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The Crystal Structure of $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot 0.3NH_3$

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The crystals of $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot 0.3$ NH_3 are tetragonal, space group $I4/m$ (No. 87) with $a = 13.996(4)$ Å, $c = 5.709(1)$ Å and $Z = 2$. The structure determination is based on 469 independent reflexions collected with a single crystal X-ray diffractometer using Cu*K*α radiation. Least-squares refinement of structural and thermal parameters yielded a final *R*-value of 0.044.

The crystals contain sodium ions, *catena*-di-μ-thiosulfatoargentate(I) ions, square planar tetraamminenickel(II) ions and, to a small extent, octahedral hexaamminenickel(II) ions. Silver is tetrahedrally surrounded by four sulfur atoms [S(2)], one from each of four thiosulfato groups. Each sulfur atom S(2) bridges two silver atoms, thus giving rise to a chain anion parallel to [001]. The thiosulfato group has an almost tetrahedral configuration. Bond distances: Ni – N 1.944(7) and 2.08(6) Å, Ag – S 2.596(2) Å, S – O 1.455 – 1.459(7) Å and S – S 2.037(3) Å.

Ferrari *et al.* in 1952 claimed to have synthesized $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2$.[1] The analytical result, however, is more consistent with the formulation $Na_4[Ni(NH_3)_5][Ag(S_2O_3)_2]_2$. The crystal structure and spectra of the product obtained by a diffusion method similar to that described by Ferrari *et al.* has been determined by Stomberg *et al.*[2] That investigation clearly indicated the presence of a fifth ammonia molecule, nickel being both four- and six-coordinated. Since the attempts to remove the fifth ammonia molecule almost completely have been successful, though the preliminary ones were not,[2] it would seem profitable to solve the structure of $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2$ in order to see the effect of the missing ammonia molecule.

EXPERIMENTAL

Preparation. $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot NH_3$ was prepared according to Stomberg *et al.*[2] The fifth ammonia molecule was removed by keeping the substance over phosphorous(V) oxide *in vacuo* for a long time (months).

Data collection. The collection of data was performed with a SYNTEX $P2_1$ automatic single crystal X-ray diffractometer at room temperature. A crystal with the dimensions $0.088 \times 0.095 \times 0.095$ mm was used.

The cell dimensions were obtained by a least-squares refinement of 15 automatically centred reflexions. The X-ray intensities were measured by the $\theta - 2\theta$ scan technique, using Cu*K*α radiation ($2\theta < 115°$). The scan rate varied between 2 and 8 °/min. The reflexion checked periodically during the data collection showed no crystal decomposition. A total of 469 independent reflexions with $I > 2\sigma(I)$ were used for the structure analysis. The intensities were corrected for Lorentz factor, polarization and absorption, but not for extinction.

Computing methods. The computational work was performed on an IBM 3033 computer using a set of crystallographic programmes described by Lindgren.[3]

CRYSTAL DATA

$Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot 0.3NH_3$; F.W. = 888.1
Space group $I4/m$ (No. 87)
$a = b = 13.996(4)$, $c = 5.709(1)$ Å, $V = 1118.3(5)$ Å^3, $Z = 2$, $D_c = 2.637$ g cm^{-3}, $\mu(\text{Cu}K\alpha) = 23.2$ mm^{-1}, $\lambda(\text{Cu}K\alpha) = 1.5418$ Å.

A list of observed and calculated structure factors is available from the author R.S. upon request.

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STRUCTURE DETERMINATION

Approximate atomic coordinates were known from the structure analysis of $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot NH_3$, the only difference being a missing ammonia molecule in $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2$. These positional parameters, together with anisotropic thermal parameters for nickel, silver and sulfur and isotropic ones for nitrogen and oxygen and and overall scale factor, were refined by the full matrix least-squares method. In a subsequent difference Fourier summation, the largest peak appeared at (0; 0; 0.360) with a peak height of approximately 15 % of that of a nitrogen peak. If significance is to be given to this, it indicates that not all of the more loosely bound ammonia molecules have been removed by the phosphorous(V) oxide. The occupation number for this residual molecule was determined to be 0.16 ± 0.03 by the least-squares method. It was included in the final refinement of the structure using an isotropic thermal parameter. For all other atoms anisotropic thermal parameters were used. The structure factors were weighted according to Cruickshank,[4]

$$w = (a + |F_o| + c|F_o|^2 + d|F_o|^3)^{-1},$$

with $a = 15$, $c = 0.006$ and $d = 0$. The contributions to the structure factors from the hydrogen atoms were not taken into account. A final R-value of 0.044 for 469 observed reflexions was obtained with the parameters given in Table 1. The atomic scattering factors were taken from Ref. 5 as were the dispersion corrections.

