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trans-Dichloro(1,5,9,13-tetramethyl-1,5,9,13-tetrazacyclohexadecane-κ^4N)-ruthenium(III) triiodide

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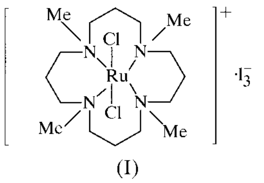
In the title complex, $[RuCl_2(C_{16}H_{36}N_4)]I_3$, the overall symmetry of the centrosymmetric cation is approximately C_{2h} and the I_3^- anions are slightly asymmetric. The I···I distance is 4.313 (1) Å. The cations and the linear anions are arranged in alternate layers and thus form the intercalating structure.

Comment

Crystal engineering has become an area of great interest in recent years (Roboson *et al.*, 1992; Desiraju, 1989; Zuo *et al.*, 1998). Different cation networks have been developed through ligand design and the use of different transition metal ions such as Zn^{2+}, Cd^{2+}, Cu^+ and Ag^+ (Xiong *et al.*, 1999, and references therein). However, the only examples of anionic and non-zeolitic supramolecular architectures are iodine-rich compounds (Blake *et al.*, 1996, 1998). The synthesis and structural characterization of polyiodides continue to be an active area of investigation. Metal thioether macrocyclic complexes have been used as templating agents in the preparation of polymeric one-dimensional chain structures or infinite two- or three-dimensional networks, in which the polyiodide arrays form unusual supramolecular inorganic matrices. High-valent oxo complexes of ruthenium are of interest because of their potential usefulness as oxidative catalysts (Mak *et al.*, 1985). Several trichlororuthenium complexes of macrocyclic amines have been studied by Che *et al.* (1986). Owing to their strong σ-donor properties, tetradentate macrocyclic tertiary amines, such as 16-TMC (1,5,9,13-tetramethyl-1,5,9,13-tetrazacyclohexadecane), are introduced which are capable of stabilizing high valent metal-oxo complexes. In this paper, we have chosen the cation $[Ru(16\text{-}TMC)Cl_2]^+$, (I), as a template to synthesize extended polyiodide arrays.



(I)

The asymmetric unit contains a half molecule and the overall symmetry of the centrosymmetric cation is approximately C_{2h}. The Ru—N bond lengths, Ru1—N1 = 2.266 (4) Å and Ru1—N2 = 2.267 (3) Å, are slightly longer than that in $[Ru(16\text{-}TMC)O_2]^{2+}$ [2.17 (2)–2.22 (2) Å; Mak *et al.*, 1985]. The I_3^- anions are slightly asymmetric with bond distances I1—I2 = 2.883 (1) Å and I2—I3 = 2.949 (1) Å, which is different from the symmetric I_3^- ion in $[Ag([18]aneS_6)I_3]$ (Blake *et al.*, 1995). The Ru—N and Ru—Cl distances are slightly longer than the values reported in the literature (Allen *et al.*, 1989). The 16-membered ring excluding the Ru and Cl atoms is essentially planar, and the C4 and C8 atoms are in axial orientations. The six-membered rings adopt twist-boat conformations.

The I···I($x - \frac{1}{2}$, y, $-z + \frac{1}{2}$) distance is 4.313 (1) Å. The cations and the linear anions are arranged as alternate layers and thus form the intercalating structure along the *b* direction.

