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The Crystal Structure and Spectra of $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2.NH_3$

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A Ni^{II} compound previously formulated as a tetraammine has been found to contain an extra ammonia molecule. The crystal structure of this compound, $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2.NH_3$, has been determined from visually estimated X-ray data collected with an integrating camera. The crystals are tetragonal, space group $I4/m$, with $a = 14.025(2)$ Å, $c = 5.761(1)$ Å, $V = 1133.09(3)$ Å^3 and $Z = 2$. Least-squares refinement based on 513 observed reflexions yielded an R value of 0.079. Difference syntheses showed that the fifth ammonia molecule is statistically distributed between (0;0;0.40) and (0;0;0.60). The in-plane Ni – N distances of 2.01 Å are intermediate between those found in square planar complexes and those in octahedral ones. In agreement with this the visible and infra-red spectra, and magnetic moment show that both $Ni(NH_3)_4^{2+}$ and $Ni(NH_3)_6^{2+}$ are present instantaneously.

In 1952, Ferrari *et al.* reported the synthesis of $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2$ and $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2$.[1,2] In 1966 the structure of the latter was solved by Ferrari *et al.*,[3] who concluded that copper(II) is surrounded by four ammonia molecules in a square planar arrangement. The preliminary analysis of the corresponding nickel complex indicated the formula $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2$. If the nickel complex were isostructural with the copper complex this would be a rare case of a square planar nickel-ammonia complex. In fact both compounds are tetragonal with very similar unit cell dimensions.[1,2]

EXPERIMENTAL

Preparation. The compound was prepared by a diffusion method, similar to the original one.[1] A solution of silver nitrate (8.5 g, 0.05 mol) and freshly-prepared nickel tetraammine sulphate dihydrate (6.5 g, 0.025 mol), in 30 ml water, was allowed to diffuse

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through a collodion membrane into a solution of sodium thiosulphate pentahydrate (21.7 g, 0.0875 mol) in 25 ml water. After nine days at room temperature, clusters of yellow needles had formed, on which there also formed some easily separated purple needles (presumably a hexaammine). Intermixed were several particles, presumably metallic silver, which were accurately separated mechanically.

Attempts to change experimental conditions slightly, so as to obtain other derivatives such as the monohydrate given by the analogous $Cu^{II}Cu^{I}$ complex,[4] were unsuccessful. Analyses, crystal structure and physical methods were all performed on the same sample although no evidence of other products was ever obtained. (Found: NH_3 9.5; Ni 6.7, S 28.9. Calc. for $N_5H_{15}O_{12}Na_4NiAg_2S_8$: NH_3 9.46; Ni 6.50; S 28.5.) These analyses were carried out by A. Bernhardt, W. Germany, and numerous other analyses, such as the volumetric determination of NH_3, Ni as dimethyl glyoximate, and $S_2O_3^{2-}$ as barium sulphate, after oxidation with bromine, are in agreement.

A thermogravimetric analysis was carried out to confirm the presence of the fifth ammonia molecule. With a heating rate of 1 K min^{-1} there was a slow weight loss of about 2.5 % up to 175°C, corresponding to approximately one ammonia group. Above this temperature the weight loss rate increased more than tenfold.

Attempts to eliminate the fifth ammonia molecule were not successful. Constant weight and good analyses were not obtained on heating *in vacuo* at 100°C for 5 h. The fifth ammonia was not removed on storage over P_2O_5 *in vacuo* for a week.

Physical methods. Magnetic measurements were carried out on a Gouy balance, calibrated with $[Nien_3](S_2O_3)$.[5] Reflectance spectra were run on a Beckmann DK 1A spectrophotometer and IR on a Perkin-Elmer 521 equipped with a cold tip.

X-Ray methods. The cell dimensions were obtained from X-ray powder photographs obtained by the Guinier-Hägg method, using $CuK\alpha_1$ radiation and $Pb(NO_3)_2$ ($a = 7.8566$ Å at 21°C) as an internal standard.

Multiple film (6 films) equi-inclination Weissenberg photographs were taken on a Nonius integrating camera with the crystal rotating about [001] (layer lines 0 – 5) using $CuK\alpha$ radiation. 513 independent reflexions were registered. The intensities were corrected for Lorentz, polarization, and absorption but not for extinction.

Computing methods. The computational work was performed at Göteborg Universities' Computing Centre using an IBM 360/65 computer and a set of crystallographic programs in use at Göteborg.[6,7]

The atomic scattering factors used in the calculation of the structure factors were taken from Cromer and Waber. [8]

RESULTS

Unit cell and space group. The unit cell dimensions were obtained from the measured $\sin^2\theta$ values by a least-squares procedure using 63 observed lines. The dimensions of the tetragonal cell thus determined, $a = b = 14.025(2)$ Å, $c = 5.761(1)$ Å, $V = 1133.09(3)$ Å^3, were in close agreement with those reported by Ferrari *et al.*, *i.e.* $a = b = 14.00(1)$ Å and $c = 5.75(3)$ Å. From the observed density $Z = 2$ was found.[1] Observed and calculated $\sin^2\theta$ values are given in Table 1. The Laue symmetry is $4/m$. Since the only missing reflexions were of the type $h+k+l = 2n+1$, possible space groups are thus $I4/m$ (No. 87), $I\bar{4}$ (No. 83), and $I4$ (No. 79). The structure can be described according to space group $I4/m$ as was also found for $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2$.

