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The Structure of Nitrosyltetracarbonylmanganese, $\text{Mn}(\text{NO})(\text{CO})_4$

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The crystal structure of nitrosyltetracarbonylmanganese, $\text{Mn}(\text{NO})(\text{CO})_4$, has been determined from three-dimensional X-ray data collected by the precession method at -110° . The material grown from the liquid phase crystallizes in space group $\text{C}_{2h}^6\text{-C2}/c$ with four molecules in a cell of dimensions $a = 11.72$ (3) Å, $b = 6.74$ (2) Å, $c = 9.65$ (2) Å, and $\beta = 107.8$ (1) $^\circ$ at -110° . Least-squares refinement of 624 independent reflections resulted in a final conventional R factor of 0.087. The $\text{Mn}(\text{NO})(\text{CO})_4$ molecule is required crystallographically to possess C_2 symmetry; the molecule is trigonal bipyramidal in shape. The metal-ligand bond distances and the root-mean-square amplitudes of vibration of the various atoms favor an ordered model with the nitrosyl group on the twofold axis and in the equatorial plane of the trigonal bipyramid. The axial Mn-C distance is 1.886 (8) Å while the equatorial Mn-C distance is 1.851 (8) Å; the Mn-N distance is 1.797 (13) Å. The Mn-C-O and Mn-N-O bonds are linear. The structure is compared with that of the isoelectronic molecule $\text{Fe}(\text{CO})_5$. The structural trends in the series of compounds $\text{Mn}(\text{NO})(\text{CO})_{4-x}(\text{P}(\text{C}_6\text{H}_5)_3)_x$ ($x = 0-2$) are discussed.

Introduction

In previous papers describing the structures of $\text{Mn}(\text{NO})(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$ ¹ and $\text{Mn}(\text{NO})(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ ² we have discussed the structural ambiguities inherent in the kinetic and spectral data for the series of compounds $\text{Mn}(\text{NO})(\text{CO})_4$, $\text{Mn}(\text{NO})(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$, and $\text{Mn}(\text{NO})(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$. We have also pointed out that this series of compounds may be a potentially useful one for evaluating the significant factors governing the stereochemistry of five-coordinate compounds. In particular, this series permits one to study the structures of a group of transition metal compounds where the coordination number and formal valence state of the central metal remain constant while the ligands are varied systematically.

This paper presents the results of a structural investigation of $\text{Mn}(\text{NO})(\text{CO})_4$, the final compound in this series. It also presents intercomparisons of the three structures, together with a rationalization of their bonding differences and the differences in the reactivity of $\text{Mn}(\text{NO})(\text{CO})_4$ and $\text{Mn}(\text{NO})(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ toward replacement of CO by $\text{P}(\text{C}_6\text{H}_5)_3$. In addition the structure is compared with that of the isoelectronic molecule $\text{Fe}(\text{CO})_5$.

Collection of X-Ray Data

A sample of $\text{Mn}(\text{NO})(\text{CO})_4$, mp $\sim 0^\circ$, was prepared by D. Keeton using King's recipe.³ A small amount of the deep red liquid was distilled under vacuum into a 0.3-mm thin-walled quartz capillary. The capillary was sealed and transferred to a precession camera, and a crystal was grown from the liquid by passing a cold stream of nitrogen gas over the sample.⁴ During data collection the temperature of the crystal was maintained at $-110 \pm 6^\circ$.

Preliminary precession photographs showed systematic absences consistent with space groups $\text{C}_{2h}^6\text{-C2}/c$

and $\text{C}_s^4\text{-Cc}$: hkl when $h + k = 2n + 1$ and $h0l$ when $l = 2n + 1$. The unit cell parameters at -110° are $a = 11.72$ (3) Å, $b = 6.74$ (2) Å, $c = 9.65$ (2) Å, and $\beta = 107.8$ (1) $^\circ$, where the error estimates have been obtained from repeated measurements and where a wavelength of 0.7107 Å has been assumed for Mo $K\alpha$ radiation. With four molecules per unit cell, the calculated density is 1.88 g/cm³. This seems reasonable when compared with the calculated density of 1.85 g/cm³ for $\text{Fe}(\text{CO})_5$.⁵

