

Paddlewheel dirhodium complexes bridged by *para*-substituted benzoates

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Received 25 July 2006

Accepted 2 August 2006

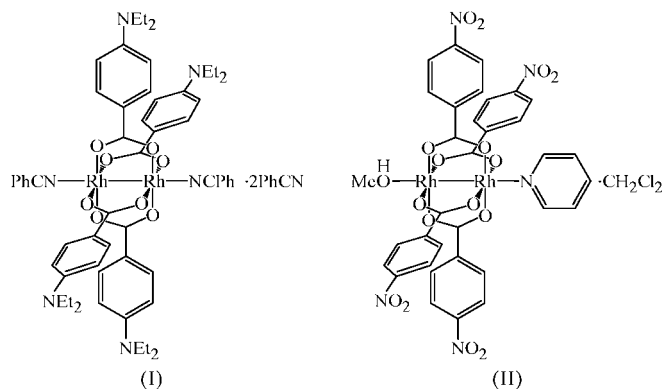
Online 31 August 2006

The dirhodium complex bis(benzonitrile)tetrakis[μ -4-(diethylamino)benzoato- $\kappa^2O:O'$]dirhodium(II)(*Rh*–*Rh*) benzonitrile disolvate, $[\text{Rh}_2(\text{C}_{11}\text{H}_{14}\text{NO}_2)_4(\text{C}_7\text{H}_5\text{N})_2] \cdot 2\text{C}_7\text{H}_5\text{N}$, lies about an inversion centre. The dirhodium complex (methanol)tetrakis(μ -4-nitrobenzoato- $\kappa^2O:O'$)(pyridine)dirhodium(II)(*Rh*–*Rh*) dichloromethane solvate, $[\text{Rh}_2(\text{C}_7\text{H}_4\text{NO}_4)_4(\text{C}_5\text{H}_5\text{N})(\text{CH}_4\text{O})] \cdot \text{CH}_2\text{Cl}_2$, lies in a general position in the unit cell, but the complexes dimerize around an inversion centre *via* O–H...O hydrogen bonding of the axial MeOH to a carboxylate O atom. In the latter crystal structure, π – π stacking interactions between the bridging 4-nitrobenzoate ligands and the axial pyridine ligand are observed between adjacent molecules.

Comment

Paddlewheel dimetal complexes have attracted much attention in recent years because they are useful modules to make assembled frameworks. Among such paddlewheel complexes, metal–metal single-bonded dirhodium(II) complexes are interesting examples that change their highest occupied molecular orbitals (HOMOs) depending on their bridging and axial ligands (Kawamura *et al.*, 1989, 1998). For example, the HOMOs of such compounds with carboxylate bridges are π^* orbitals, but amidate-bridged compounds have a δ^* HOMO. We have studied assembled structures with paddlewheel dirhodium cationic radicals constructed by π – π stacking interactions between odd electron densities on the bridging ligands (Kawamura *et al.*, 1993, 2000) or by connection with axial linker ligands (Yang *et al.*, 2000, 2001, 2006; Takazaki *et al.*, 2003; Fuma *et al.*, 2004). Substituted benzoates are interesting bridging ligands, the donor abilities and stacking patterns of which change with their substituents. In this paper, we report the crystal structures of two novel dirhodium complexes with *para*-substituted benzoate bridges, namely bis(benzonitrile)tetrakis[μ -4-(diethylamino)benzoato- $\kappa^2O:O'$]dirhodium(II)(*Rh*–*Rh*) benzonitrile disolvate, (I), and (methanol)tetrakis(μ -4-nitrobenzoato- $\kappa^2O:O'$)(pyridine)dirhodium(II)(*Rh*–*Rh*) dichloromethane solvate, (II).

