

The Crystal Structures of Tris(thiosemicarbazido)nickel(II) Nitrate and its Monohydrate

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Tris(thiosemicarbazido)nickel nitrate has been prepared in two crystalline modifications, one of which is a monohydrate. Three dimensional X-ray analyses have shown that the complex ion has the same configuration in the two forms. Nickel is octahedrally surrounded by three sulfur atoms and three terminal nitrogen atoms from the hydrazine groups. The sulfur atoms are *cis* to one another. The average distances in the octahedron are: Ni—S 2.40 Å, Ni—N 2.12 Å. In the anhydrous form one Ni—S bond is significantly longer than the others. The packing of positive and negative ions is different in the two compounds. The unit cell dimensions are for the monohydrate: orthorhombic, $a = 9.43(2)$ Å, $b = 15.71(3)$ Å, $c = 11.77(2)$ Å, space group $Pna2_1$. The anhydrous form: monoclinic, $a = 14.64(3)$ Å, $b = 9.77(2)$ Å, $c = 11.68(2)$ Å, $\beta = 101.6(2)^\circ$. Space group $P2_1/a$. After least squares refinement the R -values are 0.053 and 0.043 for 1273 and 3091 reflections, respectively.

This investigation belongs to a series of structure determinations of nickel complexes with thiosemicarbazide. The purpose is to obtain reliable bond lengths for *trans* planar,¹⁻³ *cis* planar,^{2,3} *trans* octahedral,⁴ and *cis* octahedral complexes of the same ligand to support theoretical work on the bonding in such complexes. The occurrence of two different sorts of crystals in one preparation of tris(thiosemicarbazido)nickel nitrate gave a suspicion of *cis-trans* isomerism, and we had to solve both structures to establish what was the actual difference between the two sorts of crystals.

EXPERIMENTAL

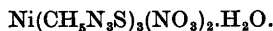
Alcoholic solutions of the stoichiometric amounts of thiosemicarbazide and of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were mixed and left to eva-

porate. Deep-blue crystals of composition $\text{Ni}(\text{CH}_5\text{N}_3\text{S})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ formed. The water could be removed when the crystals were heated to 150 °C for some hours. The crystals were destroyed by this treatment and the product was not the same as the anhydride mentioned below.

In one preparation some of the crystals that had formed first on the sides of the beaker were of a slightly different colour from that of the main product. There were not enough of these crystals to allow a chemical analysis, and no later preparation contained any of this sort. The structure analysis showed that the formula was $\text{Ni}(\text{CH}_5\text{N}_3\text{S})_3(\text{NO}_3)_2$.

Unit cell dimensions and space groups were obtained from rotation and equi-inclination Weissenberg films taken with $\text{CuK}\alpha$ radiation ($\lambda_{\text{Cu}} = 1.5418$ Å) and from precession exposures taken with $\text{CuK}\alpha$ and $\text{MoK}\alpha$ radiation ($\lambda_{\text{Mo}} = 0.7107$ Å). Intensities were collected by means of an automatic diffractometer of Arndt-Phillips design⁵ using Mo radiation and balanced filter technique together with pulse height discrimination. Later another set of data was collected for another crystal of the anhydrous compound using the same diffractometer but crystal monochromatized $\text{MoK}\alpha$ radiation. Data were collected to $\sin \theta/\lambda = 0.7$ giving 1273 significant out of 2942 reflections for the monohydrate, 3091 significant out of 4379 for the anhydrous compound. The linear dimensions of the crystals used were all of the order of 0.2–0.3 mm. No absorption correction was applied because the crystals were so equidimensioned and the absorption factors reasonably small.

CRYSTAL DATA



Orthorhombic.

$a = 9.43(2)$ Å; $b = 15.71(3)$ Å; $c = 11.77(2)$ Å;
 $V = 1742$ Å³.

$d_c = 1.81$ g/cm³ for 4 formula units per unit cell.

Table 1. Final coordinates for the monohydrate, $\text{Ni}(\text{CH}_5\text{N}_3\text{S})_3(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, in fractions of the unit cell, standard deviations $\times 10^4$ in parentheses. Hydrogen atom positions were calculated and not refined. Their temperature factor parameters B were kept at 5.0 \AA^2 .

