References

BERTRAND, J. A., SMITH, J. H. & VANDERVEER, D. G. (1977). Inorg. Chem. 16, 1484–1488.

CHING, J. C. & SCHLEMPER, E. O. (1975). Inorg. Chem. 14, 2470–2474.

FAIR, C. K. & SCHLEMPER, E. O. (1978). Acta Cryst. B34, 438–441.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

MURMANN, R. K. & SCHELEMPER, E. O. (1979). Inorg. Chem. 18, 2625–2631.

SAKHAWAT HUSSAIN, M. & SCHLEMPER, E. O. (1979). Inorg. Chem. 18, 1116–1121.

SCHLEMPER, E. O. (1968). Inorg. Chem. 7, 1130–1135.

SCHLEMPER, E. O. & FAIR, C. K. (1977). Acta Cryst. B33, 2484–2488.

SCHLEMPER, E. O., HAMILTON, W. C. & LAPLACA, S. J. (1971). J. Chem. Phys. 54, 3990–4000.

SHELDRICK, G. M. (1986). SHELXTL-Plus User's Manual. Nicolet XRD Corporation, Madison, Wisconsin, USA.

π-Arene Complexes. 5. Structure of Tricarbonyl(η⁶-hexamethylbenzene)manganese(I) Pentacarbonyliodochromate(0)

BY PETRUS H. VAN ROOYEN,* LORNA GEER AND SIMON LOTZ

Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa

Abstract. [Mn($C_{12}H_{18}$)(CO)$_3$][CrI(CO)$_5$], $M_r = 620.6$, monoclinic, $P2_1/c$, $a = 8.957$ (3), $b = 19.017$ (3), $c = 14.328$ (3) Å, $\beta = 106.96$ (2)°, $V = 2334$ (1) Å^3, $Z = 4$, $D_x = 1.77$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 2.23$ mm^{-1}, $F(000) = 1216$, $T = 298$ K. Final $R = 0.049$, $wR = 0.031$ for 2316 observed reflections with $F > 4\sigma(F_o)$ and 301 variable parameters. The structure consists of an [Mn(η^6-C$_6$Me$_6$)(CO)$_3$]$^+$ cation linked to a [Cr(CO)$_5$I]$^-$ anion in the asymmetric unit. The cation displays the well known 'piano stool' conformation found in half-sandwich complexes with the three carbonyl ligands in a staggered orientation relative to the C atoms of the substituted benzene ring. The central Cr atom of the anion is octahedrally coordinated and the iodo ligand is directed towards the arene ligand of the cation.

Introduction. The use of cationic arene complexes of manganese as starting materials for synthetic purposes is currently of interest (Bernhardt, Wilmoth, Weers, LaBrush, Eyman & Huffman, 1986; Ittel, Whitney, Chung, Williard & Sweigart, 1988). As part of our continuing interest in the activation/deactivation of the arene ring towards nucleophiles for such compounds, and the possible correlation with structural features, the crystal structure of the manganese complex with hexamethylbenzene as arene ligand (compound 1) was determined. The parent complex ion, [Mn(η^6-C$_6$Me$_6$)(CO)$_3$]$^+$, is furthermore an important reference compound for the structural studies of complexes of the type

[Mn(η^6-C$_6$Me$_6$)(CO)$_2$L]$^+$ and [Mn(η^6-C$_6$Me$_6$)(CO)$_2$X] (L = neutral and X = anionic ligands). Initial problems encountered in growing suitable diffraction-quality single crystals were solved by using [Cr(CO)$_5$I]$^-$ as a counter ion.

Experimental. The title compound was formed by the standard AlCl$_3$ reaction to yield the [Mn(η^6-C$_6$Me$_6$)(CO)$_3$]$^+$ cation (Winkhaus, Pratt & Wilkinson, 1961), followed by the addition of a THF (tetrahydrofuran) solution of Cr(CO)$_6$ and excess NaI which was irradiated with a medium-pressure mercury arc. The colour of the solution changed to orange and the solvent was removed in vacuo. Recrystallization of this compound from a CH$_2$Cl$_2$–hexane solution yielded diffraction-quality single crystals: crystal size 0.23 × 0.21 × 0.19 mm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; unit cell from 25 reflections (7 < θ < 16°); 4231 reflections for 3 < θ < 25° in the range (0 < h < 10, 0 < k < 22 and −17 < l < 17) using ω scans where ω changed as (0.57 + 0.34tanθ)° with a variable but maximum speed that corresponded to 3.30° min^{-1}. Three standard reflections varied less than 3%, measured every hour; Lorenz–polarization and empirical absorption corrections based on ψ scans of nine reflections were applied (North, Phillips & Mathews, 1968): transmission factors 0.935–1.00, av. 0.976. 2316 unique reflections were observed [$I > 2\sigma(I)$]. Structure solved using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined using SHELX76 (Sheldrick, 1976), H atoms

---

* To whom correspondence should be addressed.