Structure determination and refinement. The structure analysis was performed in the usual way by solving the Patterson function for the heavy atoms, introducing these into structure factor calculations to obtain the signs of the Fourier coefficients and thereafter making Fourier summations alternating with new structure factor calculations as more atomic positions were revealed. Thus, no assumption was made about possible isomorphism with $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2$.

Table 1. Observed lines in the powder photograph of $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2.NH_3$ at 21°C (Guinier focusing camera). $\lambda(CuK\alpha_1) = 1.54051$ Å. Internal standard: $Pb(NO_3)_2$ ($a = 7.8566$ Å at 21°C). $d_{hkl} = d_{khl}$, $F_{hkl} \neq F_{khl}$.

$h\ k\ l$ $k\ h\ l$	$10^5 \times \sin^2\theta_{obs}$	$10^5 \times \sin^2\theta_{calc}$	d_{calc}	I_{obs}	F_{hkl}	F_{khl}
1 1 0	608	603	9.917	m	161	161
2 0 0	1210	1206	7.013	m−	132	132
2 2 0	2417	2413	4.959	m−	180	180
3 1 0	3021	3016	4.435	m−	161	30
2 1 1	3308	3296	4.243	m+	211	44
3 0 1	4505	4502	3.630	vvw	60	60
4 0 0	4827	4826	3.506	w−	175	175
3 3 0	5435	5429	3.306	vw	153	153
3 2 1	5716	5709	3.224	vvw	29	59
4 2 0	6040	6032	3.136	m	234	275
4 1 1	6927	6915	2.929	m	38	174
0 0 2	7174	7152	2.880	vvw	150	150
1 1 2	7766	7755	2.766	vvw	142	142
5 1 0	7857	7842	2.751	vvw	53	131
2 0 2	8380	8358	2.664	vw	93	93
5 0 1	9340	9328	2.522	vvw	69	69
2 2 2	9579	9564	2.491	m−	161	161
4 4 0	9671	9652	2.479	vw	130	130
3 1 2	10169	10168	2.416	m+	248	222
5 3 0	10271	10255	2.405	m−	29	194
6 0 0	10883	10858	2.337	vvw	92	92
4 0 2	11986	11977	2.226	vw	107	107
6 2 0	12072	12065	2.218	vw	157	81
3 3 2	12619	12581	2.172	vvw	68	68
6 1 1	12954	12948	2.141	w+	50	171
4 2 2	13203	13184	2.121	vw	76	104
5 4 1	14171	14154	2.047	vvw	57	7
5 1 2	15006	14994	1.9892	w+	142	187
6 4 0	15683	15684	1.9449	w+	148	294
5 3 2	17422	17407	1.8462	w	242	51
7 2 1	17789	17774	1.8270	w	159	69
6 0 2	18020	18010	1.8150	vw	138	138
6 2 2	19199	19216	1.7571	vw	113	62
8 0 0	19322	19304	1.7531	vw	234	234
3 2 3	20004	20012	1.7218	vvw	9	98
6 5 1	20189	20187	1.7144	vvw	0	14
8 2 0	20542	20510	1.7008	vw	153	161
4 1 3	21214	21218	1.6722	vvw	42	90
8 1 1 7 4 1	21398	21393	1.6653	vw	37 81	83 72
6 6 0	21728	21717	1.6529	vw	147	147
5 5 2	22257	22232	1.6336	m−	100	100
6 4 2	22853	22836	1.6118	vvw	79	32
5 0 3	23668	23632	1.5845	vvw	69	69
8 4 0	24154	24130	1.5680	vw−	182	60
7 3 2 9 1 0	24697	24646 24733	1.5488	vw	45 81	135 103
7 6 1 9 2 1	27422	27426	1.4708	vvw	19 14	70 37
8 5 1	28681	28632	1.4395	vvw	47	49
7 5 2 7 7 0	29523	29559	1.4176	vvw	120 74	53 74

Table 1. Continued.

