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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: OH1067). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Dichlorotetrakis(pyridine-*N*)-ruthenium(II)

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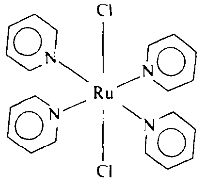
Abstract

We present here the crystal structure of *trans*-$[RuCl_2(C_5H_5N)_4]$, which exhibits notably shorter *M*—N and *M*—Cl bond lengths, and hence reduced unit-cell dimensions, when compared with the previously reported isomorphous compounds of the first transition series, $[MCl_2(C_5H_5N)_4]$ (M = Fe, Co, Ni).

Comment

As part of our studies (Elsegood & Tocher, 1988, 1989; Aronson, Elsegood, Steed & Tocher, 1991; Elsegood, 1991) on ruthenium(II)[2_2](1,4)-cyclophane compounds, we have investigated the reactivity of the dinuclear triply chloro-bridged compound $[Ru_2(\eta^6\text{-}C_{16}H_{16})_2(\mu\text{-}Cl)_3][PF_6]$ towards various reagents. Prolonged exposure (12 h) to pyridine in methanol, resulted in cleavage of the dimer and displacement of the aromatic ligands giving the well known compound *trans*-$[RuCl_2(C_5H_5N)_4]$, (I) (Long & Clarke, 1978; Robertson & Stephenson, 1976; Robertson, Stephenson & Arthur, 1978; Abel, Bennett & Wilkinson, 1959), the crystal structure of which we report here.



(I)

The structures of a number of *trans*-dichloride metal tetrakis(pyridine) complexes have been reported (Al-Zamil *et al.*, 1982; Bachman, Whitmire, Mandal & Bharadwaj, 1992; Rozière, Lehmann & Potier, 1979; Dobinson, Mason & Russell, 1967; Pullman, Hensen & Bats, 1982; Sinclair, Small & Worrall, 1981). These fall into two main categories: those with metal ions in the 2+ oxidation state and those with metal ions in the 3+ oxidation state. The most comprehensive study in this field, by Long & Clarke (1978), reports the structures of the three isomorphous anhydrous compounds *trans*-$[MCl_2(C_5H_5N)_4]$ (M = Fe, Co, Ni), and the hydrated compound *trans*-$[FeCl_2(C_5H_5N)_4].H_2O$. The structure of the Ni compound was redetermined by Bachman *et al.* (1992) at low temperature, with the cell parameters and interatomic distances being slightly smaller than those determined at ambient temperature by Long & Clarke (1978). The data from Long & Clarke's experiment is used for comparison with the present room-temperature data.

The crystals of *trans*-$[FeCl_2(C_5H_5N)_4].H_2O$ were grown by the slow evaporation of a reaction solution open to the air (Long & Clarke, 1978). The anhydrous analogue was obtained only under a moisture-free atmosphere. In contrast, the anhydrous compound *trans*-$[RuCl_2(C_5H_5N)_4]$ was obtained simply be evaporation of the methanolic reaction solution in an open vessel. The crystals of com-

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pounds of the first transition series, namely *trans*-$[M\mathrm{Cl}_2(\mathrm{C}_5\mathrm{H}_5\mathrm{N})_4]$ (M = Fe, Co, Ni) and *trans*-$[\mathrm{FeCl}_2(\mathrm{C}_5\mathrm{H}_5\mathrm{N})_4].\mathrm{H}_2\mathrm{O}$, are reported to lose pyridine from their surfaces, and were mounted in capillaries containing the mother liquor during their structure determinations. No such surface degradation has been observed for the crystals of the title compound, nor did the crystal degrade in the X-ray beam during the diffraction experiment. A displacement ellipsoid plot of *trans*-$[\mathrm{RuCl}_2(\mathrm{C}_5\mathrm{H}_5\mathrm{N})_4]$ is presented in Fig. 1.

The asymmetric unit comprises one quarter of the formula unit and the structure is isomorphous with those of the compounds *trans*-$[M\mathrm{Cl}_2(\mathrm{C}_5\mathrm{H}_5\mathrm{N})_4]$ (M = Fe, Co, Ni). Long & Clarke (1978) give a detailed description of the geometry of the molecule and the packing in the unit cell. Table 3 contains selected crystal data for the four anhydrous compounds. The most striking feature which is apparent on comparing the data in this table is the decrease in unit-cell dimensions, and hence unit-cell volume, across the first transition series, and from the first to second row in Group 8. The explanation for these trends lies in the significant decrease in the M—N distances from Fe [2.247 (4) Å] to Ni [2.133 (4) Å] and from Fe [2.247 (4) Å] to Ru [2.073 (3) Å]. There is also a small decrease in the M—Cl distances on comparing the data for Fe [2.419 (2) Å] with that for Ru [2.406 (1) Å].

