

The Crystal Structure of the *cis-α* Isomer of Nickel(II)-triethylenetetramine Isothiocyanate, $[\text{Ni}(\text{trien})(\text{NCS})_2]$

ASGER CLAUSEN and ALAN C. HAZELL

Department of Inorganic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

cis-α- $[\text{Ni}(\text{trien})(\text{NCS})_2]$, (trien = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$) is monoclinic with $a=14.14\pm 0.01$ Å, $b=12.02\pm 0.01$ Å, $c=8.395\pm 0.01$ Å, and $\beta=106.4\pm 0.2^\circ$. The space-group is $C2/c$ (C_{2h}^6 , No. 15); there are 4 molecules per unit cell. An X-ray analysis carried out using 1553 intensities measured with an automatic counter diffractometer gave the positions of all the atoms, including the hydrogen atoms. The final *R*-value attained was 0.043.

The complex is approximately octahedral and has a 2-fold axis coincident with the crystallographic 2-fold axis. The quadridentate trien group is bonded so as to be almost strain-free, leaving two *cis* positions for the thiocyanate groups which are bonded *via* their nitrogen atoms.

Although many complexes of triethylenetetramine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ = trien) have been prepared, *e.g.* by Jonassen and Douglas,¹ and the stereochemistry of octahedral M trien complexes has been discussed,² no accurate structure analysis has been reported of any of these compounds.* We have therefore determined the structure of one of the isomers of $[\text{Ni}(\text{trien})(\text{NCS})_2]$.

There are three possible modes of coordinating trien to the Ni(II) ion, these are shown schematically in Fig. 1.

In addition to these topological isomers several isomeric possibilities arise from the way in which the rings can be staggered.

The compound that we have studied has the *cis-α* configuration, *i.e.* the configuration in which all the nitrogen atoms can assume a strain-free tetrahedral arrangement, whereas in the *cis-β* configuration one secondary nitrogen atom is forced into an intermediate planar-tetrahedral configuration and in the *trans* configuration both secondary nitrogen atoms will be forced into such an arrangement.³

* A preliminary crystal structure determination of β - $[\text{Co}(\text{trien})\text{CO}_3]\text{ClO}_4$ by B. F. Hoskins is referred to by Sargeson and Searle.²

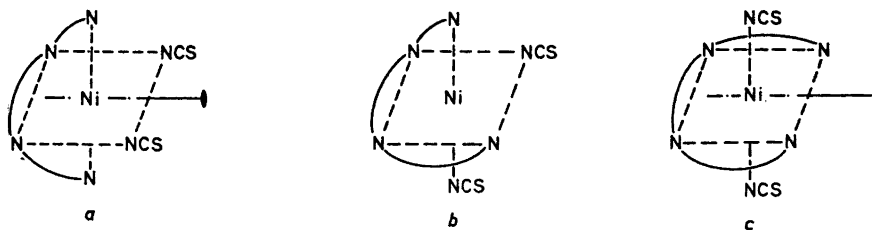


Fig. 1. The topological isomers of Ni(trien) X_2 . a) *cis-α*, b) *cis-β*, c) *trans*.

CRYSTAL DATA

$C_8H_{18}N_6NiS_2$, $M = 321.1$. Monoclinic $a = 14.14 \pm 0.01$ Å, $b = 12.02 \pm 0.02$ Å, $c = 8.395 \pm 0.01$ Å, $\beta = 106.4 \pm 0.2^\circ$, $U = 1366$ Å³, $D_M = 1.52$ (by flotation in $CCl_4/C_2H_2Cl_2$), $Z = 4$, $D_c = 1.56$, $F(000) = 336$. The crystals are paramagnetic with $\mu = 3.04$ B.M. ($23^\circ C$).

Possible space-groups $C2/c$ (C_{2h}^6 , No. 15) or Cc (C_s^4 , No. 9). $CuK\alpha$ and $MoK\alpha$ radiations, single crystal oscillation, Weissenberg, and precession photographs. No piezoelectric effect could be observed using the Giebe-Scheibe method. The implied molecular symmetry is 2 or $\bar{1}$ in $C2/c$; no conditions are imposed on the molecular symmetry in Cc .

