

structure for the incommensurate modulation. It has been claimed that some structural features of the prototype phase are the origin of these transitions (Kaltkanant, Edwardson, Hardy & Boyer, 1989). The lattice dynamic simulations performed for several A_2BX_4 compounds confirm that the relative size of the A^+ and BX_4^{2-} anions plays an important role in the sequence of transitions (Etxebarria, Pérez-Mato & Criado, 1990). In particular, calculations based on the static structural data reported here for Cs_2SeO_4 exclude the existence of an incommensurate phase for this compound.

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Structure of Di- μ -chloro-bis[dicarbonylrhodium(I)]

BY LEONHARD WALZ*

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Germany

AND PETER SCHEER

Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen, Germany

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Abstract. $[\text{Rh}_2\text{Cl}_2(\text{CO})_4]$, $M_r = 388.76$, tetragonal, $I4_2d$, $a = 14.279$ (4), $c = 9.353$ (3) Å, $V = 1907$ (2) Å³, $Z = 8$, $D_x = 2.708$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 3.666$ mm⁻¹, $F(000) = 1440$, $T = 296$ K. Final $R = 0.0398$ for 593 reflections [$F_o > 3\sigma(F_o)$]. The unit cell contains eight molecules, which are bent in a V shape, with an Rh–Rh distance of 3.138 (1) Å. The coordination at one Rh atom is distorted from exact planarity. The molecules are connected to form zigzag chains with intermolecular Rh–Rh distances of 3.324 Å.

Experimental. Prepared according to the procedure given by Powell & Shaw (1968) by bubbling carbon monoxide through a refluxing ethanolic solution of rhodium trichloride trihydrate and extracting the dried residue with boiling light petroleum. A plate-like crystal with dimensions 0.044 × 0.192 × 0.300 mm and sealed in a Lindemann-glass capillary was used for the data collection on a Huber 511 four-circle diffractometer. Lattice constants were obtained from 18 reflections in the range $20 \leq 2\theta \leq 25^\circ$. 1455 reflections were measured [one octant, $3 \leq$

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$2\theta \leq 60^\circ$, $0 \leq h(k) \leq 20$, $0 \leq l \leq 13$] leading to 593 unique reflections with $F_o > 3\sigma(F_o)$ after numerical absorption correction ($R_{\text{int}} = 0.0266$, min., max. transmission factors 0.498, 0.851, 128 reflections unobserved). The intensity variation of three standard reflections measured every 2 h was < 1%. Structure solution with direct methods (Sheldrick, 1986). The refinement (56 parameters) with anisotropic thermal parameters and isotropic extinction (6×10^{-4}) on the basis of F (Sheldrick, 1976) converged at $R = 0.0398$, $wR = 0.0238$ [$w = k/\sigma^2(F_o)$]. The ratio of max. least-squares shift to e.s.d. in the final refinement cycle was less than 0.01, max. and min. heights in the final difference Fourier synthesis were 1.42 and $-1.0 \text{ e } \text{Å}^{-3}$. The atomic scattering factors used were taken from Cromer & Mann (1968). Table 1 contains atomic parameters for (1). Bond distances and angles (Busing, Martin & Levy, 1971) are given in Table 2.† Fig. 1 shows the molecular structure of

* Present address: Daimler-Benz AG, Forschungszentrum Ulm, Postfach 800 230, D-7000 Stuttgart 80, Germany.

† Lists of structure factors, anisotropic thermal parameters and bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53496 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters and equivalent isotropic thermal displacement factors for (1)

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Rh(1)	0.27130 (4)	0.85209 (4)	0.21041 (7)	0.0531 (2)
Cl(1)	0.3609 (1)	0.7970 (1)	0.4081 (2)	0.0641 (8)
C(1)	0.1981 (6)	0.9073 (5)	0.0721 (9)	0.062 (4)
O(1)	0.1547 (4)	0.9444 (4)	-0.0112 (7)	0.091 (3)
C(2)	0.3790 (6)	0.8919 (6)	0.118 (1)	0.064 (4)
O(2)	0.4459 (4)	0.9137 (5)	0.0630 (8)	0.101 (4)

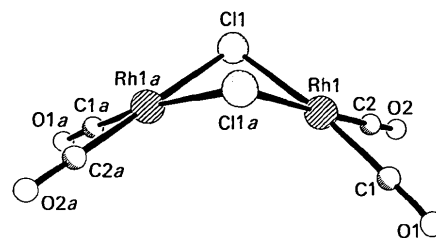


Fig. 1. Molecular structure of (1).

