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Crystal and Molecular Structures of Chlorobis(acetone thiosemicarbazone)nickel(II) Chloride Monohydrate and Nitratobis(acetone thiosemicarbazone)nickel(II) Nitrate Monohydrate

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Received July 18, 1972

The crystal structures of two isomorphous salts of the type $[Ni(acetone\ thiosemicarbazone)_2X]^+X^-\cdot H_2O$, where X = Cl or NO_3, have been determined by X-ray diffraction methods. The crystals are orthorhombic, space group $Pca2_1$, with dimensions $a = 21.934$ (3), $b = 6.920$ (1), and $c = 11.762$ (2) Å for the chloride and $a = 23.316$ (4), $b = 7.208$ (2), and $c = 11.470$ (2) Å for the nitrate. The structures were determined by the heavy-atom method and refined by least-squares methods to an R of 0.036 for 1426 observed reflections for the chloride and $R = 0.061$ for 1016 reflections for the nitrate salt. The cation in the chloro case is a trigonal bipyramid with 1 Cl (Ni–Cl = 2.305 Å) and 2 S atoms (Ni–S = 2.290 and 2.131 Å) in the equatorial plane. The pentacoordinated geometry appears to be a function of the steric constraints of the acetone thiosemicarbazone ligand. In the nitrate salt, the cation appears to be octahedral although there are only slight changes in the ligand geometry from the chloro case. In both salts, there is an extensive hydrogen-bonding network which links the anions, cations, and water molecules.

Introduction

The reaction of aldehydes or ketones with thiosemicarbazide produces derivatives known as thiosemicarbazones. Thiosemicarbazones have a very broad spectrum of biological activity which is dependent upon the nature of the parent aldehyde or ketone.

In the case of α-(N)-heterocyclic thiosemicarbazones, several were found to be good antitumor agents.[1] These carcinostatic agents were thought to function as monovalent, tridentate chelates. The chelating ability of 1-isoquinoline thiosemicarbazone, a good tumor inhibitor, was demonstrated and the crystal structure was determined.[2] To investigate the chelating properties of inactive thiosemicarbazones, some metal complexes with acetone thiosemicarbazone were prepared. The nickel chloride compound was pentacoordinated,[3] not octahedral as had been proposed.[4] Therefore, we also prepared the complex with nickel nitrate to extend our knowledge of thiosemicarbazones as chelating ligands. We report now the crystal structure of the two salts $[Ni(ATSC)_2X]^+X^-\cdot H_2O$, where ATSC is acetone thiosemicarbazone, $(CH_3)_2C{=}NNHC(S)NH_2$, and X = Cl or NO_3.

Experimental Section

The compounds were both prepared by the reaction of ATSC with the appropriate nickel salt in ethanol.[4] The chloride forms yellow-green crystals while the nitrate is very pale blue. The compounds are relatively insoluble after forming and the chloride was used without recrystallization.

Preliminary Weissenberg and precession photographs showed both compounds to be nearly isomorphous. The crystals are orthorhombic and the systematic absences of $0kl$ if $l = 2n + 1$ and $h0l$ if $h = 2n + 1$ indicated that the possible space groups were $Pca2_1$ and $Pcam$. Intensity statistics indicated that the noncentric space group $Pca2_1$ was more likely; this choice was supported by the successful structure analysis.

A small crystal mounted on the end of a glass fiber was used for the intensity measurements. The unit cell dimensions were determined from a least-squares fit of 2θ values measured using the Cu Kβ peak (λ 1.39217 Å). The crystal size and other pertinent data are presented in Table I. The intensity measurements were made with a General Electric XRD-6 diffractometer, using the stationary-crystal, stationary-counter method. A wide beam of Cu Kα radiation (λ 1.54051 Å) was used with a 0.35-mil Ni foil in front of the scintillation counter window. Four standard reflections were measured after every 100 reflections and were used to correct for a small variation (1% for X = Cl and 4% for X = NO_3) of the standards with time. All reflections with 2θ ≤ 135° were measured at least once, and for the chloride, multiple measurements were made (see Table I). An experimental background curve was derived by measurement of the background in areas of reciprocal space which were known to contain no reflections and were free from streaking. The values obtained at a given 2θ angle were then averaged. Those reflections which had intensities greater than 1.2 times the appropriate background were considered to be observed and were used in the analysis. The unobserved reflections were flagged with a minus sign and given a value of 0.1 times the appropriate background. A correction for the α_1-α_2 splitting was made for reflections with 2θ > 80°. These data were then reduced to a set of structure amplitudes on an arbitrary scale in the usual manner.

Table I. Crystal Data for the $[Ni(ATSC)_2X]^+X^-\cdot H_2O$ Salts

	X = Cl	X = NO_3
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pca2_1$	$Pca2_1$
a, Å	21.934 (3)	23.316 (4)
b, Å	6.920 (1)	7.208 (2)
c, Å	11.762 (2)	11.470 (2)
Vol., $Å^3$	1785.3	1927.7
Z	4	4
d_c, g/cm^3	1.525	1.576
d_m, g/cm^3	1.51	1.59
Crystal size, mm	0.10 × 0.12 × 0.08	0.08 × 0.08 × 0.03
No. of intensity measurements	6185	2548
No. of unique reflections	1701	1822
No. of observed reflections	1426	1016

Structure Determination and Refinement. $[Ni(ATSC)_2Cl]^+Cl^-\cdot H_2O$. A sharpened three-dimensional Patterson function was calculated and used to locate the position of the Ni atom. The remaining atoms were located in successive Fourier and difference Fourier syntheses. Three full-matrix least-squares cycles using individual isotropic thermal parameters reduced R to 0.11. An additional three least-squares cycles using anisotropic thermal parameters reduced R to 0.047. A difference Fourier synthesis was used to locate the hydrogen atoms. No other significant spurious peaks were present. The contributions of the hydrogen atoms were included in subsequent structure factor calculations but their parameters were not varied. After two more least-squares cycles, the shifts were less than 0.1 times the estimated standard deviations and the refinement was terminated. The final R was 0.036. The final positional and thermal parameters for the nonhydrogen atoms are given in Table II. An ORTEP drawing of the molecule is shown in Figure 1 which also gives the atomic numbering. The hydrogen atom parameters are tabulated in Table III.[5]

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(1) F. A. French and E. J. Blanz, Jr., *J. Med. Chem.*, **9**, 585 (1966).