The crystals which are blue, are elongated in the [001] direction and are bounded by {100} and by {110} and terminated by {011}.

Table 1. Atomic coordinates as fractions of cell edges, their estimated standard deviations are multiplied by 10^4 . The isotropic temperature factor coefficients and their estimated standard deviations (both in Å²) are also given for the hydrogen atoms.

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Ni	0	—	0.1806	0	0.25	—		
S	0.2361	1	-0.1194	1	0.4214	1		
N1	0.1104	2	0.0616	2	0.3153	4		
N2	-0.0034	2	0.1841	2	0.5009	3		
N3	0.1013	2	0.3146	2	0.3368	3		
C1	0.1635	2	-0.0124	2	0.3581	4		
C2	0.0487	3	0.2837	3	0.5869	4		
C3	0.1349	2	0.3079	4	0.5217	4		
C4	0.0557	2	0.4216	3	0.2675	4		
H1	0.0371	31	0.1227	36	0.5586	50	4.04	1.02
H2	-0.0708	31	0.1788	31	0.4968	46	2.62	0.84
H3	0.1560	30	0.3031	31	0.2973	49	3.23	0.93
H4	0.0718	28	0.2692	31	0.6998	47	2.50	0.80
H5	-0.0046	28	0.3507	31	0.5575	44	2.35	0.78
H6	0.1830	27	0.2400	30	0.5469	42	2.13	0.74
H7	0.1723	31	0.3798	34	0.5670	49	3.30	0.92
H8	0.0756	22	0.4341	25	0.1636	36	1.09	0.62
H9	0.0899	21	0.4802	26	0.3385	36	0.83	0.60

Table 2. Thermal parameters and their estimated standard deviations (both in Å² × 10⁻⁴).

Atom	<i>u</i> ₁₁	σ(<i>u</i> ₁₁)	<i>u</i> ₂₂	σ(<i>u</i> ₂₂)	<i>u</i> ₃₃	σ(<i>u</i> ₃₃)	<i>u</i> ₁₂	σ(<i>u</i> ₁₂)	<i>u</i> ₁₃	σ(<i>u</i> ₁₃)	<i>u</i> ₂₃	σ(<i>u</i> ₂₃)
Ni	314	3	233	3	434	3	0	—	187	2	0	—
S	424	5	337	5	811	6	86	4	211	5	88	4
N1	541	20	416	16	773	20	122	15	292	16	117	15
N2	493	17	426	15	490	14	-35	15	286	13	64	13
N3	250	12	408	14	417	12	-3	11	145	10	19	11
C1	357	16	277	15	599	17	-18	13	183	14	8	14
C2	425	20	595	22	394	16	-50	16	173	15	26	15
C3	290	16	679	25	437	16	-103	17	67	13	-1	17
C4	368	18	316	16	550	18	-63	13	150	15	11	15

The linear absorption coefficients are $\mu = 45.0 \text{ cm}^{-1}$ for CuK α radiation and $\mu = 17.0 \text{ cm}^{-1}$ for MoK α radiation.

Atomic coordinates and thermal parameters, bond lengths and angles, torsion angles, and the observed and calculated structure factors, are listed in Tables 1, 2, 3, 4, 5, and 6. The standard deviations quoted in these tables have been calculated neglecting the errors in the unit cell parameters.

Table 3. Bond lengths (in Å) and their estimated standard deviations.

