References

CHARVILLAT, J. P., BAND, G. & BESSE, J. P. (1970). *Mater. Res. Bull.* **5**, 933–938.

DUIVENBODEN, H. C. VAN & IJDO, D. J. W. (1986). *Acta Cryst.* C**42**, 523–525.

GROEN, W. A., VAN BERKEL, F. P. F. & IJDO, D. J. W. (1986). *Acta Cryst.* C**42**, 1472–1475.

GROEN, W. A., ZANDBERGEN, H. W. & IJDO, D. J. W. (1987). *Mater. Res. Bull.* In the press.

KEMMLER-SACK, S. & SEEMANN, I. (1975). *Z. Anorg. Allg. Chem.* **411**, 61–78.

KOESTER, L., RAUCH, H., HERKENS, M. & SCHROEDER, K. (1981). Report 1755. Kernforschungsanlage Jülich.

LOOPSTRA, B. O. & RIETVELD, H. M. (1969). *Acta Cryst.* B**25**, 787–791.

MEGAW, H. D. (1973). *Crystal Structures – A Working Approach*, ch. 12.1. Philadelphia: Saunders.

RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.

RINGWOOD, A. E. (1978). *Safe Disposal of High Level Nuclear Reactor Wastes: A New Strategy.* Australian National Univ. Press, Canberra, Australia, and Norwalk, Connecticut, USA.

RUDORF, W. & PFITZER, F. (1954). *Z. Naturforsch.* **96**, 568–569.

SHANNON, R. D. (1976). *Acta Cryst.* A**32**, 751–767.

SLEIGHT, A. W. & WARD, R. (1962). *Inorg. Chem.* **1**, 790–793.

WEBER, K. (1967). *Acta Cryst.* **23**, 720–725.

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Structure of the Binuclear Rhodium(II) Complex Dichloro-di-μ-formato-bis(1,10-phenanthroline)dirhodium(II)

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Abstract. $[Rh_2Cl_2(C_{12}H_8N_2)_2(CHO_2)_2]$, $M_r = 727{\cdot}2$, orthorhombic, *Pbca*, $a = 24{\cdot}278\,(10)$, $b = 15{\cdot}127\,(7)$, $c = 13{\cdot}398\,(7)$ Å, $V = 4920\,(5)$ Å^3, $Z = 8$, $D_m = 1{\cdot}96\,(1)$, $D_x = 1{\cdot}963$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}57$ mm^{-1}, $F(000) = 2864$, $T = 293$ K, final $R = 0{\cdot}030$ for 3244 reflections. The coordination sphere of each Rh atom is octahedral, consisting of two O atoms from different formato groups [Rh—O 2·063 (3)–2·069 (4) Å], two N atoms of a chelating 1,10-phenanthroline ligand [Rh—N 1·999 (4)–2·010 (4) Å], one Cl atom [Rh—Cl 2·496 (2), 2·504 (1) Å] and one Rh atom [Rh—Rh 2·576 (1) Å]. The Rh atoms are bridged by two formato groups.

Introduction. Rhodium(II) compounds are relatively rare. A number of dimeric and polymeric Rh^{II} carboxylates which contain Rh—Rh bonds have, however, been reported. These are mainly dirhodium(II) tetrakis(μ-carboxylates), but a few compounds with only two or three carboxylato bridges are also known (Boyar & Robinson, 1983). Thus, $Rh_2(\mu\text{-}CH_3COO)_2(dmg)_2(PPh_3)_2.H_2O$ (dmg = dimethylglyoximato) containing two carboxylato bridges and $[Rh_2(dpnp)(\mu\text{-}CH_3COO)_3].PF_6$ [dpnp = 2,7-di(2-pyridyl)-1,8-naphthyridine] with three carboxylato bridges and one naphthyridine bridge have been prepared and their crystal structures determined (Halpern, Kimura, Molin-Case & Wong, 1971; Tikkanen, Binamirs-Soriaga, Kaska & Ford, 1983).

The present paper describes the structure of $Rh_2Cl_2(HCOO)_2(phen)_2$ (phen = 1,10-phenanthroline). Such complexes, as noted in our previous paper (Pasternak, Lancman & Pruchnik, 1985) are precursors of very active ketone hydrogenation catalysts.