Timed exposures of 12 reciprocal lattice layers ($hkl0$; $h0l$; $h, k, 2k$; $h, 2l, l$; $h1l$; $h2l$; $h3l$; $hk1$; $hk2$; hkk ; $h, k, k - 1$; $h, k, k - 2$) were taken by the precession method using Mo $K\alpha$ radiation. Owing to a problem with the low-temperature system, two crystals were required to obtain these nets. Of the total of 958 reflections observed, 624 were independent. Intensities were estimated visually against a calibrated strip. Lorentz-polarization corrections were applied;⁶ no corrections for extinction effects or absorption were made. The linear absorption coefficient for $\text{Mn}(\text{NO})(\text{CO})_4$ is 19.6 cm⁻¹ for Mo $K\alpha$ radiation. The crystal was cylindrical with an estimated diameter of 0.3 mm and an estimated length of 0.5 mm. Owing to the complexity of the absorption corrections for the precession method,⁷ it is difficult to estimate the errors introduced into the data set by neglect of such corrections. For the small crystal used here, however, it is doubtful that such errors exceed those of intensity estimation.

Determination and Refinement of the Structure

With the assumption that the correct space group is $\text{C2}/c$, symmetry C_2 may be imposed on the molecule. The positions of the manganese atom and one of the carbon atoms were easily located using a three-dimensional Patterson function. Two cycles of least-squares refinement followed by a difference Fourier synthesis re-

(1) J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **6**, 1575 (1967).(2) J. H. Enemark and J. A. Ibers, *ibid.*, **7**, 2339 (1968).

(3) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, New York, N. Y., 1965, p 164.

(4) B. A. Frenz, J. H. Enemark, L. W. Schroeder, D. J. Hodgson, W. T. Robinson, R. J. Loyd, and J. A. Ibers, *J. Appl. Cryst.*, in press.(5) A. W. Hanson, *Acta Cryst.*, **15**, 930 (1962).

(6) In addition to various local programs for the CDC 6400, other programs used were local modifications of Zalkin's FORDAP Fourier program, the Busing-Levy ORFLS least-squares and ORFFE error function programs, Johnson's ORTEP plotting program, Hamilton's INSCALE data interscaling program, and Bauer's LPPPRE Lorentz-polarization program.

(7) R. D. Burbank and K. Knox, *Rev. Sci. Instr.*, **33**, 218 (1962).

vealed the locations of all of the other atoms except the carbon or nitrogen atom lying on the twofold axis. The calculated position of this atom was included with the coordinates of the others in several least-squares cycles and resulted in an agreement factor $R = (\sum ||F_o| - |F_c|| / \sum |F_o|) = 0.175$. No attempt was made to distinguish the nitrogen atom from the carbon atoms; *i.e.*, a model of five carbonyl groups surrounding a central Mn atom was refined. Atomic scattering factors for C, O, and N (used in final refinements) were taken from the tabulation by Ibers.⁸ Anomalous dispersion effects were included in F_c ;⁹ the values of $\Delta f'$ and $\Delta f''$ for Mn were those of Cromer.¹⁰ The scattering factors for Mn were taken from the calculations of Cromer and Waber.¹¹

Anisotropic least-squares refinement of 63 variables, including 12 scale factors, reduced the R factor to 0.101. At this point the data from the various layers were interscaled through the use of the Hamilton-Rollett-Sparks algorithm.¹² A weighting scheme of the following type was applied: $w = (16/|F|)^2$ for $I > 16$; $w = (I/|F|)^2$ for $I \leq 16$. Here w is the weight, $|F|$ is the observed structure amplitude, and I is the raw intensity reading where an I of 2 was barely visible on the films. The intensity of a reflection common to more than one layer was obtained as a weighted average and a new weight was assigned to the averaged intensity on the basis of the weights and number of separate observations of this reflection. The agreement among separate observations of the same reflection was generally that expected for visual estimates of intensity and further indicates that neglect of absorption corrections is not a serious approximation.

With the interscaled data two cycles of least-squares refinement resulted in an R factor of 0.090 and a weighted R factor or $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}$ of 0.085. This refinement led to a nonpositive definite thermal ellipsoid for the carbon atom on the twofold axis, indicating physically impossible thermal vibrations for the atom. The Mn-C distance with C on the twofold axis was 1.78 Å, compared with 1.85 and 1.88 Å for the equatorial and axial carbon atoms, respectively. As discussed later, in the complexes containing both nitrosyl groups and carbonyl groups for which structural work has been done, the metal-nitrogen bond distances are from 0.03 to 0.07 Å shorter than the average metal-carbon distances. Since the apical bond is 0.06 Å longer than the average equatorial bond in the present compound, it seems unlikely that the apical atoms are partly nitrosyl in character. On the basis of this evidence, although not conclusive, we assumed that the nitrogen atom lies in the basal plane and considered the two limiting models of symmetry C_2 : model 1, NO and two CO disordered in the basal plane; model 2, ordered arrangement with NO on the twofold axis.

