O12	−0.1819 (3)	0.4418 (2)	0.9778 (2)	4.15 (6)
O13	0.4319 (4)	0.6090 (2)	0.2541 (2)	5.15 (7)
O14	0.5732 (4)	0.5891 (2)	0.1353 (2)	4.91 (7)
O15	0.5474 (4)	0.1985 (3)	−0.0683 (2)	5.94 (8)
O16	0.3729 (4)	0.0638 (2)	−0.0381 (2)	4.23 (6)
O17	0.5145 (4)	0.1123 (2)	0.7099 (2)	5.31 (7)
O18	0.2777 (3)	−0.0700 (2)	0.5563 (2)	3.57 (6)
O19	0.2501 (3)	0.5834 (2)	0.4472 (2)	3.61 (6)
O20	0.9209 (5)	0.3471 (2)	0.2716 (2)	6.30 (9)
N1	0.0592 (4)	−0.0310 (3)	0.8284 (2)	3.79 (7)
N2	−0.1012 (4)	0.3563 (3)	0.9893 (2)	3.53 (7)
N3	0.4914 (4)	0.5491 (3)	0.1890 (2)	3.46 (7)
N4	0.4591 (4)	0.1596 (3)	−0.0171 (2)	3.33 (7)
C1	0.0433 (4)	0.2531 (3)	0.7585 (2)	2.32 (7)
C2	0.0637 (4)	0.1360 (3)	0.7563 (2)	2.45 (7)
C3	0.0309 (5)	0.0939 (3)	0.8318 (2)	2.59 (7)
C4	−0.0216 (5)	0.1630 (3)	0.9090 (2)	2.93 (7)
C5	−0.0433 (4)	0.2780 (3)	0.9084 (2)	2.57 (7)
C6	−0.0131 (4)	0.3262 (3)	0.8355 (2)	2.55 (7)
C7	0.0881 (5)	0.3017 (3)	0.6790 (2)	2.56 (7)
C8	0.3969 (4)	0.2527 (3)	0.2290 (2)	2.51 (7)
C9	0.4214 (4)	0.3736 (3)	0.2438 (2)	2.56 (7)
C10	0.4634 (5)	0.4211 (3)	0.1726 (2)	2.52 (7)
C11	0.4804 (5)	0.3546 (3)	0.0869 (2)	2.75 (7)
C12	0.4505 (5)	0.2348 (3)	0.0746 (2)	2.59 (7)
C13	0.4093 (5)	0.1820 (3)	0.1432 (2)	2.59 (7)
C14	0.3490 (5)	0.1989 (3)	0.3062 (2)	2.83 (7)

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

Co—O1	2.059 (2)	Co—O8	2.116 (2)
Co—O3	2.052 (2)	O1—C7	1.253 (4)
Co—O5	2.087 (2)	O2—C7	1.248 (4)
Co—O6	2.110 (2)	O3—C14	1.250 (4)
Co—O7	2.096 (2)	O4—C14	1.248 (4)
O1—Co—O3	178.53 (8)	O5—Co—O7	179.3 (1)
O1—Co—O5	90.80 (9)	O5—Co—O8	88.82 (9)
O1—Co—O6	91.4 (1)	O6—Co—O7	86.09 (9)
O1—Co—O7	88.71 (9)	O6—Co—O8	177.74 (9)
O1—Co—O8	89.0 (1)	O7—Co—O8	91.69 (9)
O3—Co—O5	88.20 (9)	Co—O1—C7	131.6 (2)
O3—Co—O6	89.7 (1)	Co—O3—C14	130.8 (2)
O3—Co—O7	92.30 (9)	O1—C7—O2	126.2 (3)
O3—Co—O8	89.9 (1)	O3—C14—O4	126.2 (3)
O5—Co—O6	93.40 (9)		
O9—N1—C3—C2	11.1 (5)	O15—N4—C12—C11	22.8 (5)
O10—N1—C3—C4	12.0 (5)	O16—N4—C12—C13	23.7 (5)
O11—N2—C5—C4	25.4 (5)	C2—C1—C7—O1	4.9 (4)
O12—N2—C5—C6	25.5 (4)	C6—C1—C7—O2	2.3 (5)
O13—N3—C10—C11	161.8 (3)	C9—C8—C14—O3	−2.4 (5)
O14—N3—C10—C9	162.2 (3)	C13—C8—C14—O4	−2.0 (5)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O5—H51···O2	0.80	2.06	2.767 (4)	146.6
O5—H52···O19	1.08	1.67	2.747 (4)	171.2
O6—H61···O19$^{\rm i}$	0.91	1.92	2.808 (4)	165.1
O6—H62···O20$^{\rm ii}$	1.03	1.72	2.704 (4)	157.6
O7—H71···O18	0.85	1.97	2.803 (3)	167.9
O7—H72···O4	0.97	1.78	2.699 (4)	156.5
O8—H81···O17	0.79	2.04	2.815 (4)	166.6
O8—H82···O18$^{\rm iii}$	0.86	1.94	2.785 (4)	167.5
O17—H171···O4$^{\rm iii}$	0.87	1.91	2.724 (4)	155.7
O18—H181···O17	0.94	2.12	3.022 (3)	161.5
O18—H182···O6$^{\rm iv}$	1.04	2.02	3.010 (3)	158.6
O19—H192···O2$^{\rm i}$	0.99	1.93	2.887 (4)	162.0
O20—H201···O2$^{\rm v}$	0.88	1.98	2.792 (3)	152.4

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $x-1, y, z$; (iii) $1-x, -y, 1-z$; (iv) $-x, -y, 1-z$; (v) $1-x, 1-y, 1-z$.

H atoms bound to C atoms were placed geometrically at a distance of 1.05 Å, while water H atoms were taken from difference maps. For all H atoms, $U_{\rm iso} = 1.3U_{\rm eq}$ for the parent atom and a riding model was adopted.

