linearity of the C(1)-Mn-C(2) vector. This latter distortion involves an angular displacement of C(1) and C(2) away from C(4) and toward C(5), with a resulting C(1)-Mn-C(2) angle of 172.2 (4)°. The Mn-C(5) distance of 2.060 (8) Å is identical within experimental error to the Mn-C(sp^2) distance of 2.072 Å found in *cis*-$(CH_3NHCO)Mn(NH_2CH_3)(CO)_4$[34] and is shorter by about 0.06 Å than the value predicted by Churchill[35] (on the basis of a Mn single-bond covalent radius of 1.39 Å[36]) for the length of a single Mn-C(sp^2) bond. The Mn-N distance of 2.070 (7) Å agrees well with that estimated from a manganese covalent radius of 1.39 Å and an N(sp^2) radius of *ca.* 0.68 Å.

The C-C distances within the phenyl rings average to 1.398 (16) Å and no individual distance deviates significantly from this value. The standard deviation of an individual C-C(phenyl) distance, as estimated from the variation in observed distances on the assumption of equivalent distances, is greater than their mean least-squares esd by a factor of about 1.3. The variations in C-C distances are comparable for the two rings. The mean Mn-carbonyl C and C-O bond distances of 1.795 and 1.153 (9) Å are of normal magnitudes; there appears to be some variation in the individual Mn-C-(carbonyl) distances. None of the Mn-C-O angles deviate from linearity by more than 2.5°.

A comparison of this structure with that of the closely related *N,N*-dimethylbenzylamine complex $(CH_3)_2NCHC_6H_4Mn(CO)_4$ may be found in the following paper.[37]

Registry No. $C_6H_5NCHC_6H_4Mn(CO)_4$, 36594-09-9.

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Crystal and Molecular Structure of an Ortho-Metalated *N,N*-Dimethylbenzylamine-Manganese Carbonyl Complex, Tetracarbonyl-2-(dimethylaminomethyl)phenylmanganese, $C_6H_4CH_2N(CH_3)_2Mn(CO)_4$

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A single-crystal X-ray structural investigation has established the crystal and molecular structure of the ortho-metalated manganese carbonyl complex derived from *N,N*-dimethylbenzylamine. Crystals of tetracarbonyl-2-(dimethylaminomethyl)phenylmanganese are monoclinic, with eight molecules in a unit cell of dimensions $a = 27.36$ (1), $b = 6.805$ (4), $c = 15.12$ (1) Å, $\beta = 93.30$ (3)°. The space group is $C2/c$. Observed and calculated densities are 1.43 and 1.35 (5) g/cm^3, respectively. Full-matrix anisotropic least-squares refinement, based upon 1989 independent nonzero diffractometer data, converged to a conventional discrepancy factor of 0.047. The discrete monomeric $C_6H_4CH_2N(CH_3)_2Mn(CO)_4$ molecules contain a manganese atom bound in a distorted octahedral configuration to four carbonyl groups and to the chelating ligand. The ligand is bound *via* a metal-nitrogen bond and a metal-carbon σ bond to the ortho position of the phenyl ring. The five-membered chelate ring is distinctly puckered. The Mn-C and Mn-N distances are 2.139 (3) and 2.070 (7) Å, respectively. Comparison of the details of the structures with those for two closely related tetracarbonylmanganese complexes leads to a number of generalizations concerning this structure type.

Introduction

In the preceding paper, we reported the results of a crystal structure analysis of the ortho-metalated product obtained from the reaction of benzylidineaniline with $CH_3Mn(CO)_5$.[1] Ortho-metalation reactions[2] are also known for benzyldialkylamines, $C_6H_5CH_2NR_2$.[3] In this paper, the results of a crystal structure analysis of a product of such a reaction, $[C_6H_4CH_2N(CH_3)_2]Mn(CO)_4$, are reported. This investigation was undertaken in order to compare the details of the structure of this compound with those for the benzylidineaniline complex and thereby to help establish the structural systematics of this important structure type.

Experimental Section

Collection and Reduction of Intensity Data. A sample of $C_6H_4CH_2N(CH_3)_2Mn(CO)_4$ was generously supplied by Dr. M. I. Bruce of the University of Bristol. Suitable single crystals were prepared by recrystallization from light petroleum ether. Precession photographs (*h*0*l*, *h*1*l*, 0*kl*, 1*kl*) displayed monoclinic symmetry with systematic absences ($h0l$, $l \neq 2n$; hkl, $h + k \neq 2n$) consistent with the space groups Cc and $C2/c$. Successful solution of the structure was achieved in the latter centrosymmetric space group. Lattice parameters were obtained by least-squares refinement[4] of the setting angles of 14 reflections with $2\theta \geq 40°$ which had been accurately centered on a Picker four-circle X-ray diffractometer. The unit cell constants (23°, λ(Mo Kα_1) 0.70926 Å) obtained in this manner are $a = 27.36$ (1), $b = 6.805$ (4), $c = 15.12$ (1) Å, and $\beta = 93.30$ (3)°. The numbers in parentheses are the standard deviations obtained from the least-squares refinement of the setting angles. Calculated ($Z = 8$)

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(2) G. W. Parshall, *Accounts Chem. Res.*, 3, 139 (1970).

