square-pyramidal conformation, no unusual bond distances or angles indicative of strain are apparent within the TMC macrocycle as a consequence of its coordination to Co^{II}.

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Structure of Dichlorobis(trimethylphosphine oxide)cobalt(II)

By Marie-Joëlle Menu, Michel Simard and André L. Beauchamp

Département de Chimie, Université de Montréal, CP 6128, *Succ. A, Montréal, Québec, H3C 3J7, Canada*

Herbert König, Michèle Dartiguenave and Yves Dartiguenave

Laboratoire de Chimie de Coordination, 205 *route de Narbonne,* 31077-*Toulouse, France*

and Hans-Friedrich Klein

Anorganische Chemie I, *Technische Hochschule, Darmstadt, Federal Republic of Germany*

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Abstract. $[CoCl_2(C_3H_9OP)_2]$, $M_r = 313{\cdot}99$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}660\,(4)$, $b = 11{\cdot}187\,(6)$, $c = 11{\cdot}807\,(3)$ Å, $V = 1408{\cdot}0$ Å^3, $Z = 4$, $D_x = 1{\cdot}481$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 15{\cdot}64$ mm^{-1}, $F(000) = 644$, $T = 170$ K, final $R = 0{\cdot}057$ for 2149 unique observed reflections. Co has a slightly distorted tetrahedral coordination [Cl—Co—Cl 113·6 (1), O—Co—O 105·6 (2)°] and forms normal Co—Cl [2·262 (2) Å] and Co—O [1·971 (5) Å av.] distances.

Introduction. Dichlorobis(tertiary phosphine oxide)cobalt(II) complexes have been known for some time (Hunter, Langford, Rodley & Wilkins, 1968; De Bolster, Boutkan, van der Knaap, van Zweeden, Kortram & Groeneveld, 1978; Schmidt & Yoke, 1971), but they still raise interest because cobalt acts as a catalyst in phosphine oxidation (Yamamoto, 1986). On the basis of X-ray diffraction studies, the triphenylphosphine oxide and tribenzylphosphine oxide complexes have been described as tetrahedral four-coordinate Co^{II} complexes (Mangion, Smith & Shore, 1976; De Almeida Santos & Mascarenhas, 1979). The present $CoCl_2(OPMe_3)_2$ compound formed as a by-product of the slow reaction of $CoCl(PMe_3)_3$ with CO_2 and of $CoCl(Ph_2C_2O)(PMe_3)_3$ with H_2, because traces of oxygen were present (König & Klein, 1989). It crystallized out in a pure state from the benzene solution as deep-blue, air-stable crystals. Increasing the amount of O_2 gave rise to untractable mixtures from which only trimethylphosphine oxide could be separated and characterized. The $CoCl_2(OPMe_3)_2$ complex is more conveniently synthesized by reacting $OPMe_3$ with $CoCl_2$ (Hunter *et al.*, 1968; De Bolster *et al.*, 1978; Schmidt & Yoke, 1971).

Experimental. Crystal, 0·065 × 0·11 × 0·19 mm, cut from a large fragment. Enraf–Nonius CAD-4 diffractometer, Niggli matrix of reduced cell indicative of orthorhombic primitive lattice, Laue symmetry and cell dimensions checked with oscillation photographs. Refined cell parameters from 25 centered reflections ($20 < \theta < 25°$), space group $P2_12_12_1$, systematic absences ($h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $00l$, $l \neq 2n$) identified in full data set. Intensity data collected by ω-scan technique, width = $(1{\cdot}00 + 0{\cdot}14\tan\theta)°$, scan speed 4° min^{-1}, graphite-monochromatized Cu $K\bar{\alpha}$ radiation, $2\theta_{\max} = 140°$, one asymmetric unit ($+h+k+l$ and $-h+k+l$ octants) measured.

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Orientation checked every 200 measurements, intensity of seven standards checked every hour, max. fluctuations ±2·9%, 2671 independent reflections, 2163 with $I > 3\sigma(I)$. Data corrected for Lp and absorption (Gaussian integration, grid 10 × 10 × 10, transmission range 0·04–0·29).