(2) M. Mathew and G. J. Palenik, *J. Amer. Chem. Soc.*, **91**, 6310 (1969).

(3) M. Mathew and G. J. Palenik, *J. Amer. Chem. Soc.*, **91**, 4923 (1969).

(4) A. V. Ablov and N. V. Gerbeleu, *Russ. J. Inorg. Chem.*, **9**, 46 (1964).

Table II. Final Parameters and Their Estimated Standard Deviations in Parentheses for $[Ni(ATSC)_2Cl]^+Cl^- \cdot H_2O$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	15,271 (4)	6,872 (14)	0,000 (0)	154 (2)	2096 (21)	838 (9)	10 (11)	15 (8)	−73 (27)
Cl1	10,866 (9)	33,697 (26)	−8,218 (23)	264 (4)	2306 (39)	1583 (25)	193 (22)	−221 (18)	776 (56)
Cl2	8,965 (7)	40,387 (30)	51,816 (23)	159 (3)	4135 (58)	1297 (22)	128 (22)	14 (14)	750 (62)
SA1	11,648 (8)	−4,966 (28)	16,874 (19)	265 (4)	2769 (45)	741 (12)	−577 (24)	−120 (13)	9 (47)
SB1	23,318 (8)	−12,898 (30)	−5,186 (24)	204 (4)	3326 (49)	1537 (24)	323 (21)	−47 (15)	−223 (60)
NA1	848 (2)	−1,152 (7)	−713 (5)	18 (1)	183 (11)	82 (5)	6 (6)	−6 (4)	4 (13)
NA2	444 (2)	−1,888 (7)	81 (5)	19 (1)	214 (11)	68 (4)	−1 (6)	−6 (4)	30 (14)
NA3	150 (3)	−2,500 (10)	1,888 (5)	24 (1)	313 (16)	85 (6)	−41 (8)	−7 (4)	75 (16)
NB1	2,222 (2)	2,360 (7)	794 (5)	15 (1)	214 (12)	91 (5)	−5 (6)	1 (4)	−12 (14)
NB2	2,802 (2)	1,903 (9)	386 (5)	14 (1)	342 (17)	80 (5)	−11 (7)	10 (3)	−38 (15)
NB3	3,465 (2)	−11 (12)	−538 (6)	17 (1)	564 (23)	96 (6)	38 (9)	4 (4)	−116 (20)
CA1	543 (3)	−1,717 (9)	1,185 (6)	20 (1)	167 (13)	84 (6)	6 (7)	−7 (5)	7 (16)
CA2	741 (3)	−1,519 (8)	−1,750 (6)	23 (1)	189 (14)	87 (6)	23 (8)	−19 (5)	−4 (17)
CA3	1,161 (3)	−738 (13)	−2,622 (7)	29 (2)	429 (25)	81 (7)	22 (12)	10 (6)	−23 (24)
CA4	214 (4)	−2,660 (12)	−2,176 (7)	34 (2)	276 (19)	91 (7)	−25 (11)	−30 (6)	−23 (20)
CB1	2,897 (2)	295 (11)	−197 (6)	16 (1)	363 (20)	72 (6)	25 (8)	3 (4)	−30 (18)
CB2	2,190 (3)	3,681 (9)	1,557 (6)	25 (2)	203 (15)	91 (6)	−9 (8)	3 (5)	−15 (17)
CB3	1,584 (3)	4,270 (10)	2,006 (9)	33 (2)	222 (16)	166 (11)	9 (11)	37 (7)	−135 (23)
CB4	2,725 (4)	4,728 (14)	2,010 (9)	30 (2)	415 (26)	166 (12)	−26 (12)	−5 (7)	−239 (30)
Ow	5,293 (2)	2,057 (8)	4,348 (6)	28 (1)	350 (15)	136 (6)	21 (7)	1 (5)	−76 (17)

[a] All values are ×10⁴ except those for Ni, Cl1, Cl2, S1, and S2 which are ×10⁵. The temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table III. Final Parameters for the Hydrogen Atoms in $[Ni(ATSC)_2Cl]^+Cl^- \cdot H_2O$[a]

Atom [bonded to]	Distance	x	y	z	B
H1[NA2]	1.02	8	−259	−27	3.7
H2[NA3]	0.83	−20	−291	155	4.8
H3[NA3]	0.92	26	−274	255	4.8
H4[CA3]	0.74	145	−23	−251	5.5
H5[CA3]	0.86	135	−148	−309	5.5
H6[CA3]	0.94	101	3	−322	5.5
H7[CA4]	1.01	19	−319	−298	5.9
H8[CA4]	0.86	21	−384	−194	5.9
H9[CA4]	1.02	−22	−213	−208	5.9
H10[NB2]	0.99	315	280	37	3.9
H11[NB3]	1.05	361	−126	−97	5.5
H12[NB3]	1.13	381	118	−39	5.5
H13[CB3]	0.86	150	538	228	5.7
H14[CB3]	0.90	131	332	189	5.7
H15[CB3]	1.08	154	389	290	5.7
H16[C4B]	0.94	258	571	250	7.0
H17[CB4]	1.01	315	420	197	7.0
H18[CB4]	1.19	286	571	122	7.0
H19[Ow]	0.89	492	257	437	6.2
H20[Ow]	0.85	558	286	443	6.2

[a] The hydrogen atom is given followed by the atom to which it is bonded in brackets, the corresponding bond distance (in Å), the positional parameters (×10³), and the isotropic thermal parameters (in Å²).