10 0 0 8 6 0	30199	30162	1.4025	vvw	121 21	121 113
10 2 0	31372	31368	1.3753	vvw	108	20
3 3 4	34068	34035	1.3203	vvw	99	99
9 3 2	34305	34297	1.3152	vvw	78	186
10 3 1	34668	34664	1.3082	vvw	88	12
8 1 3 7 4 3	35702	35696	1.2892	vvw	46 97	97 85
7 7 2	36749	36710	1.2713	vvw	120	120
10 0 2 8 6 2	37299	37314	1.2610	vvw	5 155	5 24
10 2 2	38502	38520	1.2410	vvw	88	114
5 3 4	38868	38861	1.2356	vvw	15	116
9 5 2	39179	39123	1.2314	vvw	169	117
10 5 1 11 2 1	39522	39490	1.2257	vvw	28 44	13 51
11 1 2	43959	43949	1.1619	vvw	45	119
6 4 4	44257	44290	1.1574	vvw	73	135
2 1 5	46226	46205	1.1332	vvw	91	21

The electron density function with Fourier signs based on Ag, Ni, and S showed the positions of all the light atoms. In particular a peak approximately half the height of a nitrogen peak appeared at (0;0;0.41) and at the symmetry-related position (0;0;0.59). The distance between these positions, 1.0 Å, is, however, too short to be an intermolecular distance between ammonia groups (or water molecules). A difference synthesis with all atoms introduced, except the fifth nitrogen atom, N(2), also showed a peak at (0;0;0.40). Obviously, both the analytical data and the structure analysis indicated the presence of a fifth ammonia group not expected at the start of the investigation.

Due to the troublesome distance 1.0 Å, alternative assumptions about space group and occupancy were tried. A difference synthesis with N(2) at $(0;0;\frac{1}{2})$ showed a large hole at $(0;0;\frac{1}{2})$ and a peak at (0;0;0.40). Space group $I4$ was tried in a difference synthesis with all atoms except N(2); this gave peaks at (0;0;0.385) and (0;0;0.620) with peak heights approximately half those due to nitrogen peaks.

The structure was refined by the structure factor least-squares method using a full matrix program and 513 observed, independent reflexions. A separate scale factor for each layer, atomic coordinates, and anisotropic temperature parameters for N and O were refined. The structure factors were weighted according to Cruickshank,[9] $w=(a+|F_o|+c|F_o|^2+d|F_o|^3)^{-1}$, with $a=30$, $c=0.005$, and $d=0$.

The least-squares refinement was applied to the several alternatives. Both refinement according to space group $I4/m$ and I4 converged to a final R-value of 0.079 for the 513 observed reflexions indicating approximately half a nitrogen atom at (0;0;0.40) and (0;0;0.60). We have, therefore, chosen to describe the structure according to space group $I4/m$. The parameters, together with their standard deviations, are given in Table 2, the weight analysis in Table 3, and observed and calculated structure factors in Table 4. The contributions to the structure factors from the hydrogen atoms have not been taken into consideration. The final difference synthesis showed no anomalies.

Table 2a. Atomic coordinates, expressed as fractions of the cell edges, for $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2.NH_3$. Space group $I4/m$, $Z=2$. The numbers in parentheses are the standard deviations of the last significant figures. The temperature factor $= \exp(-B\sin^2\theta/\lambda^2)$.

Atom	Position	x	y	z	B
Ni	2*a*	0	0	0	
Ag	4*d*	0	½	¼	
S(1)	8*h*	0.0936(2)	0.2642(2)	½	
S(2)	8*h*	0.1217(3)	0.4067(2)	½	
Na	8*h*	0.2927(4)	0.1669(4)	½	0.7(1)
O(1)	8*h*	−0.0080(7)	0.2445(7)	½	2.3(2)
O(2)	16*i*	0.1403(5)	0.2258(6)	0.2945(17)	2.9(1)
N(1)	8*h*	0.3619(9)	0.4618(9)	½	2.3(2)
N(2)	4*e*	0	0	0.3929(69)	1.3(5)

Table 2b. Anisotropic temperature parameters β_{ij} and their standard deviations. The expression used is $\exp -(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.0034(2)	0.0034(2)	0.0219(17)	0	0	0
Ag	0.0042(1)	0.0042(1)	0.0146(9)	0	0	0
S(1)	0.0015(1)	0.0016(1)	0.0102(11)	0.0001(2)	0	0
S(2)	0.0020(2)	0.0017(2)	0.0278(15)	−0.0003(3)	0	0

Table 3. Weight analysis for $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2.NH_3$.

$\lvert F_o \rvert$-interval	$w\Delta^2$	Number of reflexions
0.0 − 16.2	1.11	51
16.2 − 21.8	1.09	51
21.8 − 27.2	1.10	51
27.2 − 34.5	0.94	52
34.5 − 39.9	0.90	51
39.9 − 51.0	0.83	51
51.0 − 65.2	0.86	52
65.2 − 82.2	0.97	51
82.2 − 115.6	0.91	51
115.6 − 264.3	1.29	52

DISCUSSION

During the structure investigation it became apparent that the structure of $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2.NH_3$ was very similar to that reported for $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2$, the only difference being the presence of a fifth ammonia group. Curiously enough, the analytical results obtained by Ferrari

Table 4. Observed and calculated structure factors for $Na[Ni(NH_3)_4][Ag(S_2O_3)_2]_2.NH_3$. The columns are successively h, $|F_o|$ and $|F_c|$.

