

1.2U<sub>eq</sub>(C), for methyl H atoms U(H) = 1.5U<sub>eq</sub>(C)] using a riding model with C—H(methylene) = 0.99, C—H(aromatic) = 0.95 and C—H(methyl) = 0.98 Å. For each methyl group, the torsion angle H—C—O—C was refined.

Due to the negligible anomalous dispersion, the absolute structure could not be determined. The Flack (1983) absolute-structure parameter converged to  $x = -0.5(1)$ . Origin restraints were generated automatically by the program of Flack & Schwarzenbach (1988). The structure contains two nearly centrosymmetric radical anion molecules and two solvent-separated lithium countercations, each surrounded by three dimethoxyethane molecules (Fig. 3). The coordination spheres of both lithium cations differ significantly in their Li···O distances, as do the torsion angles of the solvent molecules. The structure cannot be successfully refined in the centrosymmetric space group  $P\bar{1}$ . The reciprocal space was thoroughly but unsuccessfully scanned for reflections that might give a hint of a superstructure.

Data collection: *DIF4* (Stoe & Cie, 1988a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1988b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXL93 CIFTAB*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1040). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Bock, H., Näther, C., Arad, C., John, A. & Havlas, Z. (1994). *Angew. Chem.* **106**, 931–934; *Angew. Chem. Int. Ed. Engl.* **33**, 875–878.
- Bock, H., Näther, C. & Ruppert, K. (1992). *J. Chem. Soc. Chem. Commun.* pp. 765–766.
- Bock, H., Näther, C., Ruppert, K. & Havlas, Z. (1992). *J. Am. Chem. Soc.* **114**, 6907–6908.
- Bock, H., Ruppert, K., Näther, C., Zdenek, H., Herrmann, H.-F., Arad, C., Göbel, L., John, A., Heuret, J., Nick, S., Rauschenbach, A., Seitz, W., Vaupel, T. & Solouki, B. (1992). *Angew. Chem.* **104**, 564–595; *Angew. Chem. Int. Ed. Engl.* **31**, 550–581.
- Eaborn, C., Hitchcock, P. B., Smith, J. D. & Sullivan, A. C. (1983). *J. Chem. Soc. Chem. Commun.* pp. 1390–1391.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Flack, H. D. & Schwarzenbach, D. (1988). *Acta Cryst.* **A44**, 499–506.
- Jonas, K., Pörschke, K. R., Krüger, C. & Tsay, Y.-H. (1976). *Angew. Chem.* **88**, 682–683; *Angew. Chem. Int. Ed. Engl.* **15**, 621–622.
- Jost, W., Adam, M., Enkelmann, V. & Müllen, K. (1992). *Angew. Chem.* **104**, 883–884; *Angew. Chem. Int. Ed. Engl.* **31**, 878–879.
- Schade, C. & von Schleyer, R. (1988). *Adv. Organomet. Chem.* **27**, 169–279.
- Setzer, W. N. & von Schleyer, R. (1985). *Adv. Organomet. Chem.* **24**, 353–450.
- Sheldrick, G. M. (1990a). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1990b). *SHELXTL/PC*. Version 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

Stoe & Cie (1988a). *DIF4. Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1988b). *REDU4. Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

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## *mer,trans*-[Bis(2-diphenylphosphinoethyl)(*n*-propyl)amine-*N,P,P'*]dichloro-(triphenylphosphine)ruthenium(II) 0.5-Dichloromethane Solvate

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## Abstract

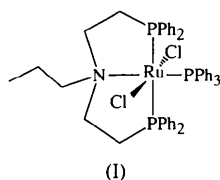
The structure consists of discrete neutral molecules of [RuCl<sub>2</sub>(PPh<sub>3</sub>)(PNP)] [PNP = CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>-PPh<sub>2</sub>)<sub>2</sub>] and dichloromethane solvent molecules. In the molecular structure of the complex a Ru<sup>II</sup> metal centre is pseudo-octahedrally coordinated by a meridional tridentate PNP ligand, by two Cl ligands *trans* to each other, and by a triphenylphosphine ligand. The latter ligand is *trans* to the N-atom donor of the amino-diphosphine.