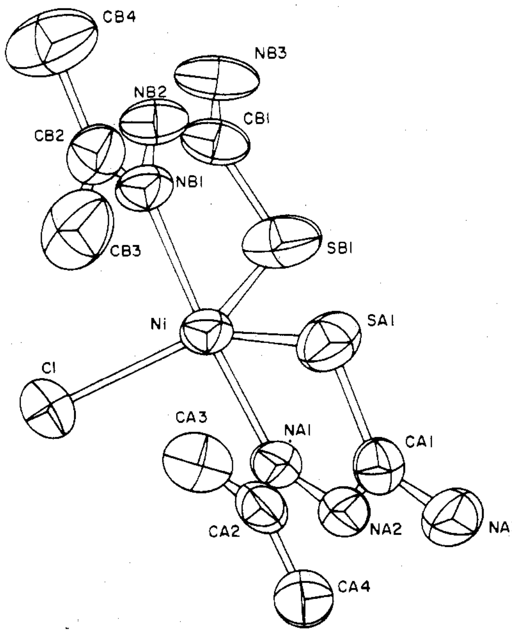

Figure 1. An ORTEP drawing for the $Ni(ATSC)_2Cl^+$ cation showing the atomic numbering and the thermal ellipsoids.

$[Ni(ATSC)_2NO_3]^+NO_3^- \cdot H_2O$. The unit cell dimensions and space group suggested that the nitrate salt was isomorphous with the chloride. A three-dimensional Patterson function confirmed that the salts were isomorphous. The parameters from the chloride salt were used as a trial structure and successive difference Fourier syntheses were used to locate the nitrate ions and water molecule. After three least-squares cycles using individual isotropic thermal parameters, R was 0.11. A block-diagonal approximation was used for the refinement with anisotropic thermal parameters. After four least-squares cycles, the R value was 0.067 and a difference Fourier synthesis was calculated to locate the hydrogen atoms. Although most of the hydrogen atoms were well defined, a number of spurious peaks were present especially in the area of the methyl groups and water molecule. Hydrogen positions were selected to give chemically reasonable bond distances and angles and their contributions were included in subsequent least-squares calculations. The hydrogen atom parameters were held constant during three more least-squares cycles. The R value of 0.061 was only slightly improved but some distances and angles changed significantly. The shifts in the parameters were less than 0.25 times the estimated standard deviations so the refinement was terminated. The final positional and thermal parameters for the nonhydrogen atoms are given in Table IV. An ORTEP drawing of the molecule showing the atomic numbering and thermal ellipsoids is given in Figure 2. The hydrogen atom parameters are given in Table V.[5]

The weighting scheme used in all the least-squares calculations was

$$\sqrt{w} = |F_o|/F(\text{low}) \text{ if } F_o < F(\text{low})$$

$$\sqrt{w} = 1 \text{ if } F(\text{low}) \leqslant |F_o| \leqslant F(\text{high})$$

$$\sqrt{w} = F(\text{high})/|F_o| \text{ if } F_o > F(\text{high})$$

where $F(\text{low})$ and $F(\text{high})$ were 16.0 and 32.0 for $[Ni(ATSC)_2Cl]^+Cl^- \cdot H_2O$ and 32.0 and 48.0 for $[Ni(ATSC)_2NO_3]^+NO_3^- \cdot H_2O$. The scattering factors were from ref 6 and the nickel atom was corrected for the

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[5] A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-446.

