

Curtis M. Whaley, Thomas B. Rauchfuss and Scott R. Wilson\*

University of Illinois, School of Chemical Sciences, Box 59-1, 505 South Mathews Avenue, Urbana, Illinois 61801, USA

Correspondence e-mail: srwilson@uiuc.edu

#### Key indicators

Single-crystal X-ray study

$T = 193\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

$R$  factor = 0.036

$wR$  factor = 0.081

Data-to-parameter ratio = 21.5

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## Bis[(1,4,7,10,13,16-hexaoxacyclooctadecane)-potassium] carbonyltricyanorhodate(I) acetonitrile solvate

In the title complex,  $[\text{K}(\text{C}_{12}\text{H}_{24})]_2[\text{Rh}(\text{CN})_3(\text{CO})] \cdot \text{C}_2\text{H}_3\text{N}$ , the Rh atom is coordinated by three cyanide ligands and one carbonyl ligand in a square-planar geometry. The K atom in each cation is coordinated by six O atoms from the crown ether and one N atom from a cyanide ligand.

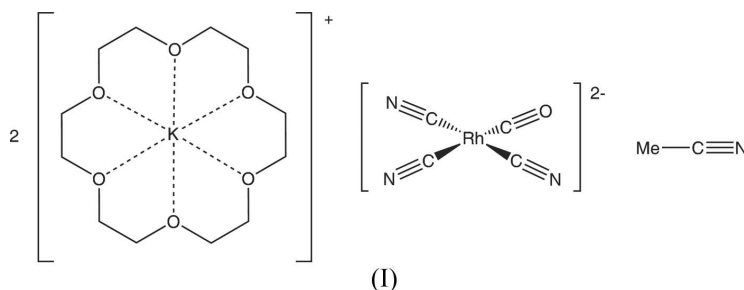
Received 18 August 2005

Accepted 30 August 2005

Online 7 September 2005

#### Comment

The carbonyltricyanorhodate(I) dianion was first proposed by Jewsbury & Maher (1971) as an intermediate in the preparation of  $\text{K}_3[\text{HRh}(\text{CN})_5]$  on the basis of visible and IR spectroscopic evidence. The complex, however, was never isolated. We report here the synthesis and structure of the title acetonitrile solvate, (I).



In the title complex, the  $\text{Rh}^{\text{I}}$  atom is coordinated in a square-planar geometry by three C atoms of cyanide ligands and one C atom from a carbonyl ligand. Each N atom of two *trans* cyanide ligands is in close contact [2.741 (2) and 2.747 (2)  $\text{\AA}$ ] with a K atom from the cations. The carbonyl ligand was identified on the basis of its shorter Rh1—C1 bond length [1.828 (3) *versus* 2.051 (3)  $\text{\AA}$  for Rh1—C3]. One of the *trans* cyanide ligands is slightly bent, having an Rh1—C2 $\equiv$ N2 bond angle of 174.2 (3)°. The other *trans* cyanide ligand is more linear, with an Rh1—C4 $\equiv$ N4 bond angle of 177.2 (2)°. The K atom of each cation is pulled toward the cyanide N atom and out of the plane of the crown ether.

#### Experimental

A flask charged with  $[\text{RhCl}(\text{cod})]_2$  (702 mg, 1.42 mmol) in MeCN (25 ml) was purged with CO for approximately 20 min. The resulting orange solution was treated with a solution of  $[\text{K}(18\text{-crown-6})]\text{CN}$  (3.14 g, 9.54 mmol). During addition, the color of the solution changed from clear orange to clear yellow to cloudy blue to cloudy yellow. Addition of diethyl ether (100 ml) resulted in the precipitation of a yellow solid. The solid was isolated by filtration, washed with more diethyl ether and dried under vacuum to yield 2.124 g (92%) of  $[\text{K}(18\text{-crown-6})]_2[\text{Rh}(\text{CN})_3(\text{CO})]$ . X-ray quality crystals were formed at room temperature by vapor diffusion of diethyl ether into an

acetonitrile solution of the product.  $\nu(\text{CO})$ , acetonitrile: 1959 and  $2084\text{ cm}^{-1}$ , consistent with the published IR data.