## Comment

As part of our effort to control the chemo-, regio-, stereo- and enantioselectivity of organometallic reactions, we have recently prepared a number of transition metal complexes containing aminodiphosphine ligands of the general formula RN(CHR'CH<sub>2</sub>PR''<sub>2</sub>)<sub>2</sub> [*R* and *R'* are (chiral) alkyl groups, *R''* is an aryl or cycloalkyl group] (Bianchini, Innocenti, Masi, Peruzzini & Zanobini, 1992; Bianchini *et al.*, 1990; Bianchini, Farnetti *et al.*, 1995). These ligands offer significant advantages over linear and tripodal polyphosphines in homogeneous catalytic reactions assisted by transition metal complexes, since the concomitant presence in the ligand framework of both hard and soft donor atoms provides easy access to coordination vacancies at the metal centre by different mechanisms.

In this paper we report the crystal structure of the title complex, *mer,trans*-[RuCl<sub>2</sub>(PPh<sub>3</sub>)(PNP)], (I), which represents the key compound for studying the organometallic chemistry of the (PNP)Ru<sup>II</sup> sys-

tem (Bianchini, Glendenning, Peruzzini, Romerosa & Zanobini, 1994; Bianchini, Peruzzini, Romerosa & Zanobini, 1995).



A perspective drawing of *mer,trans*-[RuCl<sub>2</sub>(PPh<sub>3</sub>)(PNP)] is given in Fig. 1 with the atomic numbering scheme. The structure consists of discrete *mer,trans*-[RuCl<sub>2</sub>(PPh<sub>3</sub>)(PNP)] molecules and dichloromethane solvent molecules in the asymmetric unit in a 1:0.5 ratio. The metal atom is octahedrally coordinated by the three donor atoms of a meridional PNP ligand, by two mutually *trans* Cl atoms and by one triphenylphosphine ligand *trans* to the N atom of PNP. The most relevant distortion from idealized octahedral geometry is due to bending of the two PNP phosphine groups towards the N atom [P(1)—Ru(1)—N(1) = 80.69(10), P(2)—Ru(1)—N(1) = 79.45(9)°] probably on account of the size of the chelate-ring bite. The Ru atom is displaced by 0.158(1) Å from the least-squares plane through P(1), N(1), P(2) and P(3) towards Cl(1). The Ru—P(1) and Ru—P(2) distances are similar [2.375(1) and 2.371(1) Å, respectively] and fall within the reported range for ruthenium–phosphine complexes (Sed-

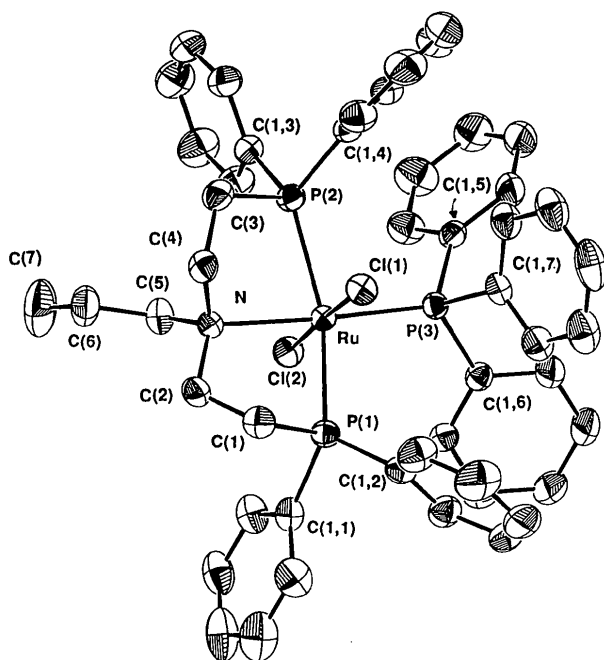


Fig. 1. ORTEP (Johnson, 1976) drawing of the complex molecule [RuCl<sub>2</sub>(PPh<sub>3</sub>)(PNP)] showing the atomic labelling scheme. Displacement ellipsoids are shown at the 50% probability level.

