Coordination of a water molecule is a common feature of H_4phdta and H_4edta complexes of the manganese(II) ion, which has a large radius (0·80 Å). Hydration in a chelated compound should result in greater exothermicity and in a smaller change in entropy (Anderegg, 1971), and this is just the case for both complexes. Hence these thermochemical data are satisfactorily interpretable in terms of $Mn(OH_2)L^{2-}$, which may be present in an aqueous solution.

References

ANDEREGG, G. (1971). *Coordination Chemistry*, edited by A. E. MARTELL, pp. 427–490. *Am. Chem. Soc. Monogr.* 168. New York: Van-Nostrand–Reinhold.

COHEN, G. H. & HOARD, J. L. (1966). *J. Am. Chem. Soc.* **88**, 3228–3234.

FURUSAKI, A. (1979). *Acta Cryst.* A**35**, 220–224.

GRIMES, J. H., HUGGARD, A. J. & WILFORD, S. P. (1963). *J. Inorg. Nucl. Chem.* **25**, 1225–1238.

International Tables for X-ray Crystallography (1974). Vol. IV, p. 95. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KATAYAMA, C., SAKABE, N. & SAKABE, K. (1972). *Acta Cryst.* A**28**, S207.

MCCANDLISH, E. F. K., MICHAEL, T. K., NEAL, J. A., LINGAFELTER, E. C. & ROSE, N. J. (1978). *Inorg. Chem.* **17**, 1383–1394.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MOTHERWELL, W. D. S. (1978). *PLUTO78*. Program for drawing crystal and molecular structures. Univ. of Cambridge, England.

NAKASUKA, N., KUNIMATSU, M., MATSUMURA, K. & TANAKA, M. (1985). *Inorg. Chem.* **24**, 10–15.

RICHARDS, S., PEDERSEN, B., SILVERTON, J. V. & HOARD, J. L. (1964). *Inorg. Chem.* **3**, 27–33.

SOLANS, X., FONT-ALTABA, M., OLIVA, J. & HERRERA, J. (1983). *Acta Cryst.* C**39**, 435–438.

WEAKLIEM, H. A. & HOARD, J. L. (1959). *J. Am. Chem. Soc.* **81**, 549–555.

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Structure of Iodotris(trimethylphosphine)cobalt(I), $[CoI(C_3H_9P)_3]$

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Abstract. $M_r = 414\cdot07$, monoclinic, $P2_1/m$, $a = 7\cdot702\ (1)$, $b = 13\cdot747\ (2)$, $c = 9\cdot304\ (1)$ Å, $\beta = 107\cdot92\ (1)°$, $U = 937\cdot3$ Å^3, $Z = 2$, $D_x = 1\cdot47$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0\cdot71069$ Å, $\mu(\mathrm{Mo}\ K\alpha) = 2\cdot848$ mm^{-1}, $F(000) = 412$, room temperature, $R = 0\cdot032$ for 1466 unique reflections. Each molecule possesses m symmetry and the central Co is found in a distorted tetrahedral coordination environment [Co—I 2·5495 (8), Co—P 2·232 (2), 2·237 (1) (×2) Å] agreeing well with predictions based on magnetic measurements.

Introduction. The four-coordinate d^8 complexes of the second- and third-row transition metals Rh and Ir adopt a square-planar geometry. This leads to a low-spin diamagnetic $e_g(4)a_{1g}(2)b_{2g}(2)$ molecule in which the strongly antibonding b_{1g} ($d_{x^2-y^2}$) orbital remains unfilled at the expense of spin-pairing of two electrons. Many examples of such compounds are known. In contrast the d^8 Co^I complexes adopt a high-spin $e(4)t_2(4)$ electronic configuration. A tetrahedral coordination geometry has been predicted but hitherto unproved as such complexes are easily oxidized to Co^{II} or react with neutral σ donors to give 18-electron five-coordinate species, generally of trigonal-bipyramidal geometry. We now report the crystal structure of $Co(PMe_3)_3I$, a tetrahedral four-coordinate Co^I d^8 complex. The complex was formed as a byproduct of the sodium-amalgam reduction of the half-sandwich complex $Co(\eta\text{-}C_5Me_5)(PMe_3)I_2$ and was isolated owing to the ease with which it crystallized from solution in petroleum ether as deep-blue, tabular, air-sensitive crystals. The complexes $Co(PMe_3)_3X$ ($X = $ Cl, Br, I) are most conveniently synthesized by alternative literature preparations (Klein & Karsch, 1975*a*,*b*).