#### Crystal data

$[\text{K}(\text{C}_{12}\text{H}_{24})]_2[\text{Rh}(\text{CN})_3(\text{CO})]\cdot\text{C}_2\text{H}_3\text{N}$

$M_r = 856.86$

Monoclinic,  $P2_1/c$

$a = 22.439\text{ (6) \AA}$

$b = 8.553\text{ (2) \AA}$

$c = 20.576\text{ (5) \AA}$

$\beta = 90.178\text{ (4)^\circ}$

$V = 3948.9\text{ (17) \AA}^3$

$Z = 4$

$D_x = 1.441\text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

Cell parameters from 949 reflections

$\theta = 2.2\text{--}26.1^\circ$

$\mu = 0.71\text{ mm}^{-1}$

$T = 193\text{ (2) K}$

Tablet, yellow

$0.40 \times 0.18 \times 0.10\text{ mm}$

#### Data collection

Bruker SMART CCD

diffractometer

$\omega$  scans

Absorption correction: integration  
[*XPRED* in *SHELXTL* (Bruker, 2001)]

$T_{\min} = 0.775$ ,  $T_{\max} = 0.935$

39007 measured reflections

9709 independent reflections

7084 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$

$\theta_{\max} = 28.3^\circ$

$h = -29 \rightarrow 29$

$k = -11 \rightarrow 11$

$l = -27 \rightarrow 27$

#### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.081$

$S = 1.02$

9709 reflections

452 parameters

H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 0.650P]$

where  $P = (F_o^2 + 2F_c^2)/3$

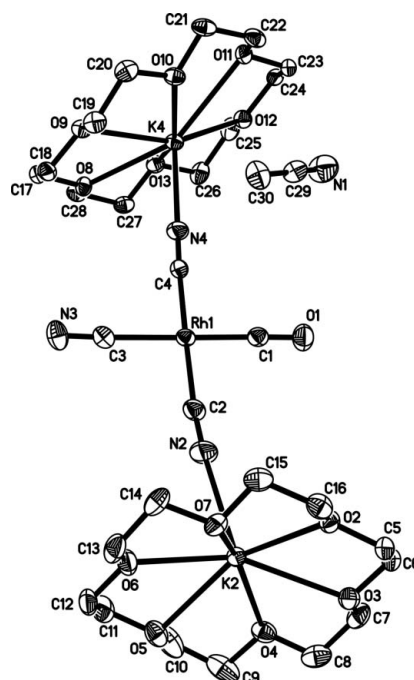
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.65\text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.27\text{ e \AA}^{-3}$

Methyl H-atom positions,  $R\text{--CH}_3$ , were optimized by rotation about  $R\text{--C}$  bonds with idealized  $\text{C--H}$ ,  $R\text{--H}$  and  $\text{H--H}$  distances. The remaining H atoms were included as riding idealized contributors. Methyl  $U_{\text{iso}}(\text{H})$  values were assigned as 1.5 times  $U_{\text{eq}}$  of the adjacent atom; the remaining  $U_{\text{iso}}(\text{H})$  values were assigned as 1.2 times the adjacent  $U_{\text{eq}}$ . A final analysis of variance between observed and calculated structure factors showed little dependence on amplitude or resolution.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine



**Figure 1**

*SHELXTL* (Bruker, 2001) plot showing 35% probability displacement ellipsoids for non-H atoms; H atoms have been omitted for clarity.

structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *CIFTAB* in *SHELXTL*.

The Materials Chemistry Laboratory at the University of Illinois was supported in part by grant No. NSF CHE 95-03145 from the National Science Foundation.

#### References

- Bruker (2001). *SMART* (Version 5.625), *SAINT* (Version 6.22) and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
- Jewsbury, R. A. & Maher, J. P. (1971). *J. Chem. Soc. A*, pp. 2847–2852.