don & Seddon, 1984). The Ru—PPh<sub>3</sub> bond *trans* to the N(1) donor [2.315(1) Å] is somewhat shorter than previously reported analogous bonds, thus indicating that the *trans* influence exerted by the P ligands is larger than that of the N donor (Bianchini *et al.*, 1992). The Ru—Cl bond lengths [Ru—Cl(1) 2.430(1), Ru—Cl(2) 2.441(1) Å] agree well with reported values for several dichloro complexes of ruthenium with a *trans* arrangement of Cl ligands (Krassowski, Nelson, Brower, Hauenstein & Jacobson, 1988; Kawamura, Ebihara, Katayama, Nishikawa & Yamabe, 1991). The Ru—N distance [2.337(4) Å] is almost equal to that found in the related complex *mer,trans*-[RuH(Cl)(PPh<sub>3</sub>)(PNP)] (Bianchini *et al.*, 1992) and is slightly longer than that reported for other Ru—N(tertiary amine) complexes (Orpen *et al.*, 1989). Finally, the intermolecular contacts appear normal and exclude forces other than the van der Waals interactions being active in the crystal packing.

## Experimental

Deep-orange crystals of *mer,trans*-[RuCl<sub>2</sub>(PPh<sub>3</sub>)(PNP)] were grown by slow diffusion of ethanol into a diluted dichloromethane solution of the crude microcrystalline material, which was prepared as previously described (Bianchini *et al.*, 1992).

### Crystal data

[RuCl<sub>2</sub>(C<sub>18</sub>H<sub>15</sub>P)-  
(C<sub>31</sub>H<sub>35</sub>NP<sub>2</sub>)]·  
0.5CH<sub>2</sub>Cl<sub>2</sub>  
M<sub>r</sub> = 960.30  
Monoclinic  
C2/c  
a = 44.117(9) Å  
b = 10.650(2) Å  
c = 18.898(4) Å  
β = 92.16(3)°  
V = 8873(3) Å<sup>3</sup>  
Z = 8  
D<sub>x</sub> = 1.436 Mg m<sup>-3</sup>

Cu Kα radiation  
λ = 1.5418 Å  
Cell parameters from 25  
reflections  
θ = 15–17.5°  
μ = 5.944 mm<sup>-1</sup>  
T = 293 K  
Needle  
0.40 × 0.35 × 0.30 mm  
Orange

### Data collection

Philips PW1100 diffractometer  
ω/2θ scans  
Absorption correction:  
refined from ΔF  
(DIFABS; Walker &  
Stuart, 1983)  
T<sub>min</sub> = 0.10, T<sub>max</sub> = 0.15  
5232 measured reflections  
5232 independent reflections

5231 observed reflections  
[I > 2σ(I)]  
θ<sub>max</sub> = 60°  
h = -49 → 49  
k = 0 → 11  
l = 0 → 21  
3 standard reflections  
monitored every 200  
reflections  
intensity decay: none

### Refinement

Refinement on F<sup>2</sup>  
R(F) = 0.0339  
wR(F<sup>2</sup>) = 0.0999

(Δ/σ)<sub>max</sub> = -0.022  
Δρ<sub>max</sub> = 0.611 e Å<sup>-3</sup>  
Δρ<sub>min</sub> = -0.672 e Å<sup>-3</sup>

S = 1.202

5232 reflections

450 parameters

H atoms: see text

$$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 41.3217P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

Extinction correction: none

Atomic scattering factors

from *International Tables*for *X-ray Crystallography*

(1974, Vol. IV) and

Stewart, Davidson &amp;

Simpson (1965) (H atoms)

Table 2. Selected geometric parameters (Å, °)