In the structure of (I) (Fig. 1 and Table 1), the rhodium complex lies on a crystallographic inversion centre. There is also one benzonitrile solvent molecule in the asymmetric unit. The O–Rh–Rh–O torsion angles are close to 0°. In one of



the two independent bridging ligands, four of the six benzene C atoms, the N atom and one ethyl group are disordered over two sets of sites, labelled *A* and *B*. In both disordered sites, the benzene groups are slightly tilted from the CO₂ plane (Table 2). The C₂N moiety of the amino group does not deviate much from the C₆H₄ plane. The ethyl groups of the diethylamino substituent point toward opposite sides of the benzene ring for the *A* site and towards the same side for the *B*

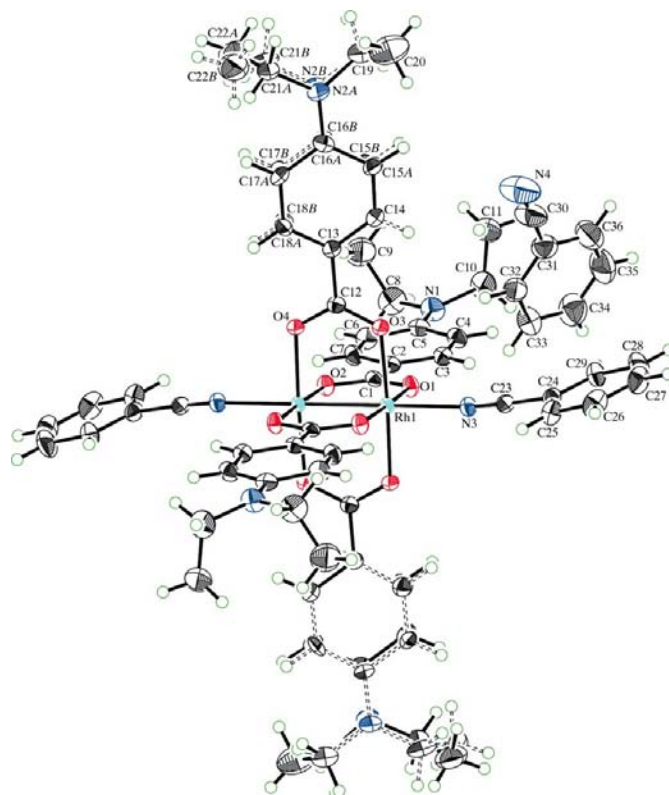


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Both disorder components are shown. Unlabelled atoms are related to labelled atoms by the symmetry operator ($-x + 1, -y + 1, -z + 1$).

site. For the other bridging ligand, the C₂N, C₆H₄ and CO₂ moieties are nearly coplanar and the ethyl groups of the amino substituent point towards the same side of the benzene ring. The near planarity of the diethylaminobenzoate group suggests that it has significant quinoid character. This is also

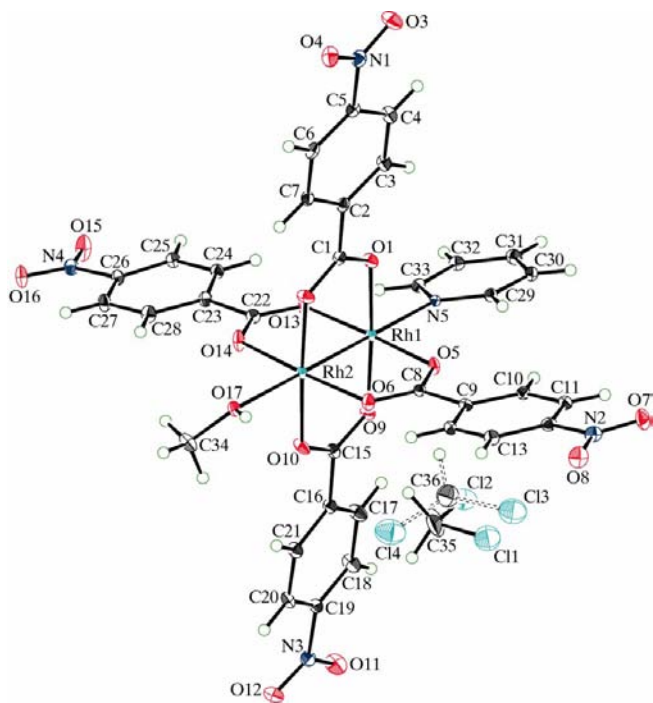


Figure 2
The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Both disorder components are shown.