Structure solved with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974). Refinement on $|F_o|$ by full-matrix least squares using the *SHELX* package (Sheldrick, 1976). Anisotropic refinement for all non-H atoms. H-atom coordinates fixed at idealized values (sp^3 hybridization, C—H = 0·97 Å, isotropic B initially refined, then fixed in last cycles, $U = 0{\cdot}064$ Å^2). Reflections (14) probably strongly affected by extinction rejected in final refinement. Final $R = 0{\cdot}057$, $wR = 0{\cdot}056$, weights based on counting statistics, $w = 1/[\sigma^2(F) + 0{\cdot}00005F^2]$, $S = 2{\cdot}12$; (shift/σ), mean = 0·007, max. = 0·04. Residual electron density on final ΔF map: peaks of $\pm$ |0·6–0·8| e Å^{-3} near Co, P and Cl, general background below $\pm$ 0·6 e Å^{-3}. Enantiomorph refined independently, $R = 0{\cdot}129$, $wR = 0{\cdot}137$ and $S = 5{\cdot}82$ (large f'' contribution). Scattering factors from Cromer & Mann (1968) for Co, Cl, P, O and C; from Stewart, Davidson & Simpson (1965) for H. Anomalous-dispersion factors f' and f'' for Co and Cl from Cromer & Liberman (1970). Coordinates and equivalent isotropic thermal parameters are given in Table 1.*

Table 1. *Refined coordinates* (× 10^5, C *and* O × 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3)

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co	57447 (12)	50471 (11)	6315 (10)	33
Cl(1)	37738 (19)	47073 (16)	12642 (16)	41
Cl(2)	58142 (21)	58451 (17)	−11278 (16)	42
P(1)	77564 (20)	68507 (17)	15945 (17)	32
P(2)	65728 (21)	24808 (17)	14629 (17)	34
O(1)	6588 (5)	6098 (4)	1723 (4)	36
O(2)	6698 (5)	3527 (5)	659 (5)	44
C(11)	7441 (8)	8159 (7)	776 (7)	44
C(12)	8970 (8)	6046 (8)	920 (7)	49
C(13)	8321 (8)	7317 (7)	2925 (7)	41
C(21)	6087 (8)	2918 (6)	2850 (7)	40
C(22)	5481 (9)	1414 (8)	946 (7)	54
C(23)	8046 (8)	1752 (7)	1615 (7)	48

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Co—Cl(1)	2·262 (2)	P(1)—C(12)	1·766 (9)
Co—Cl(2)	2·262 (2)	P(1)—C(13)	1·761 (8)
Co—O(1)	1·962 (5)	P(2)—O(2)	1·513 (6)
Co—O(2)	1·981 (5)	P(2)—C(21)	1·786 (8)
P(1)—O(1)	1·511 (6)	P(2)—C(22)	1·775 (9)
P(1)—C(11)	1·786 (8)	P(2)—C(23)	1·779 (9)
Cl(1)—Co—Cl(2)	113·6 (1)	C(11)—P(1)—C(12)	108·2 (4)
Cl(1)—Co—O(1)	108·0 (2)	C(11)—P(1)—C(13)	107·7 (4)
Cl(1)—Co—O(2)	109·2 (2)	C(12)—P(1)—C(13)	107·6 (4)
Cl(2)—Co—O(1)	110·6 (2)	Co—O(2)—P(2)	129·0 (3)
Cl(2)—Co—O(2)	109·7 (2)	O(2)—P(2)—C(21)	112·9 (3)
O(1)—Co—O(2)	105·6 (2)	O(2)—P(2)—C(22)	111·2 (4)
Co—O(1)—P(1)	130·2 (3)	O(2)—P(2)—C(23)	109·9 (4)
O(1)—P(1)—C(11)	110·8 (3)	C(21)—P(2)—C(22)	108·0 (4)
O(1)—P(1)—C(12)	111·4 (4)	C(21)—P(2)—C(23)	106·8 (4)
O(1)—P(1)—C(13)	110·9 (3)	C(22)—P(2)—C(23)	107·8 (4)

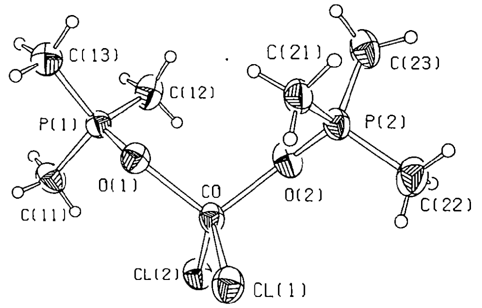

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the dichlorobis(trimethylphosphine oxide)cobalt(II) molecule. Non-H atoms are represented at 50% probability level, H atoms by spheres of arbitrary size.