	<i>x</i>	<i>y</i>	<i>z</i>
Ni	0.0487(1)	0.0082(1)	0.0021(3)
S(1)	0.0616(3)	0.1335(2)	0.1154(4)
S(2)	0.2257(3)	-0.0666(2)	0.1054(3)
S(3)	-0.1377(3)	-0.0525(2)	0.1150(4)
C(1)	-0.0869(12)	0.1814(7)	0.0614(13)
C(2)	0.3693(12)	-0.0214(7)	0.0413(14)
C(3)	-0.1423(11)	-0.1490(6)	0.0460(11)
N(11)	-0.0950(9)	0.0839(5)	-0.0927(9)
N(12)	0.2282(9)	0.0470(6)	-0.1001(9)
N(13)	0.0107(9)	-0.0981(6)	-0.1019(10)
N(21)	-0.1556(10)	0.1517(6)	-0.0276(10)
N(22)	0.3591(11)	0.0325(7)	-0.0413(12)
N(23)	-0.0641(11)	-0.1648(6)	-0.0453(10)
N(31)	-0.1384(10)	0.2515(6)	0.1106(12)
N(32)	0.4989(10)	-0.0411(8)	0.0810(13)
N(33)	-0.2237(11)	-0.2120(6)	0.0864(11)
N[O(1)]	0.1244(12)	0.3465(6)	0.3055(10)
O(1)	0.2240(10)	0.3115(6)	0.3585(10)
O(2)	0.1519(14)	0.4072(7)	0.2456(13)
O(3)	0.0030(9)	0.3166(6)	0.3192(11)
N[O(2)]	-0.0346(12)	0.7121(7)	0.3163(11)
O(4)	-0.1252(10)	0.7575(6)	0.3634(11)
O(5)	-0.0448(17)	0.6361(7)	0.3253(16)
O(6)	-0.0534(15)	0.7490(11)	0.2568(14)
O(7)	-0.1818(11)	0.4548(6)	0.3387(12)
H(111)	-0.179	0.045	-0.123
H(112)	-0.038	0.111	-0.164
H(121)	0.218	0.114	-0.121
H(122)	0.229	0.011	-0.178
H(131)	0.114	-0.123	-0.129
H(132)	-0.047	-0.078	-0.175
H(211)	-0.255	0.180	-0.050
H(221)	0.450	0.070	-0.064
H(231)	-0.059	-0.230	-0.074
H(311)	-0.100	0.266	0.170
H(312)	-0.230	0.280	0.070
H(321)	0.513	-0.070	0.150
H(322)	0.580	-0.010	0.050
H(331)	-0.270	-0.195	0.160
H(332)	-0.233	-0.270	0.050

$\mu(\text{CuK}\alpha) = 132.1 \text{ cm}^{-1}$, $\mu(\text{MoK}\alpha) = 37.8 \text{ cm}^{-1}$.

Systematic absences: $0kl$ for $k+l$ odd

$h0l$ for h odd

Space group $Pna2_1$ from systematic absences and the piezoelectric effect.

Final atomic coordinates and temperature factor parameters are given in Tables 1 and 2, and bond lengths and angles in Table 5.

$\text{Ni}(\text{CH}_5\text{N}_3\text{S})_3(\text{NO}_3)_2$

Monoclinic, b unique.

$a = 14.64(3) \text{ \AA}$; $b = 9.77(2) \text{ \AA}$; $c = 11.68(2) \text{ \AA}$;

$\beta = 101.6(2)^\circ$; $V = 1636 \text{ \AA}^3$.

$d_c = 1.85 \text{ g/cm}^3$ for 4 formula units per unit cell.

$\mu(\text{CuK}\alpha) = 138.9 \text{ cm}^{-1}$, $\mu(\text{MoK}\alpha) = 40.1 \text{ cm}^{-1}$.

Systematic absences: $h0l$ for h odd

$0k0$ for k odd

Space group: $P2_1/a$.

Final atomic coordinates and temperature factor parameters are given in Tables 3 and 4, and bond lengths and angles in Table 5. Structure factor tables can be obtained from the author on request.