Table 1. *Fractional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$) *for* (1)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq}
Mn	2968 (1)	5047 (1)	1825 (1)	50 (1)
C(1)	1976 (11)	5849 (6)	1258 (7)	72 (3)
O(1)	1330 (8)	6337 (4)	935 (6)	108 (3)
C(2)	4821 (11)	5342 (5)	1643 (6)	59 (3)
O(2)	5979 (7)	5524 (4)	1557 (5)	88 (2)
C(3)	2411 (11)	4613 (6)	655 (7)	72 (3)
O(3)	2055 (9)	4343 (4)	−77 (5)	104 (3)
C(4)	2715 (11)	5391 (4)	3235 (6)	57 (3)
C(5)	1298 (9)	5021 (5)	2703 (6)	53 (2)
C(6)	1395 (10)	4345 (5)	2331 (6)	57 (3)
C(7)	2915 (11)	4027 (4)	2526 (6)	59 (3)
C(8)	4288 (10)	4377 (5)	3056 (6)	58 (3)
C(9)	4188 (9)	5057 (5)	3410 (6)	57 (3)
C(10)	2616 (12)	6120 (5)	3627 (8)	90 (3)
C(11)	−285 (9)	5377 (5)	2569 (7)	78 (3)
C(12)	−93 (10)	3975 (6)	1755 (7)	85 (3)
C(13)	2991 (13)	3271 (5)	2180 (8)	98 (4)
C(14)	5826 (10)	3992 (6)	3216 (8)	102 (4)
C(15)	5643 (10)	5453 (6)	3966 (7)	92 (3)
I	337 (1)	3914 (1)	4616 (1)	65 (1)
Cr	719 (2)	2494 (1)	5059 (1)	56 (1)
C(16)	406 (11)	2278 (5)	3718 (8)	67 (3)
O(4)	214 (9)	2133 (4)	2918 (5)	96 (2)
C(17)	2904 (11)	2623 (5)	5229 (7)	68 (3)
O(5)	4193 (8)	2703 (4)	5330 (6)	112 (3)
C(18)	975 (10)	1562 (5)	5373 (7)	66 (3)
O(6)	1137 (8)	978 (3)	5586 (5)	84 (2)
C(19)	1091 (12)	2737 (5)	6405 (8)	69 (3)
O(7)	1295 (9)	2840 (4)	7199 (5)	102 (3)
C(20)	−1533 (12)	2452 (5)	4841 (7)	67 (3)
O(8)	−2820 (8)	2410 (4)	4691 (6)	106 (3)

Table 2. *Selected bond distances* (Å) *and bond angles* (°) *for* (1)

Mn—C(1)	1·831 (10)	Mn—C(2)	1·841 (10)
Mn—C(3)	1·804 (10)	Mn—C(4)	2·196 (9)
Mn—C(5)	2·218 (9)	Mn—C(6)	2·211 (10)
Mn—C(7)	2·191 (9)	Mn—C(8)	2·217 (8)
Mn—C(9)	2·215 (8)	C(1)—O(1)	1·119 (12)
C(2)—O(2)	1·134 (12)	C(3)—O(3)	1·126 (12)
I—Cr	2·772 (2)	Cr—C(16)	1·903 (11)
Cr—C(17)	1·916 (10)	Cr—C(18)	1·826 (10)
Cr—C(19)	1·916 (11)	Cr—C(20)	1·950 (11)
C(16)—O(4)	1·142 (13)	C(17)—O(5)	1·131 (12)
C(18)—O(6)	1·151 (12)	C(19)—O(7)	1·115 (13)
C(20)—O(8)	1·112 (12)		