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(4) Programs employed in this structural analysis included local versions of PICK (J. A. Ibers) for cell refinement and generation of diffractometer settings; PICKOUT (R. J. Doedens, J. A. Ibers) for data processing; GONO (W. C. Hamilton) for absorption correction; FORDAP (A. Zalkin) for Fourier summation; UCIGLS (derived from Busing, Martin, and Levy's ORFLS) for structure factor calculations and least-squares refinement; ORFFE (Busing, Martin, and Levy) for function and error calculations; PLANET (D. L. Smith) for least-squares plane calculations; DANFIG (R. J. Dellaca, W. T. Robinson) and ORTEP (C. K. Johnson) for preparation of figures; and RSCAN (R. J. Doedens) for evaluation of the weighting scheme. All computations were carried out on the local PDP-10 computer.

and observed (flotation in aqueous $ZnBr_2$) densities are 1.43 and 1.35 (5) g/cm^3, respectively.

Intensity data were collected from a yellow crystal of dimensions 0.57 × 0.48 × 0.43 mm mounted in a thin-walled glass capillary with its longest dimension (the crystallographic [001] direction) parallel to the capillary walls. The data were collected by use of procedures previously described.[5] A takeoff angle of 1.7° was employed. The diffracted beam was filtered through 3.0-mil Nb foil. The counter aperture was 5 × 5 mm and was positioned 28 cm from the crystal. The pulse-height analyzer was set to admit ~95% of the Mo Kα peak. Data were collected by the θ–2θ scan method. A scan range of −0.60 to +0.65° in 2θ from the calculated scattering angle was employed for reflections with $2\theta \leqslant 20°$. This range was increased to ±0.70° in 2θ for the remainder of the data. The intensities of all independent reflections with $2\theta \leqslant 53°$ were measured. The $h\bar{k}\bar{l}$ equivalent form was also collected for all data which were above background by three or more standard deviations. The scan rate was 1°/min and stationary-background counts of 20 sec were taken at each end of the scan range. Copper foil attenuators were automatically inserted whenever the count rate exceeded ~10,000 counts/sec. Three standard reflections, chosen to lie in widely separated regions of reciprocal space, were monitored regularly throughout the collection of data. During the data collection there was a 4% overall decrease in the intensity of these standards. This decrease was of a comparable magnitude for all three standards and was a roughly linear function of the time of exposure of the crystal to the X-ray beam.

Previously described methods were employed in processing the data and in averaging the equivalent forms.[5] The p factor in the expression for the standard deviation of the observed intensities was assigned a value of 0.05. Of the 2903 independent data collected, 1989 were above background by three or more standard deviations. The observed intensities were scaled upward to compensate for the systematic decrease in intensity of the standards. An absorption correction was applied; based on a linear absorption coefficient of 9.92 cm^{-1} the calculated transmission factors ranged from 0.61 to 0.73.

Solution and Refinement of the Structure. The structure was determined by standard heavy-atom methods. The metal atom coordinates were obtained from a three-dimensional Patterson map and carbon, nitrogen, and oxygen atoms were located by difference Fourier methods. Refinement of positional and isotropic thermal parameters for the 18 nonhydrogen atoms converged to discrepancy factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.122$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.177$. A difference Fourier map at this point showed peaks greater than 1.3 e/Å^3 near the manganese atom and peaks greater than 0.9 e/Å^3 in the vicinity of C8, O2, O3, and O4. Further refinement employing anisotropic thermal parameters for the manganese atom and including the phenyl hydrogen atoms as fixed contributions reduced R_1 and R_2 to 0.104 and 0.154, respectively. Refinement was continued employing anisotropic thermal parameters for all nonhydrogen atoms. After the first cycle of this refinement a partial difference Fourier map was calculated in the vicinity of the two methyl carbon atoms; peaks ranging in height from 0.40 to 0.47 e/Å^3 were found at plausible locations for the six methyl hydrogen atoms. These peaks were fit to ideal tetrahedral geometry (C–H = 1.0 Å) and included as fixed atoms in the final refinement. The final discrepancy factors were $R_1 = 0.047$ and $R_2 = 0.075$; in the final cycle the largest parameter shift was 0.3σ.