[6] "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

Table IV. Final Parameters and Their Estimated Standard Deviations in Parentheses for $[Ni(ATSC)_2NO_3]^+NO_3^-\cdot H_2O$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{23}	β_{12}	β_{13}	β_{23}
Ni	1484 (1)	212 (2)	0000 (0)	23 (1)	174 (4)	111 (2)	11 (3)	10 (3)	−4 (8)
SA1	1150 (2)	−952 (5)	1776 (4)	34 (1)	234 (9)	117 (4)	−46 (6)	11 (4)	−41 (11)
SB1	2249 (2)	−1737 (6)	−391 (6)	31 (1)	313 (11)	156 (7)	83 (6)	−13 (5)	−121 (14)
OC1	860 (4)	2453 (15)	−311 (12)	19 (3)	310 (27)	238 (20)	12 (12)	13 (13)	−40 (44)
OC2	1558 (5)	1872 (14)	−1486 (10)	31 (3)	281 (28)	133 (13)	1 (16)	−17 (10)	79 (33)
OC3	947 (6)	4063 (15)	−1881 (13)	58 (4)	215 (28)	294 (22)	13 (18)	−121 (15)	193 (41)
OD1	958 (9)	2486 (30)	5221 (21)	67 (7)	698 (68)	295 (30)	61 (43)	117 (25)	−221 (93)
OD2	576 (6)	5016 (26)	5074 (27)	38 (4)	735 (85)	540 (36)	194 (30)	−139 (27)	−657 (106)
OD3	1455 (5)	4881 (19)	4779 (16)	32 (2)	758 (42)	202 (20)	−57 (21)	59 (18)	−119 (65)
Ow	5367 (7)	1773 (25)	4310 (15)	90 (6)	921 (59)	264 (26)	−22 (33)	33 (20)	−38 (60)
NA1	813 (5)	−1467 (15)	−712 (13)	33 (3)	168 (26)	105 (16)	−17 (14)	−2 (12)	−58 (34)
NA2	400 (5)	−1916 (15)	134 (14)	18 (3)	306 (27)	119 (14)	−30 (15)	14 (13)	176 (45)
NA3	143 (5)	−2475 (20)	1990 (12)	38 (3)	358 (44)	81 (16)	−75 (20)	30 (13)	46 (39)
NB1	2108 (4)	1937 (16)	748 (11)	23 (3)	213 (29)	81 (14)	9 (15)	17 (10)	−2 (33)
NB2	2652 (5)	1468 (17)	339 (10)	27 (3)	402 (36)	77 (13)	39 (17)	−7 (10)	−98 (35)
NB3	3301 (4)	−460 (21)	−470 (11)	21 (3)	709 (56)	163 (19)	77 (22)	−12 (10)	−307 (56)
NC1	1132 (7)	2826 (18)	−1290 (17)	27 (5)	167 (34)	193 (21)	−39 (20)	−52 (17)	100 (44)
ND1	972 (9)	4162 (30)	5073 (21)	32 (5)	636 (71)	167 (22)	137 (42)	−47 (26)	−404 (97)
CA1	533 (8)	−1823 (23)	1273 (17)	44 (5)	222 (41)	103 (21)	0 (25)	8 (18)	121 (51)
CA2	679 (7)	−1877 (20)	−1799 (15)	36 (5)	153 (34)	112 (17)	44 (20)	−28 (16)	26 (41)
CA3	1129 (6)	−1470 (19)	−2727 (12)	37 (4)	411 (41)	63 (14)	40 (22)	−4 (14)	43 (41)
CA4	102 (7)	−2623 (25)	−2178 (15)	27 (5)	438 (57)	110 (25)	5 (29)	−36 (17)	5 (50)
CB1	2753 (6)	−171 (23)	−166 (16)	34 (4)	464 (51)	72 (17)	107 (27)	20 (16)	−141 (65)
CB2	2065 (6)	3316 (20)	1454 (12)	33 (4)	176 (34)	76 (15)	−6 (20)	16 (13)	18 (39)
CB3	1492 (6)	3823 (20)	1898 (15)	34 (3)	271 (38)	207 (23)	−25 (23)	29 (18)	−207 (51)
CB4	2558 (7)	4452 (19)	1907 (15)	48 (4)	457 (42)	129 (20)	18 (24)	−67 (17)	−74 (50)

[a] All values are ×10^4 and the temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table V. Final Parameters for the Hydrogen Atoms in $[Ni(ATSC)_2NO_3]^+NO_3^-\cdot H_2O$[a]

Atom [bonded to]	Distance	x	y	z	B
H1[NA2]	0.99	6	−236	−29	5.0
H2[NA3]	1.18	−33	−268	167	5.5
H3[NA3]	1.07	11	−261	292	5.5
H4[CA3]	1.15	93	−54	−344	6.0
H5[CA3]	1.18	111	−275	−338	6.0
H6[CA3]	0.84	148	−136	−256	6.0
H7[CA4]	1.14	11	−268	−317	6.0
H8[CA4]	1.01	−22	−171	−229	6.0
H9[CA4]	1.13	−6	−386	−167	6.0
H10[NB2]	1.01	293	229	77	5.0
H11[NB3]	0.90	338	−164	−67	5.5
H12[NB3]	1.09	364	11	6	5.5
H13[CB3]	1.15	133	482	119	7.5
H14[CB3]	0.75	127	314	208	7.5
H15[CB3]	1.16	147	479	271	7.5
H16[CB4]	0.85	259	500	125	7.5
H17[CB4]	1.05	274	321	219	7.5
H18[CB4]	0.94	260	500	265	7.5
H19[Ow]	1.23	494	189	495	7.5
H20[Ow]	1.28	566	321	458	7.5

[a] The hydrogen atom is given followed by the atom to which it is bonded in brackets, the corresponding bond distance (in Å), the positional parameters (×10^3), and the isotropic thermal parameters (in Å^2).

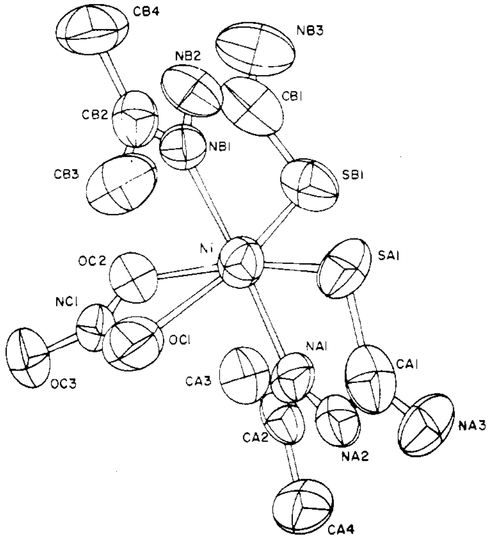

Figure 2. An ORTEP drawing for the $Ni(ATSC)_2NO_3^+$ cation showing the atomic numbering and the thermal ellipsoids.

real part of the anomalous scattering.[7] All calculations were carried out on an IBM-360 Model 75 computer.