	<i>l</i>	σ(<i>l</i>) × 10 ³	<i>l</i> _{corr}
Ni—N1	2.075	3	2.083 ^a
Ni—N2	2.121	3	2.128
Ni—N3	2.141	2	2.152
N1—C1	1.153	4	(1.174) ^b
S—C1	1.638	3	(1.651) ^b
N2—C2	1.482	5	1.490
N3—C3	1.492	4	1.497
N3—C4	1.482	4	1.490
C2—C3	1.500	5	1.506
C4—C4'	1.518	4	1.526
N2—H1	0.974	41	
N2—H2	0.947	45	
N3—H3	0.934	47	
C2—H4	0.928	37	
C2—H5	1.083	38	
C3—H6	1.045	37	
C3—H7	1.028	40	
C4—H8	1.001	34	
C4—H9	0.961	29	

^a Corrected using T, L, and S from Ni(trien) plus the two nitrogen atoms of the thiocyanate groups.

^b Values obtained on the assumption that N1 and S ride on C1.

Table 4. Angles and their standard deviations (in degrees).

	θ	$\sigma(\theta)$	θ_{corr}
N1—Ni—N1'	92.8	0.1	92.7 ^a
N1—Ni—N2	88.7	0.1	88.7 ^a
N1—Ni—N3	92.7	0.1	92.6 ^a
N2—Ni—N3	81.3	0.1	81.2
N3—Ni—N3'	82.5	0.1	82.5
Ni—N1—C1	171.5	0.3	—
N1—C1—S	178.1	0.3	—
Ni—N2—C2	110.6	0.2	110.6
N2—C2—C3	108.8	0.3	108.9
C2—C3—N3	109.7	0.2	109.6
Ni—N3—C3	107.5	0.2	107.5
Ni—N3—C4	110.1	0.2	110.1
N3—C4—C4'	112.9	0.4	112.9
C3—N3—C4	115.5	0.3	115.5
H1—N2—Ni	107.7	2.7	
H1—N2—C2	103.2	2.4	
H1—N2—H2	114.3	3.6	
H2—N2—Ni	104.6	1.1	
H2—N2—C2	115.4	2.3	
H3—N3—Ni	108.1	2.3	
H3—N3—C3	107.9	2.6	
H3—N3—C4	107.5	2.3	
H4—C2—N2	109.3	2.4	
H4—C2—C3	108.7	2.6	
H4—C2—H5	113.2	3.2	
H5—C2—N2	105.8	1.9	
H5—C2—C3	110.9	2.3	
H6—C3—C2	108.9	2.3	
H6—C3—N3	104.5	1.9	
H6—C3—H7	110.2	3.0	
H7—C3—C2	114.5	2.7	
H7—C3—N3	108.6	2.3	
H8—C4—N3	105.9	1.8	
H8—C4—C4'	111.3	1.6	
H8—C4—H9	102.3	2.6	
H9—C4—N3	107.8	1.7	
H9—C4—C4'	115.7	1.9	

^a Corrected using T, L, and S from Ni(trien) plus the two nitrogen atoms of the thiocyanate groups.

Table 5. Torsion in degrees. The torsion angles did not change on correcting the atomic coordinates for thermal vibration.

Ni—N2—C2—C3	35.6
N2—C2—C3—N3	52.7
C2—C3—N3—Ni	43.0
C2—C3—N3—C4	80.4
Ni—N3—C4—C4'	29.0
N3—C4—C4'—N3'	39.3

Table 6. Observed and calculated structure factors, both $\times 10$.