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Table 1. *Atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic vibration parameters*

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

	x	y	z	$U_{\rm eq}$(Å^2)
I(1)	0·17288 (6)	0·25	0·45067 (6)	0·0773
Co(1)	−0·14607 (10)	0·25	0·26001 (8)	0·0458
P(1)	−0·1764 (2)	0·25	0·0136 (2)	0·0603
P(2)	−0·3005 (2)	0·11934 (9)	0·2964 (1)	0·0568
C(1)	−0·0705 (11)	0·1479 (6)	−0·0517 (7)	0·1190
C(2)	−0·3995 (13)	0·25	−0·1245 (9)	0·1051
C(3)	−0·5400 (7)	0·0969 (5)	0·1927 (7)	0·0946
C(4)	−0·1972 (10)	0·0043 (4)	0·2668 (8)	0·1004
C(5)	−0·3058 (8)	0·1055 (4)	0·4906 (6)	0·0843

Experimental. Chunky crystal mounted under nitrogen in a glass capillary, dimensions 0·3 × 0·3 × 0·45 mm. Enraf–Nonius CAD-4 diffractometer. Lattice parameters from the positions of 25 carefully centred reflections ($12 < \theta < 20°$). ω–2θ scans with ω-scan width $(0·95 + 0·35\tan\theta)°$, scan speed 0·97 – 5·49° min^{-1}, graphite-monochromated Mo $K\alpha$ radiation. Absorption correction applied (North, Phillips & Mathews, 1968); max., min. transmission factors 1·10, 1·00. Data-collection range $1·0 \leq \theta \leq 30·0°$; *ca* 2·5% decay in intensity corrected during processing. 4453 reflections measured, 2834 unique (merging $R = 0·019$) giving 1466 reflections with $I > 3\sigma(I)$; index range $h \pm 10$, $k\,0/16$, $l\,0/12$. Structure solved by heavy-atom method to locate Co, I, P followed by difference Fourier syntheses revealing all non-hydrogen atoms. H atoms all located but included in calculated positions [U(iso) refined to 0·144 (7) Å^2]. Full-matrix least-squares refinement (on F) with all non-hydrogen atoms anisotropic. Correction for isotropic extinction (Larson, 1967) made during the latter stages of refinement. A Chebyshev weighting scheme (Carruthers & Watkin, 1979) with coefficients 56·0, 74·4, and 28·6 gave satisfactory agreement analyses. At convergence $R = 0·032$, $wR = 0·034$, all $\Delta/\sigma < 0·001$. Secondary-extinction parameter 25 (5). Highest peak in final difference Fourier map 0·5 e Å^{-3} located near I(1), deepest trough at atomic sites −0·06 e Å^{-3}. Structure analysis and refinement carried out using the Oxford *CRYSTALS* system (Carruthers & Watkin, 1981) on the VAX 11/750 computer in the Chemical Crystallography Laboratory, Oxford University. Scattering factors and corrections for anomalous dispersion taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.*

The molecular structure of $Co(PMe_3)_3I$ is shown in Fig. 1 (Davies, 1983) which depicts the view along the Co—I vector. The molecule has m symmetry in the solid state with the mirror plane passing through Co, I, P(1), C(2) and H(4). Intramolecular bond lengths and angles are in Table 2 confirming that the molecule is approximately tetrahedral as predicted by magnetic measurements in solution [Klein & Karsch (1975*b*); Aresta, Rossi & Sacco (1969) for the triphenylphosphine derivatives. Aresta and co-workers also postulated on the basis of spectroscopic evidence that these complexes possess the same structure in solution as in the solid state.]. In this crystal structure the Co—I, Co—P and P—C distances show no unusual variations from those found in related complexes, *e.g.* in $CoI(NO)_2PPh_3$ (Haymore, Huffman & Butler, 1983), but a significant distortion is found for the I—Co—P angles which are 119·26 (6) and 109·77 (4)°. Comparison of the various I—Co—P and P—Co—P angles does however indicate that a molecular-orbital description using a tetrahedral orientation of ligands around the Co centre is a sufficiently good first approximation to describe the electronic nature of this paramagnetic

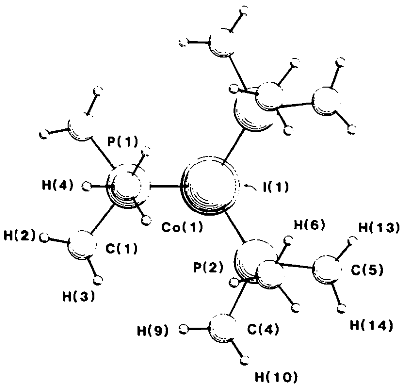

Fig. 1. Molecular structure of $Co(PMe_3)_3I$ with numbering scheme.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Primed atoms are related to the corresponding unprimed ones by the mirror plane at $y = \frac{1}{4}$.