Throughout the least-squares refinement, the weights of the observed structure amplitudes were taken as $w = 4F_o^2/\sigma^2(F_o^2)$ and the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The final standard deviation of an observation of unit weight was 2.0. Calculation of mean $w(\Delta F)^2$ values for subsets of the data as functions of uncorrected intensity, F_o, and Bragg angle revealed no significant trends, thus confirming that the relative weights were reasonable. Calculation of structure factors for data with $F_o^2 \leqslant 3\sigma(F_o^2)$ revealed 27 reflections with $|F_o - F_c|/\sigma(F_o) \geqslant 3$; only four of these had $\Delta F/\sigma > 4$. Scattering factors for Mn, C, N, and O were taken from ref 6, and those of Stewart, *et al.*,[7] were employed for H. Structure factor calculations included provisions for the real and imaginary parts of anomalous scattering by the manganese atoms, employing $\Delta f'$ and $\Delta f''$ values of Cromer.[8]

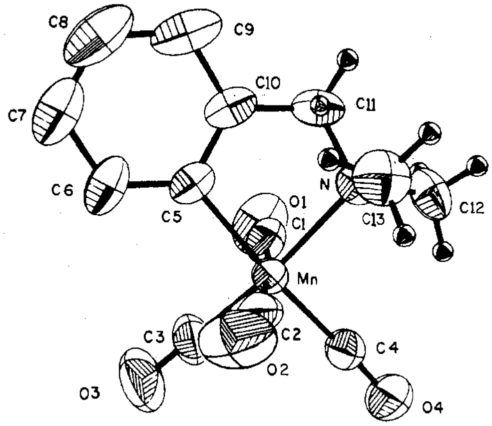

Figure 1. A perspective view of the $C_6H_4CH_2N(CH_3)_2Mn(CO)_4$ molecule. Thermal ellipsoids are drawn at the 50% probability level, with the exception that those for the hydrogen atoms are reduced for clarity.

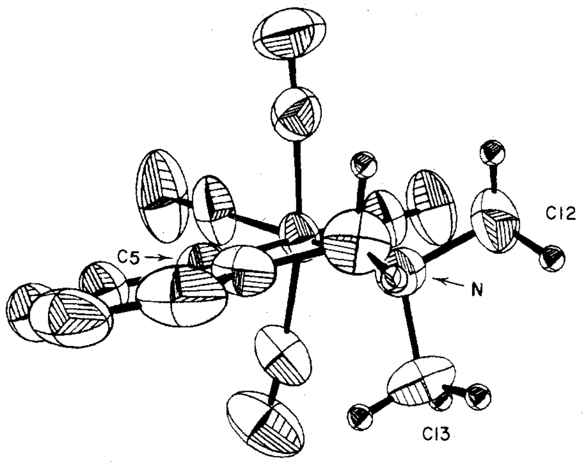

Figure 2. An alternative view of the molecular structure, showing the puckering of the chelate ring and the axial *vs.* equatorial nature of the methyl groups and methylene hydrogen atoms.

Final atomic positional and thermal parameters are listed in Table I and intramolecular distances and angles are tabulated in Tables II and III, respectively. Principal amplitudes of thermal motion are listed in Table IV and information relating to molecular planes may be found in Table V. A table of observed and calculated structure factors is available.[9]

Description and Discussion of the Structure

The crystal structure of tetracarbonyl-2-(dimethylaminomethyl)phenylmanganese (Mn(dmb)) is made up of discrete monomeric molecular units. The manganese atom is coordinated in a distorted octahedral configuration to four terminal carbonyl groups and to the chelating ligand. Two views of the molecular structure are shown in Figures 1 and 2. The organic ligand is bound *via* a metal-nitrogen bond and a metal-carbon σ bond to the ortho position of the phenyl ring. The structure is thus analogous to that of the benzylidineanilinemanganese carbonyl complex described in the previous paper (Mn(bza)).[1]

The principal differences between the structures of Mn(bza) and Mn(dmb) involve the dimensions and conformations of the five-membered chelate rings. In the former compound, the ring is essentially planar, owing to the re-

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(5) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967); R. J. Doedens and J. A. Ibers, *ibid.*, 6, 204 (1967).

(6) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962.

(7) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(8) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

(9) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-844.