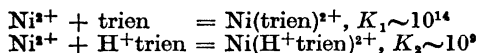
h	k	l	Obs	Calc	h	k	l	Obs	Calc	h	k	l	Obs	Calc
2	0	0	170	1259	15	1	1	270	271	-2	10	1	178	180
4	0	0	156	1059	15	1	1	194	198	0	10	1	500	500
6	0	0	129	786	15	1	1	130	107	2	4	4	531	516
8	0	0	97	542	15	1	1	97	78	4	4	4	233	231
10	0	0	70	392	-16	2	1	307	302	6	4	4	52	24
12	0	0	50	277	-18	2	1	217	215	10	4	4	112	115
14	0	0	36	198	-21	2	1	161	160	16	4	4	62	64
16	0	0	26	142	-22	2	1	117	117	19	4	4	42	42
18	0	0	19	102	-22	2	1	87	85	22	4	4	30	30
20	0	0	14	74	-22	2	1	64	64	24	4	4	22	22
22	0	0	10	54	-22	2	1	47	47	26	4	4	16	16
24	0	0	7	39	-22	2	1	34	34	28	4	4	12	12
26	0	0	5	28	-22	2	1	25	25	30	4	4	9	9
28	0	0	4	20	-22	2	1	18	18	32	4	4	6	6
30	0	0	3	14	-22	2	1	13	13	34	4	4	4	4
32	0	0	2	10	-22	2	1	9	9	36	4	4	3	3
34	0	0	1	7	-22	2	1	6	6	38	4	4	2	2
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44	0	0	1	1	-22	2	1	1	1	48	4	4	1	1
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66	0	0	1	1	-22	2	1	1	1	70	4	4	1	1
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112	0	0	1	1	-22	2	1	1	1	116	4	4	1	1
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206	0	0	1	1	-22	2	1	1	1	210	4	4	1	1

Table 6. Continued.

10	4	181	95	-5	15	86	2	10	5	193	192	-18	8	6	211	212	-10	8	7	73	56	-5	9	8	77	78		
-6	4	96	95	-16	16	142	145	4	10	5	244	250	-12	8	6	182	137	-12	8	7	77	80	-3	9	8	176	178	
-4	4	105	87	-19	1	162	150	8	10	5	149	159	-10	8	6	86	87	-6	8	7	126	132	-3	9	8	76	74	
-2	4	109	104	-17	1	168	159	8	10	5	177	180	-8	8	6	467	461	-4	8	6	152	152	-3	9	8	86	74	
0	4	147	136	-15	1	350	368	10	10	5	171	169	-6	8	6	178	172	-2	8	7	112	154	-12	10	8	69	85	
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2	4	170	168	-11	1	379	382	1	11	5	138	135	0	8	6	59	61	0	8	6	162	151	-6	10	8	106	110	
4	4	383	385	-9	1	277	291	3	11	5	156	151	0	8	6	273	270	-5	9	7	143	150	-2	10	8	101	99	
8	4	197	160	-7	1	134	131	5	11	5	83	83	4	8	6	95	107	4	8	6	180	167	-6	10	8	107	97	
8	4	122	123	-5	1	97	98	-12	12	5	102	110	10	8	6	257	228	8	8	6	173	140	-11	11	8	221	231	
12	4	71	79	-5	1	88	87	8	12	5	308	315	15	9	6	95	87	-5	9	7	170	141	-9	11	8	156	149	
14	4	102	96	5	1	956	604	-10	12	5	167	180	-15	9	6	155	141	-1	9	7	129	131	-9	11	8	160	136	
14	4	313	328	5	1	398	405	-8	12	5	175	184	-11	9	6	231	231	1	9	7	149	136	-5	11	8	167	152	
14	4	147	145	7	1	868	877	-6	12	5	166	167	-7	9	6	202	230	7	9	7	89	55	-3	11	8	167	152	
-13	4	303	356	-11	1	198	180	-2	12	5	170	178	-3	9	6	268	294	-3	9	6	165	170	-1	11	8	145	106	
-13	4	105	72	-13	1	102	83	0	12	5	219	228	-1	9	6	282	187	-14	10	7	180	161	-11	11	8	202	168	
-13	4	763	750	-10	2	2	2	2	12	5	259	267	-1	9	6	142	150	-10	10	7	154	122	-11	1	9	207	210	
-7	4	136	138	-14	2	359	371	-6	12	5	174	116	3	9	6	79	77	-6	10	7	195	183	-11	1	9	207	210	
-1	4	825	881	-12	2	112	99	-7	13	5	219	228	-5	6	6	117	112	-10	10	7	228	209	-7	1	9	119	121	
-3	4	269	256	-10	2	701	709	-5	13	5	180	174	7	9	6	111	97	-6	10	7	115	117	-1	1	9	164	184	
-1	4	920	932	-6	2	69	60	-5	13	5	176	173	-10	10	6	73	25	-2	10	7	146	143	-1	1	9	164	184	
-1	4	170	159	-8	2	263	265	-10	14	5	121	105	-4	10	6	182	162	-4	10	7	128	132	5	1	9	198	178	
3	4	186	141	-2	2	682	695	-2	14	5	154	144	2	10	6	79	81	-7	11	7	149	150	5	1	9	106	94	
3	4	486	478	-4	2	797	793	-2	14	5	135	118	6	10	6	106	101	-5	11	7	145	132	-16	2	9	106	94	
9	4	181	186	2	2	122	120	2	14	5	91	77	-11	11	6	215	221	-5	11	7	149	150	-14	2	9	106	94	
8	4	292	276	8	2	287	283	-8	15	5	152	148	-9	11	6	198	191	-11	7	7	107	78	-12	2	9	106	94	
-16	4	240	238	8	2	320	290	-10	0	6	152	158	-10	0	6	173	160	-9	11	6	107	78	-12	2	9	106	94	
-14	4	308	305	-10	10	2	2	-16	0	6	198	215	-5	11	6	181	182	-12	12	7	206	196	-6	2	9	106	94	
-10	4	410	430	-17	3	175	158	-10	0	6	152	158	-16	0	6	198	215	-5	11	6	181	182	-6	2	9	106	94	
-10	4	157	160	-15	3	135	127	-10	0	6	231	236	-11	1	6	193	182	-12	12	7	182	151	-6	2	9	106	94	
-4	4	176	170	-13	3	144	144	-10	0	6	231	236	-11	1	6	193	182	-12	12	7	182	151	-6	2	9	106	94	
-4	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
-4	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
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2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
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2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
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2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
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2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
2	4	565	557	-11	3	128	127	-10	0	6	437	424	-11	1	6	169	171	0	12	7	164	154	-10	0	2	9	106	94
2	4	565	557	-11	3	128	127																					