Data collection: *CAD*-4 *EXPRESS Software* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN SIMPEL*. Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP* (Johnson, 1965) in *MolEN*. Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1053). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Amin, A. S., El-Ansary, A. L. & Issa, Y. M. (1994). *Talanta*, **41**, 691–694.

Enraf–Nonius (1993). *CAD*-4 *EXPRESS Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Odunola, O. A. (1993). *Synth. React. Inorg. Met. Org. Chem.* **23**, 1241–1249.

Prince, P., Fronczek, F. R. & Gandour, R. D. (1991). *Acta Cryst.* C**47**, 895–898.

Acta Cryst. (1996). C**52**, 1394–1399

The Pseudo-Racemic Complex Bis[tris(2,2′-bipyridine)ruthenium(II)] Hexacyanocobaltate(III) Chloride Octahydrate, $[Ru(bpy)_3]_2[Co(CN)_6]Cl.8H_2O$

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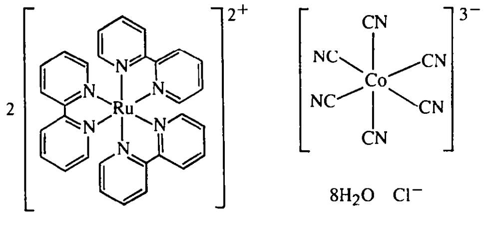
Abstract

Crystals of $[Ru(C_{10}H_8N_2)_3]_2[Co(CN)_6]Cl.8H_2O$ ($C_{10}H_8N_2$ = bpy = 2,2′-bipyridine) which belong to the space group $C2$ are characterized by two 'pseudo-racemic' crystallographically independent $[Ru(bpy)_3]^{2+}$ cations. Three kinds of layers are found in the crys-

tal structure: (i) a layer consisting of Λ-$[Ru(bpy)_3]^{2+}$ cations and water molecules; (ii) a layer of $[Co(CN)_6]^{3-}$ and Cl^- anions and water molecules; (iii) a layer of Δ-$[Ru(bpy)_3]^{2+}$ cations and water molecules. The layers are stacked in the order (i), (ii), (iii) and (ii) almost perpendicularly to the *c* axis. Some O···O, O···N(cyano) and O···Cl hydrogen bonds construct networks within and between the layers.

Comment

Photo-induced ion–ion reactions in ionic crystals such as double-complex salts have rarely been investigated. We have recently studied the quenching reactions of a metal-to-ligand charge-transfer (MLCT) excited state of Ru^{II} with Co^{III} in crystals of $[RuL_3]_2[Co(CN)_6]X.nH_2O$ [L = bpy and dmbpy (= 4,4′-dimethyl-2,2′-bipyridine); X = Cl^-, $0.5SO_4^{2-}$ and BF_4^-] (Iguro, Ikeda & Ohno, 1994). In the course of the study, it was found that the Ru^{II}–Co^{III} compounds with various simple anions (X) and bulky ligands (L) cause various quenching efficiency. The title double-complex salt, (I), for which the photo-induced quenching reaction occurs efficiently prompted the investigation of the crystal structure by means of X-ray analysis in order to gain a better understanding of the excited-state quenching.



(I)

Fig. 1 illustrates perspective views of the $[Ru(bpy)_3]^{2+}$ cations and the $[Co(CN)_6]^{3-}$ anion together with the atom-numbering scheme (*ORTEP*II; Johnson, 1976). There are crystallographically independent Δ- and Λ-$[Ru(bpy)_3]^{2+}$ cations which are approximately related to each other by a non-crystallographic centre of symmetry. The title complex is, therefore, pseudo-racemic in spite of the chiral space group. Similar complexes have been reported only for $[(\pm)\text{-}Co(en)_3](C_2O_4)I.1.5H_2O$ (Fuertes, Miravitlles, Ibáñez, Martínez-Tamayo & Beltrán-Porter, 1988) and $[Co(C_3H_{10}N_2)_2(C_2H_8N_2)](ClO_4)Cl_2.H_2O$ (Searle & Tiekink, 1989).