(8) J. A. Ibers, "International Tables for X-ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(9) J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

(10) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(11) D. T. Cromer and J. T. Waber, *ibid.*, **18**, 104 (1965).

(12) W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *ibid.*, **18**, 129 (1965).

Models 1 and 2 do not differ significantly from the five-carbonyl model in bond distances or R factors. Refinement using model 1 resulted in a positive-definite temperature factor for the disordered atom on the twofold axis, but the thermal motion of the atom is unrealistic, as shown in Figure 1. Atom 3 ($2/3$ C, $1/3$ N)

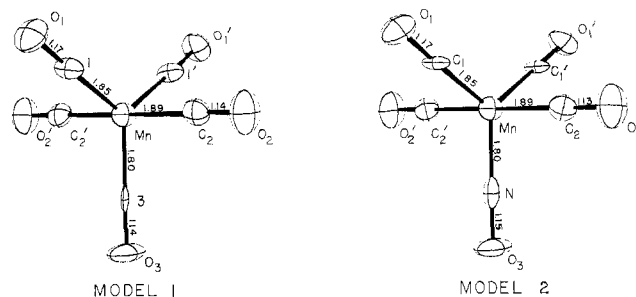


Figure 1.—View of $\text{Mn}(\text{NO})(\text{CO})_4$ after refinement as a disordered molecule with atoms labeled 1, 1', and 3 considered as $2/3$ C, $1/3$ N (model 1) and refinement as an ordered molecule with N on the twofold axis (model 2). The sizes and shapes of the atoms are determined by their final anisotropic thermal parameters and by their perspective view. Atoms with primes are related by twofold symmetry to the corresponding unprimed atoms.

is compressed onto the twofold axis; its root-mean-square (rms) amplitudes of vibration are 0.048, 0.18, and 0.19 Å (Table I). The thermal ellipsoid plot of model 2 is more reasonable; the rms amplitudes for N are 0.10, 0.22, and 0.22 Å. The selection of model 2 as the correct structure is supported by the fact that the Mn-3 (Mn-N) bond distance of 1.80 Å is shorter than the Mn-1 (Mn-C) bond distance of 1.85 Å; this difference compares well with results reported for other metal nitrosyl carbonyl complexes, as discussed later.

The final least-squares cycle gave an R factor of 0.087 and a weighted R factor of 0.085. A final difference electron density map showed no significant features. The maximum residual electron density was $0.4 \text{ e}^- \text{ \AA}^{-3}$, compared with $4.7 \text{ e}^- \text{ \AA}^{-3}$ for a C atom in the initial difference Fourier map. Table II lists values of $10|F_o|$ and $10|F_c|$ (in electrons) for the 624 reflections. The final atomic parameters are given in Table III.

The final R factors are reasonable for film data, the thermal vibrations of the atoms are realistic in magnitude and to a lesser extent in orientation, and the final difference Fourier map is essentially featureless. For these reasons the assumption that the correct space group is C_{2h}^6 - $C2/c$ seems justified; refinements based on space group C_s^4 - Cc were therefore not undertaken.

Description and Discussion

Model 2 of Figure 1 shows the most reasonable structure of $\text{Mn}(\text{NO})(\text{CO})_4$; bond lengths in ångströms are also given. Root-mean-square amplitudes of vibration are listed in Table I. Interatomic distances and bond angles calculated from the final structure parameters are tabulated in Tables IV and V, respectively.

$\text{Mn}(\text{NO})(\text{CO})_4$ forms an almost perfect trigonal bipyramid. All Mn-C-O and Mn-N-O groups are linear; the axial C-Mn-equatorial C bond angles are