Table I. Atomic Positional and Thermal Parameters for $[C_6H_4CH_2N(CH_3)_2]Mn(CO)_4$ [a]

Atom	x	y	z	β_{11} (or B)[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	0.08732 (2)	−0.17083 (9)	0.15855 (4)	102 (1)	2407 (17)	358 (3)	−73 (3)	20 (1)	−134 (5)
C(1)	0.0605 (2)	0.0263 (7)	0.0882 (3)	126 (6)	2303 (111)	709 (26)	−40 (23)	−3 (10)	−173 (46)
O(1)	0.0428 (2)	0.1550 (6)	0.0489 (4)	231 (8)	2751 (102)	1297 (36)	189 (23)	−96 (13)	312 (47)
C(2)	0.1197 (2)	−0.3364 (8)	0.2401 (3)	150 (7)	4179 (161)	428 (20)	−241 (29)	9 (9)	263 (49)
O(2)	0.1395 (2)	−0.4229 (8)	0.2952 (3)	246 (8)	6453 (174)	643 (21)	−180 (31)	−72 (10)	1023 (54)
C(3)	0.0662 (2)	−0.0392 (9)	0.2508 (3)	148 (7)	4786 (193)	613 (25)	−166 (32)	44 (11)	−860 (63)
O(3)	0.0537 (2)	0.0426 (9)	0.3110 (3)	263 (9)	7936 (222)	981 (29)	−287 (38)	169 (13)	1813 (71)
C(4)	0.0326 (2)	−0.3250 (7)	0.1485 (3)	135 (6)	3323 (130)	435 (19)	−162 (26)	24 (9)	−231 (43)
O(4)	−0.0025 (1)	−0.4186 (7)	0.1456 (3)	201 (7)	5298 (141)	691 (20)	−533 (27)	50 (9)	−417 (46)
C(5)	0.1520 (1)	−0.0167 (6)	0.1611 (3)	105 (5)	1921 (93)	582 (21)	−32 (19)	5 (8)	125 (38)
C(6)	0.1746 (2)	0.0922 (7)	0.2303 (4)	142 (7)	2331 (109)	844 (31)	−84 (24)	−123 (12)	−10 (50)
C(7)	0.2201 (2)	0.1866 (8)	0.2207 (5)	170 (8)	2600 (136)	1096 (45)	−122 (30)	−143 (17)	374 (64)
C(8)	0.2426 (2)	0.1676 (9)	0.1444 (6)	127 (7)	3264 (163)	1367 (56)	−142 (30)	−95 (18)	849 (81)
C(9)	0.2218 (2)	0.0561 (9)	0.0726 (4)	125 (7)	3637 (168)	1056 (40)	−3 (29)	74 (14)	860 (69)
C(10)	0.1765 (2)	−0.0342 (7)	0.0828 (3)	113 (5)	2384 (110)	648 (23)	−35 (21)	12 (9)	395 (43)
C(11)	0.1502 (2)	−0.1455 (7)	0.0084 (3)	175 (8)	3210 (135)	480 (21)	−50 (26)	97 (10)	271 (43)
C(12)	0.0830 (2)	−0.3716 (8)	−0.0228 (3)	230 (9)	3611 (149)	403 (20)	11 (31)	−14 (11)	−342 (45)
C(13)	0.1534 (2)	−0.4695 (7)	0.0735 (4)	199 (9)	2317 (116)	797 (30)	262 (28)	60 (13)	122 (50)
N	0.1197 (1)	−0.3010 (5)	0.0472 (2)	143 (5)	2051 (84)	383 (14)	50 (17)	30 (7)	16 (27)
H1C6[c]	0.1583	0.1037	0.2877	5.9					
H2C7	0.2354	0.2668	0.2704	7.4					
H3C8	0.2748	0.2338	0.1382	7.8					
H4C9	0.2390	0.0422	0.0163	7.1					
H5C11	0.1746	−0.2070	−0.0299	5.8					
H6C11	0.1288	−0.0538	−0.0281	5.8					
H7C12	0.0724	−0.2588	−0.0617	6.2					
H8C12	0.0982	−0.4756	−0.0590	6.2					
H9C12	0.0540	−0.4272	0.0061	6.2					
H10C13	0.1349	−0.5691	0.1070	6.5					
H11C13	0.1816	−0.4189	0.1119	6.5					
H12C13	0.1656	−0.5311	0.0190	6.5					

[a] Numbers in parentheses in tables and in the text are estimated standard deviations in the least significant figures. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{33}kl)]$. Anisotropic thermal parameters tabulated are multiplied by 10^5. [c] The designation of hydrogen atoms includes specification of the carbon atom to which they are bound. Temperature factors for the hydrogen atoms were set at one unit greater than the final isotropic B of the corresponding carbon atom.