C(1)—Mn—C(2)	91·4 (4)	C(1)—Mn—C(3)	90·1 (5)
C(2)—Mn—C(3)	91·4 (4)	C(1)—Mn—C(4)	89·6 (4)
C(1)—Mn—C(5)	87·2 (4)	C(1)—Mn—C(7)	150·2 (4)
C(1)—Mn—C(6)	112·1 (4)	C(1)—Mn—C(8)	155·3 (4)
C(1)—Mn—C(9)	118·6 (4)		

in calculated positions (C—H = 1·08 Å, H—C—H = 109·4°), F magnitudes, $\sigma^{-2}(F)$ weights, all non-H atoms were refined with anisotropic thermal parameters, H atoms with a common isotropic thermal parameter that refined to $U_{iso} = 0\cdot174$ (12) Å^2; 301 variables refined, $\Sigma w|\Delta F|^2$ minimized. Final $wR = 0\cdot031$, $R = 0\cdot049$, $(\Delta/\sigma)_{max} = 0\cdot8$, maximum residual electron density $= 0\cdot49$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974) and the anomalous-dispersion terms for Mn and Cr were taken from Cromer & Liberman (1970).

Discussion. Final fractional atomic coordinates with equivalent isotropic thermal parameters are given in

Table 1.* The geometry of the ionic units showing the atomic numbering scheme used is depicted in Fig. 1 and selected bond lengths and angles are given in Table 2. The structure consists of an $[Mn(\eta^6\text{-}C_6Me_6)(CO)_3]^+$ cation and a $[Cr(CO)_5I]^-$ anion orientated such that the Mn atom, the centre of the arene ring and the I atom are aligned. The structure of the anion is in good agreement with that published by Calhoun & Trotter (1974) as counter ion to $[N_4P_4Me_9]^+$; a slightly longer Cr—I bond [2·772 (1) vs 2·790 (2) Å] is observed in that structure. A strong *trans* effect in the anion is reflected by the Cr—C(18) distance of 1·826 (10) Å, significantly shorter than the average value for the other Cr—C bonds of 1·926 (11) Å. This shortening of the Cr—C(18) bond results in the C(17) and C(20) atoms bending away from C(18) towards the I ligand, as evidenced by the I—Cr—C(17) and I—Cr—C(20) angles of 87·6 (3) and 87·2 (3)°, respectively. The $[Mn(\eta^6\text{-}C_6Me_6)(CO)_3]^+$ cation has the typical half-sandwich structure with the carbonyl ligands orientated in a staggered configuration relative to the arene C atoms. The least-squares plane of the hexamethylbenzene group is perpendicular to the C_3 axis which passes through the centre of the ring and the Mn atom. The maximum deviation of any of the 12 atoms of this group from the plane is 0·06 (3) Å. No conclusive evidence of alternating long and short bonds due to coordination is found, and an average value of 1·422 (13) Å for the aromatic bonds is similar to that found for the neutral complex $[Mn(\eta^6\text{-}C_6Me_6)(CO)_2Cl]$ (Bernhardt, Wilmoth, Weers, LaBrush, Eyman & Huffman, 1986). The average value of 2·208 (9) Å for the Mn—C(arene) bond distances are also comparable with that of the neutral complex and of η^5-cyclohexadienyl com-
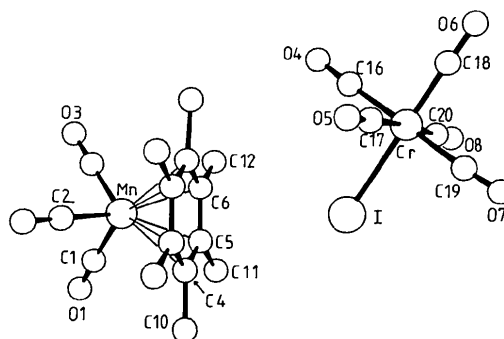
Fig. 1. Perspective view with atomic numbering scheme.

plexes $[Mn(\eta^5\text{-}C_6H_6R)(CO)_3]$, $R = H$, Ph [2·17 (1) Å] (Churchill & Scholer, 1969), as well as with the distance of 2·15 (2) Å in the neutral η^5-cyclopentadienyl complex $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$ (Berndt & Marsh, 1963).

References

BERNDT, A. F. & MARSH, R. E. (1963). *Acta Cryst.* **16**, 118–123.

BERNHARDT, R. J., WILMOTH, M. A., WEERS, J. J., LABRUSH, D. M., EYMAN, D. P. & HUFFMAN, J. C. (1986). *Organometallics*, **5**, 883–888.

CALHOUN, H. P. & TROTTER, J. (1974). *J. Chem. Soc. Dalton Trans.* pp. 377–381.