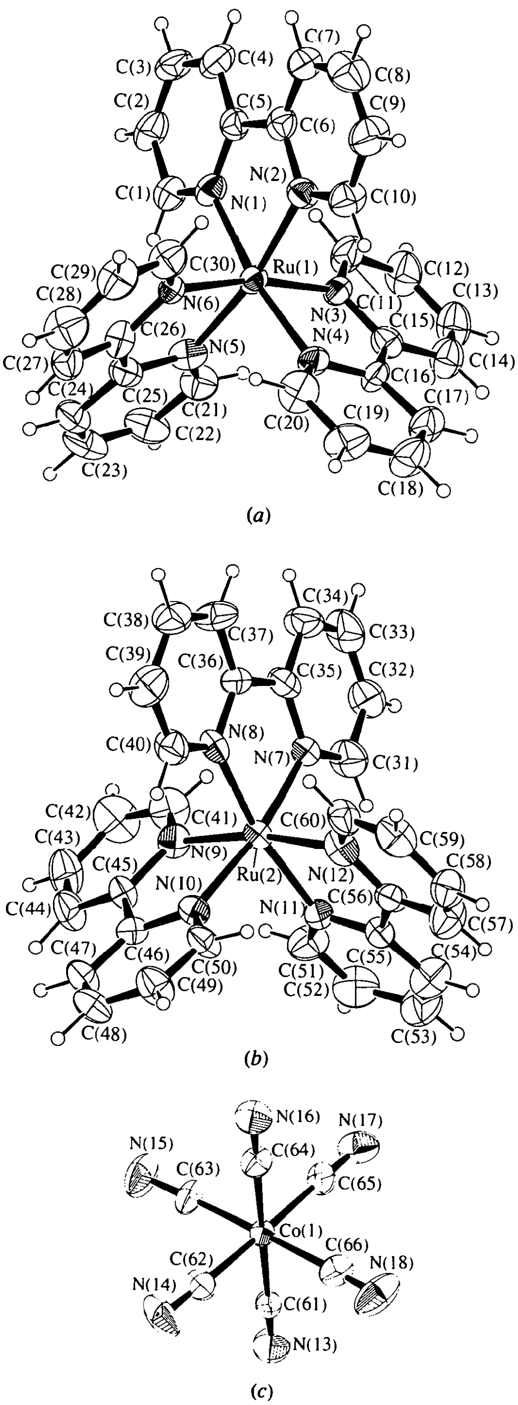


Fig. 1. *ORTEP*II (Johnson, 1976) drawings of (*a*) the Λ-Ru(1) cation, (*b*) the Δ-Ru(2) cation, and (*c*) the Co(1) anion, with the displacement ellipsoids at the 50% probability level. The atom-numbering scheme is shown.

The Ru atoms have distorted octahedral configurations. The inter-ligand *transoid* N—Ru—N angles of 169.4 (2)–170.3 (2)° are far from the ideal value of 180° for perfect octahedral geometry compared with those of related tris(bpy) complexes, such as $[Co(bpy)_3]Cl_2.2H_2O.C_2H_5OH$, (II) (average N—Ru—N angle 167.4°; Szalda, Creutz, Mahajan & Sutin, 1983), $[Ni(bpy)_3]SO_4.7.5H_2O$, (III) (169.7°; Wada, Sakabe & Tanaka, 1976), $[Ni(bpy)_3]_2Cl_2.C_4H_4O_6.nH_2O$, (IV) (170.0°; Wada, Katayama & Tanaka, 1976), $[Cr(bpy)_3](PF_6)_3$ (171.0°; Goodwin, Pennington & Petersen, 1989), $[Cr(bpy)_3](ClO_4)_3.HbpyClO_4$ (172.0°; Lee & Hoggard, 1989), $[Ru(bpy)_3](PF_6)_3$, (V) (172.3°; Biner, Bürgi, Ludi & Röhr, 1992), $[Ru(bpy)_3](PF_6)_2$ (172.6°;

Biner *et al.*, 1992), $[Ir(bpy)_3](ClO_4)_3.1.5H_2O$ (173.6°; Hazell & Hazell, 1984), $[Ni(bpy)_3](ClO_4)_3.2CH_3CN.0.5CH_2Cl_2$, (VI) (174.8°; Szalda, Macartney & Sutin, 1984), $[Fe(bpy)_3][Fe(CN)_5(NO)].4H_2O$ (175.2°; Posse *et al.*, 1984) and $[Co(bpy)_3][Fe(CN)_6].8H_2O$, (VII) (176.3°; Yanagi, Ohashi, Sasada, Kaizu & Kobayashi, 1981). The corresponding values of the bond lengths and angles in both the cations agree fairly well with one another. The average Ru—N, pyridyl C—C, N—C and the connecting C—C bond lengths are 2.072, 1.382, 1.355 and 1.456 Å for the Λ-Ru(1) cation, and 2.063, 1.379, 1.352 and 1.473 Å for the Δ-Ru(2) cation, respectively. The average N—Ru—N, Ru—N—C and N—C—C bond angles in the five-membered rings are 78.6, 115.1 and 115.3° for the Ru(1) cation, and 79.0, 115.4 and 115.0° for the Ru(2) cation, respectively. These bond lengths and angles which characterize $[Ru(bpy)_3]^{2+}$ cations are very similar to the corresponding values in other $Ru(bpy)_3$ complexes, such as $[Ru(bpy)_3](ClO_4)_2$ (Harrowfield & Sobolev, 1994), $[Ru(bpy)_3](ClO_4)_2.H_2O$ (Krausz, Riesen & Rae, 1995) and (V). The bpy ligand is not in a planar conformation. The two rings of each bpy ligand are twisted along the connecting C—C bond by 7.2–10.5°, which is similar to the twisting observed for (III) (6.8–10.9°) and (VI) (4.4–12.7°), and different from that of (II) (average 3.6°), (VII) (2.3–4.7°), $[Co(bpy)_3]Cl.H_2O$ (average 3.0°; Szalda *et al.*, 1983) and $[Mn(bpy)_3](ClO_4)_2.0.5H_2O$ (13, 25°; Chen, Wang & Xu, 1995).

The average Co—C and C—N distances (1.898 and 1.143 Å, respectively) are in good agreement with those (average 1.896 and 1.146 Å) of other hexacyanocobalt(III) complexes (Orpen *et al.*, 1989). The average Co—C—N angle (177.2°) is in the range 175.6 (8)–178.2 (6)°.

As shown in Fig. 2 (*ORTEP*II; Johnson, 1976), the crystal structure is constructed by the following three kinds of layers: (i) the layer consisting of the Λ-$[Ru(bpy)_3]^{2+}$ cation and a water molecule [O(1)]; (ii) the layer of the $[Co(CN)_6]^{3-}$ and Cl^- anions and water molecules [O(3–9)]; (iii) the layer of the Δ-$[Ru(bpy)_3]^{2+}$ cation and a water molecule [O(2)]. The layers are stacked in the order (i), (ii), (iii) and (ii) almost perpendicularly to the *c* axis. Thus the positively and negatively charged layers are stacked alternately.