Table II. Intramolecular Distances, Å

Mn–C(1)	1.839 (5)	C(1)–O(1)	1.148 (6)
Mn–C(2)	1.857 (5)	C(2)–O(2)	1.132 (6)
Mn–C(3)	1.781 (5)	C(3)–O(3)	1.136 (6)
Mn–C(4)	1.827 (4)	C(4)–O(4)	1.152 (5)
Mn–C(5)	2.055 (4)	Mean C–O	1.142 (10)[a]
Mn–N	2.139 (3)	C(5)–C(10)	1.398 (6)
C(10)–C(11)	1.504 (7)	C(5)–C(6)	1.397 (6)
C(11)–N	1.489 (5)	C(6)–C(7)	1.416 (8)
N–C(12)	1.496 (6)	C(7)–C(8)	1.346 (10)
N–C(13)	1.509 (5)	C(8)–C(9)	1.416 (10)
Mean N–C(methyl)	1.502	C(9)–C(10)	1.401 (6)
		Mean C–C(phenyl)	1.396 (26)
C(1)· · ·C(3)	2.494 (7)	C(2)· · ·C(13)	2.877 (7)
C(1)· · ·C(4)	2.685 (7)	O(2)· · ·C(13)	3.409 (7)
C(1)· · ·C(5)	2.692 (6)	C(3)· · ·C(4)	2.618 (7)
C(1)· · ·N	2.845 (6)	C(3)· · ·C(5)	2.781 (6)
C(2)· · ·C(3)	2.507 (8)	C(4)· · ·N	2.910 (6)
C(2)· · ·C(4)	2.687 (7)	C(4)· · ·C(12)	3.018 (7)
C(2)· · ·C(5)	2.657 (6)	O(4)· · ·C(12)	3.568 (7)
C(2)· · ·N	2.925 (6)		

[a] The figure in parentheses following mean values of bond distances in this table is the standard deviation of an *individual* distance as estimated by $s = [\{1/(n-1)\}\Sigma_{i=1}{}^{n}(\bar{x} - x_i)^2]^{1/2}$ where x_i is an individual distance and $\bar{x}$ is the mean value of the n measurements of presumably equivalent bond distances.

Table III. Bond Angles, Deg

C(1)–Mn–C(2)	170.4 (2)	Mn–C(4)–O(4)	176.9 (4)
C(1)–Mn–C(3)	87.1 (2)	Mn–C(5)–C(6)	128.9 (4)
C(1)–Mn–C(4)	94.2 (2)	Mn–C(5)–C(10)	113.3 (3)
C(1)–Mn–C(5)	87.3 (2)	C(6)–C(5)–C(10)	117.8 (4)
C(1)–Mn–N	91.0 (2)	C(5)–C(6)–C(7)	121.2 (6)
C(2)–Mn–C(3)	87.1 (3)	C(6)–C(7)–C(8)	119.5 (6)
C(2)–Mn–C(4)	93.7 (2)	C(7)–C(8)–C(9)	121.7 (5)
C(2)–Mn–C(5)	85.4 (2)	C(8)–C(9)–C(10)	118.0 (6)
C(2)–Mn–N	93.8 (2)	C(9)–C(10)–C(5)	121.8 (5)
C(3)–Mn–C(4)	93.1 (2)	C(9)–C(10)–C(11)	121.7 (5)
C(3)–Mn–C(5)	92.6 (2)	C(5)–C(10)–C(11)	116.4 (4)
C(3)–Mn–N	172.7 (2)	C(10)–C(11)–N	108.5 (3)
C(4)–Mn–C(5)	174.2 (2)	Mn–N–C(11)	106.4 (2)
C(4)–Mn–N	94.1 (2)	Mn–N–C(12)	113.4 (3)
C(5)–Mn–N	80.2 (2)	Mn–N–C(13)	112.4 (3)
Mn–C(1)–O(1)	175.8 (5)	C(11)–N–C(12)	108.6 (4)
Mn–C(2)–O(2)	173.5 (5)	C(11)–N–C(13)	107.3 (3)
Mn–C(3)–O(3)	178.2 (6)	C(12)–N–C(13)	108.5 (4)

stricted rotation about the C(5)–C(10) and C(11)=N bonds. On the other hand, the five-membered ring of Mn(dmb) is distinctly puckered, as is clearly evident in Figure 2. The degree of puckering may be described by slightly generalized versions of the parameters α and β[10,11] which have been employed for metal-coordinated ethylenediamine rings. The values of these parameters are $\alpha = 19.2°$ and $\beta = 32.0°$, compared to ranges of $\alpha = 18.9$-$28.9°$ and $\beta = 38.1$-$55.0°$ observed for coordinated ethylenediamine molecules in $M(en)_3$ complexes.[11] Of course, the Mn-C(5)-C(10)-C(11)-N ring is subject to somewhat different constraints than a metal-ethylenediamine ring, because of restricted rotation about the C(5)-C(10) bond and the presence of two sp^2 carbon atoms. Thus, the Mn-C(5)-C(10)-C(11) grouping is more nearly coplanar than would ordinarily be the case in a fully saturated ring. The equatorial and axial natures of the methylene protons and of the two methyl groups are evident in Figure 2.

