0042(1)	–0.0103(1)	–0.0085(1)	0.0230(1)
O1	0.7269(2)	0.4217(2)	0.5950(2)	0.0341(5)	0.0245(5)	0.0319(5)	–0.0016(4)	–0.0156(4)	–0.0028(4)	0.0322(2)
O2	0.6549(2)	0.6454(2)	0.9069(2)	0.0450(6)	0.0369(5)	0.0318(5)	0.0070(4)	–0.0233(5)	–0.0209(5)	0.0339(2)
O3	0.6404(2)	0.8045(2)	0.5891(2)	0.0405(6)	0.0317(5)	0.0306(5)	0.0127(4)	–0.0085(5)	–0.0140(5)	0.0364(2)
O4	0.1754(2)	0.1940(2)	0.8551(2)	0.0381(6)	0.0310(5)	0.0233(4)	0.0045(4)	–0.0114(4)	–0.0198(5)	0.0292(2)
O5	0.1245(2)	–0.0291(2)	0.2445(2)	0.0473(6)	0.0245(5)	0.0299(5)	0.0063(4)	–0.0240(5)	–0.0138(4)	0.0314(2)
N	0.2950(2)	0.6993(2)	0.8142(2)	0.0291(5)	0.0218(5)	0.0207(4)	0.0020(4)	–0.0112(4)	–0.0088(4)	0.0239(2)
H1	0.237(4)	0.183(3)	0.731(3)							0.036(5)
H2	0.268(4)	0.207(3)	0.896(3)							0.047(6)
H3	0.171(4)	–0.140(4)	0.272(4)							0.053(6)
H4	0.202(5)	0.021(5)	0.273(5)							0.078(8)
H5	0.261(3)	0.680(3)	0.713(3)							0.029(4)
H6	0.267(4)	0.599(3)	0.888(3)							0.039(5)

[a] U_{ij} in Å^2.
ADP = $\exp(-2\pi^2 \Sigma_i \Sigma_j U_{ij}\, h_i\, h_j\, \mathbf{a}^*_{\boldsymbol{i}}\, \mathbf{a}^*_{\boldsymbol{j}})$;
$U_{eq} = \frac{1}{3} \Sigma_i \Sigma_j U_{ij}\, \mathbf{a}^*_{\boldsymbol{i}}\, \mathbf{a}^*_{\boldsymbol{j}}\, \mathbf{a}_{\boldsymbol{i}}\, \mathbf{a}_{\boldsymbol{j}}$ (Fischer and Tillmanns, 1988).[17]

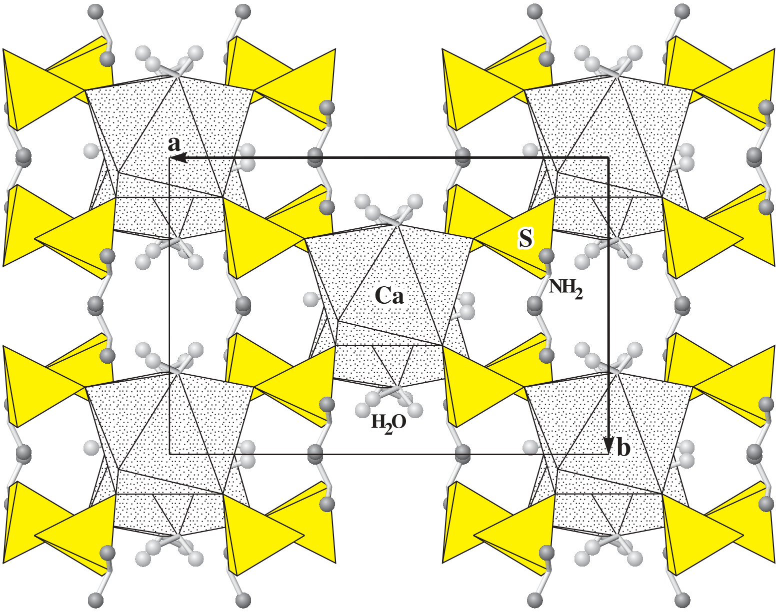

Figure 1. Projection of the crystal structure of $Ca(NH_2SO_3)_2 \cdot 4H_2O$ along [001].