Discussion. The CoCl$_2$(OPMe$_3$)$_2$ molecule is shown in Fig. 1. Intramolecular bond lengths and angles are given in Table 2. The Co coordination is approximately tetrahedral. The departure of the Cl(1)—Co—Cl(2) and O(1)—Co—O(2) angles [113·6 (1) and 105·6 (2)°, respectively] from the tetrahedral value was also noted for CoCl$_2${OP(CH$_2$Ph)$_3$}$_2$ (De Almeida Santos & Mascarenhas, 1979). In CoCl$_2$(OPPh$_3$)$_2$, the O—Co—O angle is much smaller [96·4 (3)°] (Mangion *et al.*, 1976), and the relatively long Co—O bonds [1·999 (7) Å av.] are probably correlated with this small angle. However, no similar explanation can be proposed for our Co—O distances in the PMe$_3$ complex [1·969 (5) Å] being significantly longer than those of CoCl$_2${OP(CH$_2$Ph)$_3$}$_2$ [1·928 (7) Å]. There are no unusual features in the coordinated phosphine oxide ligand, compared with Co(NO$_3$)$_2$(OPEt$_3$)$_2$ (Alnaji, Dartiguenave, Dartiguenave, Simard & Beauchamp, 1989), Co(NO$_3$)$_2$(OPMe$_3$)$_2$ (Cotton & Soderberg, 1963), CoCl$_2$(OPPh$_3$)$_2$ (Mangion *et al.*, 1976) and CoCl$_2${OP(CH$_2$Ph)$_3$}$_2$ (De Almeida Santos & Mascarenhas, 1979).

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* Lists of refined temperature factors, hydrogen coordinates, and observed and calculated structure-factor amplitudes, together with a stereoview of the unit cell, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52012 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Neutron Structure Refinement of Barium Oxalate–Oxalic Acid Dihydrate, $BaC_2O_4.H_2C_2O_4.2H_2O$ and of Related Nonstoichiometric Hydrates

BY O. CHAIX-PLUCHERY AND J. C. MUTIN*

Laboratoire de Recherche sur la Réactivité des Solides, Faculté des Sciences Mirande, BP 138,
21004 *Dijon CEDEX, France*

J. BOUILLOT

Institut Laue-Langevin, 156*X,* 38042 *Grenoble CEDEX, France*

AND J. C. NIEPCE

Laboratoire de Recherche sur la Réactivité des Solides, Faculté des Sciences Mirande, BP 138,
21004 *Dijon CEDEX, France*

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Abstract. $BaC_2O_4.H_2C_2O_4.2H_2O$, $M_r = 351{\cdot}38$, monoclinic, $C2/c$, $a = 14{\cdot}446$ (2), $b = 5{\cdot}4175$ (6), $c = 12{\cdot}450$ (1) Å, $\beta = 116{\cdot}17$ (1)°, $V = 874$ (4) Å^3, $Z = 4$, $D_x = 2{\cdot}669$ Mg m^{-3}, $\lambda = 1{\cdot}2651$ Å, $\mu(n) = 0{\cdot}137$ mm^{-1}, $F(000) = 269{\cdot}94$, room temperature, final $R = 0{\cdot}021$ for 768 independent reflections. The neutron refinement of the crystal structure of the dihydrate compound confirms the structure previously reported from X-ray measurements. The positions of the two kinds of H atoms are determined and the environment and geometry of the water molecules analysed. The crystal structures of mosaic crystals with various water contents ε, from dehydration of single crystals followed by rehydration with H_2O or D_2O, were also refined. Only limited changes of the structural parameters of the dihydrate mosaic crystals with respect to the single-crystal ones are observed ($R = 0{\cdot}022$ and $0{\cdot}045$ for the hydrogenated and deuterated crystals, respectively). In mosaic crystals with $\varepsilon \neq 2$, the initial crystallographic sites of water are preserved whatever the water content ($\varepsilon = 0{\cdot}7$, $R = 0{\cdot}072$; $\varepsilon = 0{\cdot}3$, $R = 0{\cdot}058$). However, the oxalate ions in such crystals present abnormally large displacement parameters along the y direction; this is tentatively explained by the random removal of water molecules which leads to the formation of two intermolecular distances along this direction.

Introduction. Previous thermogravimetry and X-ray diffraction studies of the thermal dehydration of barium oxalate–oxalic acid dihydrate BaC_2O_4.-

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* To whom correspondence should be addressed.

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