Ru(1)—P(1)	2.375 (1)	C(1)—C(2)	1.520 (7)
Ru(1)—P(2)	2.371 (1)	C(3)—C(4)	1.522 (7)
Ru(1)—P(3)	2.315 (1)	C(5)—C(6)	1.527 (7)
Ru(1)—Cl(1)	2.430 (1)	C(6)—C(7)	1.511 (9)
Ru(1)—Cl(2)	2.441 (1)	N(1)—C(2)	1.499 (6)
Ru(1)—N(1)	2.337 (4)	N(1)—C(4)	1.493 (6)
P(1)—C(1)	1.848 (5)	N(1)—C(5)	1.494 (6)
P(2)—C(3)	1.861 (5)		
P(3)—Ru(1)—N(1)	176.91 (10)	Cl(1)—Ru(1)—Cl(2)	177.14 (4)
P(3)—Ru(1)—P(2)	97.87 (5)	C(4)—N(1)—C(5)	110.6 (4)
N(1)—Ru(1)—P(2)	79.45 (9)	C(4)—N(1)—C(2)	108.4 (3)
P(3)—Ru(1)—P(1)	101.55 (5)	C(5)—N(1)—C(2)	108.6 (4)
N(1)—Ru(1)—P(1)	80.69 (10)	C(4)—N(1)—Ru(1)	105.3 (3)
P(2)—Ru(1)—P(1)	155.97 (4)	C(5)—N(1)—Ru(1)	111.4 (3)
P(3)—Ru(1)—Cl(1)	88.51 (4)	C(2)—N(1)—Ru(1)	112.5 (3)
N(1)—Ru(1)—Cl(1)	89.69 (10)	C(2)—C(1)—P(1)	106.4 (3)
P(2)—Ru(1)—Cl(1)	84.18 (4)	N(1)—C(2)—C(1)	112.8 (4)
P(1)—Ru(1)—Cl(1)	82.33 (4)	C(4)—C(3)—P(2)	113.6 (3)
P(3)—Ru(1)—Cl(2)	90.30 (4)	N(1)—C(4)—C(3)	111.3 (4)
N(1)—Ru(1)—Cl(2)	91.61 (10)	N(1)—C(5)—C(6)	117.1 (4)
P(2)—Ru(1)—Cl(2)	98.56 (4)	C(7)—C(6)—C(5)	110.1 (5)
P(1)—Ru(1)—Cl(2)	95.37 (4)		

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares with anisotropic displacement parameters for all non-H atoms. All phenyl rings were treated as rigid bodies with  $D_{6h}$  symmetry (C—C = 1.39 Å). H atoms were introduced at calculated positions (C—H = 1.08 Å).

The programs *SHELXS86* (Sheldrick, 1985), *SHELXTL-Plus* (Sheldrick, 1991) and *SHELXL93* (Sheldrick, 1993) were used for the structure determination and refinement.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1178). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- Bianchini, C., Farnetti, E., Glendenning, L., Graziani, M., Nardin, G., Peruzzini, M., Rocchini, E. & Zanobini, F. (1995). *Organometallics*, **14**, 1489–1502.
- Bianchini, C., Farnetti, E., Graziani, M., Nardin, G., Vacca, A. & Zanobini, F. (1990). *J. Am. Chem. Soc.* **112**, 9190–9197.
- Bianchini, C., Glendenning, L., Peruzzini, M., Romerosa, A. & Zanobini, F. (1994). *J. Chem. Soc. Chem. Commun.* p. 2219.
- Bianchini, C., Innocenti, P., Masi, D., Peruzzini, M. & Zanobini, F. (1992). *Gazz. Chim. Ital.* **122**, 461–470.
- Bianchini, C., Peruzzini, M., Romerosa, A. & Zanobini, F. (1995). *Organometallics*, **14**, 3152–3153.
- Johnson, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kawamura, T., Ebihara, M., Katayama, H., Nishikawa, H. & Yamabe, T. (1991). *J. Chem. Soc. Dalton Trans.* pp. 2703–2706.
- Krassowski, W., Nelson, J. H., Brower, K. R., Hauenstein, D. & Jacobson, R. A. (1988). *Inorg. Chem.* **27**, 4294–4307.
- Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–S83.
- Seddon, E. A. & Seddon, K. R. (1984). *The Chemistry of Ruthenium*, ch. 9. Amsterdam: Elsevier.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