Table 2. Temperature factor parameters, u_{ij} , for the monohydrate in Å² × 10⁻⁴ with standard deviations in parentheses. The expression for the temperature factor is: $\exp[-2\pi^2(u_{11}(ha^*)^2 + \dots + 2u_{23}k lb^*c^*)]$

	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Ni	305(6)	318(6)	486(6)	-11(6)	1(10)	1(8)
S(1)	314(14)	344(13)	545(15)	5(11)	-41(16)	13(14)
S(2)	370(14)	404(14)	617(19)	26(11)	-98(17)	24(16)
S(3)	367(14)	321(13)	566(16)	-38(11)	109(16)	-82(15)
C(1)	373(64)	356(58)	784(91)	28(48)	-125(65)	107(62)
C(2)	286(63)	521(69)	886(118)	-66(58)	-55(66)	-48(76)
C(3)	355(61)	273(50)	622(81)	2(50)	-102(63)	-101(54)
N(11)	389(50)	390(50)	538(59)	1(40)	-189(47)	12(46)
N(12)	355(49)	565(59)	403(53)	-101(46)	2(48)	40(48)
N(13)	404(51)	424(50)	538(55)	-58(41)	-43(47)	-29(48)
N(21)	472(58)	421(53)	821(87)	53(46)	-205(61)	51(53)
N(22)	412(60)	663(66)	942(97)	-183(59)	100(66)	156(69)
N(23)	472(58)	394(50)	876(83)	12(44)	132(61)	-168(52)
N(31)	584(62)	491(51)	959(80)	259(52)	-80(74)	-48(71)
N(32)	299(53)	1182(94)	992(116)	71(62)	-41(65)	-31(92)
N(33)	674(68)	494(53)	771(79)	-194(49)	107(64)	-93(56)
N[O(1)]	623(74)	350(55)	613(68)	-71(53)	-30(64)	-35(50)
O(1)	651(63)	807(66)	990(91)	-173(51)	-238(65)	234(61)
O(2)	1344(112)	705(68)	1351(113)	-136(72)	166(89)	474(78)
O(3)	456(54)	511(54)	1194(86)	-41(41)	-21(57)	-59(57)
N[O(2)]	408(66)	693(78)	759(77)	53(58)	-30(65)	-144(63)
O(4)	552(57)	745(61)	1068(79)	-89(50)	120(61)	-171(61)
O(5)	1895(150)	455(65)	2129(169)	245(79)	-1293(139)	-147(79)
O(6)	888(91)	2198(155)	1216(108)	-236(103)	480(89)	-517(119)
O(7)	965(78)	858(68)	1260(102)	485(58)	407(76)	388(70)

Table 3. Final coordinates for the anhydrous compound, Ni(CH₃N₃S)₃·2NO₃, in fractions of the unit cell, standard deviations × 10⁴ in parentheses. For hydrogen atoms isotropic temperature factor parameters, B , are also given.

	x	y	z	B
Ni	0.3512(0.3)	0.1781(0.4)	0.2185(0.4)	
S(1)	0.1816(1)	0.1997(1)	0.1743(1)	
S(2)	0.3723(1)	0.3474(1)	0.0786(1)	
S(3)	0.3524(1)	-0.0107(1)	0.0870(1)	
C(1)	0.1635(3)	0.0562(3)	0.2494(3)	
C(2)	0.3535(2)	0.4842(3)	0.1597(3)	
C(3)	0.4656(2)	-0.0504(3)	0.1291(3)	
N(11)	0.3216(2)	0.0470(3)	0.3477(2)	
N(12)	0.3619(2)	0.3497(2)	0.3319(2)	
N(13)	0.4944(2)	0.1285(3)	0.2717(3)	
N(21)	0.2301(2)	-0.0039(3)	0.3254(3)	
N(22)	0.3519(2)	0.4757(3)	0.2726(3)	
N(23)	0.5246(2)	0.0197(3)	0.2098(3)	
N(31)	0.0800(2)	0.0004(4)	0.2331(4)	
N(32)	0.3419(3)	0.6085(3)	0.1119(3)	
N(33)	0.5009(2)	-0.1566(3)	0.0809(3)	
N[O(1)]	-0.0492(2)	0.7464(3)	0.4305(3)	
O(1)	-0.1111(2)	0.7406(3)	0.3423(3)	
O(2)	-0.0076(2)	0.6425(3)	0.4705(3)	
O(3)	-0.0328(3)	0.8566(3)	0.4795(4)	

Table 3. Continued.