Discussion

Both salts consist of a cation, anion, and water molecule held together by strong hydrogen bonds. The molecular packing for the chloride salt is given in Figure 3, with the nitrate salt being virtually identical, except for a nitrate group substituted for a chlorine atom. In both cases the ATSC functions as a neutral bidentate N,S ligand, with the coordination sphere around the nickel being completed with either a chloride or a nitrate ion. The distances and angles in the two salts are given in Table VI.

The $[Ni(ATSC)_2Cl]^+$ cation is best described as a trigonal bipyramid with Ni, SA1, SB1, and Cl1 in the equatorial plane and NA1 and NB1 in the axial positions. Although the atoms in the equatorial plane are coplanar, the various angles do differ by about ±13° from the ideal value of 120°. Similarly, the NA1-Ni-NB1 angle of 175.9 (2)° is smaller than 180° which is probably a consequence of the "bite" of the ATSC ligand. The ATSC ligands are not planar in the cation (Table VII) nor in the free ligand.[8] The C2-C3-C4 group is displaced away from the plane defined by N1-N2-N3-C1-S in a direction opposite from that of the nickel atom. The direction of the displacement results from steric effects related to the geometry of the complex.

The equatorial Ni-S and Ni-Cl bond distances are about 0.1 Å shorter than in octahedral complexes.[9] However,

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[7] D. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

[8] D. Rendle, G. J. Palenik, and W. S. Carter, unpublished results.

[9] L. Sacconi, *Transition Metal Chem.*, 4, 199 (1968), has summarized much of the structural data on nickel complexes.

Table VI. Bond Lengths (Å) and Bond Angles (deg) in the $[Ni(ATSC)_2X]^+X^- \cdot H_2O$ Salts

(a) Bond Lengths Involving the ATSC Ligands

	$NiCl(ATSC)_2$		$Ni(NO_3)(ATSC)_2$	
	A	B	A	B
Ni-S	2.290 (2)	2.315 (2)	2.337 (5)	2.315 (5)
Ni-N1	2.131 (5)	2.129 (5)	2.139 (12)	2.098 (11)
C1-S	1.710 (7)	1.698 (7)	1.674 (18)	1.650 (16)
C1-N2	1.323 (9)	1.324 (9)	1.344 (25)	1.337 (21)
C1-N3	1.311 (9)	1.326 (8)	1.313 (23)	1.339 (18)
N2-N1	1.384 (8)	1.397 (7)	1.405 (18)	1.392 (17)
N1-C2	1.267 (9)	1.283 (9)	1.319 (22)	1.286 (19)
C2-C3	1.481 (11)	1.485 (11)	1.523 (22)	1.475 (20)
C2-C4	1.487 (11)	1.478 (11)	1.511 (23)	1.504 (21)

(b) Bond Angles Involving the ATSC Ligands

	$NiCl(ATSC)_2$		$Ni(NO_3)(ATSC)_2$	
	A	B	A	B
N1-Ni-S	83.4 (2)	83.7 (2)	83.5 (4)	84.5 (3)
Ni-S-C1	98.9 (2)	96.7 (2)	96.9 (6)	96.0 (6)
S-C1-N2	120.9 (5)	122.9 (5)	123.5 (1.3)	123.1 (1.3)
S-C1-N3	120.7 (5)	121.0 (5)	120.9 (1.4)	122.1 (1.3)
N2-C1-N3	118.4 (6)	116.0 (6)	115.6 (1.5)	114.8 (1.4)
C1-N2-N1	121.7 (5)	120.7 (5)	120.1 (1.3)	121.5 (1.2)
N2-N1-Ni	113.7 (4)	112.3 (4)	111.6 (9)	110.5 (8)
N2-N1-C2	117.2 (5)	116.8 (5)	116.0 (1.2)	118.1 (1.2)
Ni-N1-C2	128.9 (5)	130.9 (5)	131.4 (1.0)	131.4 (1.0)
N1-C2-C3	118.6 (6)	119.3 (6)	117.0 (1.3)	118.7 (1.3)
N1-C2-C4	125.1 (6)	123.9 (7)	124.2 (1.4)	125.3 (1.3)
C3-C2-C4	116.4 (6)	116.7 (7)	118.8 (1.3)	115.9 (1.2)

(c) Coordination around Ni in $NiCl(ATSC)_2$

Ni-Cl1	2.305 (2)		
SA1-Ni-SB1	106.4 (1)	NA1-Ni-SB1	94.4 (2)
SA1-Ni-Cl1	120.4 (1)	NB1-Ni-SA1	93.6 (2)
SB1-Ni-Cl1	133.2 (1)	NB1-Ni-Cl1	92.7 (2)
NA1-Ni-Cl1	91.3 (2)	NB1-Ni-NA1	175.9 (2)

(d) Coordination around Ni in $Ni(NO_3)(ATSC)_2$

Ni-OC1	2.204 (10)	Ni-OC2	2.090 (11)
SA1-Ni-SB1	102.0 (2)	NB1-Ni-SA1	95.0 (3)
SA1-Ni-OC1	100.7 (3)	NB1-Ni-OC1	95.2 (4)
SB1-Ni-OC2	97.2 (3)	NB1-Ni-OC2	86.4 (4)
OC1-Ni-OC2	60.2 (4)	NB1-Ni-NA1	176.9 (5)
NA1-Ni-SB1	98.4 (4)	SA1-Ni-OC2	160.8 (3)
NA1-Ni-OC1	82.5 (5)	SB1-Ni-OC1	157.3 (3)
NA1-Ni-OC2	94.2 (4)		