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

	x	y	z	$U_{eq}$
Ru(1)	0.3667 (1)	0.2927 (1)	0.0966 (1)	0.025 (1)
P(1)	0.3149 (1)	0.2321 (1)	0.0890 (1)	0.030 (1)
P(2)	0.4125 (1)	0.3773 (1)	0.0552 (1)	0.030 (1)
P(3)	0.3715 (1)	0.3647 (1)	0.1211 (1)	0.027 (1)
Cl(1)	0.3456 (1)	0.4956 (1)	0.0628 (1)	0.036 (1)
Cl(2)	0.3858 (1)	0.0871 (1)	0.1342 (1)	0.035 (1)
N(1)	0.3634 (1)	0.2294 (4)	−0.0218 (2)	0.030 (1)
C(1)	0.3076 (1)	0.2626 (5)	−0.0063 (2)	0.038 (1)
C(2)	0.3319 (1)	0.1917 (5)	−0.0451 (2)	0.037 (1)
C(3)	0.4038 (1)	0.3869 (5)	−0.0418 (2)	0.041 (1)
C(4)	0.3721 (1)	0.3421 (5)	−0.0634 (2)	0.036 (1)
C(5)	0.3843 (1)	0.1224 (5)	−0.0351 (2)	0.040 (1)
C(6)	0.3891 (1)	0.0874 (6)	−0.1123 (3)	0.054 (2)
C(7)	0.4074 (2)	−0.0322 (8)	−0.1159 (4)	0.088 (2)
C(2,1)	0.2673 (1)	0.0574 (3)	0.0813 (2)	0.053 (1)
C(3,1)	0.2547 (1)	−0.0613 (4)	0.0724 (2)	0.063 (2)
C(4,1)	0.2733 (1)	−0.1667 (3)	0.0731 (2)	0.061 (2)
C(5,1)	0.3045 (1)	−0.1534 (2)	0.0825 (2)	0.055 (2)
C(6,1)	0.3172 (1)	−0.0347 (3)	0.0914 (2)	0.045 (1)
C(1,1)	0.2986 (1)	0.0708 (2)	0.0907 (2)	0.035 (1)
C(2,2)	0.2732 (1)	0.4305 (3)	0.1106 (2)	0.051 (1)
C(3,2)	0.2525 (1)	0.4950 (3)	0.1506 (2)	0.069 (2)
C(4,2)	0.2444 (1)	0.4478 (3)	0.2158 (2)	0.061 (2)
C(5,2)	0.2569 (1)	0.3359 (4)	0.2409 (1)	0.053 (2)
C(6,2)	0.2777 (1)	0.2713 (3)	0.2009 (2)	0.042 (1)
C(1,2)	0.2858 (1)	0.3186 (3)	0.1358 (2)	0.034 (1)
C(2,3)	0.4550 (1)	0.1797 (3)	0.0798 (2)	0.046 (1)
C(3,3)	0.4826 (1)	0.1196 (3)	0.0710 (2)	0.058 (2)
C(4,3)	0.5054 (1)	0.1795 (3)	0.0351 (2)	0.059 (2)
C(5,3)	0.5006 (1)	0.2994 (3)	0.0078 (2)	0.055 (2)
C(6,3)	0.4730 (1)	0.3594 (2)	0.0166 (2)	0.046 (1)
C(1,3)	0.4502 (1)	0.2996 (3)	0.0526 (2)	0.037 (1)
C(2,4)	0.4462 (1)	0.5537 (3)	0.1336 (2)	0.042 (1)
C(3,4)	0.4542 (1)	0.6737 (3)	0.1563 (2)	0.057 (2)
C(4,4)	0.4405 (1)	0.7780 (2)	0.1246 (2)	0.066 (2)
C(5,4)	0.4188 (1)	0.7624 (2)	0.0702 (2)	0.061 (2)
C(6,4)	0.4107 (1)	0.6424 (3)	0.0475 (2)	0.048 (1)
C(1,4)	0.4244 (1)	0.5380 (2)	0.0792 (2)	0.036 (1)
C(2,5)	0.4206 (1)	0.4767 (3)	0.2943 (2)	0.045 (1)
C(3,5)	0.4498 (1)	0.4763 (3)	0.3243 (2)	0.056 (2)
C(4,5)	0.4691 (1)	0.3757 (4)	0.3126 (2)	0.057 (2)
C(5,5)	0.4591 (1)	0.2755 (3)	0.2708 (2)	0.060 (2)
C(6,5)	0.4298 (1)	0.2758 (3)	0.2408 (2)	0.046 (1)
C(1,5)	0.4106 (1)	0.3764 (3)	0.2525 (2)	0.032 (1)
C(2,6)	0.3533 (1)	0.3342 (2)	0.3514 (2)	0.046 (1)
C(3,6)	0.3389 (1)	0.2747 (3)	0.4063 (1)	0.052 (1)
C(4,6)	0.3256 (1)	0.1578 (3)	0.3953 (1)	0.048 (1)
C(5,6)	0.3266 (1)	0.1003 (2)	0.3294 (2)	0.042 (1)
C(6,6)	0.3410 (1)	0.1598 (3)	0.2745 (1)	0.033 (1)
C(1,6)	0.3544 (1)	0.2767 (3)	0.2855 (1)	0.030 (1)
C(2,7)	0.3720 (1)	0.6291 (3)	0.2092 (2)	0.043 (1)
C(3,7)	0.3594 (1)	0.7477 (2)	0.2179 (2)	0.054 (2)
C(4,7)	0.3306 (1)	0.7599 (2)	0.2440 (2)	0.060 (2)
C(5,7)	0.3142 (1)	0.6536 (3)	0.2616 (2)	0.056 (2)
C(6,7)	0.3267 (1)	0.5350 (3)	0.2530 (2)	0.044 (1)
Cl(1,7)	0.3556 (1)	0.5228 (2)	0.2268 (2)	0.034 (1)
Cl(1S)	1/2	0.9410 (3)	1/4	0.114 (1)
CS†	0.5347 (4)	0.9357 (18)	0.2087 (8)	0.096 (5)
Cl(2S)†	0.5306 (1)	0.8301 (5)	0.1417 (3)	0.114 (2)