H 0 0		
2	130	132
4	162	175
6	99	92
8	229	234
10	120	121
12	107	98
14	51	47
16	16	17
H 1 0		
1	127	-161
3	156	-161
5	67	53
7	20	-19
9	86	-81
11	99	-91
13	13	6
15	-	-8
17	33	-36
H 2 0		
2	159	180
4	224	234
6	156	157
8	139	153
10	105	108
12	65	64
14	-	-5
16	80	82
H 3 0		
1	25	30
3	160	-153
5	33	-29
7	163	-150
9	73	-65
11	25	-27
13	12	10
15	-	1
17	39	-43
H 4 0		
2	242	275
4	125	130
6	150	148
8	177	182
10	63	66
12	113	114
14	45	37
16	38	37
H 5 0		
1	134	-131
3	189	-194
5	131	-128
7	33	26
9	15	8
11	73	-71
13	40	-37
15	32	-33
17	21	20
H 6 0		
2	71	81
4	262	294
6	149	147
8	37	-21
10	43	41
12	82	78
14	98	89
16	28	31
H 7 0		
1	90	-82
3	18	-14
5	111	-100
7	81	-74
9	26	-23
11	44	-38
13	24	-21
15	59	-58
H 8 0		
2	149	161
4	52	60
6	106	113
8	111	112
10	115	105
12	46	44
14	58	57
H 9 0		
1	113	-103
3	23	-13
5	21	11
7	25	-19
9	56	-52
11	14	-13
13	41	-46
15	20	16
H 10 0		
2	21	20
4	92	99
6	105	102
8	108	89
10	27	28
12	44	46
14	26	30
H 11 0		
1	27	-27
3	25	18
5	73	-69
7	63	-59
9	93	-89
11	54	46
13	10	7
H 12 0		
2	47	49
4	96	90
6	13	12
8	124	119
10	53	53
12	19	21
H 13 0		
1	67	-60
3	67	-63
5	-	-1
7	-	-8
9	-	-9
11	33	-38
H 14 0		
2	105	96
4	89	87
6	35	31
8	-	4
10	-	2
H 15 0		
1	-	-4
3	64	-61
5	-	-9
7	33	-33
9	25	26
H 16 0		
2	62	60
4	39	40
6	27	29
H 17 0		
1	14	-13
3	-	-5
5	-	-5
H 0 1		
1	10	-6
3	56	60
5	73	69
7	52	-46
9	28	24
11	19	-10
13	27	26
15	-	-1
17	-	-7
H 1 1		
2	177	211
4	41	38
6	47	50
8	43	-37
10	23	27
12	-	-11
14	31	39
16	-	11
H 2 1		
1	40	44
3	46	-29
5	-	2
7	166	159
9	-	14
11	50	44
13	25	20
15	-	-11
17	-	-4
H 3 1		
2	51	59
4	-	12
6	22	24
8	16	19
10	84	88
12	19	-6
14	38	37
16	24	-29
H 4 1		
1	178	-174
3	32	39
5	60	57
7	75	81
9	37	-37
11	35	-33
13	-	-10
15	68	65
17	20	26
H 5 1		
2	32	31
4	-	7
6	-	0
8	57	-47
10	-	27
12	79	69
14	-	-2
16	27	-27
H 6 1		
1	160	171
3	-	2
5	18	-14
7	20	19
9	39	37
11	36	29
13	-	-4
15	29	27
H 7 1		
2	62	-67
4	77	72
6	63	70
8	83	79
10	43	-40
12	-	-7
14	-	-3
16	24	28
H 8 1		
1	85	83
3	19	23
5	51	49
7	40	-43
9	-	-4
11	51	42
13	-	11
15	-	-14
H 9 1		
2	32	37
4	23	21
6	46	45
8	-	-9
10	-	-17
12	-	17
14	27	29
H 10 1		
1	-	3
3	18	12
5	19	13
7	-	0
9	91	84
11	-	7
13	24	22
H 11 1		
2	55	51
4	31	-25
6	56	51
8	-	-7
10	47	41
12	-	-13
H 12 1		
1	39	-42
3	-	9
5	82	75
7	-	3
9	37	-39
11	-	-17
H 13 1		
2	71	68
4	36	-36
6	35	-39
8	-	-5
10	50	54
H 14 1		
1	-	-9
3	28	26
5	-	-4
7	34	37
9	-	-10
H 15 1		
2	20	-23
4	47	45
6	30	31
8	-	2
H 16 1		
1	38	38
3	23	24
5	17	-26
7	-	10
H 17 1		
2	-	1
4	28	30
H 0 2		
2	97	-93
4	109	-107
6	138	-138
8	40	-23
10	-	-5
12	-	-3
14	61	-58
16	28	-34
H 1 2		
1	125	142
3	220	248
5	143	142
7	193	201
9	85	86
11	45	45
13	68	66
15	64	60
17	18	21
H 2 2		
2	154	-161
4	84	-76
6	121	-113
8	35	35
10	84	-88
12	40	-40
14	75	-77
16	32	29
H 3 2		
1	198	222
3	62	68
5	238	242
7	47	45
9	77	78
11	62	58
13	127	124