The water molecules containing O(1) and O(2) are surrounded by six Λ- and six Δ-$[Ru(bpy)_3]^{2+}$ cations, respectively. On the other hand, in the other complexes (III), (IV) and $Na_{0.5}\{\Delta\text{-}[Co(bpy)_3]Cl_{0.5}(\text{D-tart})\}.6.5H_2O$ (Tada, 1982) having layered structures, the simple anions (Cl^-, SO_4^{2-}) are surrounded by the cations. In the double-complex salt (VII), having a bulky anion, the alternate arrangement of the columns of cations and anions is found. The O(1) and O(2) atoms are linked to N(13) [2.793 (7) Å] and N(16) [2.805 (7) Å] of $[Co(CN)_6]^{3-}$, respectively, by hydrogen bonds, by which layer (i) or (iii) is joined to layer (ii). Some O···O, O···N(cyano) and O···Cl hydrogen bonds form a two-dimensional network within layer (ii) [Fig. 3 (*CHARON*; Lauher, 1989)]. Some intermolecular O···C(pyridyl) non-bonded contacts within 3.60 Å are shown in Table 3. They may be related to the electronic interaction between the $[Ru(bpy)_3]^{2+}$ cations and the $[Co(CN)_6]^{3-}$ anions through the hydrogen bonds.

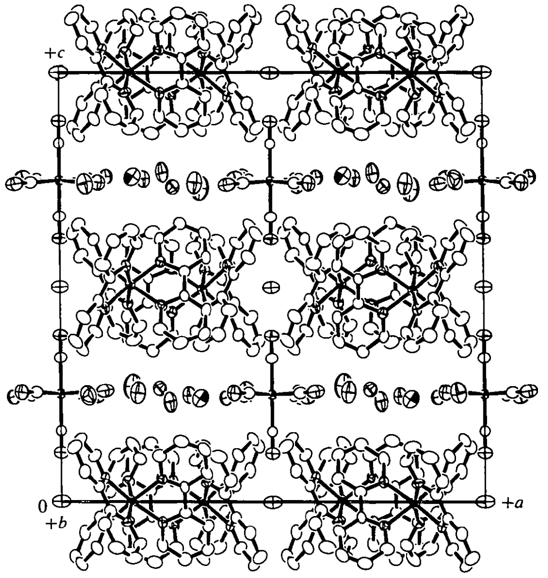


Fig. 2. Crystal structure projected along the *b* axis. All H atoms are omitted for clarity.

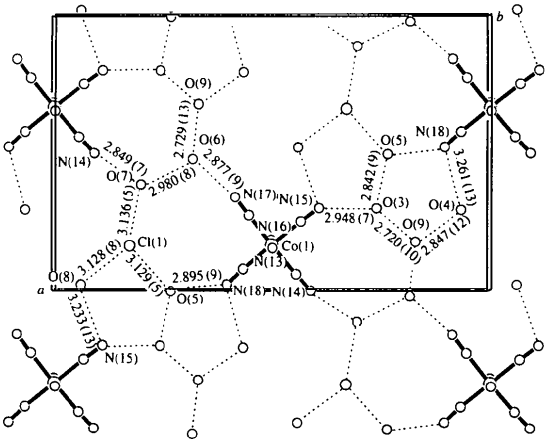


Fig. 3. The hydrogen-bonded network within layer (ii) projected along the *c* axis. Dashed lines indicate the hydrogen bonds.

Further structural investigations of $[RuL_3]_2[Co(CN)_6]X.nH_2O$ (L = bpy and dmbpy, $X = 0.5SO_4^{2-}$ and BF_4^-) are in progress in order to reveal how the crystal structures contribute to the excited-state quenching.

Experimental

The title crystals were grown by a diffusion method from aqueous solutions of $[Ru(bpy)_3]Cl_2$ and $K_3[Co(CN)_6]$ at room temperature (Iguro, Ikeda & Ohno, 1994).

Crystal data

$[Ru(C_{10}H_8N_2)_3]_2[Co(CN)_6]$-$Cl.8H_2O$
$M_r = 1533.87$
Monoclinic
$C2$
$a = 22.201\ (5)$ Å
$b = 13.667\ (3)$ Å
$c = 22.087\ (4)$ Å
$\beta = 90.43\ (2)°$
$V = 6701\ (2)$ Å^3
$Z = 4$
$D_x = 1.520$ Mg m^{-3}
$D_m = 1.52$ Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 19.61$–$20.00°$
$\mu = 0.80$ mm^{-1}
$T = 296$ K
Prismatic
0.50 × 0.50 × 0.30 mm
Orange

Data collection

Rigaku AFC-7R diffractometer
$\theta/2\theta$ scans
Absorption correction:
  ψ scan (North, Phillips & Mathews, 1968)
  $T_{\min} = 0.909$, $T_{\max} = 1.000$
10396 measured reflections
10151 independent reflections

8740 observed reflections $[I > 3.0\sigma(I)]$
$R_{\rm int} = 0.058$
$\theta_{\max} = 30.11°$
$h = 0 \rightarrow 31$
$k = 0 \rightarrow 19$
$l = -31 \rightarrow 31$
3 standard reflections
  monitored every 150 reflections
  intensity decay: 2.40%

Refinement

Refinement on F
$R = 0.035$
$wR = 0.060$
$S = 1.56$
8740 reflections
866 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.0009F_o^2]$