N[O(2)]	0.1881(2)	0.6634(3)	0.3740(3)	
O(4)	0.1911(2)	0.5396(3)	0.3970(3)	
O(5)	0.1685(2)	0.7003(3)	0.2698(3)	
O(6)	0.2063(3)	0.7498(3)	0.4537(3)	
H(111)	0.359(3)	-0.030(5)	0.348(4)	4.2(1.2)
H(112)	0.333(3)	0.085(5)	0.425(4)	2.4(1.1)
H(121)	0.305(3)	0.351(4)	0.370(3)	2.5(0.9)
H(122)	0.411(3)	0.352(4)	0.382(4)	3.4(1.0)
H(131)	0.537(3)	0.209(5)	0.260(4)	4.9(1.3)
H(132)	0.507(3)	0.098(4)	0.348(3)	2.5(1.0)
H(211)	0.224(3)	-0.077(4)	0.366(3)	2.3(0.9)
H(221)	0.351(3)	0.547(4)	0.316(3)	1.3(0.9)
H(231)	0.587(3)	-0.004(4)	0.239(3)	2.2(0.9)
H(311)	0.073(3)	-0.069(5)	0.270(4)	3.8(1.2)
H(312)	0.029(3)	0.037(5)	0.174(4)	4.9(1.2)
H(321)	0.331(3)	0.673(4)	0.158(4)	3.5(1.0)
H(322)	0.334(3)	0.623(5)	0.031(4)	4.4(1.3)
H(331)	0.462(3)	-0.209(5)	0.014(4)	4.2(1.3)
H(332)	0.557(3)	-0.167(4)	0.106(4)	2.8(0.9)

Table 4. Temperature factor parameters, u_{ij} , for the anhydride in $\text{Å}^2 \times 10^{-4}$ with standard deviations in parentheses.

	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Ni	238(2)	286(2)	64(2)	28(2)	9(2)	-27(2)
S(1)	250(4)	331(3)	29(5)	47(3)	23(4)	36(3)
S(2)	362(5)	362(4)	81(4)	25(4)	74(4)	-32(4)
S(3)	255(5)	395(4)	388(5)	20(4)	5(4)	-126(4)
C(1)	291(19)	404(16)	436(22)	16(15)	59(16)	65(16)
C(2)	277(18)	302(13)	288(18)	-40(13)	17(14)	-11(13)
C(3)	268(18)	297(13)	357(19)	17(13)	107(15)	25(13)
N(11)	294(16)	356(12)	313(16)	37(12)	-1(13)	38(12)
N(12)	363(17)	295(11)	283(15)	51(12)	13(13)	-10(11)
N(13)	249(15)	393(13)	364(17)	15(12)	-17(13)	-61(13)
N(21)	358(18)	355(13)	489(20)	-38(13)	18(15)	138(14)
N(22)	479(19)	276(12)	292(16)	35(13)	80(14)	-31(11)
N(23)	223(15)	392(13)	456(18)	48(12)	21(13)	-31(13)
N(31)	314(20)	866(26)	1031(34)	-178(20)	-37(21)	473(25)
N(32)	752(26)	340(13)	375(19)	-28(15)	176(18)	22(13)
N(33)	266(19)	426(15)	560(21)	53(14)	146(16)	-101(15)
N[O(1)]	528(22)	346(13)	549(22)	-46(15)	-194(17)	37(14)
O(1)	866(25)	466(14)	559(20)	-121(16)	-355(18)	102(14)
O(2)	648(21)	437(13)	600(20)	127(14)	-119(16)	95(13)
O(3)	1593(45)	454(17)	1617(42)	150(22)	-1133(35)	-334(22)
N[O(2)]	427(20)	507(16)	428(19)	-121(15)	104(16)	15(15)
O(4)	621(20)	473(13)	551(19)	-8(14)	109(15)	37(13)
O(5)	811(25)	736(19)	444(18)	-275(18)	-86(17)	126(16)
O(6)	1209(32)	566(16)	465(19)	-270(19)	306(19)	-100(15)

STRUCTURE DETERMINATION

Both structures were solved by Patterson and Fourier methods. For the monohydrate a few cycles of Fourier refinement were needed before the positions of all the oxygen atoms were determined; temperature factors after refinement show that the nitrate groups in

this compound oscillate considerably although they do not have a free rotation.