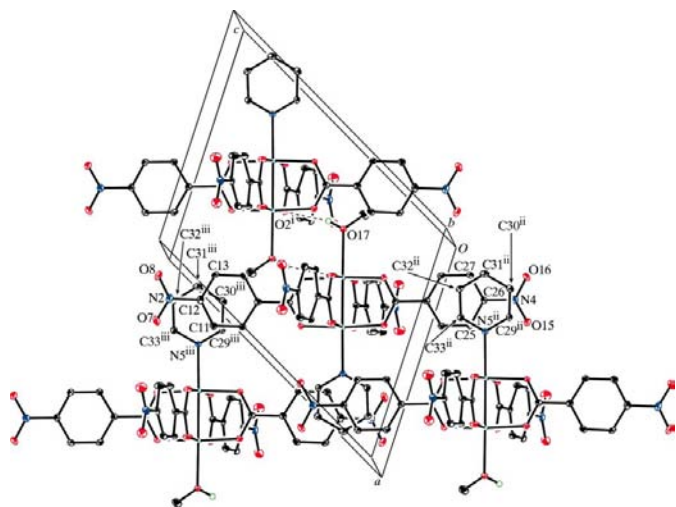


Figure 3
The crystal packing of (II). For the sake of clarity, H atoms except H1 have been omitted. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, -z$; (iii) $2 - x, 1 - y, 1 - z$.]

reflected in the bond-length pattern of the ligand [average distances are: C2–C3 and C2–C7 = 1.390 (2) Å; C3–C4 and C6–C7 = 1.378 (2) Å; C4–C5 and C5–C6 = 1.408 (2) Å]. The axial positions are occupied by benzonitrile molecules, with almost straight Rh1–Rh1–N3 and the slightly bent Rh1–N3–C23 angles. The Rh–Rh distance of 2.3920 (9) Å is very close to the values observed for dirhodium complexes bridged by benzoate or its derivatives and axially bonded by N-donors [2.3882 (4)–2.4037 (4) Å; Castro *et al.*, 2002; Cotton & Thompson, 1984; Cotton *et al.*, 2002; Hikichi *et al.*, 2003; Mehmet & Tocher, 1991]. In the crystal structure of (I), π – π stacking interactions are not observed.

In the structure of (II) (Fig. 2 and Table 3), there is one independent molecule in the asymmetric unit with a disordered dichloromethane molecule. The Rh₂O₈ skeleton is in a nearly complete eclipsed conformation, as was found for (I). The bridging nitrobenzoate ligands are almost planar: dihedral angles between the O₂C and benzene groups and between the benzene and NO₂ groups for each ligand are close to 0° (Table 4). The axial sites are occupied by one MeOH and one pyridine ligand. Only two dirhodium compounds with an N and an O atom at the axial positions have been reported to date (Cogne *et al.*, 1987, 1989). The pyridine ring is slightly tilted from the plane of the nearer carboxylate groups, with a torsion angle between them of *ca* 15°. The Rh–Rh distance [2.3936 (10) Å] is very similar to that of (I).

In the crystal structure of (II), the MeOH ligand donates a H atom to an O atom of the bridging carboxylate [O2ⁱ; Fig. 3 and Table 5; symmetry code: (i) $1 - x, 1 - y, 1 - z$]. This type of hydrogen bonding has also been observed in some paddlewheel complexes with axial alcohol ligands (Rao *et al.*, 1983; Noinville *et al.*, 1993; Agterberg *et al.*, 1997). Strong π – π stacking interactions between *p*-nitrobenzoate and pyridine are observed between the complex molecules at (x, y, z) and $(1 - x, 1 - y, -z)$, and between those at (x, y, z) and $(2 - x, 1 - y, 1 - z)$ (Fig. 3). In the former pair, representative short contacts (Å) are as follows: N2···C32ⁱⁱ = 3.177 (6), C11···C29ⁱⁱ = 3.252 (7), O7···C33ⁱⁱ = 3.320 (6), C12···C31ⁱⁱ = 3.342 (7) and C13···C31ⁱⁱ = 3.394 (8) [symmetry code: (ii) $1 - x, 1 - y, -z$]. In the latter pair, very similar contacts (Å) are observed: N4···C30ⁱⁱⁱ = 3.172 (7), C25···C33ⁱⁱⁱ = 3.270 (7), O16···C30ⁱⁱⁱ = 3.230 (5), C27···C31ⁱⁱⁱ = 3.386 (7) and C26···C31ⁱⁱⁱ = 3.403 (8) [symmetry code: (iii) $2 - x, 1 - y, 1 - z$]. These interactions result in the nitrobenzoate ligands sandwiching the pyridine ligand.