15	45	45
H 4 2		
2	115	-104
4	36	-31
6	88	-79
8	37	-37
10	53	-47
12	-	12
14	34	-36
16	31	-33
H 5 2		
1	188	187
3	52	51
5	100	100
7	121	120
9	170	169
11	36	39
13	23	25
15	24	27
H 6 2		
2	81	-62
4	35	-32
6	15	-10
8	151	-155
10	60	-54
12	51	-44
14	31	27
H 7 2		
1	126	124
3	139	135
5	56	53
7	121	120
9	54	51
11	64	57
13	46	46
15	-	6
H 8 2		
2	50	-49
4	98	-91
6	20	-24
8	36	-29
10	-	-15
12	-	-9
14	-	-15
H 9 2		
1	-	5
3	181	186
5	115	117
7	80	79
9	49	45
11	77	69
13	-	10
H 10 2		
2	107	-114
4	21	-19
6	64	-59
8	25	14
10	53	-53
12	22	-24
H 11 2		
1	116	119
3	86	88
5	45	45
7	35	33
9	-	6
11	73	77
13	52	59
H 12 2		
2	91	-83
4	-	-16
6	51	-52
8	24	18
10	-	-10
12	21	-30
H 13 2		
1	29	30
3	26	24
5	86	89
7	47	45
9	38	40
11	20	22
H 14 2		
2	45	39
4	-	-4
6	37	-37
8	50	-54
H 15 2		
1	66	63
3	-	11
5	26	26
7	32	32
H 16 2		
2	-	-11
4	14	-15
6	13	-18
H 17 2		
1	14	18
H 0 3		
1	24	29
3	10	8
5	70	69
7	31	-24
9	38	37
11	33	-32
13	37	34
15	-	4
H 1 3		
2	87	95
4	49	42
6	68	65
8	47	-46
10	33	26
12	-	-5
14	40	44
16	-	0
H 2 3		
1	40	43
3	16	-9
5	25	29
7	93	91
9	-	11
11	52	54
13	-	12
15	-	-10
H 3 3		
2	92	98
4	-	-9
6	22	22
8	18	13
10	85	87
12	-	-15
14	30	29
H 4 3		
1	91	-90
3	55	50
5	15	10
7	98	97
9	37	-34
11	20	-22
13	14	-13
15	54	62
H 5 3		
2	11	9
4	17	15
6	11	8
8	19	-20
10	-	1
12	75	70
14	-	0
H 6 3		
1	83	85
3	19	19
5	-	4
7	-	10
9	34	28
11	31	29
13	-	6
15	10	14
H 7 3		
2	55	-54
4	82	85
6	33	30
8	72	70
10	21	-23
12	-	-5
14	-	-5
H 8 3		
1	96	97
3	-	8
5	43	46
7	40	-39
9	14	15
11	29	24
13	-	10
H 9 3		
2	38	35
4	-	-1
6	57	52
8	-	-9
10	-	-9
12	15	11
H 10 3		
1	-	2
3	-	2
5	21	20
7	-	7
9	54	59
11	17	13
H 11 3		
2	49	51
4	17	-14
6	46	46
8	-	-11
10	36	38
H 12 3		
1	36	-33
3	32	27
5	51	47
7	-	6
9	25	-28
11	10	-10
H 13 3		
2	56	53
4	26	-27
6	33	-34
8	-	8
10	29	38
H 14 3		
1	-	-9
3	14	16
5	-	3
7	28	33
H 15 3		
2	25	-25
4	40	46
6	26	28
H 16 3		
1	29	36
H 0 4		
2	75	76
4	89	88
6	39	41
8	111	116
10	75	77
12	67	66
14	21	23
H 1 4		
1	80	-93
3	81	-76
5	33	-25
7	19	-15
9	50	-52
11	66	-62
13	-	-15
H 2 4		
2	86	81
4	122	118
6	80	76
8	56	103
10	49	44
12	43	41
14	-	-3
H 3 4		
1	14	-13
3	108	-59
5	18	-15
7	118	-105
9	56	-49
11	35	-32
13	17	9
H 4 4		
2	121	121
4	78	77
6	79	73
8	89	95
10	54	45
12	72	73
14	24	22
H 5 4		
1	71	-68
3	119	-116
5	75	-73
7	-	-12
9	15	6
11	56	-56
13	33	-34
H 6 4		
2	74	69
4	127	135
6	92	97
8	25	-17
10	32	31
12	36	36
H 7 4		
1	58	-56
3	23	-23
5	78	-76
7	48	-44
9	39	-36
11	25	-28
13	13	-14
H 8 4		
2	81	86
4	32	30
6	70	69
8	74	63
10	65	64
12	32	30
H 9 4		
1	88	-91
3	-	-7
5	-	-11
7	20	-19
9	37	-40
11	12	-13
H 10 4		
2	16	12
4	69	70
6	55	50
8	55	58
10	16	13
H 11 4		
1	13	-14
3	11	-7
5	48	-53
7	38	-42
9	53	-60
H 12 4		
2	22	18
4	50	55
6	13	8
8	64	73
H 13 4		
1	39	-46
3	40	-48
5	-	0
7	-	-16
H 14 4		
2	54	68
4	48	50
H 0 5		
1	7	-7
3	44	37
5	40	39
7	18	-15