I(1)—Co(1)	2·5495 (8)	P(1)—Co(1)—I(1)	119·26 (6)
Co(1)—P(1)	2·232 (2)	P(2)—Co(1)—I(1)	109·77 (4)
Co(1)—P(2)	2·237 (1)	P(2)—Co(1)—P(1)	105·24 (4)
		P(2)—Co(1)—P(2′)	106·84 (7)
P(1)—C(1)	1·819 (7)	C(1)—P(1)—Co(1)	115·3 (2)
P(1)—C(2)	1·801 (8)	C(2)—P(1)—Co(1)	120·5 (3)
		C(2)—P(1)—C(1)	100·9 (3)
P(2)—C(3)	1·826 (5)	C(1)—P(1)—C(1′)	101·0 (6)
P(2)—C(4)	1·828 (6)	C(3)—P(2)—Co(1)	123·6 (2)
P(2)—C(5)	1·830 (5)	C(4)—P(2)—Co(1)	113·3 (2)
		C(4)—P(2)—C(3)	101·0 (3)
		C(5)—P(2)—Co(1)	114·0 (2)
		C(5)—P(2)—C(3)	100·3 (3)
		C(5)—P(2)—C(4)	101·6 (3)

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42203 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

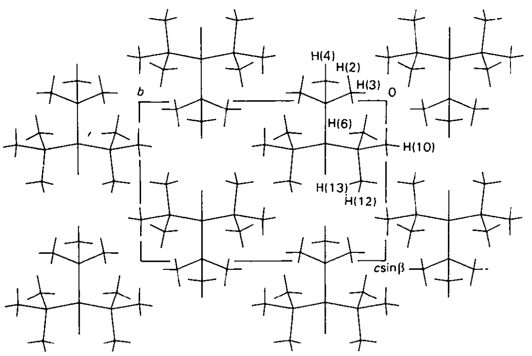

Fig. 2. Packing of adjacent molecules viewed along **a**.

compound. The molecular packing is shown in Fig. 2. The molecules pack in interlocking layers along **b** with the iodine 'head' fitting into the $(PMe_3)_3$ 'tail'. The closest contacts within the layers are H(1)···H(6)-$(1+x,y,z)$ 2·59 and H(2)···H(12)$(x,y,-1+z)$ 2·56 Å. Between layers the closest contacts are H(11)···H(12)-$(-x,-y,1-z)$ 2·45 and H(14)···H(14)$(-1-x,-y,1-z)$ 2·54 Å.

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References

Aresta, M., Rossi, M. & Sacco, A. (1969). *Inorg. Chim. Acta*, **3**, 227–231.
Carruthers, J. R. & Watkin, D. J. (1979). *Acta Cryst.* A**35**, 698–699.
Carruthers, J. R. & Watkin, D. J. (1981). *CRYSTALS User Manual.* Oxford Univ. Computing Laboratory.
Davies, E. K. (1983). *CHEMGRAF User Manual.* Chemical Crystallography Laboratory, Oxford Univ.
Haymore, B. L., Huffman, J. C. & Butler, N. E. (1983). *Inorg. Chem.* **22**, 168–170.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
Klein, H.-F. & Karsch, H. H. (1975*a*). *Chem. Ber.* **108**, 944–955.
Klein, H.-F. & Karsch, H. H. (1975*b*). *Inorg. Chem.* **14**, 473–477.
Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

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Structure of Bis(acetylacetonato)beryllium(II), $Be(C_5H_7O_2)_2$, at 119 K

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Abstract. $M_r = 207·2$, monoclinic, $P2_1$, $a = 13·437$ (1), $b = 11·196$ (2), $c = 7·656$ (1) Å, $\beta = 100·79$ (1)°, $V = 1131·4$ (3) Å^3, $Z = 4$, $D_x = 1·22$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 0·94$ cm^{-1}, $F(000) = 452$, $T = 119$ (1) K, final $R = 0·037$ for 3114 unique observed reflections. The two independent molecules are similar and each Be atom is chelated in a distorted tetrahedron by the two ligands with a Be—O distance of 1·618 (5) Å and an O—Be—O angle of 107·5 (4)°. The chelate rings of one molecule are planar while those of the other molecule are folded about the bites by 13·7 (2) and 8·7 (3)°.

Introduction. The structure of the title compound has been determined at room temperature (Stewart & Morosin, 1975). However, examination of this structure shows that equivalent bond distances are distributed over wide ranges, for example, for O—C from 1·24 (1) to 1·29 (1) Å. Stewart & Morosin collected various data sets over several years because of instrumental changes and serious radiation degradation of crystals for different specimens. Their structure analysis was based on 1929 averaged intensities of these data sets, which were corrected for degradation individually. As part of our structural studies on β-diketonato complexes, the refinement of the title complex was undertaken at low temperature in order to obtain more accurate information concerning the molecular geometry and the location of H atoms, and further to compare the molecular structure with that observed by gas electron diffraction (Shibata, Ohta & Iijima, 1980).

Experimental. Colorless crystals of title compound obtained by crystallization from benzene. Crystal specimen cooled by blowing cold N_2 gas evaporated from liquid N_2 and kept at 119 (1) K. Lattice constants by least-squares refinement of setting angles of 50 reflections ($20 < 2\theta < 30°$). Cell-volume contraction on cooling 3·7%. Graphite-monochromated Mo $K\alpha$ radiation, Rigaku four-circle diffractometer AFC-5.

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