Experimental

Tetra- μ -acetato-bis(methanol)dirhodium was prepared according to the literature procedure of Rempel *et al.* (1972). 4-(Diethylamino)benzoic acid and 4-nitrobenzoic acid were used as received. Both complexes were prepared by a modification of the procedure reported by Doyle *et al.* (1990) for tetra- μ -acetamidato-dirhodium.

For the preparation of compound (I), [Rh₂(O₂CMe)₄(MeOH)₂] (0.327 g, 0.65 mmol) and 4-(diethylamino)benzoic acid (2.95 g, 1.53 mmol) dissolved in chlorobenzene (90 ml) were placed in a 200 ml round-bottomed flask. A Soxhlet apparatus, in which sodium

carboxylate (3 g) and molecular sieves (1 g) were mixed in a filter, was placed on the flask. The solution was refluxed under an Ar atmosphere for 3 d. The resulting green precipitate was filtered off, dissolved in CH₂Cl₂-PhCN (1:1 v/v), washed with saturated aqueous NaHCO₃ and water, and dried over MgSO₄. Diffusion of ethanol into the solution gave a red-purple precipitate. Recrystallization from PhCN by slow diffusion of ethanol gave red crystals of (I).

For the preparation of compound (II), [Rh₂(O₂CMe)₄(MeOH)₂] (1.019 g, 2.01 mmol) and 4-nitrobenzoic acid (6.00 g, 35.9 mmol) were reacted in a similar method to (I). The resulting green precipitate was filtered off and dissolved in PhCN-hexane (1:1 v/v). The solution was washed with saturated aqueous NaHCO₃ and water, and dried over MgSO₄. Diffusion of hexane gave a red precipitate. This was dissolved in CH₂Cl₂ and pyridine (py) was added until the colour of the solution changed to orange. The solid obtained by the evaporation of this solution to dryness was recrystallized from CH₂Cl₂ by slow diffusion of MeOH. Two types of crystals were obtained in an almost 1:1 ratio; one type was (II) and the other was poor quality crystals of [Rh₂(O₂CC₆H₄NO₂)₂(py)₂].

Compound (I)

Crystal data

[Rh₂(C₁₁H₁₄NO₂)₄(C₇H₅N)₂]-
2C₇H₅N
M_r = 1387.23
Triclinic, P $\bar{1}$
a = 10.049 (4) Å
b = 12.752 (6) Å
c = 13.479 (6) Å
α = 98.641 (6)°
β = 90.781 (6)°

γ = 99.424 (6)°
V = 1683.3 (13) Å³
Z = 1
D_x = 1.368 Mg m⁻³
Mo Kα radiation
μ = 0.55 mm⁻¹
T = 296 (2) K
Block, dark-red
0.20 × 0.10 × 0.10 mm

Data collection

Rigaku/MSC Mercury CCD area-detector diffractometer
ω scans
13963 measured reflections

7660 independent reflections
5661 reflections with I > 2σ(I)
R_{int} = 0.046
θ_{max} = 27.5°

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.055
wR(F²) = 0.104
S = 1.05
7660 reflections
475 parameters

H-atom parameters constrained
w = 1/[σ²(F_o²) + (0.0391P)²]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.016
Δρ_{max} = 0.52 e Å⁻³
Δρ_{min} = -0.71 e Å⁻³

Table 1

Selected bond lengths (Å) for (I).