$(\Delta/\sigma)_{\max} = 0.14$
$\Delta\rho_{\max} = 0.59$ e Å^{-3}
$\Delta\rho_{\min} = -0.74$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2A)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ru(1)	0.16489 (2)	0.1860	0.00198 (2)	0.0299 (1)
Ru(2)	0.16525 (2)	0.13811 (3)	0.50735 (2)	0.0297 (1)
Co(1)	0.50009 (3)	0.16039 (8)	0.25011 (3)	0.0266 (1)
Cl(1)	0.82898 (9)	0.1565 (2)	0.2400 (1)	0.0668 (6)
O(1)	1/2	0.2400 (7)	0	0.061 (2)
O(2)	0	0.5847 (7)	1/2	0.058 (2)
O(3)	0.2582 (2)	0.2960 (5)	0.2320 (3)	0.074 (2)
O(4)	0.0648 (3)	0.2888 (8)	0.2480 (4)	0.096 (3)
O(5)	0.7331 (2)	−0.0067 (4)	0.2635 (2)	0.057 (1)
O(6)	0.6819 (2)	0.4754 (4)	0.2558 (3)	0.082 (2)
O(7)	0.8027 (2)	0.3817 (4)	0.2465 (2)	0.054 (1)
O(8)	0.9400 (3)	0.0178 (7)	0.2562 (4)	0.097 (3)
O(9)	0.1694 (3)	0.1729 (8)	0.2689 (5)	0.121 (3)
N(1)	0.1026 (2)	0.2601 (4)	−0.0520 (2)	0.036 (1)
N(2)	0.1574 (2)	0.3189 (4)	0.0469 (2)	0.036 (1)
N(3)	0.2377 (2)	0.2344 (4)	−0.0470 (2)	0.032 (1)
N(4)	0.2361 (2)	0.1336 (5)	0.0544 (2)	0.034 (1)
N(5)	0.1558 (2)	0.0551 (4)	−0.0437 (2)	0.038 (1)
N(6)	0.1018 (2)	0.1152 (4)	0.0547 (2)	0.031 (1)
N(7)	0.1035 (2)	0.0695 (4)	0.4521 (2)	0.036 (1)
N(8)	0.1557 (2)	0.0084 (4)	0.5513 (2)	0.035 (1)
N(9)	0.2374 (2)	0.0858 (4)	0.4580 (2)	0.039 (1)
N(10)	0.2364 (2)	0.1870 (4)	0.5598 (2)	0.033 (1)
N(11)	0.1589 (2)	0.2693 (4)	0.4619 (2)	0.033 (1)
N(12)	0.1013 (2)	0.2127 (5)	0.5592 (2)	0.042 (1)
N(13)	0.5002 (3)	0.1480 (6)	0.1129 (2)	0.054 (2)
N(14)	0.4097 (3)	−0.0040 (7)	0.2547 (3)	0.066 (2)
N(15)	0.3907 (3)	0.2963 (7)	0.2420 (3)	0.063 (2)
N(16)	0.5003 (2)	0.1811 (6)	0.3879 (2)	0.049 (1)
N(17)	0.5859 (3)	0.3353 (5)	0.2429 (3)	0.054 (2)
N(18)	0.6037 (4)	0.0183 (7)	0.2579 (3)	0.073 (2)
C(1)	0.0820 (3)	0.2286 (6)	−0.1066 (3)	0.045 (2)
C(2)	0.0466 (3)	0.2883 (7)	−0.1441 (3)	0.050 (2)
C(3)	0.0325 (3)	0.3799 (6)	−0.1272 (3)	0.046 (2)
C(4)	0.0544 (2)	0.4134 (6)	−0.0714 (3)	0.050 (2)
C(5)	0.0894 (3)	0.3517 (5)	−0.0353 (3)	0.036 (1)
C(6)	0.1155 (2)	0.3843 (5)	0.0233 (2)	0.037 (2)
C(7)	0.1025 (3)	0.4691 (6)	0.0521 (3)	0.046 (2)
C(8)	0.1299 (4)	0.4882 (7)	0.1071 (4)	0.059 (2)
C(9)	0.1691 (3)	0.4280 (8)	0.1314 (4)	0.064 (3)
C(10)	0.1845 (3)	0.3421 (6)	0.0998 (3)	0.046 (2)
C(11)	0.2365 (3)	0.2837 (6)	−0.0997 (3)	0.050 (2)
C(12)	0.2895 (3)	0.3019 (7)	−0.1330 (3)	0.055 (2)
C(13)	0.3442 (3)	0.2769 (7)	−0.1098 (3)	0.053 (2)
C(14)	0.3458 (3)	0.2326 (6)	−0.0550 (3)	0.046 (2)
C(15)	0.2919 (2)	0.2089 (5)	−0.0242 (2)	0.035 (1)
C(16)	0.2901 (2)	0.1597 (5)	0.0343 (2)	0.033 (1)
C(17)	0.3430 (3)	0.1384 (7)	0.0675 (3)	0.047 (2)
C(18)	0.3371 (3)	0.0886 (8)	0.1224 (3)	0.056 (2)
C(19)	0.2829 (3)	0.0620 (7)	0.1410 (3)	0.056 (2)
C(20)	0.2310 (3)	0.0864 (7)	0.1077 (3)	0.056 (2)
C(21)	0.1834 (3)	0.0320 (6)	−0.0967 (3)	0.046 (2)
C(22)	0.1686 (3)	−0.0529 (6)	−0.1290 (3)	0.052 (2)
C(23)	0.1281 (3)	−0.1162 (5)	−0.1046 (3)	0.052 (2)
C(24)	0.1003 (3)	−0.0963 (5)	−0.0496 (3)	0.045 (2)
C(25)	0.1145 (3)	−0.0093 (5)	−0.0193 (3)	0.038 (2)
C(26)	0.0884 (3)	0.0225 (6)	0.0362 (3)	0.040 (2)
C(27)	0.0553 (3)	−0.0406 (6)	0.0716 (3)	0.046 (2)
C(28)	0.0320 (3)	−0.0043 (8)	0.1286 (4)	0.062 (3)
C(29)	0.0452 (3)	0.0877 (7)	0.1459 (3)	0.053 (2)
C(30)	0.0787 (3)	0.1455 (7)	0.1077 (3)	0.048 (2)
C(31)	0.0824 (3)	0.1029 (6)	0.3982 (3)	0.051 (2)
C(32)	0.0502 (3)	0.0440 (7)	0.3582 (3)	0.055 (2)
C(33)	0.0361 (3)	−0.0499 (8)	0.3760 (3)	0.062 (2)
C(34)	0.0550 (3)	−0.0845 (6)	0.4310 (3)	0.051 (2)
C(35)	0.0895 (3)	−0.0236 (6)	0.4688 (3)	0.040 (2)
C(36)	0.1165 (3)	−0.0550 (5)	0.5259 (3)	0.037 (1)
C(37)	0.1009 (3)	−0.1438 (6)	0.5545 (3)	0.051 (2)
C(38)	0.1265 (3)	−0.1680 (6)	0.6097 (3)	0.052 (2)
C(39)	0.1686 (3)	−0.1016 (7)	0.6343 (3)	0.056 (2)
C(40)	0.1803 (3)	−0.0165 (6)	0.6055 (3)	0.047 (2)
C(41)	0.2353 (3)	0.0413 (7)	0.4041 (3)	0.056 (2)
C(42)	0.2830 (4)	0.0152 (8)	0.3720 (3)	0.066 (2)
C(43)	0.3393 (3)	0.0476 (8)	0.3927 (3)	0.058 (2)
C(44)	0.3439 (3)	0.0966 (6)	0.4471 (3)	0.047 (2)
C(45)	0.2932 (2)	0.1139 (5)	0.4798 (2)	0.033 (1)
C(46)	0.2934 (2)	0.1676 (4)	0.5373 (2)	0.033 (1)
C(47)	0.3443 (2)	0.1916 (7)	0.5698 (3)	0.042 (1)
C(48)	0.3409 (3)	0.2349 (7)	0.6249 (3)	0.050 (2)
C(49)	0.2835 (3)	0.2552 (7)	0.6490 (3)	0.051 (2)
C(50)	0.2341 (2)	0.2329 (5)	0.6136 (3)	0.041 (1)
C(51)	0.1856 (3)	0.2919 (6)	0.4088 (3)	0.049 (2)
C(52)	0.1728 (4)	0.3737 (8)	0.3776 (3)	0.060 (2)
C(53)	0.1294 (4)	0.4396 (7)	0.3968 (4)	0.065 (2)
C(54)	0.1040 (4)	0.4169 (7)	0.4518 (3)	0.054 (2)
C(55)	0.1183 (2)	0.3326 (5)	0.4824 (3)	0.035 (1)
C(56)	0.0883 (2)	0.3034 (5)	0.5400 (3)	0.035 (1)
C(57)	0.0498 (3)	0.3652 (7)	0.5730 (3)	0.054 (2)
C(58)	0.0307 (3)	0.3363 (6)	0.6277 (3)	0.047 (2)
C(59)	0.0447 (3)	0.2420 (7)	0.6475 (3)	0.055 (2)
C(60)	0.0797 (2)	0.1817 (7)	0.6119 (3)	0.044 (2)
C(61)	0.5004 (2)	0.1506 (5)	0.1640 (2)	0.031 (1)
C(62)	0.4442 (3)	0.0559 (6)	0.2544 (3)	0.041 (2)
C(63)	0.4333 (3)	0.2461 (6)	0.2445 (3)	0.040 (2)
C(64)	0.5000 (2)	0.1709 (5)	0.3357 (2)	0.037 (1)
C(65)	0.5531 (3)	0.2698 (5)	0.2465 (2)	0.036 (1)
C(66)	0.5667 (3)	0.0742 (5)	0.2546 (3)	0.042 (2)