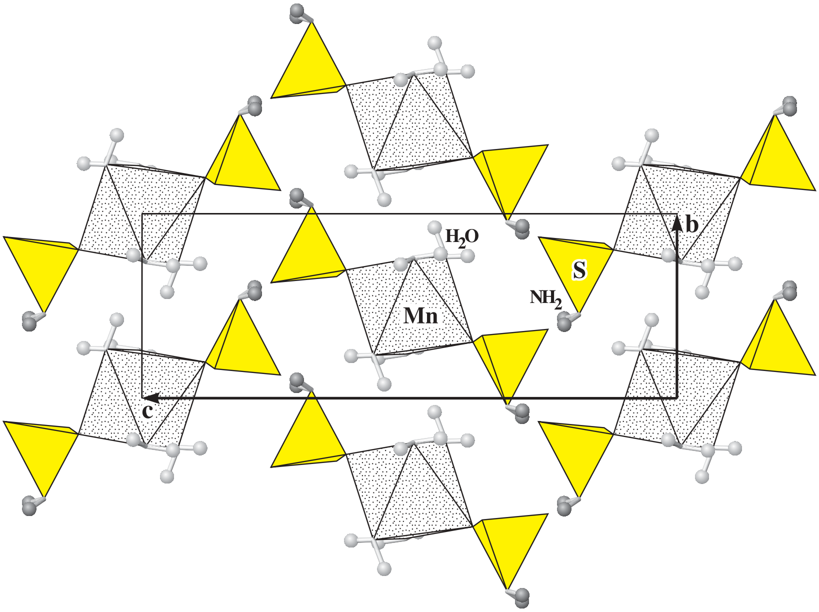

Figure 2. Projection of the crystal structure of $Mn(NH_2SO_3)_2 \cdot 4H_2O$ along [100].

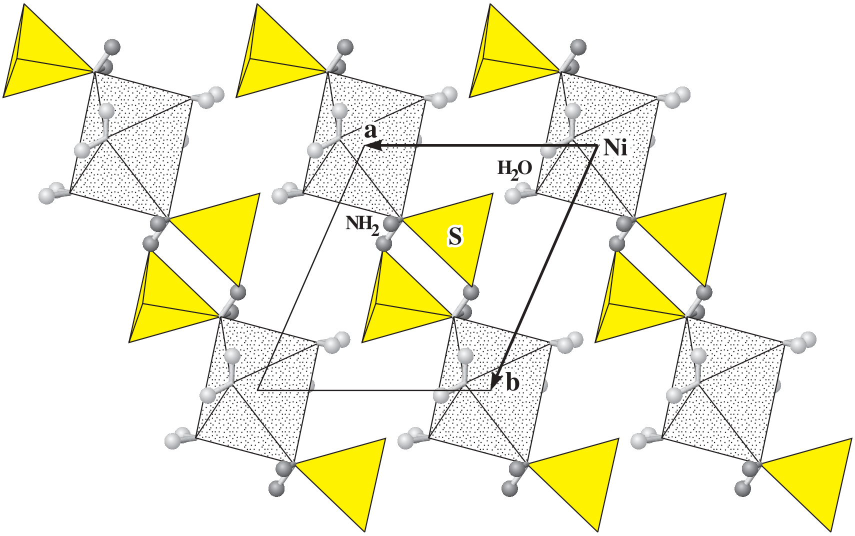

Figure 3. Projection of the crystal structure of $Ni(NH_2SO_3)_2 \cdot 4H_2O$ along [001].

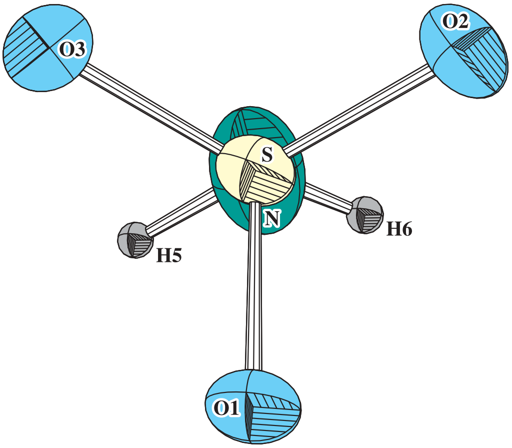

Figure 4. Typical geometry and displacement behaviour of the $[NH_2SO_3]^-$ groups in the $M^{2+}(NH_2SO_3)_2 \cdot 4H_2O$ compounds, showing the pronounced pseudo-mirror symmetry (ellipsoids represent 50% probability, isotropic H-atoms are scaled down).