Rh1—Rh1 ⁱ	2.3920 (9)	Rh1—O3	2.0407 (12)
Rh1—O1	2.0463 (10)	Rh1—O4 ⁱ	2.0318 (12)
Rh1—O2 ⁱ	2.0276 (10)	Rh1—N3	2.2194 (14)

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

Table 2

Dihedral angles (°) in the 4-(diethylamino)benzoate ligand for (I).

O ₂ C	C ₆ H ₄	NC ₂	O ₂ C—C ₆ H ₄	C ₆ H ₄ —NC ₂
O1/C1/O2	C2—C7	C8/N1/C10	3.83 (14)	16.54 (16)
O3/C12/O4	C13—C18	C19/N2/C21	20.28 (17)†	22.8 (2)†
			11.27 (18)‡	6.7 (3)‡

† Site A. ‡ Site B.

Compound (II)

Crystal data

[Rh₂(C₇H₄NO₄)₄(C₅H₅N)-
(CH₄O)]·CH₂Cl₂
M_r = 1066.34
Triclinic, P $\bar{1}$
a = 12.750 (6) Å
b = 13.290 (4) Å
c = 14.773 (5) Å
α = 96.55 (3)°
β = 109.42 (1)°

γ = 118.43 (1)°
V = 1961.0 (13) Å³
Z = 2
D_x = 1.806 Mg m⁻³
Mo Kα radiation
μ = 1.06 mm⁻¹
T = 113 (2) K
Block, dark-red
0.30 × 0.10 × 0.10 mm

Data collection

Rigaku/MSC Mercury CCD area-detector diffractometer
ω scans
16189 measured reflections

8932 independent reflections
6931 reflections with I > 2σ(I)
R_{int} = 0.047
θ_{max} = 27.5°

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.047
wR(F²) = 0.116
S = 1.05
8932 reflections
577 parameters
H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(F_o²) + (0.0533P)² + 2.6928P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.82 e Å⁻³
Δρ_{min} = -1.05 e Å⁻³

Table 3

Selected bond lengths (Å) for (II).

Rh1—Rh2	2.3937 (10)	Rh2—O2	2.037 (3)
Rh1—O1	2.051 (3)	Rh2—O6	2.028 (3)
Rh1—O5	2.039 (3)	Rh2—O10	2.022 (3)
Rh1—O9	2.050 (3)	Rh2—O14	2.030 (3)
Rh1—O13	2.042 (3)	Rh2—O17	2.291 (3)
Rh1—N5	2.218 (3)		

Table 4

Dihedral angles (°) in the 4-nitrobenzoate ligand for (II).

O ₂ C	C ₆ H ₄	NO ₂	O ₂ C—C ₆ H ₄	C ₆ H ₄ —NO ₂
O1/C1/O2	C2—C7	O3/N1/O4	7.1 (4)	5.8 (4)
O5/C8/O6	C9—C14	O7/N2/O8	6.2 (2)	4.5 (2)
O9/C15/O10	C16—C21	O11/N3/O12	6.4 (4)	4.7 (4)
O13/C22/O14	C23—C28	O15/N4/O16	7.1 (3)	6.4 (2)

Table 5

Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O17—H1···O2 ⁱ	0.65 (5)	2.42 (5)	2.963 (4)	143 (6)

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

For compound (I), one diethylaminophenyl group is disordered over two sites. Atoms C15A–C18A/C21A/C22A/N2A constitute one group and atoms C15B–C18B/C21B/C22B/N2B form the other, sharing atoms C13, C14, C19 and C20. The occupancies of sets A and B were refined and converged to 0.530 (1) and 0.470 (1), respectively. For compound (II), the dichloromethane solvent molecule is disordered over two sites, viz. C11/C12/C35 and C13/C14/C36. The occupancies were refined and converged to 0.672 (3) and 0.328 (3),

respectively. The positional parameters of the O-bound H atom in (II) were refined (Table 5), with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. All other H atoms were placed in idealized positions and treated as riding atoms, with C–H distances in the range 0.93–0.98 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

For both compounds, data collection: *CrystalClear* (Molecular Structure Corporation & Rigaku, 2001); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Rigaku/MS, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97* and *TEXSAN*.

This work was supported by the Research Foundation for Electrotechnology of Chubu.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3029). Services for accessing these data are described at the back of the journal.