Table 2. *Selected bond lengths (Å) and angles (°)*

Ru(1)—N(1)	2.082 (5)	Ru(2)—N(10)	2.063 (4)
Ru(1)—N(2)	2.078 (5)	Ru(2)—N(11)	2.059 (5)
Ru(1)—N(3)	2.060 (4)	Ru(2)—N(12)	2.095 (5)
Ru(1)—N(4)	2.080 (4)	Co(1)—C(61)	1.906 (4)
Ru(1)—N(5)	2.063 (6)	Co(1)—C(62)	1.895 (7)
Ru(1)—N(6)	2.067 (4)	Co(1)—C(63)	1.893 (6)
Ru(2)—N(7)	2.055 (5)	Co(1)—C(64)	1.896 (5)
Ru(2)—N(8)	2.033 (6)	Co(1)—C(65)	1.905 (7)
Ru(2)—N(9)	2.072 (5)	Co(1)—C(66)	1.892 (7)
N(1)—Ru(1)—N(2)	78.0 (2)	N(8)—Ru(2)—N(12)	95.2 (2)
N(1)—Ru(1)—N(3)	93.6 (2)	N(9)—Ru(2)—N(10)	79.3 (2)
N(1)—Ru(1)—N(4)	170.1 (2)	N(9)—Ru(2)—N(11)	95.4 (2)
N(1)—Ru(1)—N(5)	94.5 (2)	N(9)—Ru(2)—N(12)	170.1 (2)
N(1)—Ru(1)—N(6)	95.7 (2)	N(10)—Ru(2)—N(11)	92.4 (2)
N(2)—Ru(1)—N(3)	92.1 (2)	N(10)—Ru(2)—N(12)	93.2 (2)
N(2)—Ru(1)—N(4)	95.6 (2)	N(11)—Ru(2)—N(12)	78.4 (2)
N(2)—Ru(1)—N(5)	169.7 (2)	C(61)—Co(1)—C(62)	90.3 (3)
N(2)—Ru(1)—N(6)	94.8 (2)	C(61)—Co(1)—C(63)	89.2 (2)
N(3)—Ru(1)—N(4)	78.9 (2)	C(61)—Co(1)—C(64)	179.6 (4)
N(3)—Ru(1)—N(5)	95.5 (2)	C(61)—Co(1)—C(65)	90.4 (2)
N(3)—Ru(1)—N(6)	169.4 (2)	C(61)—Co(1)—C(66)	90.0 (3)
N(4)—Ru(1)—N(5)	92.6 (2)	C(62)—Co(1)—C(63)	87.5 (3)
N(4)—Ru(1)—N(6)	92.4 (2)	C(62)—Co(1)—C(64)	90.1 (3)
N(5)—Ru(1)—N(6)	78.8 (2)	C(62)—Co(1)—C(65)	177.2 (4)
N(7)—Ru(2)—N(8)	79.3 (2)	C(62)—Co(1)—C(66)	92.3 (3)
N(7)—Ru(2)—N(9)	92.6 (2)	C(63)—Co(1)—C(64)	90.7 (2)
N(7)—Ru(2)—N(10)	170.3 (2)	C(63)—Co(1)—C(65)	89.8 (3)
N(7)—Ru(2)—N(11)	93.7 (2)	C(63)—Co(1)—C(66)	179.2 (3)
N(7)—Ru(2)—N(12)	95.4 (2)	C(64)—Co(1)—C(65)	89.3 (3)
N(8)—Ru(2)—N(9)	92.0 (2)	C(64)—Co(1)—C(66)	90.1 (3)
N(8)—Ru(2)—N(10)	95.5 (2)	C(65)—Co(1)—C(66)	90.5 (3)
N(8)—Ru(2)—N(11)	170.1 (2)		