1.74 Å, the value of a single S–N bond and 1.54 Å, the respective value for a double S–N bond according to Pauling[14] (1960). The tetrahedral O–S–X bond angles deviate from the ideal tetrahedral value on an average by about 3°: mean O–S–O angles are expanded to 112.4°, mean O–S–N angles are reduced to 106.2°. The average geometrical data observed for the three $[NH_2SO_3]^-$ tetrahedra in the present structure investigations are practically identical with mean values calculated from 15 $[NH_2SO_3]^-$ groups found in 13 well refined structures of amido sulfate compounds, *i.e.* S–O = 1.456 Å, S–N = 1.651 Å, O–S–O = 112.4°, and O–S–N = 106.3° (Angerer,[9] 1997).

$Ca(NH_2SO_3)_2 \cdot 4H_2O$, $Mn(NH_2SO_3)_2 \cdot 4H_2O$, and $Ni(NH_2SO_3)_2 \cdot 4H_2O$ belong to three different structure types. The structure of $Ca(NH_2SO_3)_2 \cdot 4H_2O$

TABLE V

Interatomic bond lengths /Å and bond angles /° in $Ca(NH_2SO_3)_2 \cdot 4H_2O$[a]

CaO_8 polyhedron						
Ca–O2	2*x*	2.426(1)	O2–Ca–O4	2*x*	90.83(4)	[3.458(2)]
Ca–O4	2*x*	2.430(1)	O2–Ca–O5	2*x*	72.31(4)	[2.888(2)]
Ca–O5	2*x*	2.469(2)	O2–Ca–O5	2*x*	76.90(5)	[3.044(2)]
Ca–O1	2*x*	2.499(1)	O2–Ca–O1	2*x*	79.54(4)	[3.150(2)]
<Ca–O>		2.456	O4–Ca–O5	2*x*	74.64(5)	[2.971(2)]
			O4–Ca–O1	2*x*	76.38(4)	[3.048(2)]
			O4–Ca–O1	2*x*	68.67(4)	[2.781(2)]
			O5–Ca–O1	2*x*	72.05(5)	[2.922(2)]
NH_2SO_3 group						
S–O2		1.448(1)	O2–S–O1		111.91(7)	[2.401(1)]
S–O1		1.450(1)	O2–S–O3		112.36(7)	[2.418(2)]
S–O3		1.462(1)	O1–S–O3		111.06(7)	[2.401(2)]
<S–O>		1.453	O2–S–N		105.38(8)	[2.446(2)]
			O1–S–N		108.94(9)	[2.504(2)]
S–N		1.624(2)	O3–S–N		106.84(8)	[2.480(2)]
<S–X>		1.496	<O–S–O>		111.78	[2.407]
			<O–S–N>		107.05	[2.477]
N–H5		0.88(3)	H5–N–H6		115(3)	[1.35(4)]
N–H6		0.71(3)	N–H5···O1		155(2)	[3.047(2)]
			N–H6···O5		152(3)	[3.076(2)]
Water molecules						
O4–H1		0.75(3)	H1–O4–H2		98(3)	[1.22(4)]
O4–H2		0.86(3)	H3–O5–H4		110(3)	[1.12(4)]
O5–H3		0.75(3)	O4–H1···O3		172(2)	[2.906(2)]
O5–H4		0.72(3)	O4–H2···O3		172(3)	[2.861(2)]
			O5–H3···O3		158(3)	[2.908(2)]
			O5–H4···O4		164(3)	[2.964(2)]

[a] Polyhedral edge lengths /Å, hydrogen bond lengths /Å, and H–H distances /Å are given in squared brackets.