CHURCHILL, M. R. & SCHOLER, F. R. (1969). *Inorg. Chem.* **8**, 1950–1955.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **54**, 1891–1898.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

ITTEL, S. D., WHITNEY, J. F., CHUNG, Y. K., WILLIARD, P. G. & SWEIGART, D. A. (1988). *Organometallics*, **7**, 1323–1328.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

WINKHAUS, G., PRATT, L. & WILKINSON, G. (1961). *J. Chem. Soc.* pp. 3807–3813.

Structures of Bis{N-[1-(2-pyrrolyl)ethylidene]ethylaminato}zinc(II) and Bis{N-[1-(2-pyrrolyl)ethylidene]ethylaminato}copper(II)

BY MASOOD PARVEZ

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA

AND WILLIAM J. BIRDSALL

Department of Chemistry, Albright College, Reading, PA 19603, USA

Abstract. $[Zn(C_8H_{11}N_2)_2]$, (1), $M_r = 335\cdot75$, triclinic, $P\bar{1}$, $a = 7\cdot849$ (1), $b = 9\cdot783$ (1), $c = 12\cdot097$ (2) Å, $\alpha = 77\cdot12$ (1), $\beta = 87\cdot06$ (1), $\gamma = 67\cdot20$ (1)°, $V = 834\cdot1$ Å^3, $Z = 2$, $D_x = 1\cdot337$ Mg m^{-3}, $\lambda(Cu\ K\alpha) = 1\cdot54184$ Å, $\mu = 2\cdot035$ mm^{-1}, $F(000) = 352$, $T = 293$ (1) K, $R = 0\cdot038$ for 2660 reflections with $I > 3\sigma(I)$. $[Cu(C_8H_{11}N_2)_2]$, (2), $M_r = 333\cdot92$, monoclinic, $P2_1/c$, $a = 14\cdot405$ (4), $b = 8\cdot281$ (6), $c = 14\cdot205$ (7) Å, $\beta = 104\cdot49$ (3)°, $V = 1640\cdot6$ Å^3, $Z = 4$, $D_x = 1\cdot352$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0\cdot71069$ Å, $\mu = 1\cdot332$ mm^{-1}, $F(000) = 700$, $T = 293$ (1) K, $R = 0\cdot039$ for 1929 reflections with $I > 3\sigma(I)$. The geometry around the Zn atom in (1) is distorted tetrahedral with Zn—N distances in the range 1·962 (2)–2·041 (2) Å and N—Zn—N *cis* angles involving N atoms of the same ligand 84·2 (1) and 84·1 (1)° and *trans* angles in the range 118·2 (1)–129·5 (1)°. The Cu atom in (2) has distorted square-planar geometry with Cu—N distances in the range 1·935 (3)–2·000 (4) Å and N—Cu—N *cis* angles 82·8 (2) and 83·0 (2)° involving the N atoms of the same ligand and 102·3 (2) and 103·3 (2)° involving N atoms of the two ligands; the *trans* angles are 152·6 (2) and 156·0 (2)°.

Introduction. We have recently reported the crystal structure of (2-acetylpyrolato){N-[1-(2-pyrrolyl)-ethylidene]ethylaminato}copper(II), (3) (Parvez & Birdsall, 1988), a mixed-ligand complex containing one ethylamine Schiff base and one 2-acetylpyrrole chelate per Cu^{II} center. This compound formed upon spontaneous hydrolysis of bis{N-[1-(2-pyrrolyl)-ethylidene]ethylaminato}copper(II), and exhibits a distorted square-planar geometry. The mixed-ligand nature of (3) is unusual, but bond angles and bond distances fall within the range reported for bis-bidentate Schiff-base complexes of Zn^{II} (Kanters, Spek, Postma, van Stein & van Koten, 1983), Co^{II} (Wei, 1972a), Ni^{II} (Wei & Einstein, 1972), and two modifications of Cu^{II} with the same ligand (Wei, 1972b).

We have now synthesized bis{N-[1-(2-pyrrolyl)-ethylidene]ethylaminato}zinc(II), (1) and bis{N-[1-(2-pyrrolyl)ethylidene]ethylaminato}copper(II), (2). Compound (1) was prepared by published methods (Holm, Chakravorty & Theriot, 1966; Yeh & Barker, 1967). Compound (2) resulted from attempts to hydrolyze the second Schiff-base ligand on (3) to form a bis-bidentate 2-acetylpyrrole Cu^{II} product;