Table 3. *Contact distances (Å)*

O(1)···C(24$^{\rm i}$)	3.346 (9)	O(5)···C(39$^{\rm vi}$)	3.387 (9)
O(1)···C(24$^{\rm ii}$)	3.346 (9)	O(5)···C(40$^{\rm vi}$)	3.464 (8)
O(2)···C(54)	3.428 (10)	O(6)···C(42$^{\rm i}$)	3.441 (10)
O(2)···C(54$^{\rm iii}$)	3.428 (10)	O(6)···C(19$^{\rm i}$)	3.597 (10)
O(2)···C(57)	3.577 (12)	O(6)···C(41$^{\rm i}$)	3.590 (9)
O(2)···C(57$^{\rm iii}$)	3.577 (12)	O(7)···C(42$^{\rm i}$)	3.351 (8)
O(3)···C(10)	3.395 (8)	O(7)···C(12$^{\rm vii}$)	3.402 (8)
O(3)···C(9)	3.469 (10)	O(7)···C(19$^{\rm i}$)	3.417 (9)
O(3)···C(22$^{\rm ii}$)	3.484 (9)	O(7)···C(49$^{\rm vi}$)	3.471 (8)
O(4)···C(2$^{\rm iv}$)	3.360 (9)	O(8)···C(32$^{\rm viii}$)	3.332 (10)
O(4)···C(59$^{\rm iii}$)	3.425 (10)	O(8)···C(33$^{\rm viii}$)	3.509 (11)
O(4)···C(58$^{\rm iii}$)	3.541 (10)	O(8)···C(28$^{\rm viii}$)	3.506 (11)
O(4)···C(29)	3.579 (12)	O(8)···C(29$^{\rm viii}$)	3.520 (11)
O(5)···C(52$^{\rm v}$)	3.296 (9)	O(9)···C(51)	3.508 (12)
O(5)···C(9$^{\rm v}$)	3.358 (8)	O(9)···C(31)	3.589 (12)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, -z$; (iii) $-x, y, 1-z$; (iv) $-x, y, -z$; (v) $\frac{1}{2}+x, y-\frac{1}{2}, z$; (vi) $1-x, y, 1-z$; (vii) $1-x, y, -z$; (viii) $1+x, y, z$.

The systematic absences indicated possible space groups *C*2/*m*, *Cm* and *C*2. The bulky cations, having no mirror symmetry, make it difficult to adopt the space group *C*2/*m* or *Cm* because of the mirror planes perpendicular to the shortest *b* axis. The solution of the structure, therefore, was successful only for *C*2. Since the intensities of the reflections $00l$, $l = 2n + 1$; $h0l$, $l = 2n + 1$, were weak and the structure obtained for *C*2 was found to be pseudo-centrosymmetric, the structure for the centrosymmetric space group *C*2/*c* was also determined; it afforded the *R* value of 0.073 ($wR = 0.110$). This structure was almost the same as that for *C*2 except that the Cl(1) and O(9) atoms were found to be disordered. That is to say, Cl(1) of occupancy factor 0.5 is located at the same position as the O(9) atom of occupancy factor 0.5. The hydrogen bonds around Cl(1) or O(9), therefore, range from 2.912 (7) to 2.990 (7) Å, which are the average of Cl(1)···O and O(9)···O as a matter of course, whereas in the structure for *C*2 the Cl(1)···O and O(9)···O hydrogen bonds can be clearly distinguished by the lengths. The large *R* value obtained for *C*2/*c* indicates that the space group of the title complex is not *C*2/*c* but *C*2. 1878 diffraction data (a Bijvoet set) with $I > 3\sigma(I)$ were collected for the same crystal used for the structure determination. On the basis of the data, absolute-configuration analysis failed to determine the handedness of the structure. The positions of the H atoms of the water molecules were not determined. All H atoms of the bipyridine rings were fixed at geometrically calculated positions. Calculations were carried out on an IRIS INDIGO workstation at the Faculty of Science, Osaka University.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989). Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1068). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Biner, M., Bürgi, H.-B., Ludi, A. & Röhr, C. (1992). *J. Am. Chem. Soc.* **114**, 5197–5203.

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Chen, X.-M., Wang, R.-Q. & Xu, Z.-T. (1995). *Acta Cryst.* **C51**, 820–822.

Fuertes, A., Miravitlles, C., Ibáñez, R., Martínez-Tamayo, E. & Beltrán-Porter, A. (1988). *Acta Cryst.* **C44**, 417–421.

Goodwin, K. V., Pennington, W. T. & Petersen, J. D. (1989). *Inorg. Chem.* **28**, 2016–2018.