is illustrated in Figure 1 in a projection along [001]. It is built up from distorted CaO_8 antiprisms (point symmetry 2) which are linked by four common oxygen corners with four NH_2SO_3 groups forming sheets parallel to (001). These sheets are interconnected by hydrogen bonds only which are donated by water molecules occupying the remaining four oxygen corners of the CaO_8 antiprism. The mean Ca–O distance of 2.456 Å agrees well with the value predicted from the ionic radii (Shannon,[15] 1976). O–Ca–O bond angles range from 68.7(1)° (O4–Ca–O1) to 90.8(1)° (O2–Ca–O4) with corresponding shortest and longest edge lengths of 2.781(2) Å and 3.458(2) Å.

TABLE VI

Interatomic bond lengths /Å and bond angles /° in $Mn(NH_2SO_3)_2 \cdot 4H_2O$[a]

MnO_6 polyhedron						
Mn–O5	2*x*	2.155(1)	O5–Mn–O1	2*x*	87.77(4)	[2.993(1)]
Mn–O1	2*x*	2.163(1)	O5–Mn–O1	2*x*	92.23(4)	[3.112(1)]
Mn–O4	2*x*	2.201(1)	O5–Mn–O4	2*x*	90.35(4)	[3.090(1)]
<Mn–O>		2.173	O5–Mn–O4	2*x*	89.65(4)	[3.071(1)]
			O1–Mn–O4	2*x*	85.15(4)	[2.953(1)]
			O1–Mn–O4	2*x*	94.85(4)	[3.214(1)]
NH_2SO_3 group						
S–O3		1.439(1)	O3–S–O2		111.78(7)	[2.390(2)]
S–O2		1.448(1)	O3–S–O1		113.61(6)	[2.421(1)]
S–O1		1.454(1)	O2–S–O1		111.17(6)	[2.395(1)]
<S–O>		1.447	O3–S–N		105.69(7)	[2.464(2)]
			O2–S–N		109.91(6)	[2.538(2)]
S–N		1.648(1)	O1–S–N		104.22(6)	[2.451(2)]
<S–X>		1.497	<O–S–O>		112.19	[2.402]
			<O–S–N>		106.61	[2.484]
N–H5		0.79(3)	H5–N–H6		107(3)	[1.30(4)]
N–H6		0.82(3)	N–H5···O2		157(3)	[3.339(2)]
			N–H6···O2		152(3)	[3.118(2)]
Water molecules						
O4–H1		0.71(2)	H1–O4–H2		104(2)	[1.23(3)]
O4–H2		0.84(3)	H4–O4–H3		109(3)	[1.28(4)]
O5–H3		0.90(3)	O4–H1···O3		150(2)	[2.750(2)]
O5–H4		0.66(3)	O4–H2···N		150(2)	[2.905(2)]
			O5–H3···O4		171(2)	[2.807(1)]
			O5–H4···O2		156(3)	[2.738(1)]

[a] Polyhedral edge lengths /Å, hydrogen bond lengths / Å, and H–H distances / Å are given in squared brackets.

The structure of $Mn(NH_2SO_3)_2 \cdot 4H_2O$ projected along [100] is shown in Figure 2. It is composed of isolated units which are interconnected to a three-dimensional framework structure by hydrogen bonds only. Such structural units consist of one MnO_6 octahedron (symmetry $\overline{1}$) sharing common oxygen corners with two amide sulfate groups. Four octahedral corners are occupied by water molecules. The bond length and angle distortion of the $MnO_2(H_2O)_4$ octahedra are comparatively small. The O–Mn–O angles differ by at most 4.8° from 90°, the octahedral O–O edge lengths are observed between 2.953(1) Å and 3.214(1) Å. The average Mn–O distance is 2.173 Å. This is somewhat short compared to 2.205 Å given by Baur[13] (1981) for

TABLE VII

Interatomic bond lengths /Å and bond angles /° in $Ni(NH_2SO_3)_2 \cdot 4H_2O$[a]