Experimental. The compound was prepared by the method described by Pasternak & Pruchnik (1976), dimensions 0·35 × 0·35 × 0·40 mm; density measured in a mixture of CCl_4 and $C_2H_4Br_2$; orthorhombic from Weissenberg photographs, *Pbca*; Syntex $P2_1$ computer-controlled four-circle diffractometer, scintillation counter, Mo $K\alpha$ radiation, graphite monochromator; cell parameters by least squares from setting angles of 15 reflections $20° \le 2\theta \le 30°$ measured on diffractometer; 4336 independent reflections measured; variable θ–2θ scan, scan rate 2·0–29·3° min^{-1} (depending on intensity), $2\theta \le 50°$; index range h 0 to 28, k 0 to 17, l 0 to 15; two standards measured every 50 reflections, variation in their intensities was ±2·5%; corrected for Lorentz and polarization, not for absorption; 3244 with $I \ge 3{\cdot}0\sigma(I)$ used for structure determination; calculation performed with Syntex (1976) *XTL/XTLE*; neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); structure determined by heavy-atom method, full-matrix least-squares refinement (on F); $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1/\sigma^2(F)$; the positions of all H atoms were calculated, non-H atoms refined with anisotropic thermal parameters; H atoms with fixed coordinates ($B = 5{\cdot}00$ Å^2); $(\Delta/\sigma)_{\max} = 0{\cdot}01$, $(\Delta\rho)_{\max} = 0{\cdot}3$ e Å^{-3}; $(\Delta\rho)_{\min} = 0{\cdot}3$ e Å^{-3}; $R = 0{\cdot}030$, $wR = 0{\cdot}031$, $S = 2{\cdot}048$; 343 variables, no correction

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for secondary extinction. Final atomic parameters are given in Table 1;* bond lengths and selected angles are in Table 2.

Discussion. The structure of $Rh_2Cl_2(HCOO)_2(phen)_2$ is presented in Fig. 1. Each Rh atom has coordination number 6, the formato groups bridge the Rh atoms and the molecules of 1,10-phenanthroline act as chelates. Only slightly differing distances Rh—O [2·063 (3)–2·069 (4) Å], C—O [1·234 (7)–1·253 (7) Å] and Rh—N [1·999 (4)–2·010 (4) Å] indicate that the formato groups and phenanthroline molecules are coordinated symmetrically with the Rh atoms. Large Rh—Cl distances (Table 2) indicate that these bonds are weak. For this reason the Cl ions dissociate in solution and are substituted by solvent molecules. The Rh—Rh distance of 2·576 (1) Å indicates a strong Rh–Rh interaction, weaker than in $Rh_2(HCOO)_4.2H_2O$ where this distance is shorter by 0·196 Å (Shustorovich, Porai-Koshits & Buslayev, 1975). The Rh—Rh bond length in the title compound is, however, close to that between the Rh atoms in the complex with two carboxylato bridges $Rh_2(CH_3COO)_2(dmg)_2(PPh_3)_2.H_2O$, in which it is 2·618 (5) Å (Halpern *et al.*, 1971).

Table 1. *Fractional atomic coordinates* (*for* C, N *and* O $\times 10^4$; *for* Rh $\times 10^5$) *and equivalent isotropic thermal parameters* ($Å^2$) *for the non*-H *atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{1}{3}(B_{11} + B_{22} + B_{33}).$$