The coordination about the metal atom is distorted octa-

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(10) These parameters may be defined, for the present system, as follows: α = dihedral angle between the Mn-C(5)-N and Mn-C(10)-C(11) planes; β = the angle between C(5) and (N) in projection down the C(10)-C(11) bond, *i.e.*, the torsional angle about the C(10)-C(11) bond. See ref 11 for a further discussion of these parameters and a tabulation of their values for $M(en)_3$ complexes.

(11) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 7, 842 (1968).

Table IV. Principal Root-Mean-Square Amplitudes of Thermal Motion, Å

Atom	Max	Intermed	Min
Mn	0.247 (1)	0.197 (1)	0.190 (1)
C(1)	0.291 (5)	0.233 (6)	0.211 (6)
O(1)	0.403 (6)	0.307 (5)	0.220 (5)
C(2)	0.333 (6)	0.226 (5)	0.204 (6)
O(2)	0.432 (6)	0.298 (5)	0.213 (5)
C(3)	0.378 (7)	0.232 (6)	0.204 (6)
O(3)	0.508 (7)	0.303 (5)	0.214 (6)
C(4)	0.296 (6)	0.220 (5)	0.206 (6)
O(4)	0.400 (5)	0.274 (4)	0.209 (5)
C(5)	0.263 (5)	0.211 (5)	0.195 (5)
C(6)	0.338 (6)	0.240 (6)	0.192 (6)
C(7)	0.388 (8)	0.237 (7)	0.221 (6)
C(8)	0.430 (9)	0.240 (7)	0.206 (6)
C(9)	0.390 (7)	0.243 (6)	0.205 (6)
C(10)	0.297 (5)	0.213 (5)	0.200 (6)
C(11)	0.289 (6)	0.273 (6)	0.192 (5)
C(12)	0.307 (6)	0.292 (6)	0.198 (5)
C(13)	0.318 (6)	0.286 (6)	0.195 (6)
N	0.239 (4)	0.214 (4)	0.207 (4)

Table V. Molecular Planes and Dihedral Angles

1. Plane Containing C(5), C(6), C(7), C(8), C(9), C(10)

Equation of Plane:[a] $-0.4496X + 0.8188Y - 0.3570Z = -2.7745$

Distances to Plane, Å

C(5)	0.0074	C(8)	0.0025
C(6)	−0.0094	C(9)	−0.0044
C(7)	0.0044	C(10)	−0.0005

2. Plane Containing C(3), C(4), C(5), N[b]

Equation of Plane: $-0.4039X + 0.6814Y - 0.6104Z = -3.1599$

Distances to Plane, Å

C(3)	0.0245	N	0.0227
C(4)	−0.0234	Mn	−0.0017
C(5)	−0.0237		

3. Plane Containing C(1), C(2), C(4), C(5)[b]

Equation of Plane: $0.3697X - 0.5024Y - 0.7816Z = -0.4529$

Distances to Plane, Å

C(1)	−0.0944	C(5)	0.0954
C(2)	−0.0957	Mn	−0.0011
C(4)	0.0947		

4. Plane Containing C(1), C(2), C(3), N

Equation of Plane: $-0.8099X - 0.5785Y - 0.0969Z = -1.5067$

Distances to Plane, Å

C(1)	−0.0035	N	0.0029
C(2)	−0.0033	Mn	0.1246
C(3)	0.0039		

5. Plane Containing C(5), C(10), C(11)

Equation of Plane: $-0.4040X + 0.8499Y - 0.3383Z = -2.5417$

6. Plane Containing C(10), C(11), N

Equation of Plane: $0.7688X - 0.6393Y - 0.0160Z = 3.7848$

Angles between Perpendiculars to These Planes

Planes	Angle, deg	Planes	Angle, deg
1-2	16.8	2-4	90.4
1-4	85.7	2-6	42.6
1-5	3.3	3-4	86.2
1-6	30.3	5-6	32.0
2-3	90.8		

[a] Unit weights were employed in the calculation of all planes. The equations of the planes are expressed with respect to coordinates (*X, Y, Z*) referred to an orthogonal system (*A, B, C*) oriented with respect to the crystallographic axes such that *A* is parallel to *a*, *B* is parallel to $c^* \times a$, and *C* is parallel to $A \times B$.