EXPERIMENTAL

Chemistry. The equilibrium constants ⁴ for the formation of complexes of trien with nickel are:



An aqueous solution of nickel thiocyanate was titrated with trien until a pH of 9 was reached. At first a blue oil was formed which later dissolved to give a clear blueviolet solution from which the complex crystallized on standing.

X-Ray intensity measurements. Data for the *hk0* and *h0l* zones were measured photometrically from integrating-Weissenberg photographs taken using Ni-filtered CuK α radiation.

Intensities *hkl* (*l*=0 to 10) were recorded with a linear diffractometer of the Arndt-Phillips design.⁵ Balanced filters (SrO, ZrO₂) and a pulse height analyser were used in conjunction with a scintillation counter. The radiation used was MoK α and reflections were measured out to a Bragg-angle of 30°. A total of 1934 intensities were recorded of which 1585 were greater than 2 σ_c (*I*), where σ_c^2 (*I*) is the total number of counts in an intensity measurement. Each intensity is the mean of the intensity of two symmetry related reflections.

The crystal used for the intensity measurements was approximately 0.46 mm by 0.33 mm in cross-section. No corrections were made for absorption.

STRUCTURE DETERMINATION AND REFINEMENT

The approximate structure was determined from the *hk0* and the *h0l* data which had been recorded with CuK α radiation. The space-group was assumed to be *C2/c*. Patterson projections *P(u,v)* and *P(u,w)* yielded the positions of the nickel and the sulphur atoms. The nickel atom is on a 2-fold axis and hence the molecule has 2-fold symmetry. Fourier syntheses calculated using signs determined from the positions of the heavy atoms showed peaks corresponding to the remaining carbon and nitrogen atoms.

The three-dimensional MoK α data were used for refinement of the coordinates and anisotropic temperature factor coefficients. Refinement using Grønbaek Hazell's ⁶ block-diagonal least squares program, (G403), reduced the *R*-factor to 0.060 for reflections for which $|F_{\text{obs}}|^2 > 2\sigma_c(F_{\text{obs}}^2)$.

