

Tetrachlorobis(*N*¹-phenylacetamidino- κ *N*²)rhenium(IV) at 11 K by X-ray diffraction and at 20 K by neutron diffraction

Brian N. Figgis,^{a*} Alexandre N. Sobolev,^a Arthur J. Schultz^b and Philip A. Reynolds^c

^aChemistry Department, University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia, ^bIntense Pulsed Neutron Source, Argonne National Laboratory, Argonne, IL 60439-4814, USA, and ^cResearch School of Chemistry, Australian National University, Canberra, ACT 0200, Australia
Correspondence e-mail: bnf@crystal.uwa.edu.au

Received 4 April 2001

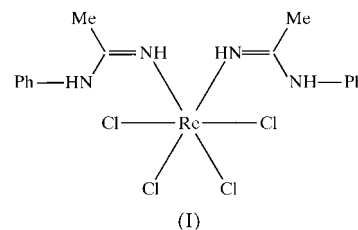
Accepted 10 July 2001

The crystal structure of the title compound, $[\text{ReCl}_4(\text{C}_8\text{H}_{10}\text{N}_2)_2]$, has been determined by X-ray diffraction at 11 K and by neutron diffraction at 20 K. The accurate and extensive data sets lead to more precise determinations than are available from earlier work. The agreement in atomic positional and displacement parameters at these very low temperatures is good. The results will facilitate re-examination of the magnetic structure of the complex. The Re atom lies on a special position and the molecule has twofold crystallographic symmetry.

Comment

The magnetic structure of tetrachlorobis(*N*-phenylacetamidino)rhenium(IV), $[\text{ReCl}_4(\text{C}_8\text{H}_{10}\text{N}_2)_2]$, (I), is of interest in chemistry and physics, as the complex is a metamagnet. It has been investigated by polarized neutron diffraction (Reynolds *et al.*, 1997), and by examining its powder neutron diffraction structure factors at very low temperatures with and without the presence of a large magnetic field (Reynolds *et al.*, 1999). However, the powder data do not determine the molecular structure with worthwhile accuracy, so that the interpretation of the magnetization data (Reynolds *et al.*, 1997) depends to a large extent on the 92 K X-ray

structure of Engelhardt *et al.* (1996). We report here the structure of (I) determined by single-crystal X-ray diffraction at 11 K and by neutron diffraction at 20 K. These results will allow a more accurate definition of the magnetic structure of (I) to be made.



Selected bond lengths and angles for (I) from both sets of data are given in Table 1. The molecular structure and the thermal motion obtained at 11 K by X-ray diffraction are illustrated in Fig. 1. Lists of calculated and observed structure factors are given in the supplementary material.

At 11 and 20 K, only zero-point thermal motion is expected to remain, so ideally the X-ray and neutron position and the atomic displacement parameters should be the same. The agreement between the X-ray and neutron positional parameters is good for the C and N atoms, with average difference/sum(s.u.) = 1.2. However, for the heavier Cl and Re atoms, the results are less satisfactory, with the ratio averaging 2.5 for Cl and 5.6 for the sole parameter, *z*, of Re. It may be that the s.u. for that parameter is unrealistically low. The agreement for the non-H atomic displacement parameters is quite satisfactory, with an average difference/sum(s.u.) of 1.1, although *U*₁₁ for Re is an exception. Probably because the X-ray experiment involved only a quadrant rather than a full sphere of data, the position is a little poorer than we have obtained previously with other very low-temperature X-ray and neutron diffraction structure studies, such as for (ND₄)₂Cu(SO₄)₂·6D₂O (Iversen *et al.*, 1994), Ni(ND₃)₄(NO₂)₂ (Iverson *et al.*, 1996), (ND₄)₂Fe(SO₄)₂·6D₂O (Figgis *et al.*, 1998) and Na₂Fe(CN)₅(-NO)·2D₂O (Schultz *et al.*, 2000). As pointed out by Abrahams (1997) after a detailed statistical analysis of our Ni(ND₃)₄(NO₂)₂ results, it appears probable that here, as in the earlier studies, our s.u.'s are probably underestimated by a factor approaching 2.

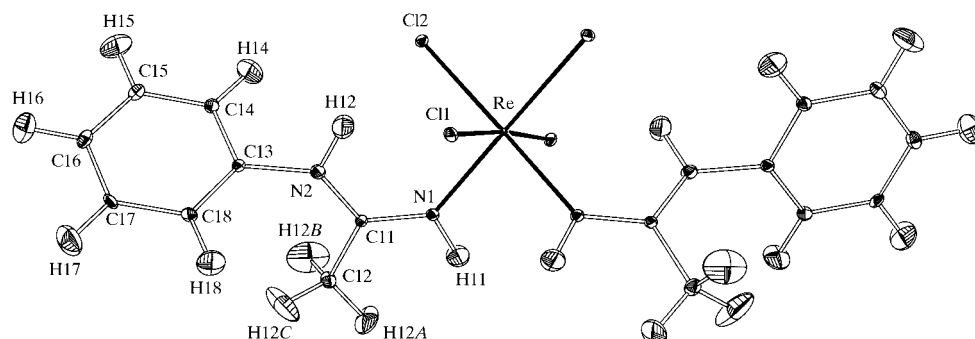


Figure 1

The molecular structure of (I) at 11 K from X-ray data. Displacement ellipsoids are shown at the 75% probability level.