Table 1. Continued.

9	16	13	1	22	21	10	43	40	4	17	16	H	7	5	H	9	5	H	11	5
11	9	-5	3	-	6	12	-	-8	6	10	-5	2	35	-38	2	25	26	2	28	22
13	13	11	5	17	-15				8	24	-23	4	32	31	4	23	17	4	16	-13
			7	65	74	H	4	5	10	23	15	6	39	36	6	12	13	6	31	36
H	1	5	9	17	9	1	62	-63	12	27	37	8	45	43	6	-	-3			
2	82	91	11	25	25	3	36	32				10	25	-23				H	12	5
4	24	17	13	15	15	5	42	37	H	6	5				H	10	5	1	16	-15
6	19	18				7	40	34	1	71	84	H	8	5	1	11	7	3	8	5
8	17	-17	H	3	5	9	21	-19	3	8	-5	1	35	33	3	-	6	5	36	45
10	17	18	2	10	3	11	10	-10	5	14	-12	3	21	15	5	11	3			
12	7	-1	4	17	13				7	21	15	5	35	37	7	-	-1	H	13	5
			6	18	19	H	5	5	9	26	24	7	15	-16				2	27	41
H	2	5	8	20	18	2	29	23	11	24	19	9	-	-10						

et al. for the copper compound, 10.7 % NH_3 on the average,[2] is more consistent with the formulation $Na_4[Cu(NH_3)_5][Cu(S_2O_3)_2]_2$ (theoretical amount 10.43 % NH_3) than with $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2$ (theoretical amount 8.55 % NH_3). At the final stage of this structure determination the structure investigation performed by Ferrari *et al.* was doubted. Refinement of the original X-ray data [4,10] as well as a new structure investigation by Hathaway *et al.*[4] have shown that the formulation $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2$ is incorrect. There exist, in fact, both a monoaquo- and a mono-ammonia-adduct, which they formulate $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]_2L$ ($L = H_2O$ or NH_3).

The present investigation of $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2.NH_3$ has shown a similar situation, the only difference being that while Morosin *et al.* on the one hand and Hathaway *et al.* on the other both report the adduct ammonia molecule at $(0;0;\frac{1}{2})$ our data are more consistent with describing the adduct molecule statistically at (0;0;0.39) and (0;0;0.61). Despite this difference there can be no doubt that there is a fifth ammonia molecule between the two nickel atoms. A further indication that the nickel atom is coordinated to more than four ligands is the in-plane Ni – N distance of 2.01 Å, which is significantly longer than those, 1.82 – 1.92 Å, found in square planar complexes (see Table 8 in Ref. 11). This distance is shorter than Ni – N distances, 2.04 – 2.15 Å, observed in octahedral complexes of nickel(II).[11]

Bond distances are given in Table 5 and packing distances in Table 6. Apart from the fifth ammonia molecule, the structural description given by Ferrari *et al.*[3] for the copper complex applies.

Table 5. Bond distances and angles with their standard deviations in $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2.NH_3$.

	Distance (Å)		Angle (°)
Ni – N(1)	2.010(13)	S(2) – Ag – S(2) ($\bar{x}$, $1-y$, z)	112.38(9)
– N(2)	2.263(40)	S(2) – Ag – S(2) ($\frac{1}{2}-y$, $\frac{1}{2}+x$, $\frac{1}{2}-z$)	108.04(5)
Ag – S(2)	2.588(3)	S(2) – S(1) – O(1)	112.1(4)
S(1) – O(1)	1.451(10)	S(2) – S(1) – O(2)	106.0(4)
– O(2)	1.456(9)	O(1) – S(1) – O(2)	111.8(4)
– S(2)	2.037(4)	O(2) – S(1) – O(2) (x, y, $1-z$)	108.8(7)
		Ag – S(2) – Ag (x, y, $1-z$)	67.62(9)
		Ag – S(2) – S(1)	111.62(16)

Table 6. Interatomic distances other than bond distances in $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2.NH_3$. Distances less than 4.0 Å are included.