TABLE I
ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)^a

Atom	Minimum		Intermediate		Maximum	
	1 ^b	2 ^c	1 ^b	2 ^c	1 ^b	2 ^c
Mn	0.120 (3) ^d	0.119 (3)	0.165 (3)	0.164 (3)	0.200 (3)	0.197 (3)
1, C ₁	0.14 (2)	0.10 (2)	0.16 (1)	0.13 (1)	0.20 (1)	0.18 (1)
C ₂	0.14 (2)	0.12 (2)	0.18 (1)	0.18 (1)	0.19 (1)	0.19 (1)
3, N	0.05 (4)	0.10 (2)	0.18 (2)	0.22 (1)	0.19 (1)	0.22 (2)
O ₁	0.15 (1)	0.15 (1)	0.22 (1)	0.21 (1)	0.25 (1)	0.24 (1)
O ₂	0.16 (1)	0.15 (1)	0.23 (1)	0.23 (1)	0.27 (1)	0.27 (1)
O ₃	0.12 (2)	0.10 (3)	0.20 (1)	0.20 (1)	0.33 (1)	0.33 (1)

^a Figure 1 provides an indication of the direction of these principal axes of vibration. ^b From refinement of the disordered model 1. ^c From refinement of the ordered model 2. ^d Standard deviations of the last significant figures are given in parentheses here and in subsequent tables.

TABLE II
VALUES OF 10|F_o| AND 10|F_c| (IN ELECTRONS) FOR Mn(NO)(CO)₄

K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	K	L	FO	FC	
*****	H	0	*****	5	-3	117	126	6	0	156	99	0	-10	210	187	1	8	58	69	4	-2	103	99	0	-4	589	515	3	1	6	4	6	4	3	-6	89	75			
0	2	513	493	5	-1	247	238	6	4	184	157	0	-8	292	268	5	-10	63	68	4	0	178	122	0	0	394	394	3	3	2	129	122	1	0	63	44	3	-3	63	57
0	4	410	388	5	-1	318	294	6	5	232	203	0	-8	284	283	5	-8	137	149	4	1	284	268	0	4	432	432	3	4	196	146	1	2	64	64	184	184			
0	6	202	192	5	2	53	40	6	6	97	93	0	-2	1038	1034	3	-7	46	41	4	2	97	74	0	4	186	182	3	6	98	59	1	3	59	61	3	0	77	79	

TABLE III
FINAL ATOMIC PARAMETERS FOR Mn(NO)(CO)₄^a

Atom	x	y	z	10 ⁴ β ₁₁	10 ⁴ β ₂₂	10 ⁴ β ₃₃	10 ⁴ β ₁₂	10 ⁴ β ₁₃	10 ⁴ β ₂₃
Mn	0	0.1592 (3)	1/4	29 (1)	117 (5)	90 (3)	0	28 (1)	0
C ₁	-0.0832 (5)	0.2989 (10)	0.0850 (9)	35 (4)	47 (22)	55 (11)	6 (6)	0 (6)	1 (11)
C ₂	0.1334 (5)	0.1601 (16)	0.1794 (9)	47 (4)	127 (22)	66 (11)	16 (10)	11 (6)	19 (16)
N	0	-0.1075 (18)	1/4	66 (7)	214 (38)	66 (14)	0	51 (9)	0
O ₁	-0.1360 (5)	0.3883 (10)	-0.0181 (8)	63 (4)	181 (20)	99 (10)	29 (7)	19 (6)	49 (11)
O ₂	0.2140 (4)	0.1590 (13)	0.1376 (8)	51 (3)	323 (24)	119 (10)	8 (9)	42 (6)	0 (14)
O ₃	0	-0.2785 (14)	1/4	101 (8)	47 (25)	234 (22)	0	95 (12)	0

^a x, y, and z are in fractional coordinates. Thermal parameters are in the form: exp[-(h²β₁₁ + k²β₂₂ + l²β₃₃ + 2hkβ₁₂ + 2hlβ₁₃ + 2klβ₂₃)]. The standard deviations of the least significant figures are given in parentheses.

within 2° (5σ) of 90°, while angles in the equatorial plane are within 2σ of 120°. The nitrosyl group has been assigned the unique position on the twofold axis on the basis of reasonableness of thermal vibrations and bond lengths. The two carbonyl groups in the apical plane are related by the twofold symmetry, as are the apical carbonyl groups.

CO stretching bands.¹³ Treichel, *et al.*,¹³ considered four possible structures for the compound: tetragonal pyramidal structures of symmetry C_{4v} or C_s; and trigonal bipyramidal structures of symmetry C_{3v} or C_{2v}. They argue that while the C_{3v} structure is compatible with the presence of three infrared-active CO stretching

(13) P. M. Treichel, E. Pitcher, R. B. King, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 2593 (1961).