The bond lengths between Re and Cl, and within the *N*-phenylacetamide ligand, agree well between the X-ray and neutron methods [average difference/sum(s.u.) = 0.6]. However, the Re—N1 bond length does not agree well, that ratio having a value of 4.3, with the length difference being 0.013 Å. This bond is directed roughly along the *c* crystal axis, so the discrepancy is associated with the disagreement in the Re *z* positional parameter.

On lowering the temperature from 92 to 11 K, the light-atom bond lengths within the *N*-phenylacetamide ligand increase very slightly, but not at the significance level. The Re—N1 bond is also unchanged, but the Re—Cl bonds lengthen by ~0.05 Å, which is several times the significance level.

The refined neutron scattering length of 0.94×10^{-5} Å is greater by about 2% than the accepted source value of 0.92×10^{-5} Å (Sears, 1992). A similar difference was observed for another rhenium complex (Bullock *et al.*, 1992).

Experimental

For the X-ray structural determination, a crystal of (I) was selected from material used in previous X-ray and magnetic structural measurements (Engelhardt *et al.*, 1996; Reynolds *et al.*, 1999). For the neutron diffraction experiment, a crystal was chosen from the batch prepared for magnetic susceptibility measurements (Reynolds *et al.*, 1997).

X-ray data for compound (I) at 11 K

Crystal data

[ReCl₄(C₈H₁₀N₂)₂]
 $M_r = 596.36$
 Orthorhombic, *Pccn*
 $a = 21.604$ (4) Å
 $b = 7.268$ (1) Å
 $c = 12.436$ (2) Å
 $V = 1952.7$ (5) Å³
 $Z = 4$
 $D_x = 2.029$ Mg m⁻³

Mo *K*α radiation
 Cell parameters from 14 reflections
 $\theta = 15.3$ – 17.9°
 $\mu = 6.78$ mm⁻¹
 $T = 11$ (2) K
 Bipyramid, purple
 $0.26 \times 0.26 \times 0.25$ mm

Data collection

Huber 512 goniometer diffractometer
 $\omega/2\theta$ scans
 Absorption correction: Gaussian (*Xtal3.7*; Hall *et al.*, 2000)
 $T_{\min} = 0.238$, $T_{\max} = 0.297$
 5671 measured reflections
 2873 independent reflections
 2406 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 30.1^\circ$
 $h = -30 \rightarrow 30$
 $k = 0 \rightarrow 10$
 $l = 0 \rightarrow 17$
 3 standard reflections every 100 reflections
 intensity decay: 1%
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.58$ e Å⁻³
 $\Delta\rho_{\text{min}} = -2.01$ e Å⁻³
 Extinction correction: *SHELXL97* (Sheldrick, 1997)
 Extinction coefficient: 0.00123 (10)

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.051$
 $S = 1.10$
 2873 reflections
 131 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0228P)^2 + 1.5368P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Table 1

Bond lengths (Å) for non-H atoms and bond angles (°) at Re in (I), as determined by X-ray diffraction (X) at 92 and 11 K, and by neutron diffraction (N) at 20 K.

	92 K (X)	11 K (X)	20 K (N)
Re—N1	2.077 (2)	2.076 (2)	2.089 (1)
Re—Cl1	2.3484 (6)	2.3539 (7)	2.3532 (9)
Re—Cl2	2.3741 (6)	2.3778 (6)	2.3764 (12)
N1—C11	1.316 (3)	1.327 (3)	1.321 (2)
N2—C11	1.328 (3)	1.331 (3)	1.335 (2)
N2—C13	1.432 (3)	1.439 (3)	1.433 (2)
C11—C12	1.496 (3)	1.501 (4)	1.499 (2)
C13—C18	1.389 (3)	1.400 (3)	1.396 (2)
C13—C14	1.390 (3)	1.392 (3)	1.394 (2)
C14—C15	1.387 (3)	1.393 (4)	1.390 (2)
C15—C16	1.387 (4)	1.389 (4)	1.401 (2)
C16—C17	1.381 (4)	1.393 (4)	1.399 (2)
C17—C18	1.389 (3)	1.393 (4)	1.395 (2)
N1—Re—N1 ⁱ	87.73 (10)	87.38 (12)	87.16 (7)
N1—Re—Cl1 ⁱ	89.68 (6)	89.91 (6)	89.80 (4)
N1—Re—Cl1	86.83 (6)	86.73 (6)	86.69 (4)
N1—Re—Cl2	91.85 (5)	91.91 (6)	91.90 (3)
N1—Re—Cl2 ⁱ	179.37 (6)	179.12 (6)	178.88 (3)
Cl1—Re—Cl1 ⁱ	175.16 (3)	175.35 (3)	175.16 (9)
Cl1—Re—Cl2 ⁱ	93.65 (2)	93.79 (2)	93.90 (4)
Cl1—Re—Cl2	89.81 (2)	89.53 (2)	89.55 (4)
Cl2—Re—Cl2 ⁱ	88.56 (3)	88.80 (3)	89.05 (6)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, z$

