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## [Ru(ND<sub>3</sub>)<sub>6</sub>](SCN)<sub>3</sub> at 20 K by Time-of-Flight Neutron Diffraction

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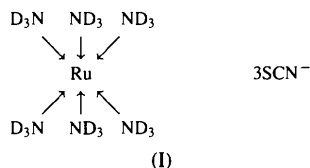
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### Abstract

Hexaammineruthenium(III) trithiocyanate has space group  $P2_1/n$  at 20 K with typical bond lengths and angles, with two of the six ammine groups rotationally disordered. Eight further limited data sets from 100 to 290 K show a reversible, probably second-order, phase transition to a  $C2/c$  cell at 283 (2) K. The  $C2/c$  cell contents are derived from those of  $P2_1/n$  by orientationally disordering one thiocyanate site together with small but well defined displacements of the other atoms.

### Comment

The structure of the title compound, (I), has been determined at 295 K (Blake *et al.*, 1993) and at 92 K (Figgis, Reynolds & Sobolev, 1994) by X-ray diffraction. These studies also examined the charge density, the magnetic susceptibility and the e.s.r. of single crystals. As a



precursor to further polarized neutron diffraction and theoretical work, we present here the structure at 20 K determined by neutron diffraction.

The geometry and thermal motion of the molecular fragments are as expected, and warrant no special comment except to note that two of the six independent ammonia molecules are disordered in their deuterium positions. On each of the two disordered ammonia sites there are two fractional molecules with significant population. These are related by a predominant rotation of *ca* 45° in the torsion angle. The refined deuterium scattering lengths imply 0.46 (2)/0.54 (2) and 0.45 (2)/0.55 (2) occupancies on each molecular site. The large and anisotropic thermal motion of N5 and N9, compared with the remaining N atoms, shows that there is also a small nitrogen translation associated with this deuterium rotation. We note that the *R* factors seem high, but this is because of the large amount of useful, but weak, high  $\sin\theta/\lambda$  data collected by the time-of-flight method.

The data show no evidence of a supercell (which this time-of-flight SCD experiment would reveal clearly) so it would appear that there is true disorder even at this very low temperature.

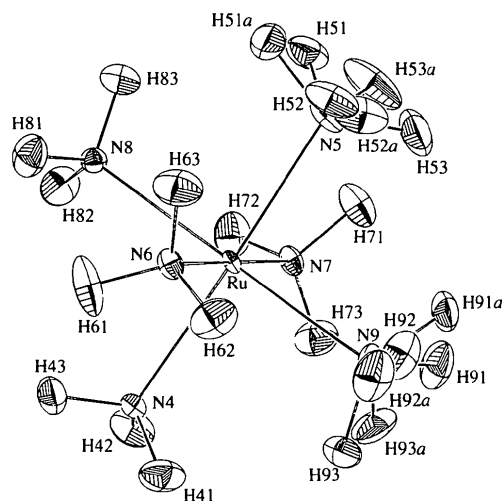


Fig. 1. Molecular structure of  $[\text{Ru}(\text{ND}_3)_6]^{3+}$  showing 50% probability displacement ellipsoids (*ac* projection).

The structure is close to  $C2/c$ . If we compare the 20 K  $P2_1/n$  and the 295 K  $C2/c$  structures, the major difference is that an SCN site is disordered in the latter. In addition the Ru atom moves onto  $\frac{1}{4}, \frac{3}{4}, \frac{1}{2}$ ; the ammonia molecules, in pairs, develop strict centrosymmetry, as do a pair of thiocyanate ions. Nevertheless, as can be seen in Fig. 2, these displacements are small. The largest changes, apart from the SCN disordering, are the alterations in the ND<sub>3</sub> torsional arrangements. The RuN<sub>6</sub> and SCN fragments move 0.1–0.2 Å, with

translation, not rotation, dominating the shift. Although small, these changes from strict *C*-centring are well defined. There are, at higher wavevectors, many strong *C*-forbidden peaks at 20 K. In Table 2 we show the evolution of the intensities of four *C*-allowed and four *C*-forbidden reflections with temperature. They are all relatively intense at 20 K, and we show their intensity normalized by the 20 K intensity.