Ni	$-N(2)\ (x, y, 1-z)$	3.50 Å
Ag	$-Ag\ (x, y, \bar{z})$	2.88
	$-S(1)$	3.84
	$-O(1)$	3.86
S(1)	$-Na$	3.11
	$-Na\ (\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z)$	3.43
	$-Na\ (\bar{y}, x, z)$	3.68
	$-N(1)\ (y-\frac{1}{2}, \frac{1}{2}-x, \frac{1}{2}-z)$	3.85
	$-N(2)$	3.98
S(2)	$-O(2)$	2.81
	$-O(1)$	2.91
	$-Na\ (\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z)$	3.29
	$-N(1)$	3.46
	$-O(1)\ (\frac{1}{2}-y, \frac{1}{2}+x, \frac{1}{2}-z)$	3.64
Na	$-O(1)\ (y, \bar{x}, z)$	2.33 Å
	$-O(2)\ (\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z)$	2.46
	$-O(2)\ (x, y, 1-z)$	2.58
O(1)	$-O(2)$	2.41
	$-N(1)\ (-\frac{1}{2}+y, \frac{1}{2}-x, \frac{1}{2}+z)$	3.27
	$-N(2)$	3.49
	$-O(2)\ (\bar{y}, x, z)$	3.59
O(2)	$-O(2)\ (x, y, 1-z)$	2.37
	$-N(1)\ (\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z)$	3.13
	$-O(2)\ (\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z)$	3.19
	$-N(1)\ (y-\frac{1}{2}, \frac{1}{2}-x, \frac{1}{2}-z)$	3.26
	$-O(2)\ (x, y, \bar{z})$	3.39
	$-N(2)$	3.77
N(1)	$-N(1)\ (y, 1-x, z)$	2.84
	$-N(2)\ (\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z)$	3.03

There are several possible structures for the complex as a result of the presence of the fifth ammonia molecule. These are:

(a) this ammonia molecule undergoes free rotation, and N(2) lies at $(0;0;\frac{1}{2})$;

(b) as well as rotating, the ammonia molecule inverts in a 'synchronised' fashion, along the *c* axis, giving instantaneously a five-coordinate structure;

(c) the ammonia molecule inverts in a 'non-synchronised' fashion, giving instantaneously one six-coordinated and one square planar nickel;

(d) the 'fifth ammonia' molecules are situated at (0;0;0.39) in a given row of unit cells in the *c*-direction and at (0;0;0.61) in a neighbouring, parallel, row of unit cells. This means on OD-structure with alternating octahedral and square planar nickel complexes in static coordination. There were, however, no visible signs that the structure was an OD-structure. The possibility cannot, however, be excluded since the difference between the contributions from nitrogen to the structure factors in cases (a) – (d) is so small that it is highly unlikely to be observable (the rotation photograph about [001] ought in case (d) to have shown extra streaks between the layer lines.

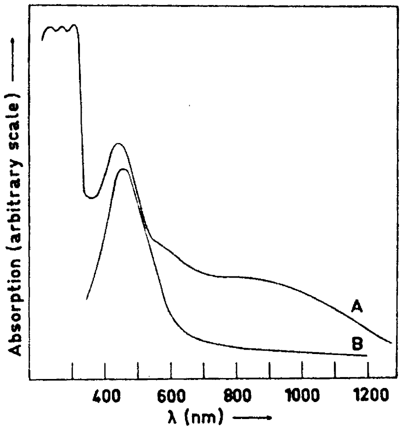

Fig. 1. Reflectance spectra. A. $Na_4[Ni(NH_3)]_4[Ag(S_2O_3)_2]_2.NH_3$ B. $[Ni(en)_2][AgBr_2]_2$.

If (a) were the case, either diamagnetic square planar or strongly tetragonal octahedral (since Ni – N(2) = 2.88 Å) structures would be present. According to Ballhausen and Liehr[12] the latter may be either diamagnetic or paramagnetic. The reflectance spectrum (Fig. 1) shows two ill-resolved bands at *ca.* 11 000 cm^{-1} and *ca.* 17 000 cm^{-1}, followed by a more intense band at 22 500 cm^{-1}. This type of spectrum is not in agreement with the strongly tetragonal paramagnetic possibility, which should give only very weak bands in the visible region since all transitions would be spin-forbidden in character.[12] The compound is not diamagnetic and the reflectance spectrum is different from that of $[Ni(en)_2][AgBr_2]_2$ (see Fig. 1). Since the latter compound is strictly square planar in structure,[11] then all possibilities under (a) may be eliminated.

Possibility (b) may also be discounted, both on the grounds of the spectrum being very different from that expected for a high spin five-coordinate structure[13] and also because such a structure should give a magnetic moment of *ca.* 3.2 BM.[14] Instead, the magnetic moment is *ca.* 2.2 BM.

The results are consistently interpreted assuming the presence of both octahedral and square planar nickel complexes. Thus, the peak at 22 500 cm^{-1} in the electronic spectrum arises from the spin-allowed transitions ${}^1A_{1g} \rightarrow {}^1A_{2g}$, *etc.* of $Ni(NH_3)_4^{2+}$, which are, in fact, very close to those in $Ni(en)_2^{2+}$. The $Ni(NH_3)_6^{2+}$ ion gives a spectrum with bands at 10 750, 17 500 and 27 200 cm^{-1},[15] which is in reasonable agreement with Fig. 1 if it is assumed that the

Table 7. Magnetic properties of the compound.