Neutron data for compound (I) at 20 K

Crystal data

[ReCl₄(C₈H₁₀N₂)₂]
 $M_r = 596.36$
 Orthorhombic, *Pccn*
 $a = 21.604$ (4) Å
 $b = 7.268$ (1) Å
 $c = 12.436$ (2) Å
 $V = 1952.7$ (5) Å³
 $Z = 4$
 $D_x = 2.029$ Mg m⁻³

Pulsed neutron radiation
 $\lambda = 0.7$ – 4.2 Å (time of flight)
 Cell parameters from 14 reflections
 $\theta = 15.3$ – 17.9°
 $\mu = 1.28 + 1.05\lambda$ cm⁻¹
 $T = 20$ (1) K
 Prism, purple
 $3.0 \times 2.0 \times 2.0$ mm

Data collection

IPNS single-crystal diffractometer
 Time-of-flight scans
 Absorption correction: Gaussian (IPNS program *ANVRED*)
 $T_{\min} = 0.350$, $T_{\max} = 0.704$
 5705 measured reflections

5705 independent reflections
 4488 reflections with $I > 3\sigma(I)$
 $h = -47 \rightarrow 46$
 $k = -15 \rightarrow 3$
 $l = -3 \rightarrow 27$

Refinement

Refinement on F
 $R = 0.072$
 $wR = 0.059$
 $S = 1.44$
 4488 reflections
 131 parameters
 All H-atom parameters refined
 $w = [2F_o\sigma(F_o^2)]^2$

$(\Delta/\sigma)_{\text{max}} = 0.01$
 $\Delta\rho_{\text{max}} = 0.38$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³
 Extinction correction: secondary, Type I
 Extinction coefficient: 0.0 – 1.4 (2) $\times 10^{-5}$

The H atoms were refined as riding on their attached C or N atom. In the case of the methyl group, rotation of the H atoms about the C11—C12 bond was allowed with individual lengths to C12, but the H—C12—H angles were kept constant.

For X-ray data at 11 K, data collection: local diffractometer control software; cell refinement: local diffractometer control software; data reduction: *PROFIT* (Streltsov & Zavodnik, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990);

program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

For neutron data at 20 K, data collection: IPNS data acquisition software; cell refinement: *LATCON* (local Argonne program); data reduction: *ANVRED* (local Argonne program); program(s) used to refine structure: *ANVLS* (local version of *ORFLS*; Busing *et al.*, 1962); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996).

BNF and ANS are grateful to the Australian Research Council for financial support. The work at Argonne National Laboratory was supported by the US Department of Energy, Basic Energy Sciences – Materials Sciences, under contract No. W-31-109-ENG-38.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1153). Services for accessing these data are described at the back of the journal.

References

- Abrahams, S. C. (1997). *Acta Cryst.* **A53**, 673–675.
- Bruker (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bullock, R. M., Brammer, L., Schultz, A. J., Albinati, A. & Koetzle, T. F. (1992). *J. Am. Chem. Soc.* **114**, 5125–5130.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.
- Engelhardt, L. M., Figgis, B. N., Sobolev, A. N. & Reynolds, P. A. (1996). *Aust. J. Chem.* **49**, 489–496.
- Figgis, B. N., Sobolev, A. N., Young, D. M., Schultz, A. J. & Reynolds, P. A. (1998). *J. Am. Chem. Soc.* **120**, 8715–8723.
- Hall, S. R., du Boulay, D. J. & Olthof-Hazekamp, R. (2000). Editors. *Xtal3.7 System of Crystallographic Programs*. University of Western Australia, Australia.
- Iversen, B. B., Larsen, F. K., Figgis, B. N., Reynolds, P. A. & Schultz, A. J. (1996). *Acta Cryst.* **B52**, 923–931.
- Iversen, B. B., Larsen, F. K., Reynolds, P. A. & Figgis, B. N. (1994). *Acta Chim. Scand.* **48**, 800–809.
- Reynolds, P. A., Figgis, B. N. & Martin y Marero, D. (1999). *J. Chem. Soc. Dalton Trans.* pp. 945–950.
- Reynolds, P. A., Moubaraki, B., Murray, K. S., Cable, J. W., Engelhardt, L. M. & Figgis, B. N. (1997). *J. Chem. Soc. Dalton Trans.* pp. 263–267.
- Schultz, A. J., Figgis, B. N. & Sobolev, A. N. (2000). *Acta Cryst.* **C56**, 1289–1291.
- Sears, V. F. (1992). *Neutron News*, **3**, 26–37.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Streltsov, V. A. & Zavodnik, V. E. (1989). *Sov. Phys. Crystallogr.* **34**, 824–828.