Long & Clark (1978) suggest in their paper that if the M—N distance becomes too short, unfavourable pyridine–pyridine interactions at H(1) and C(5) would result. On the basis of the trend in M—N distances across the first transition period, *trans*-$[\mathrm{ZnCl}_2(\mathrm{C}_5\mathrm{H}_5\mathrm{N})_4]$ is predicted to have a Zn—N distance of *ca* 1.99 Å. However, the compound *trans*-$[\mathrm{ZnCl}_2(\mathrm{C}_5\mathrm{H}_5\mathrm{N})_4]$ is not known and it is $[\mathrm{ZnCl}_2(\mathrm{C}_5\mathrm{H}_5\mathrm{N})_2]$ which is observed. The metal ion in this compound of course displays tetrahedral geometry and also exhibits a notably longer Zn—N distance [2.049 (6) Å]. The Ru—N distance of 2.073 (3) Å in *trans*-$[\mathrm{RuCl}_2(\mathrm{C}_5\mathrm{H}_5\mathrm{N})_4]$ is, therefore, long enough for these unfavourable interactions to be small and not cause such a geometry change, which would no doubt have been unlikely in any case given the t_{2g}^6 electronic configuration of the octahedral metal ion.

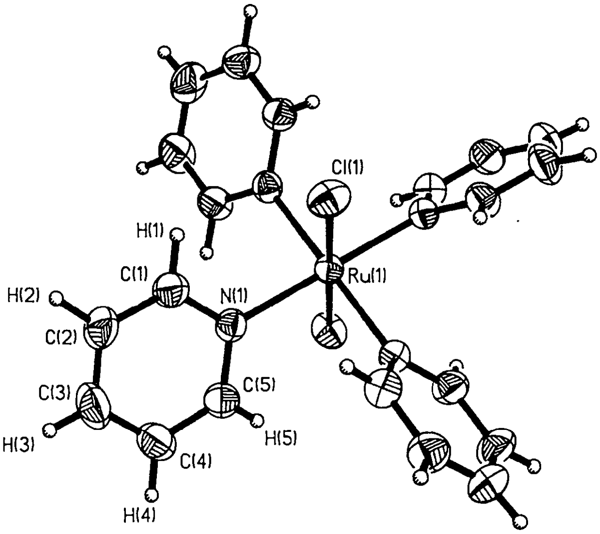

Fig. 1. Displacement ellipsoid plot of the molecule *trans*-$[\mathrm{RuCl}_2(\mathrm{C}_5\mathrm{H}_5\mathrm{N})_4]$. Atoms are represented by displacement ellipsoids at the 50% probability level and the atom-labelling scheme is shown.

Experimental

Crystal data

$[\mathrm{RuCl}_2(\mathrm{C}_5\mathrm{H}_5\mathrm{N})_4]$
$M_r = 488.4$
Tetragonal
$I4_1/acd$
$a = 15.664$ (2) Å
$c = 16.970$ (2) Å
$V = 4164$ (1) Å^3
$Z = 8$
$D_x = 1.56$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6$–15.5°
$\mu = 0.97$ mm^{-1}
$T = 293$ K
Block
0.40 × 0.16 × 0.13 mm
Red

Data collection

Nicolet $R3m/V$ diffractometer
ω/θ scans
Absorption correction: empirical
$T_{\min} = 0.582$, $T_{\max} = 0.626$
4139 measured reflections
933 independent reflections
757 observed reflections $[I \geq 1.5\sigma(I)]$

$R_{\mathrm{int}} = 0.0306$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 19$
$l = 0 \rightarrow 21$
3 standard reflections monitored every 97 reflections intensity variation: none

Refinement

Refinement on F
$R = 0.0453$
$wR = 0.0320$
$S = 2.2258$
757 reflections
83 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.000029F^2]$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.45$ e Å^{-3}
$\Delta\rho_{\min} = -0.53$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

U_{iso} for H atoms; $U_{\mathrm{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	$U_{\mathrm{eq}}/U_{\mathrm{iso}}$
Ru(1)	0	1/4	1/8	0.029 (1)
Cl(1)	0.1086 (1)	0.1414 (1)	1/8	0.045 (1)
N(1)	0.0668 (2)	0.3155 (2)	0.0386 (2)	0.034 (1)
C(1)	0.1042 (3)	0.2752 (3)	−0.0221 (3)	0.043 (2)
C(2)	0.1487 (3)	0.3173 (3)	−0.0798 (3)	0.055 (2)