References

- Agterberg, F. P. W., Kluit, H. A. J. P., Driessen, W. L., Oevering, H., Buijs, W., Lakin, M. T., Spek, A. L. & Reedijk, J. (1997). *Inorg. Chem.* **36**, 4321–4328.
- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Castro, M. A., Chaia, Z. D., Piro, O. E., Cukiernik, F. D., Castellano, E. E. & Rusjan, M. (2002). *Acta Cryst.* **C58**, m393–m395.
- Cogne, A., Grand, A., Rey, P. & Subra, R. (1987). *J. Am. Chem. Soc.* **109**, 7927–7929.
- Cogne, A., Grand, A., Rey, P. & Subra, R. (1989). *J. Am. Chem. Soc.* **111**, 3230–3238.
- Cotton, F. A., Hillard, E. A., Liu, C. Y., Murillo, C. A., Wang, W. & Wang, X. (2002). *Inorg. Chim. Acta*, **337**, 233–246.
- Cotton, F. A. & Thompson, J. L. (1984). *Inorg. Chim. Acta*, **81**, 193–203.
- Doyle, M. P., Bagheri, V., Wandless, T. J., Harn, N. K., Brinker, D. A., Eagle, C. T. & Loh, K. L. (1990). *J. Am. Chem. Soc.* **112**, 1906–1912.
- Fuma, Y., Ebihara, M., Kutsumizu, S. & Kawamura, T. (2004). *J. Am. Chem. Soc.* **126**, 12238–12239.
- Hikichi, K., Kitagaki, S., Anada, M., Nakamura, S., Nakajima, M., Shiro, M. & Hashimoto, S. (2003). *Heterocycles*, **61**, 391–401.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Kawamura, T., Ebihara, M. & Miyamoto, M. (1993). *Chem. Lett.* pp. 1509–1512.
- Kawamura, T., Kachi, H., Fujii, H., Kachi-Terajima, C., Kawamura, Y., Kanematsu, N., Ebihara, M., Sugimoto, K., Kuroda-Sowa, T. & Munakata, M. (2000). *Bull. Chem. Soc. Jpn.* **73**, 657–668.
- Kawamura, T., Katayama, H., Nishikawa, H. & Yamabe, T. (1989). *J. Am. Chem. Soc.* **111**, 8156–8160.
- Kawamura, T., Maeda, M., Miyamoto, M., Usami, H., Imaeda, K. & Ebihara, M. (1998). *J. Am. Chem. Soc.* **120**, 8136–8142.
- Mehmet, N. & Tocher, D. A. (1991). *Inorg. Chim. Acta*, **188**, 71–77.
- Molecular Structure Corporation & Rigaku (2001). *Crystal Clear*. Version 1.3. MSC, The Woodlands, Texas, USA, and Rigaku Corporation, Tokyo, Japan.
- Noinville, V., Viostat, B. & Dung, N.-H. (1993). *Acta Cryst.* **C49**, 1297–1298.
- Rao, V. M., Sathyanarayana, D. N. & Manohar, H. (1983). *J. Chem. Soc. Dalton Trans.* pp. 2167–2173.
- Rempel, G. A., Legzdins, P., Smith, H. & Wilkinson, G. (1972). *Inorg. Synth.* **13**, 90–91.
- Rigaku/MS (2004). *TEXSAN*. Version 2.0. Rigaku/MS Inc., The Woodlands, Texas, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Takazaki, Y., Yang, Z., Ebihara, M., Inoue, K. & Kawamura, T. (2003). *Chem. Lett.* **32**, 120–121.
- Yang, Z., Ebihara, M. & Kawamura, T. (2006). *Inorg. Chim. Acta*, **359**, 2465–2471.
- Yang, Z., Ebihara, M., Kawamura, T., Okubo, T. & Mitani, T. (2001). *Inorg. Chim. Acta*, **321**, 97–106.
- Yang, Z., Fujinami, T., Ebihara, M., Nakajima, K., Kitagawa, H. & Kawamura, T. (2000). *Chem. Lett.* pp. 1006–1007.