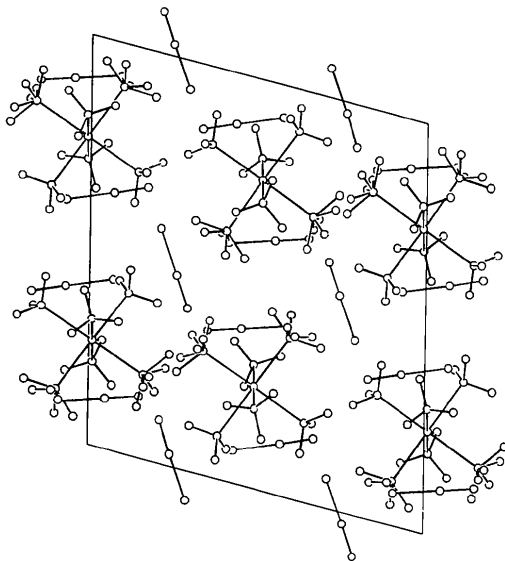


Fig. 2. Cell packing diagram (*ac* projection, *a* vertical). Atom sites are implied by the topology, except to distinguish N and S atoms in SCN we note that the N—C bond is shorter than the S—C bond.

The *C*-allowed,  $h + k$  even, reflections generally decrease in intensity following the increase in thermal parameters. This is shown in Table 2 for N and D sites. There is no dramatic change from 280 to 290 K. We note that due to changes in the way terms cancel,  $40\bar{6}$ , for example, increases in intensity for a while as temperature increases. This illustrates the need for modelling; individual reflection intensities are complex to interpret. The *C*-forbidden,  $h + k$  odd, reflections also decrease in intensity, very steeply after *ca* 260 K. We can interpolate to say that at 283 (2) K the *C*-forbidden reflections go to zero intensity. We are clearly observing the transition from  $P2_1/n$  to  $C2/c$  at this temperature. This steep change is reflected in the order parameter,  $p$ , for end-over-end SCN disordering. There is also a concomitant change in apparent RuN<sub>6</sub> centre position (shown in Table 2) and the SCN coordinates (not shown). Thermal parameters do not show this dramatic change.

These changes are all consistent with a second-order phase transition. We note that the positional parameter changes for the Ru atom do not go to zero because, although the Ru site shift in  $C2/c$  is at zero, we have isotropic thermal parameters. As a consequence, the refinement gives non-zero values in an attempt to better

fit the Ru-atom motion, which is actually anisotropic. Thus, in our refinement, the positional parameters also reflect anisotropy in thermal motion. We do not have enough data at intermediate temperatures to test a better model. The 92 K X-ray data were refined in the  $C2/c$  space group (Figgis *et al.*, 1994), giving a final  $R(F)$  of 0.015. It was noted that the temperature dependence of the thermal parameters and the significant anharmonic parameters indicated static disorder. It is probable, though not certain, that this actually reflects a  $P2_1/n$  symmetry crystal at that temperature. Since the charge density analysis was made by least-squares methods, possible use of a partial data set does not invalidate the conclusions made there about chemical bonding.

A final unusual feature of this crystal, which again indicates that the transition is second order, is that cycling the crystal several times through the transition changed neither the crystal appearance nor its apparent mosaic spread. The crystal maintained its mirror-like facets.

## Experimental

The crystal was grown by slow evaporation from D<sub>2</sub>O and mounted using epoxy on an aluminium pin in an Air Products Displex refrigerator installed on the single-crystal time-of-flight diffractometer, SCD, at the Intense Pulsed Neutron Source, Argonne National Laboratory. The density  $D_m$  was measured by flotation at 295 K with a homogeneous crystal.