Refinement proceeded by the method of least squares. With anisotropic temperature factors the R -values, ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) decreased to 0.07–0.08 at which stage difference Fourier maps were calculated.

Table 5. Bond lengths and angles in tris(thiosemicarbazido)nickel nitrate. M indicates the anhydrous form, O the monohydrate. The three thiosemicarbazido groups of each complex are designated by numbers 1, 2, and 3 corresponding to the second digit of atom identifiers on Figs. 1 and 2.

Bond	M1	M2	M3	O1	O2	O3
Ni-S	2.441(1)	2.389(1)	2.402(1)	2.380(4)	2.376(4)	2.400(4)
Ni-N(1)	2.089(3)	2.123(3)	2.120(3)	2.119(9)	2.163(10)	2.101(10)
S-C	1.703(4)	1.693(3)	1.677(3)	1.712(12)	1.705(13)	1.721(11)
C-N(2)	1.317(4)	1.323(4)	1.333(4)	1.317(18)	1.292(16)	1.326(17)
C-N(3)	1.317(5)	1.333(4)	1.333(5)	1.336(16)	1.344(16)	1.339(14)
N(1)-N(2)	1.404(4)	1.405(4)	1.406(4)	1.430(14)	1.433(14)	1.428(14)
N-O	{ 1.229(4)	{ 1.226(4)	{ 1.220(5)	{ 1.255(15)	{ 1.213(16)	{ 1.247(14)
	{ 1.238(4)	{ 1.247(4)	{ 1.245(4)	{ 1.243(16)	{ 1.202(16)	{ 1.231(20)
N(1)-H(1)	{ 0.93(5)	{ 0.83(4)	{ 0.92(4)			
N(2)-H(2)	{ 0.95(4)	{ 1.02(4)	{ 1.03(5)			
N(3)-H(3)	{ 0.87(4)	{ 0.86(4)	{ 0.93(4)			
	{ 0.82(5)	{ 0.86(4)	{ 0.82(4)			
	{ 0.98(4)	{ 0.94(5)	{ 1.01(5)			
Angle						
S-Ni-N(1)	81.8(1)	82.9(1)	83.0(1)	82.2(3)	82.8(3)	83.2(3)
Ni-N(1)-N(2)	114.3(2)	113.4(2)	114.7(2)	113.0(7)	110.5(8)	113.3(8)
Ni-S-C	94.4(1)	96.1(1)	97.1(1)	96.5(5)	97.1(5)	91.5(5)
S-C-N(2)	122.9(3)	123.0(2)	123.4(3)	122.8(9)	122.2(9)	122.6(8)
N(1)-N(2)-C	121.2(3)	121.6(3)	121.7(3)	119.6(9)	123.4(10)	121.0(9)
N(2)-C-N(3)	117.0(3)	116.6(3)	116.6(3)	117.4(11)	120.5(12)	117.4(10)
S-C-N(3)	120.2(3)	120.4(3)	120.0(2)	119.9(11)	117.2(11)	119.9(9)

They confirmed the presence of hydrogen atoms at approximately the expected positions. The introduction of these hydrogen atoms lowered the *R*-values considerably and further least squares refinement gave some changes in the positions of the atoms to which the hydrogen atoms were attached. The final *R*-values were 0.053 for both compounds for 1788 and 1273 significant reflections for the anhydride and monohydrate, respectively. At this point one Ni-S bond in the anhydrous compound seemed definitely longer than the others but since no obvious explanation for this was found, another crystal was selected and a new set of data measured in order to safeguard against accidentally introduced errors. The refinement with the new data proceeded to *R* = 0.043 for 3091 reflections and gave nearly the same coordinates as had been found with the first set of data.

In the latest refinements reflections for which $F_o^2 < 2\sigma(F^2)_{\text{count}}$ were left out of the *R*-values and of the least squares totals. The standard deviations found from counting statistics were found not to account for all errors and for the weighting of reflections for the least squares

refinement they were modified: $\sigma(F^2) = \sigma(F^2)_{\text{count}} + \alpha F^2$; $w = 1/[\sigma(F^2) + F^2]^2 - |F|^2$; α is a parameter which was adjusted so that the average of $w[|F_o| - |F_c|]^2$ was nearly independent of $|F|$. The final values for α were 0.05 for the monohydrate and 0.024 for the anhydrous, monoclinic form.