A three-dimensional difference-Fourier synthesis revealed the positions of all the hydrogen atoms. Further refinement, in which the hydrogen atoms were allowed to vibrate isotropically, by means of a full-matrix least-squares program reduced the *R*-value to 0.043. Towards the end of refinement an empirical correction for extinction was made.

Atomic coordinates and their standard deviations are given in Table 1, thermal parameters in Table 2, the observed and calculated structure factors are listed in Table 6.

Thermal vibration analysis. The thermal vibration of the molecule was analysed by the method of Schomaker and Trueblood.⁷ Three cases were considered: a) the entire molecule was considered as a rigid body; b) the molecule except for the carbon atoms and the sulphur atoms of the thiocyanate groups were taken as the rigid body; c) the molecule without the thiocyanate groups was taken as the rigid body. The hydrogen atoms were excluded in all cases. The r.m.s. Δu_{ij} ($\Delta u_{ij} = u_{ij} \text{ observed} - u_{ij} \text{ calculated from T, L, and S}$) were a) 0.0072, b) 0.0026, c) 0.0017. The values of T, L, and S for c) are given in

Table 7. T, L, and S and their standard deviations, calculated from model c) *i.e.* all atoms bar hydrogen atoms and those of the thiocyanate group included. T is in Å², L in degree², S in degree Å. Terms given as 0 are zero from symmetry requirements. T and L are symmetric so only the upper right hand triangles are given.

$$\begin{array}{l}
 T = \begin{pmatrix} 0.0286 & 0 & 0.0102 \\ & 0.0258 & 0 \\ & & 0.0451 \end{pmatrix} \quad \sigma(T) = \begin{pmatrix} 0.0013 & - & 0.0009 \\ & 0.0010 & \\ & & 0.0009 \end{pmatrix} \\
 L = \begin{pmatrix} 15.61 & 0 & -5.08 \\ & 9.21 & 0 \\ & & 21.01 \end{pmatrix} \quad \sigma(L) = \begin{pmatrix} 0.65 & - & 0.72 \\ & 0.74 & \\ & & 1.76 \end{pmatrix} \\
 S = \begin{pmatrix} -0.136 & 0 & -0.312 \\ 0 & 0.131 & 0 \\ 0.466 & 0 & 0.267 \end{pmatrix} \quad \sigma(S) = \begin{pmatrix} 0.045 & - & 0.020 \\ - & 0.038 & \\ 0.045 & - & 0.119 \end{pmatrix}
 \end{array}$$

Table 7, these values were used in correcting the coordinates of the atoms in the rigid body. To obtain corrections for distances and angles involving the atom N1 of the thiocyanate group the values of T, L, and S for b) were used.

The high value of r.m.s. Δu_{ij} for a) would seem to indicate that it would be incorrect to use the values of T, L, and S from a) for correcting the bond lengths in the thiocyanate group. It is not possible to treat a linear triatomic group by Schomaker and Trueblood's method. The thiocyanate group librates so that the carbon atom has the smallest temperature factors. Corrections to the bond lengths were calculated using the riding-motion model of Busing and Levy⁸ with the nitrogen atom riding on the carbon atom and the sulphur atom riding on the carbon atom. These corrections are given to show the magnitude of the shifts obtained by the riding motion model rather than in the belief that these are the correct values.

Computational details. The weighting scheme used for the block-diagonal least-squares program was $w = 1/\sigma_c(F^2)$ for reflections with $F^2 > 2\sigma_c(F^2)$ and zero otherwise. Reflections $\bar{2}04$ and $\bar{4}08$ were omitted as the reciprocal lattice points corresponding to these reflections were on the rotation axis of the crystal and so these reflections could not be measured accurately with the crystal setting used. An analysis of $w(F_o - F_c)^2$ showed that the scheme used had greatly overestimated the weights of both the large and the small reflections. Therefore, $w = 1/(\sqrt{\sigma_c(F^2) + (A+1)F_o^2} - |F_o|)^2$ was used, A was chosen so as to make $w(F_o - F_c)^2$ independent of $|F|$. The value of A chosen was 0.02.