### Crystal data

[Ru(ND<sub>3</sub>)<sub>6</sub>](SCN)<sub>3</sub>

$M_r = 395.4$

Monoclinic

$P2_1/n$

$a = 13.50(2) \text{ \AA}$

$b = 9.24(2) \text{ \AA}$

$c = 11.74(2) \text{ \AA}$

$\beta = 104.4(2)^\circ$

$V = 1418(4) \text{ \AA}^3$

$Z = 4$

$D_x = 1.85 \text{ Mg m}^{-3}$

$D_m = 1.71(1) \text{ Mg m}^{-3}$

Pulsed neutron radiation

Cell parameters from

extrapolated X-ray results

$T = 20 \text{ K}$

Prism

$5 \times 1.8 \times 1 \text{ mm}$

Amber

### Data collection

SCD diffractometer

Absorption correction:

spherical

$T_{\min} = 0.756$ ,  $T_{\max} =$

0.794

15507 measured reflections

12807 independent

reflections

15507 reflections used in

refinement [minimum

$I = -1.7\sigma(I)$ ]

$R_{\text{int}}(F^2) = 0.074$

$h = 0 \rightarrow 33$

$k = -21 \rightarrow 3$

$l = -26 \rightarrow 9$

### Refinement

Refinement on  $F^2$

$R(F) = 0.133$

$wR(F^2) = 0.110$

$S = 0.84$

$(\Delta/\sigma)_{\text{max}} = 0.05$

Extinction correction:

Zachariasen (1963) type

1 isotropic

15 507 reflections  
 402 parameters  
 All H-atom parameters refined  
 Weighting scheme based on measured e.s.d.'s

Extinction coefficient: 2.41 (8)  
 Atomic scattering factors from Sears (1986)

Temp. (K)	<i>hkl</i>			Shift		Mean <i>U</i>	
	7,0,11	7,0,13	<i>p</i>	Ru <i>x</i>	Ru <i>z</i>	N	D
100	1.010	1.028	1.00 (3)	-26 (3)	-95 (2)	144	338
180	0.935	0.913	1.10 (3)	-22 (3)	-92 (2)	216	400
200	0.872	0.732	1.19 (4)	-13 (3)	-83 (2)	235	561
220	0.658	0.637	1.09 (4)	-11 (3)	-77 (2)	245	520
240	0.478	0.388	1.13 (4)	-5 (3)	-71 (2)	276	569
260	0.271	0.236	0.98 (4)	-17 (4)	-63 (2)	318	636
280	0.061	0.036	0.36 (3)	41 (5)	-7 (2)	354	753
290	0.019	0.014	0.09 (7)	110 (12)	59 (5)	390	634

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Ru	0.24611 (4)	0.75680 (6)	0.49017 (5)	0.0065 (2)
N4	0.19213 (3)	0.71357 (5)	0.64134 (4)	0.0091 (1)
N5	0.29892 (4)	0.80395 (5)	0.33849 (4)	0.0148 (2)
N6	0.19336 (3)	0.97258 (5)	0.49221 (4)	0.0106 (1)
N7	0.29883 (3)	0.54221 (5)	0.48899 (4)	0.0101 (1)
N8	0.10399 (3)	0.69055 (5)	0.38412 (4)	0.0101 (1)
N9	0.38947 (3)	0.81792 (5)	0.59583 (5)	0.0131 (2)
S1	0.0807 (1)	0.3196 (2)	0.4304 (1)	0.0107 (4)
C1	0.12690 (4)	0.35679 (7)	0.57054 (6)	0.0106 (2)
N1	0.16115 (3)	0.38695 (5)	0.66986 (4)	0.0136 (2)
S2	0.4180 (1)	0.1922 (2)	0.5925 (1)	0.0132 (5)
C2	0.38012 (5)	0.15835 (7)	0.45100 (6)	0.0130 (2)
N2	0.35290 (5)	0.13121 (6)	0.35022 (5)	0.0218 (8)
S3	0.42634 (9)	0.5313 (2)	0.7904 (1)	0.0106 (4)
C3	0.52909 (4)	0.50404 (7)	0.74241 (5)	0.0111 (2)
N3	0.60402 (4)	0.48982 (7)	0.71037 (5)	0.0214 (2)
H41	0.23159 (9)	0.7709 (1)	0.71273 (9)	0.0235 (5)
H42	0.19600 (9)	0.6070 (1)	0.6641 (1)	0.0213 (4)
H43	0.11753 (9)	0.7420 (2)	0.6298 (1)	0.0238 (6)
H51	0.2684 (2)	0.7460 (3)	0.2726 (2)	0.023 (1)
H51a	0.2313 (3)	0.816 (1)	0.2611 (3)	0.054 (3)
H52	0.3002 (4)	0.9106 (6)	0.3213 (6)	0.025 (1)
H52a	0.3280 (6)	0.8978 (8)	0.3377 (7)	0.027 (2)
H53	0.3792 (2)	0.7775 (5)	0.3566 (3)	0.035 (1)
H53a	0.3319 (4)	0.7251 (4)	0.3055 (4)	0.035 (2)
H61	0.12549 (9)	0.9806 (2)	0.5148 (2)	0.0302 (6)
H62	0.2427 (1)	1.0372 (1)	0.5496 (1)	0.0252 (5)
H63	0.1833 (1)	1.0224 (1)	0.4129 (1)	0.0256 (5)
H71	0.34454 (8)	0.5280 (1)	0.4315 (1)	0.0222 (4)
H72	0.24059 (8)	0.4695 (1)	0.4618 (1)	0.0225 (5)
H73	0.3378 (1)	0.5077 (2)	0.5699 (1)	0.0228 (5)
H81	0.04638 (8)	0.7634 (1)	0.3791 (1)	0.0221 (5)
H82	0.07928 (9)	0.5947 (1)	0.4107 (1)	0.0214 (5)
H83	0.10993 (8)	0.6722 (1)	0.29968 (9)	0.0219 (4)
H91	0.4477 (2)	0.7525 (3)	0.5991 (3)	0.026 (1)
H91a	0.4434 (2)	0.7968 (4)	0.5427 (3)	0.023 (1)
H92	0.4138 (3)	0.9215 (6)	0.5885 (5)	0.025 (1)
H92a	0.3953 (4)	0.9222 (8)	0.6103 (7)	0.028(2)
H93	0.3850 (2)	0.8246 (4)	0.6889 (2)	0.024 (1)
H93a	0.4067 (2)	0.7579 (4)	0.6628 (3)	0.025 (1)