† Occupancy = 0.5.

- Sheldrick, G. M. (1991). *SHELXTL-Plus User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3181.
- Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–167.

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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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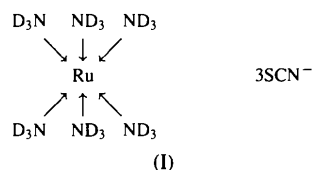
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### Abstract

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.

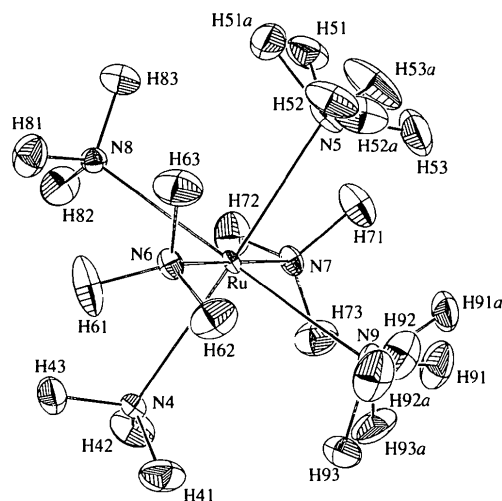


Fig. 1. Molecular structure of  $[\text{Ru}(\text{ND}_3)_6]^{3+}$  showing 50% probability displacement ellipsoids (*ac* projection).

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