(e) Dimensions of Nitrate Ion

NC1-OC1	1.317 (23)	OC1-NC1-OC2	115.6 (1.4)
NC1-OC2	1.229 (18)	OC1-NC1-OC3	117.4 (1.5)
NC1-OC3	1.200 (20)	OC2-NC1-OC3	127.1 (1.6)
ND1-OD1	1.220 (31)	OD1-ND1-OD2	121.7 (2.5)
ND1-OD2	1.111 (27)	OD1-ND1-OD3	117.4 (2.1)
ND1-OD3	1.285 (25)	OD2-ND1-OD3	120.4 (2.3)

there are no reported structures of a high-spin trigonal bipyramidal nickel complex with a 2 N, 2 S, 1 Cl donor set for a direct comparison. The best comparison appears to be with *N*-methyl-1,4-diazabicyclo[2.2.2]octonium trichloroaquonickelate(II),[10] where the average Ni-Cl(equatorial) distance of 2.320 Å and the axial Ni-N distance of 2.140 Å compare favorably with the values of Ni-Cl (2.305 Å) and Ni-N (average 2.130 Å) found in our study.

The $[Ni(ATSC)_2NO_3]^+$ ion appears to be a distorted octahedron with 2 S, 2 O, and 2 N atoms surrounding the central Ni atom. The Ni-S bond lengths are increased slightly (average 2.326 Å) but the Ni-N distances (average 2.12 Å) are virtually the same as in the chloro derivative. The larger bond distances usually found in octahedral complexes are not present in this case. Furthermore, to a first approximation, the $Ni(ATSC)_2$ skeleton is virtually the same in the two complexes. The main difference is that the displacements from planarity in the ATSC ligands are more pronounced in the nitrate compound. The two cations can almost be described as being trigonal bipyramidal with the NO_3^- ion occupying only one coordination site. The concept of the NO_3^- ion utilizing only one coordination site has been discussed in connection with other nitrato complexes[11,12] and may be a useful model in certain compounds.

The two NO_3^- ions are planar. The Ni atom is slightly displaced from the plane of the coordinated NO_3^- group. The NC1-OC3 distance is longer while the NC1-OC1 and NC1-OC2 distances appear shorter than the values usually founded in coordinated nitrato groups.[12] The reasons for this reversal of dimensions is not understood although the presence of hydrogen bonds to the nitrato group may influence the bond lengths. The ionic NO_3^- is not as symmetrical as would be expected but the large thermal motion which was evident in the electron-density maps may affect the distances. In addition, there are some indications of hydrogen bonds involving the NO_3^- ion which again could affect the bond distances.

In the uncomplexed ATSC ligand the S1 and N1 atoms are trans relative to the C1-N2 bond; however, the orientation must be cis if the molecule is to function as a bidentate chelating ligand. The C-S bond length increases slightly from 1.690 (5) Å in ATSC[8] to 1.704 (7) Å in $[Ni(ATSC)_2Cl]^+$ and 1.712 (6) Å in $ZnCl_2(ATSC)_2$.[13] Although the change is barely significant, the trend is in the anticipated direction of increasing the C-S bond length with coordination. In the $Ni(ATSC)_2NO_3^+$ ion the C-S bonds appear shorter (average 1.66 (2) Å) although the esd is sufficiently large to make the difference not significant. The remaining bond distances show only slight variations in the four compounds and none of the differences are significant. The major changes in the ATSC ligand after coordination are a rotation about the C1-N2 bond, a change in the planarity of the C2-C3-C4 grouping, and a slight increase in the C-S bond length. The approximate planarity of the ATSC ligand, together with the distances and angles in the molecule, accounts for the pentacoordinated geometry found in $[Ni(ATSC)_2Cl]^+$. The C3 or C4 methyl group blocks the coordination site trans to the Ni-S bond. The importance of the molecular dimensions is seen in the case of the acetone semicarbazone derivative where the octahedral $Ni[(CH_3)_2CNNHC(O)NH_2]_2(H_2O)_2{}^{2+}$ ion is formed.[14] The shorter Ni-O bond must relieve some of the steric effects of the methyl groups trans to the Ni-O bond since the remaining bond distances are virtually the same.

In each salt there are eight hydrogen atoms which could form hydrogen bonds and seven of these are definitely hydrogen bonded. The pertinent data have been summarized in Table VIII for both salts, with the packing for the chloride salt illustrated in Figure 3. The main feature of the crystalline arrangement is a network in the *XY* plane of hydrogen-bonded cations, anions, and water molecules involving six of the seven "good" hydrogen bonds. The seventh hydrogen bond, involving NA3-H3· · ·Ow, links the sheets together. The intermolecular contacts involving the eighth hydrogen atom, H11, appear to be simply van der Waals contacts between sheets. The H11· · ·SA1 distance of 2.85 Å is certain-

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Table VII. Least-Squares Planes for the $[Ni(ATSC)_2X]^+X^-\cdot H_2O$ Salts, $X^- = NO_3^-$ and Cl^- [a]