[b] Inclusion of planes 2 and 3 in this tabulation should not be taken to imply that we consider these groups of atoms accurately coplanar; rather the data are presented to provide a comparison with corresponding planes in the preceding paper.

Table VI. Comparison of Metal-Ligand Distances in Mn(bza), Mn(dmb), and $Mn(CO)_4(NH_2CH_3)(CONHCH_3)$[a]

	Mn(bza)	Mn(dmb)	$Mn(CO)_4$-(NH_2CH_3)-$(CONHCH_3)$
Mn-C(1)	1.823 (9)	1.839 (5)	1.839 (13)
Mn-C(2)	1.799 (10)	1.857 (5)	1.856 (12)
Mn-C(3)	1.764 (10)	1.781 (5)	1.775 (13)
Mn-C(4)	1.796 (10)	1.827 (4)	1.845 (12)
Mn-C(5)	2.060 (8)	2.055 (4)	2.072 (11)
Mn-N	2.070 (7)	2.139 (3)	2.111 (8)

[a] The atom numbering scheme for the *N*-methylcarboxamido complex has been changed to conform to our system. The structural parameters tabulated for this complex are those of the tetragonal form,[12] for which the bond lengths are substantially more precise than are those for the monoclinic form.[13]

hedral, with a pattern of distortions qualitatively very similar to that found in Mn(bza). The angle subtended by the chelating atoms is comparable in the two structures (80.2 (2)° in Mn(dmb) and 79.4 (3)° in Mn(bza)). The C(1)-Mn-C(2) angle of 170.4 (2)° observed in the present case is slightly smaller than the value of 172.4 (4)° for the corresponding angle in the benzylidineaniline complex. The principal difference in coordination geometry between these two complexes involves the C(2)-Mn-N angle, which is 93.8° in Mn(dmb) and 89.6° in Mn(bza). This difference can be attributed to the steric effects of the axial methyl group, as evidenced by the C(2)· · ·C(13) contact of 2.877 (7) Å.

In Table VI, the bond distances within the metal coordination sphere are tabulated and compared with the corresponding distances for Mn(bza) and the carboxamidomanganese carbonyl complex $Mn(CO)_4(NH_2CH_3)(CONHCH_3)$.[12,13] The latter complex (henceforth denoted as Mn(mca)) also contains a $Mn(CO)_4$ moiety with Mn-N and Mn-C σ bonds in a cis configuration but lacks the constraint of a chelate ring. The Mn-N distance of 2.139 (3) Å in Mn(dmb) is significantly larger than the corresponding distance of 2.070 (7) Å in Mn(bza) and slightly longer than the 2.111 (8) Å Mn-N distance observed in Mn(mca). On the basis of a Mn covalent radius of 1.39 Å[14] and an $N(sp^3)$ radius of 0.70 Å, the estimated length of a single $Mn-N(sp^3)$ bond is 2.09 Å.[15] Factors in Mn(dmb) which could cause a lengthening from this value include residual strain in the chelate ring, the steric crowding of the axial methyl group, and a trans effect of the carbonyl group. The Mn-C(5) distances for the three complexes are identical within experimental error; the weighted average of the three values is 2.058 Å. As previously noted,[15] this is shorter than has been predicted for a $Mn-C(sp^2)$ single bond.

Some trends also are evident in the Mn-C(carbonyl) distances tabulated in Table V. In each case, the Mn-C bond trans to the nitrogen atom is the shortest, consistent with a smaller structural trans effect for an amino or imino nitrogen atom than for a carbonyl group or a σ-bonded phenyl group. Also, the longest of the four Mn-C(carbonyl) distances in each case occurs for an axial carbonyl group (C(1) or C(2)). Finally it may be noted that the Mn-C(carbonyl) distances as a group are shorter for Mn(bza) than for the other two complexes. This latter trend is only marginally significant on a statistical basis, though the fact that it holds for all four carbonyl groups lends it some credence.

Other structural features of the Mn(dmb) molecule are

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unremarkable. The thermal motion of some of the atoms is relatively large in amplitude (see Table IV and the figures); this undoubtedly lowers the accuracy of some of the bond distances and angles, particularly those toward the periphery of the molecule. The N-C(methyl) distances of 1.496 (6) and 1.509 (5) Å are slightly longer than the N-C distance of 1.474 Å in methylamine.[16] The C-O distances average to 1.142 (10) Å and the mean C-C(phenyl) distance is 1.396 (26) Å. The variation in the distances in the phenyl ring is substantially greater than would be expected on the basis of the tabulated esd's. This problem stems primarily from the short C(7)-C(8) distance and may well be related to the high thermal motion of the phenyl carbon atoms. Three of the four Mn-C-O angles are somewhat nonlinear.