NiN_2O_4 polyhedron						
Ni–O4	2*x*	2.033(2)	O4–Ni–O5	2*x*	86.48(7)	[2.807(3)]
Ni–O5	2*x*	2.065(2)	O4–Ni–O5	2*x*	93.52(7)	[2.985(1)]
Ni–N	2*x*	2.153(1)	O4–Ni–N	2*x*	83.84(5)	[2.797(2)]
<Ni–X>		2.083	O4–Ni–N	2*x*	96.16(5)	[3.115(1)]
			O5–Ni–N	2*x*	92.94(5)	[3.059(1)]
			O5–Ni–N	2*x*	87.06(5)	[2.906(2)]
NH_2SO_3 group						
S–O3		1.440(1)	O3–S–O2		112.81(10)	[2.406(2)]
S–O2		1.449(2)	O3–S–O1		114.15(6)	[2.426(1)]
S–O1		1.450(1)	O2–S–O1		112.68(8)	[2.413(2)]
<S–O>		1.446	O3–S–N		105.48(9)	[2.496(3)]
			O2–S–N		104.22(9)	[2.482(3)]
S–N		1.690(1)	O1–S–N		106.48(10)	[2.520(2)]
<S–X>		1.507	<O–S–O>		113.21	[2.414]
			<O–S–N>		105.39	[2.490]
N–H5		0.82(3)	H5–N–H6		102(3)	[1.31(3)]
N–H6		0.87(2)	N–H5···O1		165(3)	[2.975(2)]
			N–H6···O2		153(4)	[2.966(1)]
Water molecules						
O4–H1		0.77(2)	H2–O4–H1		106(4)	[1.23(4)]
O4–H2		0.77(4)	H3–O5–H4		102(4)	[1.17(5)]
O5–H3		0.74(2)	O4–H1···O3		172(2)	[2.793(1)]
O5–H4		0.77(5)	O4–H2···O2		151(3)	[2.680(3)]
			O5–H3···O1		170(2)	[2.799(1)]
			O5–H4···O3		169(3)	[2.968(3)]

[a] Polyhedral edge lengths /Å, hydrogen bond lengths /Å, and H–H distances /Å are given in squared brackets.

$Mn^{[6]}$–O bonds or compared with the sum of the respective ionic radii (Shannon,[15] 1976).

Figure 3 illustrates the polyhedral arrangement in $Ni(NH_2SO_3)_2 \cdot 4H_2O$ in a projection along [001]. Similar to the manganese compound, this structure is also composed of separate units – consisting of one cation octahedron and two amide sulfate tetrahedra – which are connected among themselves by hydrogen bonds only. But contrary to the situation in $Mn(NH_2SO_3)_2 \cdot 4H_2O$, the Ni atoms (point symmetry $\bar{1}$) are coordinated to two nitrogen atoms shared with amide sulfate groups and four H_2O molecules. The mean

TABLE VIII

Compilation of donor–hydrogen distances, D–H···A hydrogen bond lengths, and D–H···A bond angles of all hydrogen bonds occuring in the title compounds

Compound		D–H / Å	D–H···A / Å	D–H···A / °
Ca	O4–H1···O3	0.75(3)	2.906(2)	172(2)
Ca	O4–H2···O3	0.86(3)	2.861(2)	172(3)
Ca	O5–H3···O3	0.75(3)	2.908(2)	158(3)
Ca	O5–H4···O4	0.72(3)	2.964(2)	164(3)
Mn	O4–H1···O3	0.71(2)	2.750(2)	150(2)
Mn	O5–H3···O4	0.90(3)	2.807(1)	171(2)
Mn	O5–H4···O2	0.66(3)	2.738(1)	156(3)
Ni	O4–H1···O3	0.77(2)	2.793(1)	172(2)
Ni	O4–H2···O2	0.77(2)	2.680(3)	151(3)
Ni	O5–H3···O1	0.74(2)	2.799(1)	170(2)
Ni	O5–H4···O3	0.77(5)	2.968(3)	169(3)
Ca, Mn, Ni	<O–H···O>	0.76	2.834	164
Ca	N–H5···O1	0.88(3)	3.047(2)	155(2)
Ca	N–H6···O5	0.71(3)	3.076(2)	152(3)
Mn	N–H5···O2	0.79(3)	3.339(2)	157(3)
Mn	N–H6···O2	0.82(3)	3.118(2)	152(3)
Ni	N–H5···O1	0.82(3)	2.975(2)	165(3)
Ni	N–H6···O2	0.87(2)	2.966(1)	153(4)
Ca, Mn, Ni	<N–H···O>	0.82	3.087	156
Mn	O4–H2···N	0.84(3)	2.905(2)	150(2)
Mn	<O–H···N>	0.84	2.905	150
Ca, Mn, Ni	<D–H···A>	0.79	2.922	161