The scattering curves used were those of Table A of International Tables.⁶ Anomalous dispersion effects for the nickel atoms were taken into account. The data for the acentric monohydrate had been collected from two symmetry related octants and the two possible polarities had to be tried, one gave a significantly better fit than the other.

At the end of refinement an extinction parameter was introduced according to formula 3 in Larson's paper.⁷ Little improvement was achieved and the extinction parameters are small in both cases.

DISCUSSION

The NiThio₃²⁺ ions have the all *cis* configuration in both compounds. The average Ni-S distance of 2.40 Å agrees well with that in

Table 6. Intermolecular contacts.

Anhydride		Monohydrate	
N(11)–O(1)	2.982	N(11)–O(7)	3.037
N(11)–O(4)	3.026	N(12)–O(2)	3.069
N(12)–O(3)	2.983	N(13)–O(1)	2.911
N(12)–O(6)	3.037	N(21)–O(4)	2.945
N(13)–O(2)	2.982	N(22)–O(5)	2.860
N(21)–O(6)	2.893	N(23)–O(1)	2.976
N(22)–O(1)	2.910	N(23)–O(3)	2.921
N(23)–O(4)	2.985	N(31)–O(3)	2.980
N(23)–O(5)	2.992	N(33)–O(6)	2.963
N(31)–O(5)	3.199	O(7)–O(3)	2.792
N(32)–O(1)	3.025	N(12)–S(3)	3.460
N(33)–O(5)	2.982	N(13)–S(1)	3.442
N(32)–S(1)	3.409	N(31)–S(1)	3.356
N(31)–S(2)	3.536	N(32)–S(3)	3.453
N(32)–S(3)	3.490	O(7)–S(2)	3.375

NiThio₂(H₂O)₂(NO₃)₂^a (2.41 Å), and the mean distance in NiThio₂Cl₂·H₂O^a (2.41 Å). In the latter compound the three sulfur atoms are located in an equatorial plane whereas in both compounds of the present investigation the sulphur atoms are found at the corners of a face of the octahedron. Within the accuracy of the two investigations this does not lead to any differences in bond lengths. In the chloride

there are differences between Ni–S bond lengths but standard deviations are so high that no conclusion can be drawn. In the monohydrate the three Ni–S bonds are also equal within experimental error, whereas the anhydrous form has one long and two short bonds. Several unsuccessful attempts have been made to get the structure out of a suspected false minimum but the two different sets of data for this compound gave the same results within the standard deviations. We are thus led to believe that the complex does exist in a symmetric and a slightly distorted form. The difference in colour of the two sorts of crystals may be related to this fact. The dimensions of the thiosemicarbazide are similar in all six independent ligands and are also similar to those found in related complexes,^{4,5} thus offering no explanation of the distortion.

The only feature of the structure that would seem to give an indication is the fact that a nitrogen atom is found only 3.41 Å from the sulfur atom of the long bond and with a hydrogen atom pointing exactly towards sulfur. This could indicate some degree of hydrogen bonding, a hypothesis which is corroborated by the fact that this bond forms angles of about 100° with the Ni–S and C–S bonds. N–S

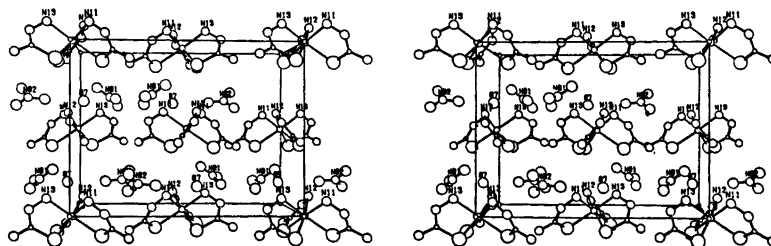


Fig. 1. The structure of nickel trithiosemicarbazide dinitrate monohydrate viewed along *a*.