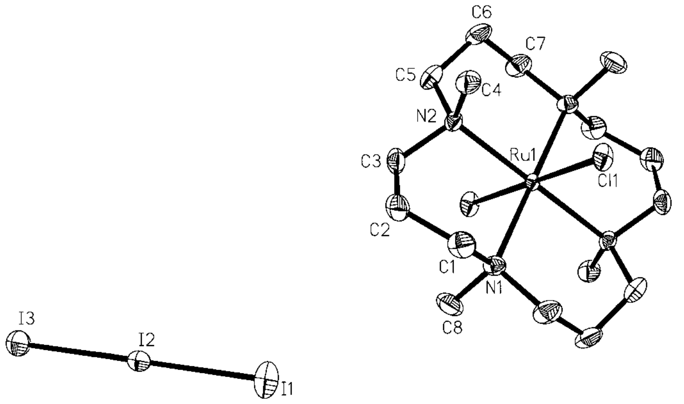


Figure 1
The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

A solution of diiodine (76.2 mg, 0.30 mmol) in acetonitrile (5 ml) was added to a solution of $[Ru(16\text{-}TMC)Cl_2]Cl$ (98.3 mg, 0.20 mmol) in acetonitrile (10 ml). After slow evaporation of the solvent, dark-red crystals were formed and washed with acetonitrile [yield 125.6 mg (75.0%)].

Crystal data

$[RuCl_2(C_{16}H_{36}N_4)]I_3$
$M_r = 837.16$
Orthorhombic, *Pnma*
$a = 7.7198$ (1) Å
$b = 20.4639$ (3) Å
$c = 15.9112$ (2) Å
$V = 2513.61$ (6) Å^3
$Z = 4$
$D_x = 2.212$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 6317 reflections
$\theta = 1.62$–$28.35°$
$\mu = 4.531$ mm^{-1}
$T = 293$ (2) K
Needle, red
0.18 × 0.16 × 0.14 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.462$, $T_{\max} = 0.530$
18757 measured reflections
3199 independent reflections
2682 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.052$
$\theta_{\max} = 28.26°$
$h = -10 \rightarrow 10$
$k = -27 \rightarrow 27$
$l = -11 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.087$
$S = 1.159$
3199 reflections
124 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 6.6027P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.29$ e Å^{-3}
$\Delta\rho_{\min} = -1.96$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ru1—N1	2.266 (3)	I1—I2	2.883 (1)
Ru1—N2	2.266 (3)	I2—I3	2.949 (1)
Ru1—Cl1	2.339 (1)		
N1—Ru1—N1$^{\rm i}$	180.0 (2)	N2$^{\rm i}$—Ru1—Cl1	88.1 (1)
N1—Ru1—N2$^{\rm i}$	91.4 (1)	N2—Ru1—Cl1	91.94 (9)
N1—Ru1—N2	88.6 (1)	Cl1—Ru1—Cl1$^{\rm i}$	180.0 (1)
N1—Ru1—Cl1	88.3 (1)	I1—I2—I3	177.25 (3)
N1$^{\rm i}$—Ru1—Cl1	91.7 (1)		

Symmetry code: (i) $-x, 1-y, -z$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1397). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1989). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Blake, A. J., Devillanova, F. A., Gould, R. O., Li, W. S., Lippolis, V., Parsons, S., Radek, C. & Schroder, M. (1998). *Chem. Soc. Rev.* **27**, 195–216.
Blake, A. J., Gould, R. O., Parsons, S., Radek, C. & Schroder, M. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2374–2376.
Blake, A. J., Lippolis, V., Parsons, S. & Schroder, M. (1996). *Chem. Commun.* pp. 293–295.
Che, C. M., Wong, K. Y. & Poon, C. W. (1986). *Inorg. Chem.* **25**, 1809–1813.
Desiraju, G. R. (1989). In *Crystal Engineering*: *Design of Organic Solids.* Amsterdam: Elsevier.
Mak, T. C. W., Che, C. M. & Wong, K. Y. (1985). *J. Chem. Soc. Chem. Commun.* pp. 986–988.
Roboson, R., Abrahams, B. F., Batlen, S. R., Gable, R. W., Hoskins, B. F. & Liu, J. (1992). *Supramolecular Architecture*, ch. 19. Washington, DC: American Chemical Society.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL Software Reference Manual.* Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Xiong, R. G., Liu, C. M., Zuo, J. L. & You, X. Z. (1999). *Inorg. Chem. Commun.* **2**, 292–297.
Zuo, J. L., Fun, H.-K., Chinnakali, K., You, X. Z. & Che, C. M. (1998). *New J. Chem.* **22**, 923–925.