DISCUSSION

A stereoscopic view of the unit cell is shown in Fig. 1. Bond distances and angles are given in Table 2 and other interatomic distances in Table 3. In

Table 1a. Atomic coordinates, expressed as fractions of the cell edges, for $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot 0.3NH_3$. Space group $I4/m$, $Z = 2$.

Atom	Position	x	y	z
Ni	2a	0	0	0
Ag	4d	0	$\frac{1}{2}$	$\frac{1}{4}$
S(1)	8h	0.0937(1)	0.2636(1)	$\frac{1}{2}$
S(2)	8h	0.1233(2)	0.4061(2)	$\frac{1}{2}$
Na	8h	0.2930(3)	0.1664(2)	$\frac{1}{2}$
O(1)	8h	−0.0085(5)	0.2442(5)	$\frac{1}{2}$
O(2)	16i	0.1405(4)	0.2251(3)	0.292(1)
N(1)	8h	0.3660(5)	0.4633(5)	$\frac{1}{2}$
N(2)	4e[a]	0	0	0.364(10)

[a] Occupation number = 0.16(3).

Table 1b. Anisotropic thermal parameters U_{ij} for $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot 0.3NH_3$. The expression used is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{23}klb^*c^*)]$.

Atom	U_{11} or U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.016(1)	0.016(1)	0.021(2)	0	0	0
Ag	0.043(1)	0.043(1)	0.025(1)	0	0	0
S(1)	0.017(1)	0.019(1)	0.022(1)	−0.001(1)	0	0
S(2)	0.018(1)	0.020(1)	0.041(1)	0.000(1)	0	0
Na	0.031(2)	0.021(2)	0.037(2)	−0.001(2)	0	0
O(1)	0.022(3)	0.028(4)	0.041(4)	−0.001(3)	0	0
O(2)	0.034(3)	0.032(3)	0.041(3)	−0.004(2)	0.009(2)	−0.010(2)
N(1)	0.020(4)	0.020(4)	0.047(5)	0.001(3)	0	0
N(2)	0.009(12)					

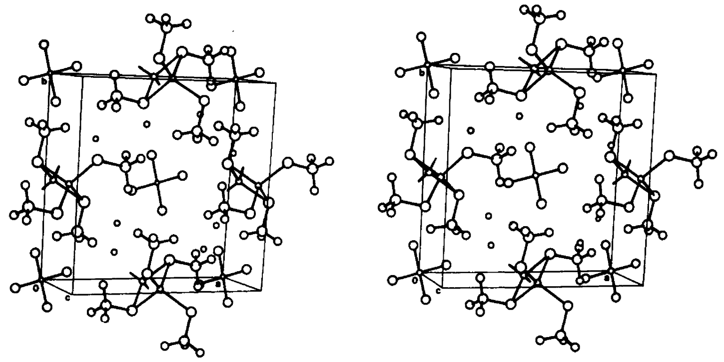

Fig. 1. Stereoscopic drawing of the unit cell of $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot 0.3NH_3$. N(2) is omitted.

Table 2. Bond distances and angles in $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot 0.3NH_3$.

	Distance/Å		Angle/°
Ni – N(1)	1.944(7)	S(2) – Ag – S(2) ($\bar{x}$,1 – y,z)	113.30(5)
Ni – N(2)	2.08(6)	S(2) – Ag – S(2) ($\frac{1}{2}-y,\frac{1}{2}+x,\frac{1}{2}-z$)	107.59(3)
Ag – S(2)	2.596(2)	S(2) – S(1) – O(1)	112.5(3)
S(1) – O(1)	1.455(7)	S(2) – S(1) – O(2)	105.6(2)
S(1) – O(2)	1.459(5)	O(1) – S(1) – O(2)	111.9(3)
S(1) – S(2)	2.037(3)	O(2) – S(1) – O(2) ($x,y,1-z$)	108.9(4)
		Ag – S(2) – Ag ($x,y,1-z$)	66.70(5)
		Ag – S(2) – S(1)	111.14(9)

$Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot 0.3NH_3$ most of the nickel atoms are surrounded by four ammonia molecules in a square planar arrangement, while silver is tetrahedrally coordinated to four sulfur atoms [S(2)], one from each of four thiosulfato groups. Each sulfur atom S(2) bridges two silver atoms, thus giving rise to a chain anion parallel to [001]. The thiosulfato group has an almost tetrahedral configuration. The structure description given by Ferrari *et al.*[6] for $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2$ is applicable to $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot 0.3NH_3$ (see Figs. 1 and 2 in Ref. 6 and exchange Cu(II) for Ni and Cu(I) for Ag). Notice, however, that there is, in fact, an extra ammonia molecule in the copper compound, not reported by Ferrari *et al.*, but established through the work by Morosin *et al.*[7]

The attempts to remove the fifth ammonia molecule in $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot NH_3$ were, thus, not completely successful. According to the interpretation put forward by Stomberg *et al.*[2] for $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot NH_3$ with both

Table 3. Interatomic distances (Å) other than bond distances in $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot 0.3NH_3$. Distances less than 3.5 Å are included.

Ag – Ag (x, y, $\bar{z}$)	2.855(0)
S(1) – Na	3.103(4)
S(1) – Na ($\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$)	3.410(2)
S(2) – Na($\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$)	3.249(2)
S(2) – O(1)	2.922(7)
S(2) – O(2)	2.807(5)
S(2) – N(1)	3.491(8)
Na – O(1) (y, $\bar{x}$, z)	2.313(7)
Na – O(2)	2.577(6)
Na – O(2) ($\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$)	2.440(6)
O(1) – O(2)	2.414(8)
O(1) – N(1) ($-\frac{1}{2}+y$, $\frac{1}{2}-x$, $\frac{1}{2}-z$)	3.268(5)
O(2) – O(2) (x, y, $\bar{z}$)	3.335(11)
O(2) – O(2) (x, y, $1-z$)	2.374(11)
O(2) – O(2) ($\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$)	3.180(10)
O(2) – N(1) ($\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$)	3.122(8)
O(2) – N(1) ($-\frac{1}{2}+y$, $\frac{1}{2}-x$, $\frac{1}{2}-z$)	3.249(8)
N(1) – N(1) (y, $1-x$, z)	2.749(10)
N(1) – N(2) ($\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{1}{2}-z$)	2.85(4)

Table 4. Ni – N distances in some Ni(II) complexes.

Complexes	Distance/Å	Ref.
Octahedral complexes		
[$NiCl_2$(*meso*-Me_6[14]aneN_4)] · $2CHCl_3$	2.060(3), 2.102(3)	9[a]
[$Ni(ClO_4)_2(C_7H_9N)_4$]	2.093(2)	10
Square planar complexes		
[Ni(*meso*-Me_6[14]aneN_4)]Cl_2 · $2H_2O$	1.957(1), 1.961(1)	9[a]
[$Ni(C_7H_9N)_4(ClO_4)_2$	1.897(3)	11
[$Ni(C_{18}H_{40}N_4)](ClO_4)_2$	1.926(2), 1.931(2)	12

[a] *meso*-Me_6[14]aneN_4 = [7*R*(*S*),14*S*(*R*)]-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

square planar and tetragonally distorted octahedra, statistically about 15 % of the nickel atoms are octahedrally coordinated in $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot 0.3NH_3$. This is reflected by the observed in-plane Ni – N distance, 1.944 Å, which ought to be the weighted mean of square planar and octahedral Ni – N distances. In square planar complexes, Ni – N distances usually range between 1.82 and 1.92 Å, while in octahedral complexes Ni – N distances are significantly longer, 2.04 – 2.15 Å (see Table 8 in Ref. 8 and Table 4 in the present investigation). In the parent compound $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot NH_3$, with statistically 50 % of the nickel atoms being six-coordinated and the rest four-coordinated, the in-plane Ni – N distance, 2.01 Å, is significantly longer.

All other bond distances and angles are not significantly different in $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot 0.3NH_3$ and $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2 \cdot NH_3$.

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