To summarize, a detailed comparison of the three closely related complexes Mn(bza), Mn(dma), and Mn(mca) has revealed many similarities among their structures, including parallel trends in Mn-C(carbonyl) distances and nearly identical Mn-C(sp^2) distances. Significant differences are also observed; many of these may be attributed to hybridization differences at the N atom or to constraints associated with the chelate rings present in two of the complexes. It would be of interest to determine whether the relatively small variations in Mn-C(carbonyl) distances we see may be correlated with trends in chemical reactivity. One might ask, for example, whether the substitutional lability of the various carbonyl groups in a given complex parallels the observed trends in bond distances. One could also inquire whether the generally shorter Mn-C(carbonyl) bonds in Mn(bza) are associated with a lesser tendency of this complex to undergo carbonyl exchange or substitution reactions.

Registry No. $C_6H_4CH_2N(CH_3)_2Mn(CO)_4$, 38162-89-9.

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Crystal and Molecular Structure of Tris(tetracarbonylcobalt)indium(III), In[$Co(CO)_4$]$_3$

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Tris(tetracarbonylcobalt)indium(III) crystallizes in the monoclinic space group $P2_1/n$ with 4 molecules in a unit cell of dimensions a = 18.834 (8), b = 6.806 (3), c = 16.606 (7) Å, and β = 113.91 (4)°. Using a data set of 1898 observed reflections collected by counter methods with an automated diffractometer and corrected for absorption, the structure was solved by Patterson and Fourier techniques and refined to a final R of 0.067. The structure consists of discrete molecules of In[$Co(CO)_4$]$_3$ with approximate C_{3h}-$\bar{6}$ symmetry. The average In-Co bond distance of 2.594 (3) Å is not consistent with dπ-pπ bonding between the empty valence p orbital of the indium and the filled d orbitals of the cobalt. The coordination geometry about the cobalt resembles the approximate trigonal bipyramid observed in other $Co(CO)_4$ derivatives except that the indium is displaced from an axial position toward two of the equatorial carbonyl groups. From a comparison with other In(III) structures, it is suggested that this displacement reflects primarily a In-C interaction rather than a steric effect although the latter effect may also be important.

Introduction

Compounds containing hetronuclear metal-metal bonds between the elements of groups IIb and IVa and transition metal carbonyl derivatives have been the subject of extensive synthetic, physical, and structural studies.[1-6] Similar investigations with elements of group IIIa have been restricted for the most part to synthetic studies. The structures of M[$Co(CO)_4$]$_3$[7], M[$Mn(CO)_5$]$_3$[8-10] (M = In or Tl), and Tl[$(h_5$-$C_5H_5)Mo(CO)_3$]$_3$[11] have been inferred as trigonal planar in solution from limited spectroscopic characterizations. Since no crystal structure data were available for these systems, we have determined the structure of In[$Co(CO)_4$]$_3$ and found that the trigonal planar structure suggested for this compound in solution is retained in the solid state. This molecule constitutes one of the rare examples of three-coordinate indium(III).

Experimental Section

Tris(tetracarbonylcobalt)indium(III) was prepared by the reaction of 5 g of Hg[$Co(CO)_4$]$_2$ in 30 ml of toluene under nitrogen with an excess of a 1% indium amalgam. Following 6 hr of stirring, the amalgam was removed and the solution filtered, concentrated to a volume of 10 ml, and cooled to −78°. The red crystals which formed were filtered from the solvent, washed with 10 ml of cold pentane, and dried *in vacuo*. *Anal.* Calcd for In[$Co(CO)_4$]$_3$: C, 23.0; H, 0.0; In, 18.3. Found: C, 22.9; H, 0.0; In, 18.2.

Space Group and Unit Cell. A needlelike crystal was mounted in a Lindemann capillary and $h0l$-$h2l$ Weissenberg levels and $0kl$ and $hk0$ precession levels were collected. These photographs displayed $2/m$ diffraction symmetry. From the systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) the space group was identified as $P2_1/c$ (No. 14). In order to work in a more nearly orthogonal unit cell, the space group $P2_1/n$ was used in subsequent steps. The unit cell dimensions were determined from measurements from the different crystals used in data collection using an Enraf-Nonius Inc. CAD-4 automated diffrac-

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