C(3)	0.1566 (4)	0.4040 (4)	−0.0771 (3)	0.059 (2)
C(4)	0.1188 (3)	0.4466 (3)	−0.0154 (3)	0.050 (1)
C(5)	0.0749 (3)	0.4016 (3)	0.0402 (3)	0.040 (1)
H(1)	0.0993 (27)	0.2135 (27)	−0.0236 (23)	0.051 (12)
H(2)	0.1744 (28)	0.2849 (27)	−0.1226 (25)	0.060 (13)
H(3)	0.1803 (33)	0.4315 (33)	−0.1138 (30)	0.079 (15)
H(4)	0.1220 (29)	0.5080 (31)	−0.0132 (28)	0.073 (16)
H(5)	0.0492 (24)	0.4278 (25)	0.0767 (22)	0.037 (12)

Table 2. *Selected geometric parameters* (Å, °)

Ru(1)—Cl(1)	2.406 (1)	Ru(1)—N(1)	2.073 (3)
N(1)—C(1)	1.341 (5)	N(1)—C(5)	1.355 (5)
C(1)—C(2)	1.371 (6)	C(1)—H(1)	0.970 (40)
C(2)—C(3)	1.365 (7)	C(2)—H(2)	0.974 (42)
C(3)—C(4)	1.375 (7)	C(3)—H(3)	0.843 (49)
C(4)—C(5)	1.365 (6)	C(4)—H(4)	0.964 (46)
C(5)—H(5)	0.845 (36)		
N(1)—Ru(1)—Cl(1)	89.6 (1)	C(1)—N(1)—Ru(1)	122.1 (3)
C(5)—N(1)—Ru(1)	121.7 (3)	C(5)—N(1)—C(1)	116.3 (3)
C(2)—C(1)—N(1)	123.0 (4)	H(1)—C(1)—N(1)	117.0 (25)
H(1)—C(1)—C(2)	120.0 (25)	C(3)—C(2)—C(1)	120.0 (5)
H(2)—C(2)—C(1)	119.5 (26)	H(2)—C(2)—C(3)	120.4 (26)
C(4)—C(3)—C(2)	118.0 (4)	H(3)—C(3)—C(2)	121.5 (37)
H(3)—C(3)—C(4)	120.3 (38)	C(5)—C(4)—C(3)	119.6 (4)
H(4)—C(4)—C(3)	119.5 (29)	H(4)—C(4)—C(5)	120.9 (29)
C(4)—C(5)—N(1)	123.2 (4)	H(5)—C(5)—N(1)	117.0 (27)
H(5)—C(5)—C(4)	119.8 (27)		

Table 3. *Crystal data for trans*-$[M\mathrm{Cl}_2(C_5H_5N)_4]$ *compounds*

	$[Fe(py)_4Cl_2]^a$	$[Co(py)_4Cl_2]^a$	$[Ni(py)_4Cl_2]^{a,b}$	$[Ru(py)_4Cl_2]^c$
a (Å)	15.945 (2)	15.966 (2)	15.920 (3)	15.664 (2)
c (Å)	17.287 (6)	17.153 (6)	17.046 (12)	16.970 (2)
D_x (Mg m^{-3})	1.34	1.36	1.37	1.56
μ (mm^{-1})	0.96	1.07	1.16	0.97
No. parameters refined	63	63	63	83^d
No. observed reflections	533	686	848	757
R	0.0477	0.0483	0.0489	0.0453
wR	0.0652	0.0668	0.0748	0.0320
M—Cl (Å)	2.430 (3)	2.444 (2)	2.437 (2)	2.406 (1)
M—N (Å)	2.229 (6)	2.183 (4)	2.133 (4)	2.073 (3)

Notes: (*a*) Long & Clarke (1978); (*b*) crystal corresponds to the formulation $Ni_{0.97}Fe_{0.03}(py)_4Cl_2$; (*c*) this work; (*d*) H atoms refined.

The positions of all the non-H atoms were found by direct methods. Iterative application of least-squares refinement and difference Fourier synthesis led to the development of the entire structure, including the H atoms. All non-H atoms were refined anisotropically, while the H atoms were freely refined using an isotropic model. Crystallographic calculations were performed using the *SHELXTL-Plus* program package (Sheldrick, 1987).

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$(\mu\text{-H})(\mu\text{-OH})Os_3(CO)_{10}$

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Abstract

The title compound, decacarbonyl-1κ^4C,2κ^3C,3κ^3C-μ-hydrido-2:3κ^2H-μ-hydroxy-2:3κ^2O-trisosmium-(3 *Os*—*Os*), consists of an Os triangle, doubly bridged on one side by a hydrido and a hydroxy group. The coordination around the Os atoms was found to be octahedral.

Comment

The triosmium complex $(\mu\text{-H})(\mu\text{-OH})Os_3(CO)_{10}$, (I), was first reported in 1968 as the product of the reduction of $Os_3(CO)_{12}$ by $Na^+.BH_4^-$ (Johnson, Lewis & Kilty, 1968). Since then two other synthetic

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