	x	y	z	B_{eq}
Rh(1)	11950 (2)	16638 (2)	13921 (3)	2·01 (2)
Rh(2)	20666 (2)	9740 (2)	21642 (3)	2·34 (2)
Cl(1)	439 (1)	2592 (1)	673 (1)	3·08 (9)
Cl(2)	2976 (1)	471 (1)	2822 (1)	4·90 (13)
O(11)	1725 (2)	2113 (2)	294 (3)	3·1 (3)
O(12)	2436 (2)	1291 (2)	819 (3)	3·2 (3)
O(21)	1390 (2)	2754 (2)	2248 (3)	3·1 (3)
O(22)	2217 (1)	2238 (2)	2686 (3)	3·2 (3)
N(11)	682 (2)	1095 (2)	2366 (3)	2·1 (3)
N(12)	972 (2)	618 (2)	561 (3)	2·0 (3)
N(21)	1913 (2)	−275 (3)	1764 (3)	2·5 (3)
N(22)	1738 (2)	556 (3)	3455 (3)	2·5 (3)
C(1)	2199 (2)	1796 (4)	231 (4)	3·0 (4)
C(2)	1854 (3)	2823 (3)	2616 (4)	3·1 (4)
C(12)	510 (2)	1387 (3)	3247 (4)	2·9 (4)
C(13)	154 (3)	889 (4)	3850 (4)	3·5 (5)
C(14)	−20 (2)	81 (4)	3555 (4)	3·3 (4)
C(15)	151 (2)	−256 (3)	2626 (4)	2·7 (4)
C(16)	492 (2)	293 (3)	2049 (3)	2·0 (3)
C(17)	650 (2)	32 (3)	1079 (3)	1·8 (3)
C(18)	456 (2)	−758 (3)	670 (4)	2·5 (4)
C(19)	584 (2)	−930 (3)	−343 (4)	2·7 (4)
C(110)	890 (2)	−325 (4)	−853 (4)	3·0 (4)
C(111)	1082 (2)	446 (3)	−381 (4)	2·6 (4)
C(112)	−19 (3)	−1083 (4)	2223 (4)	3·6 (5)
C(113)	132 (2)	−1322 (3)	1277 (4)	3·2 (4)
C(22)	2019 (2)	−664 (4)	883 (4)	3·1 (4)
C(23)	1912 (3)	−1563 (4)	745 (5)	3·8 (5)
C(24)	1724 (3)	−2070 (3)	1505 (5)	4·0 (5)
C(25)	1609 (2)	−1677 (3)	2439 (4)	3·2 (4)
C(26)	1709 (2)	−771 (3)	2528 (4)	2·6 (4)
C(27)	1615 (2)	−329 (3)	3441 (4)	2·6 (4)
C(28)	1425 (2)	−779 (4)	4282 (4)	3·3 (4)
C(29)	1381 (3)	−309 (4)	5164 (4)	4·0 (5)
C(210)	1492 (3)	586 (4)	5176 (4)	4·0 (5)
C(211)	1673 (2)	990 (3)	4305 (4)	3·3 (4)
C(212)	1399 (3)	−2139 (4)	3295 (5)	4·4 (5)
C(213)	1311 (3)	−1707 (4)	4160 (5)	4·4 (6)

Table 2. *Bond distances* (Å) *and bond angles* (°) *at* Rh *atoms with e.s.d.'s in parentheses*