Ni–O bond length in the NiN_2O_4 octahedron is 2.049 Å, the Ni–N distance 2.153(1) Å. The bond angle distortion is moderate with a maximal deviation of 6.2° from the ideal octahedral angle.

From the above discussion it follows that hydrogen bonding plays an important role in the structures of all three compounds. Three different types of hydrogen bonds occur in the title compounds, most commonly O–H···O bonds, furthermore some N–H···O type bonds, as well as one O–H···N hydrogen bond found in the structure of the manganese compound. A possible N–H···N bond is not realized. Relevant interatomic distances and angles for all hydrogen bonds are summarized in Table VIII. The mean donor–acceptor distances are 2.843 Å for the O–H···O type, 2.905 Å for the O–H···N type, and 3.087 Å for the N–H···O type, the respective average D–H···A angles of these hydrogen bonds are 164°, 150°, and 156°.

TABLE IX

Bond valence calculations in v.u. (valence units) for the amide sulfate tetrahydrates $M^{2+}(NH_2SO_3)_2 \cdot 4H_2O$ (M^{2+} = Ca, Mn, Ni) according to Brese and O'Keeffe (1991)

Cation polyhedra

M^{2+} = Ca	v	$v\,x$	M^{2+} = Mn	v	$v\,x$	M^{2+} = Ni	v	$v\,x$
Ca–O2 2*x*	0.289	0.578	Mn–O5 2*x*	0.373	0.746	Ni–O4 2*x*	0.359	0.718
Ca–O4 2*x*	0.286	0.572	Mn–O1 2*x*	0.365	0.730	Ni–O5 2*x*	0.329	0.659
Ca–O5 2*x*	0.257	0.515	Mn–O4 2*x*	0.329	0.659	Ni–N 2*x*	0.336	0.673
Ca–O1 2*x*	0.237	0.475						
Ca–O Σv		2.141	Mn–O Σv		2.134	Ni–X Σv		2.050

Amide sulfate groups

M^{2+} = Ca	v	M^{2+} = Mn	v	M^{2+} = Ni	v
S–O2	1.609	S–O3	1.649	S–O3	1.644
S–O1	1.600	S–O2	1.609	S–O2	1.605
S–O3	1.549	S–O1	1.583	S–O1	1.600
S–N	1.368	S–N	1.282	S–N	1.145
S–X Σv	6.127	S–X Σv	6.123	S–X Σv	5.994

Ligand atoms

M^{2+} = Ca	Σv	M^{2+} = Mn	Σv	M^{2+} = Ni	Σv
O1	1.837	O1	1.948	O1	1.600
O2	1.898	O2	1.609	O2	1.605
O3	1.549	O3	1.583	O3	1.644
O4	0.286	O4	0.329	O4	0.359
O5	0.257	O5	0.373	O5	0.329
N	1.368	N	1.282	N	1.481