These weights were calculated at the end of refinement with G403 and were used for further refinement with the full-matrix program of Busing and Levy¹⁰ as incorporated in Stewart's X-ray 63 system.¹¹ Bond lengths and angles and torsion angles were also calculated using the X-ray 63 system.

For G403 the atomic scattering curves used were those of *International Tables*¹² approximated as Bassi¹³ polynomials. For the full-matrix program the scattering curves of Doyle and Turner were used.¹⁴

G403 is written in GIER Algol and calculations were carried out at Aarhus University's Regnecenter, calculations with the X-ray 63 systems were carried out at NEUCC at Lundtofte. Fourier syntheses were calculated on GIER using a machine order program written by S. Lauesen. Thermal vibration analysis,

and correction of bond lengths and angles were carried out using an adapted version of the TLS and local T omega programs of Gantzel, Coulter, and Trueblood.⁹

DISCUSSION

The molecule, which lies on a 2-fold axis, has the *cis- α* configuration, that is the configuration in which the coordinated nitrogen atoms of the amine come closest to forming a strain-free tetrahedral arrangement. Bond lengths and angles are given in Tables 3 and 4, torsion angles in the amine other than those involving hydrogen atoms, are given in Table 5. Atoms related about the 2-fold axis are designated by primes. The molecule is depicted in Fig. 2.

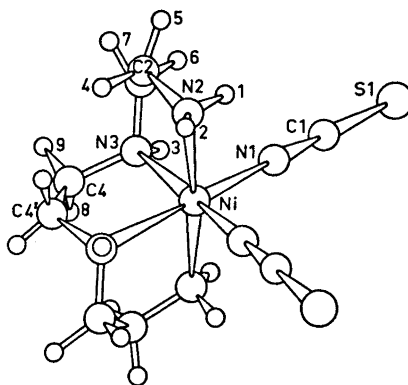


Fig. 2. The $\text{Ni}(\text{trien})(\text{NCS})_2$ molecule; the small circles represent hydrogen atoms.

The nickel-nitrogen bond distances fall within the range, 1.99 to 2.17 Å, expected for octahedral Ni(II) complexes, (see for example the values tabulated by Nardelli, Gasparri, Musatti, and Manfredotti).¹⁶ The Ni–N1 (thiocyanate) distance, 2.083 Å e.s.d. 0.003 Å, is much shorter than either of the other two Ni–N bonds (2.128 Å e.s.d. 0.003 Å, and 2.152 Å e.s.d. 0.002 Å), this is in agreement with the relative positions of the –NCS group and amines in the nephelauxetic series.

The thiocyanate group, which is linear within experimental error, is bonded to the nickel atom *via* nitrogen. The S–C and C–N bond distances and the Ni–N–C angle lie within the range of values observed previously (for example see values tabulated by Hazell).¹⁶ The difficulty in making adequate corrections for thermal vibrations of non-rigid molecules precludes detailed discussion of the relation between bond lengths and angles in M–NCS systems.

In the trien part of the molecule the C–N bond distances are typical¹⁷ for a paraffinic carbon atom to a 4-covalent nitrogen atom. The C–C bond distances are shorter than the value for a simple C–C bond (1.537 ± 0.005).¹⁷ This shortening has been observed¹⁸ in other amines and is attributed to the effect of the nitrogen atoms. The carbon to secondary-nitrogen atom distance is not significantly different from the carbon to primary nitrogen distance.

The mean value for the C-H bond distance is 1.01 Å e.s.d. 0.015 Å and for the N-H bond distance 0.95 Å e.s.d. 0.026 Å.

We have not, as yet, been able to obtain either the *cis-β* or the *trans*-[Ni(trien)(NCS)₂] compound for a comparison of their structures with that of the *cis-α* compound.

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