T/K	$10^6\chi_{corr}$/c.g.s.u.	$\mu_{eff.}$/BM
112	4717	2.07
116	4924	2.14
121	4606	2.12
126	4358	2.10
130	4257	2.11
133	4187	2.12
138	4046	2.12
143	4035	2.16
153	3783	2.16
156	3720	2.16
160	3620	2.16
167	3554	2.19
175	3317	2.16
188	3135	2.18
196	2561	2.01
215	2376	2.03
223	2305	2.03
240	2316	2.12
302	2005	2.21
314	1946	2.22
318	1916	2.22
295	2028	2.20

Diamagnetic correction = -338.4×10^{-6} c.g.s.u. (from Selwood, P. W. *Magnetochemistry*, Wiley, New York 1956).

highest energy band is covered by the onset of c.t. transitions at 27 000 cm^{-1}. The broadening at lower energy could be caused by the 'tail' of the more intense 22 500 cm^{-1} band, and also by some splitting of the $^3T_{1g}$ and $^3T_{2g}$ (F) energy levels of $Ni(NH_3)_6^{2+}$ (since $Ni-N(2)=2.26$ Å represents sensible tetragonal character).[16]

Strong evidence for the presence of both octahedral and square planar nickel complexes is provided by the magnetic properties. At room temperature the magnetic moment is 2.2 BM decreasing to 2.07 BM at 112 K. In this range the susceptibility obeys the Curie-Weiss law with θ (extrapolated) *ca.* 5 K (Table 7). Almost identical magnetic moments have been found in other cases of simultaneous presence of diamagnetic and paramagnetic octahedral chromophores of Ni^{2+} in the unit cell.[17] The corrected magnetic moments then become 2.99 (r.t.) and 2.87 (112 K) BM, assuming 50 % diamagnetic and 50 % paramagnetic (2 electrons). Hexaammine nickel(II) complexes typically show magnetic moments between 3.04 and 3.11 BM.[18]

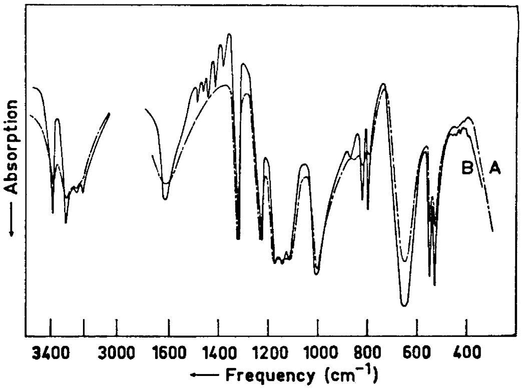

Fig. 2. IR spectra of $Na_4[Ni(NH_3)_4][Ag(S_2O_3)_2]_2.NH_3$. A. Room temperature. B. 100 K.

The IR spectrum of the compound is also in agreement with this interpretation. The split bands at 1180, 1145, 1120 and 530, 550 cm^{-1} are ascribed to $\nu_4(S_2O_3)^{2-}$ and $\nu_5(S-O)$, respectively, and the strong, broad bands at 650 and 1010 cm^{-1} to $\nu_2(S-O)$ and $\nu_1(S-O)$, respectively.[19] There is no absorption due to water molecules at *ca.* 3600 cm^{-1}, and the remaining strong bands are presumably due solely to NH_3 vibrations. It is immediately seen that there are two symmetric deformation modes, $\delta_{sym}(NH_3)$, at 1330 and 1235 cm^{-1}. The latter may be assigned to that arising from the $Ni(NH_3)_6^{2+}$ part (although at rather higher frequency than in many hexaamminenickel(II) complexes, possibly due to the tetragonal chromophore present [20]) and the former to $Ni(NH_3)_4^{2+}$. A further NH_3 symmetric deformation mode expected to arise from $Ni(NH_3)_6^{2+}$ may be hidden under $\nu_4(S_2O_3)^{2-}$. Also, there is clearly more than one $\varrho(NH_3)$ mode, at 862, 834, and 800 cm^{-1}, all of which are considerably more intense at *ca.* 100 K.

Apart from better resolution, there is almost no significant change in the other IR bands at 100 K, apart from the appearance of many weak-medium bands between 1385 and 1480 cm^{-1}. These may be combination bands between

ν_1(S – O) at 1010 cm^{-1} and several very weak bands at 410, 420, 438, 460, and 470 cm^{-1}, the origin of which is unclear, but which may include S – S stretching vibrations. The lack of a sensible temperature effect on the NH_3 vibrations favours the interpretation according to (d).

It is interesting to note that the analogous Cu^{II}Cu^{I} compound has electronic properties which are not consistent with a $CuN_4 - CuN_6$ formulation[4] and shows only one band in the IR ascribable to $\delta_{sym}(NH_3)$. (The 1180 cm^{-1} band previously assigned to δ_{sym}('NH_3') is more reasonably attributed to one of the components of $\nu_4(S_2O_3)$,$^{2-}$ and that assigned to $\varrho(NH_3)$ at 655 cm^{-1} is probably due to ν_2(S – O)). These differences indicate that the difference in position of the fifth ammonia molecule in these two compounds as found in the difference syntheses is, in fact, real.

To date we have no reasonable explanation to account for the differences between the Ni^{II}Ag^{I} and Cu^{II}Cu^{I} compounds.

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