Table IX lists the results of bond valence calculations (according to Brese and O'Keeffe,[16] 1991) for the cation polyhedra, the amide sulfate groups, and for the oxygen and nitrogen ligands (neglecting the contributions of the hydrogen atoms) in the title compounds. The bond valence sums for the cations are in good agreement with the expected values of 2 v.u. (valence units) for Ca, Mn, and Ni, and of 6 v.u. for the sulfur atom of the $[NH_2SO_3]^-$ tetrahedra. As a consequence of the hydrogen bonding system, the results for the anions are more complex. The oxygen atoms can be divided on one hand into hydrogen donors and on the other hand into acceptors or oxygen atoms not involved in the hydrogen bonding system. In the first group the bond valence sums range from 0.26 to 0.37 v.u., in the second group from 1.55 to 1.95 v.u. For the trivalent nitrogen donor of the NH_2 group values between 1.28 and 1.48 v.u. are calculated. The lowest of these values occurs in $Mn(NH_2SO_3)_2 \cdot 4H_2O$, where the nitrogen atom in addition acts as an acceptor of a hydrogen bond. In $Ca(NH_2SO_3)_2 \cdot 4H_2O$ the oxygen O3 accepts three hydrogen bonds, in agreement with its significantly lower bond valence sum (1.55 v.u.) compared to O1 and O2 (> 1.83 v.u.). In both compounds the respective highest values are observed for those oxygen atoms which are not involved in hydrogen bonding, *i.e.* O2 with 1.90 v.u. in the Ca and O1 with 1.95 v.u. in the Mn compound. In $Ni(NH_2SO_3)_2 \cdot 4H_2O$ the bond valence sums of O1, O2, and O3 are practically equal (≈1.6 v.u.). This complies with the fact that these atoms act as acceptors in two hydrogen bonds each.

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SAŽETAK

Istraživanje kristalne strukture amidosulfatnih tetrahidrata s dvovalentnim kationima

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Jedinični kristali triju amidosulfatnih tetrahidrata, s općim formulama $Ca(NH_2SO_3)_2 \cdot 4H_2O$, $Mn(NH_2SO_3)_2 \cdot 4H_2O$ i $Ni(NH_2SO_3)_2 \cdot 4H_2O$ priređeni su opreznim uparavanjem odgovarajućih vodenih otopina. Kristalne su im strukture određene postupkom difrakcije rentgenskih zraka na monokristalima. Rentgenografskim istraživanjem određeni su sljedeći kristalografski parametri: $Ca(NH_2SO_3)_2 \cdot 4H_2O$, prostorna grupa $C2/c$, Z = 4, a = 11,616(3) Å, b = 7,761(2) Å, c = 11,638(3) Å, β = 98,93(1)°, V = 1036,47 Å^3, $R1$ = 0,026; $Mn(NH_2SO_3)_2 \cdot 4H_2O$, prostorna grupa $P2_1/c$, Z = 2, a = 6,143(2) Å, b = 5,324(2) Å, c = 15,441(5) Å, β = 91,72(1)°, V = 504,78 Å^3, $R1$ = 0,024; $Ni(NH_2SO_3)_2 \cdot 4H_2O$, prostorna grupa $P\overline{1}$, Z = 1, a = 6,331(8) Å, b = 6,731(9) Å, c = 6,784(8) Å, α = 88,93(9)°, β = 67,87(5)°, γ = 67,76(6)°, V = 245,27 Å^3, $R1$ = 0,030.

U $Ca(NH_2SO_3)_2 \cdot 4H_2O$ antiprizmatski poliedri CaO_8 dijele četiri kisikova atoma s tetraedrima NH_2SO_3, stvarajući na taj način slojeve usporedne s (001). U $Mn(NH_2SO_3)_2 \cdot 4H_2O$ i $Ni(NH_2SO_3)_2 \cdot 4H_2O$, oktaedri MnO_6, odnosno NiN_2O_4, povezani su zajedničkim uglovima s dva NH_2SO_3 tetraedra stvarajući na taj način izdvojene skupine. Te jedinke, povezane međusobno samo vodikovim vezama, stvaraju trodimenzijsku mrežastu strukturu. Amidosulfatna skupina posjeduje nepravilnu tetraedarsku konfiguraciju s prosječnim veznim udaljenostima S–O, odnosno S–N od 1,449 i 1,654 Å. Srednje vrijednosti veznih udaljenosti kationa do kisika su 2,456 Å (Ca–O), 2,173 Å (Mn–O) i 2,049 Å (Ni–O), dok obadvije duljine veza Ni–N iznose 2,153 Å. U istraživanim spojevima opažene su tri različite vrste vodikovih veza i to redom: O–H···O u rasponu od 2,680 do 2,968 Å, N–H···O koje se kreću od 2,966 do 3,339 Å i O–H···N koja iznosi 2,905 Å. Općenito, opažene međuatomske udaljenosti i vezni kutovi dobro se slažu s kristalokemijskim očekivanjima.