Table 2. Temperature dependence of selected reflection intensities (normalized to 1 at 20 K), SCN order parameter (*p*), *x* and *z* Ru coordinate shift ( $\times 10^4$ ) from the constrained refinement and mean isotropic displacement parameters ( $U_2 \times 10^4 \text{\AA}^2$ ) for the 6 ammonia N atoms and 18 D atoms

Temp. (K)	Reflection ( <i>hkl</i> )					
	2,0,12	4,0,6	6,0,12	2,0,8	3,0,13	5,0,17
100	0.946	0.983	0.964	0.880	0.883	0.737
180	0.937	1.113	0.799	0.824	0.662	0.491
200	0.932	1.125	0.759	0.809	0.563	0.470
220	0.784	0.994	0.603	0.696	0.425	0.212
240	0.674	0.888	0.508	0.627	0.324	0.179
260	0.596	0.751	0.366	0.537	0.187	0.077
280	0.501	0.668	0.289	0.445	0.037	0.004
290	0.435	0.571	0.233	0.408	0.003	0.004

Most of a unique quadrant of data were measured by counting at 25 fixed crystal orientations. The non-standard setting was chosen to maintain comparability with the *C2/c* structure at room temperature. An area position-sensitive <sup>6</sup>Li-glass scintillation detector, 28 × 28 cm in size, counted the neutrons, sorted by time-of-flight. At each orientation all peaks in a volume of reciprocal space were sampled. Scattered neutrons were counted in the wavelength range 0.7–4.2 Å. For a reflection in the sampling volume, the neutron wavelength reflected, and thus time of arrival at the detector (*t*) is governed by the diffraction angle, which can be calculated from the position at which the neutrons struck the detector (*x*, *y*). Thus, each Bragg peak *hkl* appeared in the data as a position on the detector and time-of-flight, *i.e.* *x*, *y*, *t*. Since all peaks were counted during each pulse no standards were required, only scaling between different crystal orientations. Integrated intensities were evaluated from either 3 × 3 × 3 or 5 × 5 × 5 three-dimensional arrays of *xyt* channels, the former when  $\sigma(t)/I < 1/36$  (Wilkinson & Schultz, 1989).

A unit cell was derived from the time-of-flight and position of the 660 most intense reflections. When compared with a cell derived by extrapolation of the X-ray derived cells at 295 and 92–20 K, the neutron cell was 1.4% larger in all dimensions. We have used the X-ray diffraction derived cell in further analysis, since we believe the large crystal size introduces a significant uncertainty in the effective neutron path length.