Rh(1)—Rh(2)	2·576 (1)		
Rh(1)—Cl(1)	2·504 (1)	Rh(2)—Cl(2)	2·496 (2)
Rh(1)—O(11)	2·069 (4)	Rh(2)—O(12)	2·069 (4)
Rh(1)—O(21)	2·063 (3)	Rh(2)—O(22)	2·068 (3)
Rh(1)—N(11)	1·999 (4)	Rh(2)—N(21)	1·999 (4)
Rh(1)—N(12)	2·010 (4)	Rh(2)—N(22)	2·008 (4)
O(11)—C(1)	1·248 (7)	O(21)—C(2)	1·234 (7)
O(12)—C(1)	1·240 (6)	O(22)—C(2)	1·253 (7)
N(11)—C(12)	1·327 (6)	N(21)—C(22)	1·343 (17)
N(11)—C(16)	1·366 (6)	N(21)—C(26)	1·363 (6)
N(12)—C(17)	1·370 (6)	N(22)—C(27)	1·371 (6)
N(12)—C(111)	1·315 (6)	N(22)—C(211)	1·324 (7)
C(12)—C(13)	1·403 (8)	C(22)—C(23)	1·397 (8)
C(13)—C(14)	1·351 (8)	C(23)—C(24)	1·353 (8)
C(14)—C(15)	1·407 (7)	C(24)—C(25)	1·412 (8)
C(15)—C(16)	1·405 (7)	C(25)—C(26)	1·397 (7)
C(15)—C(112)	1·424 (7)	C(25)—C(212)	1·437 (8)
C(16)—C(17)	1·411 (6)	C(26)—C(27)	1·412 (7)
C(17)—C(18)	1·396 (6)	C(27)—C(28)	1·395 (7)
C(18)—C(19)	1·416 (7)	C(28)—C(29)	1·383 (8)
C(18)—C(113)	1·417 (7)	C(28)—C(213)	1·441 (8)
C(19)—C(110)	1·362 (7)	C(29)—C(210)	1·380 (8)
C(110)—C(111)	1·407 (7)	C(210)—C(211)	1·389 (8)
C(112)—C(113)	1·368 (8)	C(212)—C(213)	1·347 (9)
Rh(1)—Rh(2)—Cl(2)	172·7 (1)	Rh(2)—Rh(1)—Cl(1)	169·7 (1)
Rh(1)—Rh(2)—O(12)	85·0 (1)	Rh(2)—Rh(1)—O(11)	84·7 (1)
Rh(1)—Rh(2)—O(22)	84·6 (1)	Rh(2)—Rh(1)—O(21)	85·0 (1)
Rh(1)—Rh(2)—N(21)	97·0 (1)	Rh(2)—Rh(1)—N(11)	94·3 (1)
Rh(1)—Rh(2)—N(22)	98·5 (1)	Rh(2)—Rh(1)—N(12)	97·2 (1)
Cl(2)—Rh(2)—O(12)	89·7 (1)	Cl(1)—Rh(1)—O(11)	89·9 (1)
Cl(2)—Rh(2)—O(22)	90·4 (1)	Cl(1)—Rh(1)—O(21)	86·2 (1)
Cl(2)—Rh(2)—N(21)	88·4 (1)	Cl(1)—Rh(1)—N(11)	92·1 (1)
Cl(2)—Rh(2)—N(22)	87·2 (1)	Cl(1)—Rh(1)—N(12)	91·8 (1)
O(12)—Rh(2)—O(22)	90·2 (1)	O(11)—Rh(1)—O(21)	89·5 (1)
O(12)—Rh(2)—N(21)	93·8 (2)	O(11)—Rh(1)—N(11)	173·3 (1)
O(12)—Rh(2)—N(22)	174·8 (2)	O(11)—Rh(1)—N(12)	91·8 (1)
O(22)—Rh(2)—N(21)	175·8 (2)	O(21)—Rh(1)—N(11)	97·1 (1)
O(22)—Rh(2)—N(22)	94·0 (2)	O(21)—Rh(1)—N(12)	177·6 (1)
N(21)—Rh(2)—N(22)	81·9 (2)	N(11)—Rh(1)—N(12)	81·7 (2)

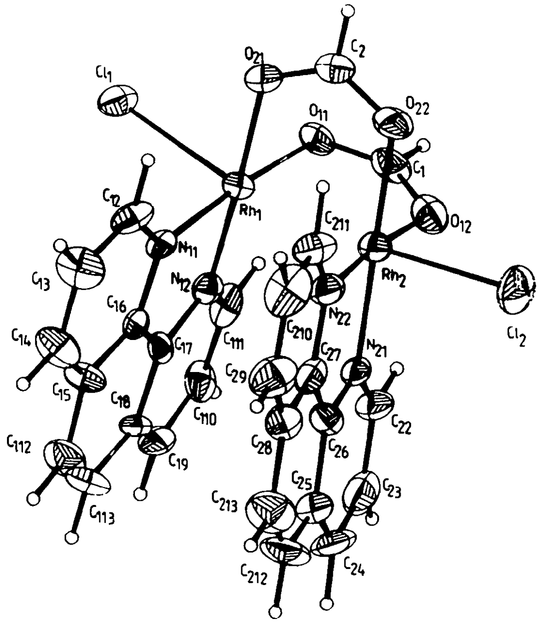

Fig. 1. The structure of the binuclear complex and the numbering system used.

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom coordinates and bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43670 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The Rh—Rh distance is significantly affected by the carboxylato groups. In the title complex, it is intermediate between the Rh—Rh distance in complexes with four carboxylato bridges, 2·38 Å in $Rh_2(HCOO)_4.2H_2O$ (Shustorovich *et al.*, 1975) or 2·386 (3) Å in $Rh_2(CH_3COO)_4(H_2O)_2$ (Cotton, De Boer, La Prade, Pipal & Ucko, 1970) and the analogous distance in complexes which contain no carboxylato bridging groups, *e.g.* 2·936 (2) Å in $Rh_2(dmg)_4(PPh_3)_2C_3H_7OH.H_2O$ (Caulton & Cotton, 1971).