Table 2. Bond distances (Å) and angles (°) for (1) with e.s.d.s in parentheses

Rh(1)—Cl(1)	2.381 (2)	C(1)—O(1)	1.128 (8)
Rh(1)—Cl(1a)*	2.386 (2)	C(2)—O(2)	1.128 (8)
Rh(1)—C(1)	1.841 (9)	Rh(1)—Rh(1a)*	3.138 (1)
Rh(1)—C(2)	1.854 (9)	Rh(1)—Rh(1b)†	3.324 (1)
Cl(1)—Rh(1)—Cl(1a)*	85.18 (6)	Cl(1a)—Rh(1)—C(2)	176.2 (3)
Cl(1)—Rh(1)—C(1)	172.7 (2)	Rh(1)—C(1)—O(1)	177.3 (7)
Cl(1)—Rh(1)—C(2)	91.0 (2)	Rh(1)—C(2)—O(2)	177.9 (8)
C(1)—Rh(1)—C(2)	90.7 (3)	Rh(1)—Cl(1)—Rh(1)	82.3 (1)
Cl(1a)—Rh(1)—C(1)	93.1 (3)		

* Atom on the position (0.5 - x, y, 0.75 - z) related to the position given in Table 1.

† Atom on the position (x, 1.5 - y, 0.25 - z) related to the position given in Table 1.

(1), Fig. 2 contains a stereoscopic view of the unit cell (Sheldrick, 1987).

Related literature. The structure of (1) consists of bent molecules containing a central Rh_2Cl_2 moiety. Distinct differences to the bond distances given by Dahl, Martell & Wampler (1961), where the two carbon monoxide fragments are not kept apart, are observed for one of the two $\text{Rh}(1)\text{—Cl}(1)$ distances and for one $\text{Rh}(1)\text{—C—O}$ fragment. Our refinement yielded nearly equal bond lengths $\text{Rh}(1)\text{—Cl}(1)$ and $\text{Rh}(1)\text{—Cl}(1a)$ whereas Dahl *et al.* (1961) give values of 2.38 and 2.33 Å (there are no e.s.d.s, either for the lattice constants or for distances and angles). For one C—O group, Dahl *et al.* give an Rh—C distance of 1.77 Å and for the corresponding C—O distance 1.21 Å. We assume that the positional parameter of the C atom was determined incorrectly, since the difference can be understood with a shift of the C atom of about 0.1 Å from its position in the direction towards the Rh atom.

An interesting feature concerning the distortion at Rh(1) from an exact planar coordination may be of some interest with respect to theoretical calculations on (1), which assume planarity around the Rh atom (Norman & Gmur, 1977; Serafini, Poilblanc, Labarre & Barthelat, 1978). Calculating the best plane through Rh(1), Cl(1) and Cl(1a), one can see that the carbon monoxide molecule $\text{C}(1)\text{—O}(1)$ deviates distinctly from this plane [$\text{C}(1) + 0.224(8)$, $\text{O}(1) + 0.411(8)$ Å], while C(2) and O(2) are situated almost exactly on this plane. The angle between the

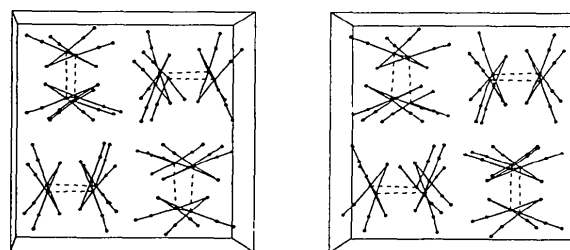


Fig. 2. Stereoscopic view of the unit cell (view along [001]).

two planes defined by the atoms Cl(1), Rh(1), Cl(1a) and by Cl(1), Rh(1a), Cl(1a) is $126.8(3)^\circ$ corresponding to an angle of $53.2(3)^\circ$ between the normals of these planes. Since Dahl *et al.* (1961) give no explanations of the planes and the atoms used for their definition we cannot decide whether the differences ($124/56^\circ$) are due to incorrect positional parameters or due to different definitions of the planes.

The stereoscopic view (Fig. 2) shows the arrangement of the molecules. The linkage between the molecules results from the contact between Rh atoms. The coordination planes of the Rh(1) atoms at (x, y, z) and at (x, 1.5 - y, 0.25 - z) are essentially coplanar, leading to a metal-metal distance of 3.324 (1) Å. Taking this distance as well as the intramolecular one into account, the arrangement of the Rh atoms is like an infinite stretched square wave along [001].

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