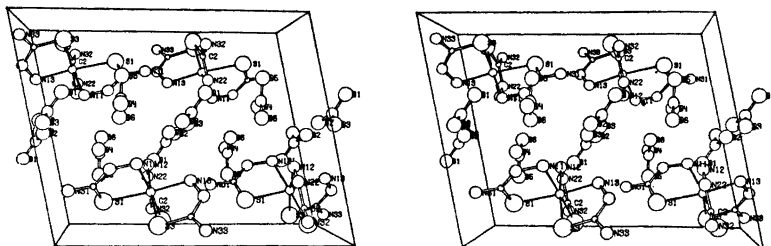


Fig. 2. The structure of anhydrous nickel trithiosemicarbazide dinitrate viewed along *a*.

contacts of similar length (see Table 6) are found as the other sulfur atoms but in those cases the hydrogen atoms are not so close to the line N—S. The Ni—S bond seems to be sensitive to changes in the coordination of the sulfur atom as evidenced by the difference between the bonds in dichlorotetrakis-thiourea-nickel(II),⁹ 2.46 Å, and those in bis-thiourea-nickel(II) thiocyanate,¹⁰ 2.53 Å and 2.56 Å, where each sulfur atom is coordinated to two nickel atoms. We might therefore take the long bond in the present compound as an indication of a relatively strong N—H...S hydrogen bond.

Table 6 also shows that there are a number of weak N—H...O hydrogen bonds in both structures though not all hydrogen atoms are involved in these. The water molecule in the monohydrate is probably contributing to the hydrogen bonding but the hydrogen atoms could not be located in this investigation. The nitrate groups have large thermal movements, but the hydrogen bonding and in the case of the anhydrous compound close distances between nitrate groups prevent actual rotation.

Ballard *et al.*⁸ noticed that the S—C bond was longer in octahedral thiosemicarbazide nickel complexes than in planar ones, though barely significantly when only one structure of each sort was considered, but from a comparison of the planar complexes in Refs. 1, 2, and 3 with the octahedral ones in Refs. 4 and 8 and the present investigation and also with free thiosemicarbazide^{11,12} it is found that the π -bonding that takes place in the planar complexes leads to a lengthening of the S—C bond by 0.03 Å and the N—N bond by 0.01–0.02 Å, whereas differences between free and octahedrally bonded thiosemicarbazide are insignificant. To decreasing π -bond character in the S—C bond corresponds shorter C—N bonds ($\Delta(\text{C—N}_2) \sim 0.015$ Å, $\Delta(\text{C—N}_1) \sim 0.03$ Å). Although the smaller differences are not highly significant, the effect is probably real.

Both structures contain layers of positive ions alternating with layers of anions. In the monohydrate these layers are only one molecule thick (Fig. 1), whereas those of the anhydrous compound are twice as thick (Fig. 2), the complex cations packing with their sulfur sides together.

Acknowledgements. Thanks are due to Professor S. E. Rasmussen for his continued interest in this work and for excellent working conditions. Carlsbergfonden put the diffractometer at our disposal.

REFERENCES

1. Grønbaek, R. and Rasmussen, S. E. *Acta Chem. Scand.* 16 (1962) 2325.
2. Hazell, R. G. *Acta Chem. Scand.* 22 (1968) 2171.
3. Hazell, R. G. *Acta Chem. Scand.* 26 (1972) 1365.
4. Hazell, R. G. *Acta Chem. Scand.* 22 (1968) 2809.
5. Arndt, U. W. and Phillips, D. C. *Acta Crystallogr.* 14 (1961) 807.
6. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III, p. 202.
7. Larson, A. C. *Acta Crystallogr.* 23 (1967) 664.
8. Ballard, R. E., Powell, D. B. and Jaysooriya, U. A. *Acta Crystallogr. B* 30 (1974) 1111.
9. Lopez-Castro, A. and Truter, M. R. *J. Chem. Soc.* (1963) 1309.
10. Nardelli, M., Gasparri, G. F., Battistini, G. G. and Domiano, P. *Acta Crystallogr.* 20 (1966) 349.
11. Hansen, F. V. and Hazell, R. G. *Acta Chem. Scand.* 23 (1969) 1359.
12. Andreotti, G. D., Domiano, P., Gasparri, G. F., Nardelli, M. and Sgarabotto, P. *Acta Crystallogr. B* 26 (1970) 1005.

Received May 20, 1976.