	$NiCl(ATSC)_2$			$Ni(NO_3)(ATSC)_2$			
Atom	I	II	III	IV	V	VI	VII
Ni	287	−495	−3*	434	−522	8*	−52
SA1	3*		1*	9*		14*	
NA1	−13*		−2118	−46*		−2097	
NA2	17*		−2513	61*		−2403	
NA3	−9*		−2111	−37*		−1971	
CA1	2*		−1657	13*		−1533	
CA2	−103		−3025	−205		−3084	
CA3	−125		−2634	−377		−2791	
CA4	−166		−4474	−156		−4445	
SB1		−2*	1*		−2*	−20*	
NB1		4*	2113		16*	2089	
NB2		−7*	2493		−20*	2409	
NB3		2*	2087		13*	1991	
CB1		4*	1624		−7*	1525	
CB2		297	3058		311	3051	
CB3		298	2717		358	2726	
CB4		606	4495		661	4514	
Cl1			1*				
OC1						−29*	2*
OC2						27*	2*
OC3						−62	2*
NC1						−29	−6*
			Parameters for the Planes[b]				
l	−5252	1862	6331	−4063	1930	6026	5735
m	8510	−4975	5915	9137	−4094	6268	6577
n	−0019	8472	4994	0126	8917	4917	4885
p	−1.6409	0.8820	2.4044	−1.7000	1.1269	2.1732	2.1366

[a] The deviations ($\times 10^3$) from the plane (in Å) are given for the specified atom. [b] Equation of the plane in the form: deviation (Å) $= lX + mY + nZ - p$ where X, Y, Z are the orthogonal coordinates (in Å) and p is the distance of the plane from the origin. The atoms used to define the plane are noted by an asterisk following the deviation.

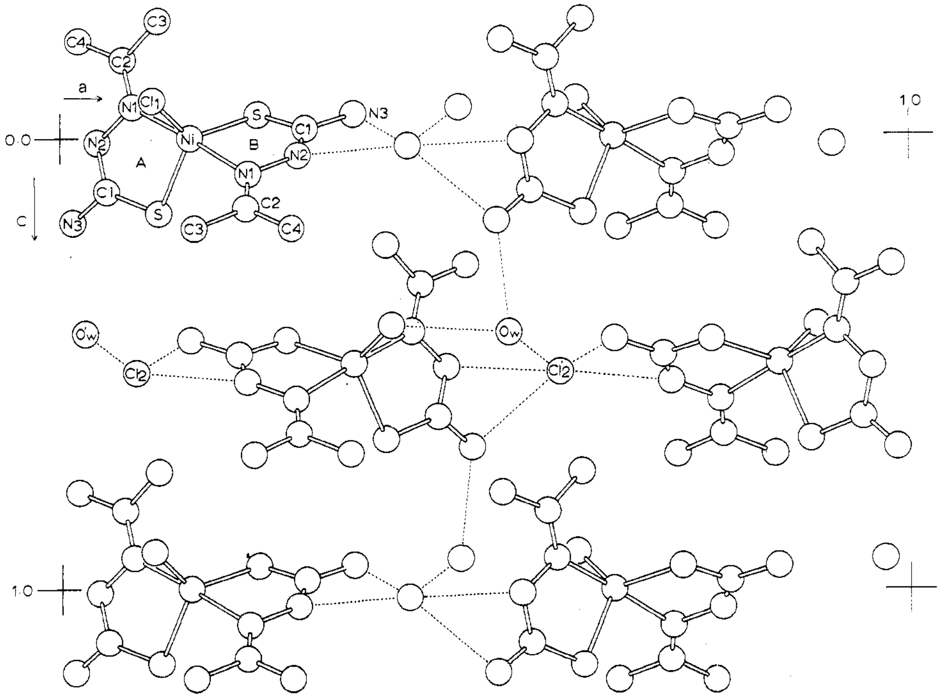

Figure 3. A projection down the *b* axis of the contents of the unit cell for $[Ni(ATSC)_2Cl]^+Cl^-\cdot H_2O$. The various hydrogen bonds are shown as dotted lines.

ly longer than the sum of the van der Waals radii of 2.75 Å, while the H11· · ·Ow distance of 2.49 Å is only slightly shorter than the expected van der Waals contact of 2.6 Å. The nitrate salt is a bit more complicated because of the nonspherical nature of the NO_3^- ion. The hydrogen bonds to the chloride ion in the chloro case become either strong hydrogen bonds involving the nitrate oxygens or just normal intermolecular contacts. For example, the NA3-H2· · ·Cl2 hydrogen bond is replaced by a strong hydrogen bond to OD1; however, the NA2-H1· · ·Cl2 contact is replaced by two interactions to OD1 and OD2 both of which are either weak bifurcated hydrogen bonds or just intermolecular contacts. A one to one correspondence can be made between the hydrogen atom contacts in the two salts except for the van der Waals contact between NA3 and OC3 which must arise because of the slightly larger nature of the nitrato group.

Table VIII. Hydrogen Bonds and Short Contacts in $[Ni(ATSC)_2X]^+X^-\cdot H_2O$ Salts, $X^- = NO_3^-$ and Cl^-