Harrowfield, J. M. & Sobolev, A. N. (1994). *Aust. J. Chem.* **47**, 763–767.

Hazell, A. C. & Hazell, R. G. (1984). *Acta Cryst.* **C40**, 806–811.

Iguro, T., Ikeda, N. & Ohno, T. (1994). *Inorg. Chim. Acta*, **226**, 203–211.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Krausz, E., Riesen, H. & Rae, A. D. (1995). *Aust. J. Chem.* **48**, 929–954.

Lauher, J. W. (1989). *CHARON. A Graphics Program for Postscript Printers*. The Research Foundation of the State University of New York, USA.

Lee, K.-W. & Hoggard, P. E. (1989). *Polyhedron*, **8**, 1557–1560.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation. (1992). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* S1–83.
Posse, M. E. G., Juri, M. A., Aymonino, P. J., Piro, O. E., Negri, H. A. & Castellano, E. E. (1984). *Inorg. Chem.* **23**, 948–952.
Searle, G. H. & Tiekink, E. R. T. (1989). *Acta Cryst.* C**45**, 1300–1303.
Szalda, D. J., Creutz, C., Mahajan, D. & Sutin, N. (1983). *Inorg. Chem.* **22**, 2372–2379.
Szalda, D. J., Macartney, D. H. & Sutin, N. (1984). *Inorg. Chem.* **23**, 3473–3479.
Tada, T. (1982). *J. Sci. Hiroshima Univ. Ser. A*, **46**, 73–93.
Wada, A., Katayama, C. & Tanaka, J. (1976). *Acta Cryst.* B**32**, 3194–3199.
Wada, A., Sakabe, N. & Tanaka, J. (1976). *Acta Cryst.* B**32**, 1121–1127.
Yanagi, K., Ohashi, Y., Sasada, Y., Kaizu, Y. & Kobayashi, H. (1981). *Bull. Chem. Soc. Jpn*, **54**, 118–126.

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tert-Butylbis(dimethylglyoximato-*N*,*N*′)(triphenylphosphine-*P*)rhodium

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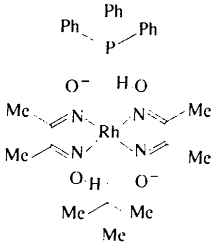
Abstract

The title structure {bis[2,3-butanedione dioximato(1−)-*N*,*N*′](*tert*-butyl)(triphenylphosphine-*P*)rhodium, [Rh($C_4H_7N_2O_2$)$_2$(C_4H_9)($C_{18}H_{15}P$)]} consists of discrete complexes in which the Rh atom displays distorted octahedral coordination, with the two dimethylglyoxime ligands in the equatorial plane and the *tert*-butyl and triphenylphosphine groups in the axial positions. The Rh atom is displaced by 0.048 (1) Å from the mean plane through the four oxime N donor atoms towards the P atom. The Rh—N distances range from 1.930 (3) to 1.982 (2) Å, while the axial Rh—P and Rh—C distances are 2.492 (1) and 2.216 (3) Å, respectively. Comparison of the results with those obtained previously for other compounds of this type indicates that the *trans* influence of *R* in the axial fragment Ph_3P—Rh—*R* is determined by its σ-donor power, while the Rh—C bond distance depends on the steric interaction of *R* with the equatorial moiety.

Comment

This work is a continuation of a project aimed at understanding the mutual electronic influence of ligands in organometallic compounds (Steinborn, 1992). The *trans* influence of σ-organo ligands is of particular interest. In previous papers of this series we have demonstrated (Steinborn & Ludwig, 1993; Dunaj-Jurčo, Kettmann, Steinborn & Ludwig, 1994; Kettmann, Dunaj-Jurčo, Steinborn & Ludwig, 1994) that in complexes of the type [Rh(dmgH)$_2$(PPh_3)*R*] (where dmgH is the monoanion of dimethylglyoxime and *R* is an organo group) the *trans* influence of *R*, as measured by ${}^1J({}^{103}\mathrm{Rh}\text{–}{}^{31}\mathrm{P})$ coupling constants and the Rh—P bond distance, is determined by the σ-donating power of *R*, irrespective of the hybridization state of the C atom. To examine the possibility that introduction of an electron-donating substituent in *R* would enhance the *trans* influence, we prepared and determined the crystal structure of a *tert*-butyl analogue, (I). The results are described here and compared with those for other compounds of the series.



(I)

The complex crystallizes as discrete molecules in which the Rh atom exhibits distorted octahedral stereochemistry, with four oxime N donors in the equatorial positions. The two dimethylglyoximato ligands are stabilized by two intramolecular hydrogen bonds acting between atoms O(1) and O(4) [O···O 2.652 (3) Å], and O(2) and O(3) [O···O 2.694 (3) Å]. The polar H atoms were clearly located from the Δρ map and are bonded to atoms O(1) and O(3) (Fig. 1).

The Rh—N(1) and Rh—N(3) bond distances involving the N atoms bearing the unprotonated OH groups are equal within experimental error (Table 2) and are much shorter than the other two Rh—N distances. As found in other derivatives of the series, the two dmgH$^-$ ligands are tilted away from the triphenylphosphine ligand so that their normal vectors make an angle of 9.5 (4)° with each other. As a result, though the four oxime N donors are coplanar to within ±0.005 Å, the Rh atom is displaced by 0.048 (1) Å from their mean plane towards the P atom. The dmgH$^-$ ligands themselves are also not strictly planar. This lack of planarity originates from twisting of the two halves of the ligand about the central C—C bond, the twist angles being 3.5 (4) and 4.1 (4)° for the ligands comprising N(1), N(2), O(1), O(2) and C(1)–C(4) and N(3), N(4), O(3), O(4) and C(5)–C(8), respectively.

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