The Rh—O distance in $Rh_2Cl_2(HCOO)_2(phen)_2$ is about 0·04 Å longer than the Rh—O distance in the tetraformato complex (2·03 Å) (Shustorovich *et al.*, 1975) and in $Rh_2Cl_2(HCOO)_2(dipy)_2.4H_2O$ [2·033 (4) Å (Głowiak, Pasternak & Pruchnik, 1984); 2·039 (9), 2·049 (8) Å (Sokol, Porai-Koshits, Kochetkova & Svieshnikova, 1984)]. It is most probable that elongation of the Rh—O bond in the phenanthroline complex results from steric interactions of the dinitrogen ligands, since the *trans* effect of dipyridyl and phenanthroline is practically the same.

References

BOYAR, E. B. & ROBINSON, S. D. (1983). *Coord. Chem. Rev.* **50**, 109–208.
CAULTON, K. G. & COTTON, F. A. (1971). *J. Am. Chem. Soc.* **93**, 1914–1918.
COTTON, F. A., DE BOER, B. G., LA PRADE, M. D., PIPAL, J. R. & UCKO, D. A. (1970). *J. Am. Chem. Soc.* **92**, 2926–2927.
GŁOWIAK,, T., PASTERNAK, H. & PRUCHNIK, F. (1984). Unpublished results.
HALPERN, J., KIMURA, E., MOLIN-CASE, J. A. & WONG, C. S. (1971). *J. Chem. Soc. Chem. Commun.* pp. 1207–1208.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
PASTERNAK, H., LANCMAN, E. & PRUCHNIK, F. (1985). *J. Mol. Catal.* **29**, 13–18.
PASTERNAK, H. & PRUCHNIK, F. (1976). *Inorg. Nucl. Chem. Lett.* **12**, 591–598.
SHUSTOROVICH, E. M., PORAI-KOSHITS, M. A. & BUSLAYEV, YU. A. (1975). *Coord. Chem. Rev.* **17**, 1–98.
SOKOL, W. I., PORAI-KOSHITS, M. A., KOCHETKOVA, A. P. & SVIESHNIKOVA, L. B. (1984). *Koord. Chim.* **10**, 844–849.
Syntex (1976). *XTL/XTLE Structure Determination System.* Syntex Analytical Instruments, Cupertino, California.
TIKKANEN, W. R., BINAMIRS-SORIAGA, E., KASKA, W. C. & FORD, P. C. (1983). *Inorg. Chem.* **22**, 1147–1148.

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The Structure of Ni(cyclam)$(ClO_4)_2$

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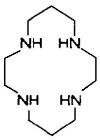
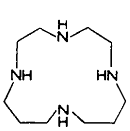
Abstract. Perchlorato(1,4,8,11-tetraazacyclotetradecane)nickel(II) perchlorate, $[Ni(ClO_4)(C_{10}H_{24}N_4)]ClO_4$, $M_r = 457{\cdot}9$, monoclinic, $P2_1/n$, $a = 9{\cdot}596\ (2)$, $b = 13{\cdot}887\ (6)$, $c = 13{\cdot}137\ (3)$ Å, $\beta = 90{\cdot}78\ (2)^\circ$, $V = 1750{\cdot}5$ Å^3, $Z = 4$, D_m not determined, $D_x = 1{\cdot}74$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7093$ Å, $\mu(\text{Mo } K\alpha) = 1{\cdot}47$ mm^{-1}, $F(000) = 952$, $R(F) = 0{\cdot}075$ for 1367 reflections at $T = 158$ K. Known unsubstituted cyclam/isocyclam complexes of Ni^{II} fall into two groups. In the former, the coordination is that of isolated octahedra; these complexes are mauve and paramagnetic. In the latter group (including the present complex) the axially disposed anions are shared between octahedra. These complexes are orange and diamagnetic.

Introduction. Several N_4 macrocycles are known which will act as ligands for transition-metal ions. Crystal structures are known for a number of complexes of one such, 1,4,8,11-tetraazacyclotetradecane (cyclam), (I). Similar complexes are known for isocyclam, 1,4,7,11-tetraazacyclotetradecane, (II). (The structures of many transition-metal complexes with substituted and partially reduced cyclams are also known.)



(I)



(II)

The present structure analysis brings to five the number of unsubstituted cyclam/isocyclam complexes

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