In addition, at a single fixed crystal orientation, a limited set of Bragg peaks were counted at each of the temperatures 100, 180, 200, 220, 240, 260, 280 and 290 K.

The integrated intensities were reduced to scaled  $F^2$  data by applying the incident neutron spectrum, absorption, dead-time, Lorentz and detector efficiency corrections. Linear absorption coefficients at each wavelength were calculated from the sum of the wavelength-dependent true absorption and the wavelength-independent total scattering;  $\mu(\lambda) = 0.086 + 0.0083\lambda$  (Å), with  $\mu$  in  $\text{mm}^{-1}$ . A full anisotropic refinement was performed including H-atom and disordered sites.

Cell refinement: *PEAKS*, *INDEX*, *LS* (Schultz *et al.*, 1984). Data reduction: *ANVRED* (Schultz *et al.*, 1984). Program(s) used to refine structure: *ANVLS* (Schultz *et al.*, 1984). Molecular graphics: *ORTEP* (Johnson, 1965) in *Xtal* (Hall, Flack & Stewart, 1992). Software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: CR1174). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## {1-[(2-Hydroxybenzylidene)aminomethyl]-naphthalen-2-olato(2-)-N,O,O'}(piperidine-N)nickel(II)

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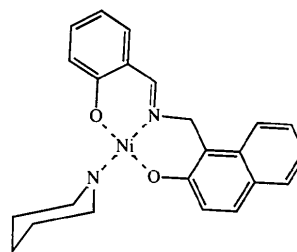
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## Abstract

The crystal structure of the title compound, [Ni(C<sub>18</sub>H<sub>13</sub>NO<sub>2</sub>)(C<sub>5</sub>H<sub>11</sub>N)], has been determined. The molecules have the *trans* form, as imposed by the geometry of the tridentate and monodentate ligands, and the Ni is in a slightly distorted square-planar environment.

## Comment

Schiff base complexes are considered to be among the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety (Garnovskii, Nivorozhkin & Minkin, 1993). Recently, the structure of {1-[(2-hydroxyphenyl)aminomethyl]-naphthalen-2-olato-*O,O',N*}piperidinenickel(II) (Elerman, Paulus & Fuess, 1991) was reported in which the nickel(II) ion reacts with both the monodentate piperidine ligand and the tridentate ligand *N*-(2-hydroxyphenyl)-2-hydroxy-1-naphthaldimine. The purpose of this study is to examine the molecular configuration when the Ni atom reacts with both the tridentate ligand *N*-(2-hydroxy-1-naphthyl-methyl)salicylaldimine, instead of *N*-(2-hydroxyphenyl)-2-hydroxy-1-naphthaldimine in the previous work, and the monodentate piperidine ligand. Both coordinate to nickel(II), producing the title compound, (I).



(I)

In the previous work (Elerman *et al.*, 1991), the coordination of the ligands around the Ni atom was found to be almost planar and the angles between the planar organic groups were found to be smaller than 8°. In the title compound, (I), however, the methyl group plays a predominant role in the distortion of the molecule as a whole. The title molecule is twisted about the C1—O1 direction with torsion angles N1—C1—C2—C11 = -56.5 (6), C2—C11—O1—Ni = 55.1 (5), N1—C1—C2—C3 = 122.8 (5) and C10—C11—O1—Ni = -126.7 (4)°. The angle between the naphthaldimine ligand and the coordination plane of nickel(II) was found to be 49°, whereas the angle between the salicylaldimine and the coordination plane of nickel(II) is only 7°. The distortion can be seen in the crystal packing diagram (Fig. 2).

A strictly planar or slightly distorted *trans* configuration is characteristic for transition metal complexes of Ni<sup>II</sup> with an NiN<sub>2</sub>O<sub>2</sub> coordination sphere (Garnovskii *et al.*, 1993). In agreement with this, the Ni atom is in a slightly distorted *trans*-square-planar environment of two O atoms [1.829 (4) and 1.857 (4) Å] and two N atoms [1.859 (4) and 1.943 (4) Å] with O—Ni—N angles between 84.8 (2) and 95.2 (2)°. The Ni—O and Ni—N distances are longer than the values determined by the previous work.