Bond D-H···A[a]	Position of A	D-H, Å	H···A, Å	D···A, Å	D-H···A, deg
	(a) $NiCl_2(ATSC)_2\cdot H_2O$				
NA2-H1···Cl2	B(00$\bar{1}$)	1.02	2.43	3.298 (5)	143
NA3-H2···Cl2	B(00$\bar{1}$)	0.92	2.35	3.230 (6)	162
NA3-H3···Ow	D($\bar{1}$00)	0.83	2.17	2.927 (9)	152
NB2-H10···Cl2	C(00$\bar{1}$)	0.99	2.27	3.223 (6)	163
NB3-H12···Cl2	C(00$\bar{1}$)	1.13	2.19	3.245 (8)	154
Ow-H19···Cl1	C(000)	0.89	2.29	3.166 (6)	168
Ow-H20···Cl2	D(010)	0.85	2.42	3.164 (6)	147
NB3-H11···Ow	B(10$\bar{1}$)	1.05	2.49	3.072 (8)	114
NB3-H11···SA1	C(00$\bar{1}$)	1.05	2.85	3.380 (7)	111
	(b) $Ni(NO_3)_2(ATSC)_2\cdot H_2O$				
NA2-H1···OD1	B(00$\bar{1}$)	0.99	2.44	3.194	133
NA2-H1···OD2	B(00$\bar{1}$)	0.99	2.45	3.190	131
NA3-H2···OD1	B(00$\bar{1}$)	1.18	2.21	3.271	147
NA3-H3···Ow	D(000)	1.07	1.81	2.758	145
NB2-H10···OD1	C(00$\bar{1}$)	1.01	2.67	3.328	123
NB2-H10···OD3	C(00$\bar{1}$)	1.01	2.61	3.287	124
NB3-H12···OD1	C(00$\bar{1}$)	1.09	1.96	2.852	137
Ow-H19···OC1	C(000)	1.23	1.94	2.935	134
Ow-H20···OD2	D(010)	1.28	1.41	2.522	140
NB3-H11···Ow	B(10$\bar{1}$)	0.90	2.93	3.257	105
NB3-H11···SA1	C(00$\bar{1}$)	0.90	3.17	3.426	99
NA3-H2···OC3	B(000)	1.18	2.41	3.074	114
NA3-H3···OC3	B(000)	1.07	2.69	3.074	101

[a] Donor-hydrogen···acceptor. D-H at x, y, z. (A) x, y, z; (B) $\bar{x}, \bar{y}, {}^1/_2 + z$; (C) ${}^1/_2 - x, y, {}^1/_2 + z$; (D) ${}^1/_2 + x, \bar{y}, z$. The numerals after the molecular designation give the unit cell translations in the order a, b, c.

In summary, we see that ATSC is capable of functioning as a bidentate, chelating S,N ligand, with resulting severe steric constraints. The question of whether a more bulky ketone would lead to tetrahedral complexes while aldehydes might give octahedral complexes is being pursued. In addition, the soft-hard combination of donor atoms might be utilized to prepare complexes of heavier transition elements in unusual or distorted geometries.

Registry No. $[Ni(ATSC)_2X]^+X^-\cdot H_2O$ (X = Cl), 25087-96-1; $[Ni(ATSC)_2X]^+X^-\cdot H_2O$ ($X = NO_3$), 37523-49-2.

Acknowledgment. We wish to thank the National Research Council of Canada and the U. S. Public Health Service, National Cancer Institute (Grant CA-12390), for partial financial support of this research which was carried out, in part, at the University of Waterloo, Waterloo, Ontario, Canada.

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Chelative Addition of Hydrazines to Coordinated Isocyanides. The Structure of Chugaev's Red Salt

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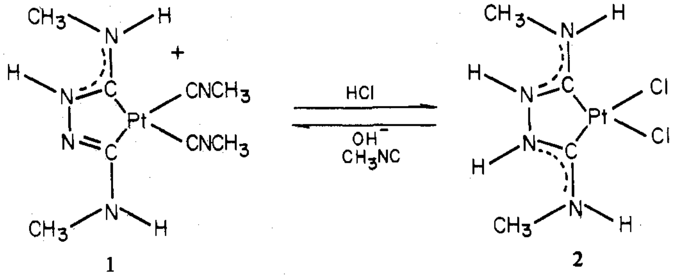
Received August 23, 1972

The structures of the monocations produced by the addition of hydrazines to $(CH_3NC)_4M^{2+}$ (M = Pd, Pt) have been elucidated by X-ray diffraction and nuclear magnetic resonance data. The compound $[(C_4H_8N_4CH_3)Pt(CNCH_3)_2][B(C_6H_5)_4]$, which was prepared by adding methylhydrazine to $(CH_3NC)_4Pt^{2+}$, crystallizes in the space group $C2/c$ with eight molecules in a unit cell of $a = 25.64$ (2), $b = 12.23$ (1), $c = 21.34$ (1) Å; $\beta = 105.5$ (2)°. The observed and calculated densities are 1.52 (2) and 1.489 (2) g cm^{-3}, respectively. Full-matrix least-squares refinement of the structure has resulted in $R = 0.053$ for the 1563 data having $F_o^2 > 3\sigma(F_o^2)$. The Pt atom is coordinated by two methyl isocyanide ligands and by two C atoms of the $(CH_3)_3N_4H_2C_2^-$ chelating ligand formed by the addition of methylhydrazine to two methyl isocyanide ligands. The entire cation is nearly planar, but steric interactions result in angular distortions within the plane. The Pt-C(chelate) distances are 1.95 (2) and 2.06 (3) Å; the average Pt-$CNCH_3$ distance is 1.96 (2) Å. The distances in the chelate ring are C-N = 1.24 (3) and 1.32 (2) Å and N-N = 1.45 (2) Å. The H atoms were not located directly, but the C-N distances and the nmr spectra show that a proton has been lost from an N atom of the chelate ring. In acidic media the N atom can be protonated to yield cations of the type $[(C_4H_9N_4R)M(CNCH_3)_2]^{2+}$ which have been isolated and characterized by their nmr spectra.

Introduction

Some years ago Chugaev and coworkers reported that hydrazine reacts with isocyanide complexes of Pt(II) to yield bright red compounds for which binuclear, hydrazine-bridged structures were proposed.[2] These complexes were converted by treatment with hydrochloric acid into yellow compounds which could be transformed back to the red forms by treatment with isocyanide and base.[2] Recent investigations have revealed that these complexes are formed by the chelative addition of hydrazine to coordinated isocyanide and that the red and yellow complexes should be formulated as 1 and 2, respectively. The assignment of structure 2 to Chugaev's yellow compound is supported by the X-ray structure deter-



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