TABLE IV
INTERATOMIC DISTANCES (Å)

Atoms ^a	Distance	Atoms ^a	Distance
Mn-C ₁	1.851 (8)	C ₁ -C ₂	2.60 (1)
Mn-C ₂	1.886 (8)	C ₁ -C ₂ '	2.69 (1)
Mn-N	1.797 (13)	C ₁ -N	3.17 (1)
C ₁ -O ₁	1.167 (9)	C ₂ -C ₂ '	3.77 (2)
C ₂ -O ₂	1.135 (9)	C ₂ -N	2.61 (1)
N-O ₃	1.152 (15)	O ₁ -O ₁ '	5.19 (2)
Mn-O ₁	3.017 (8)	O ₁ -O ₂	4.21 (1)
Mn-O ₂	3.021 (7)	O ₁ -O ₂ '	4.33 (1)
Mn-O ₃	2.949 (13)	O ₁ -O ₃	5.19 (2)
C ₁ -C ₁ '	3.187 (17)	O ₂ -O ₃	4.22 (1)

^a Atoms with primes are related by twofold symmetry to the corresponding unprimed atoms.

TABLE V
BOND ANGLES (DEG)

Atoms	Angle	Atoms	Angle
C ₁ -Mn-C ₂	88.0 (4)	Mn-C ₁ -O ₁	179.3 (7)
C ₁ '-Mn-C ₂	91.8 (4)	Mn-C ₂ -O ₂	179.3 (9)
N-Mn-C ₂	90.2 (3)	Mn-N-O ₃	180
C ₁ -Mn-C ₁ '	118.9 (5)	C ₂ -Mn-C ₂ '	179.6 (7)
C ₁ -Mn-N	120.6 (2)	O ₂ -Mn-O ₂ '	179.9 (4)

bands. Such an argument fails to take account of the possibility of an infrared-active band too weak to be observed or of accidental coincidence of two bands. The evidence, as presented here, is in favor of the C_{2v} structure, with NO on the twofold axis. In principle such a molecule would be expected to show four infrared vibrations in the CO stretching region. However, since the symmetry of the molecule, neglecting substitution of N for C, is very nearly D_{3h}, it is likely that one of these modes would be too weak to be observed owing to the lack of coupling of apical carbonyls with those in the basal plane. Thus the observation of only three bands in the CO stretching region of the infrared spectrum is compatible with either C_{3v} or C_{2v} symmetry. Similar discrepancies between predictions based on infrared bands and results of diffraction studies have been observed for other compounds, e.g., HMn(CO)₅.^{14,15}

The average Mn-C bond distance is 1.87 (1) Å. This bond length is greater than other Mn-C distances reported for several five- and six-coordinate Mn compounds, e.g.: (C₆H₅)₃SnMn(CO)₅, 1.76 Å;¹⁶ Mn(NO)(CO)₂(P(C₆H₅)₃)₂, 1.77 Å;¹ (C₆H₅)₃SnMn(CO)₄P(C₆H₅)₃, 1.79 Å;¹⁷ π-C₅H₅Mn(CO)₃, 1.80 Å;¹⁸ trans-C₁₀H₈Mn₂(CO)₈, 1.803 Å;¹⁹ Mn₂(CO)₈Br₂, 1.81 Å;²⁰ Mn₂(CO)₁₀, 1.82 Å;²¹ Mn₂Fe(CO)₁₄, 1.823 Å;²² HMn(CO)₅, 1.836 Å.¹⁵ The standard deviations are less than 0.02 Å.

The Mn-N distance of 1.797 (13) Å is also long. In a recent tabulation²³ of metal-N distances in metal

nitrosyls the values ranged from 1.57 to 2.03 Å. Only two of the complexes have metal-N distances greater than that in Mn(NO)(CO)₄. The Ir-N bonding in [IrCl(CO)(NO)(P(C₆H₅)₃)₂][BF₄]²³ (Ir-N = 1.97 Å) is not analogous to the Mn-N bonding in Mn(NO)(CO)₄, because the Ir-N-O bond angle is 124.1 (9)°. [Co(NH₃)₅(NO)]Cl₂ has been reported to have a Co-N distance of 1.99²⁴ or 2.03 Å.²⁵ The nature of the bonding of NO to the metal has been debated²⁶ and the possibility of an O-bonded group could explain the unusually long M-(NO) and N-O bond lengths. Omission of the Ir and Co complexes leaves Mn(NO)(CO)₄ with the longest M-N bond length of the complexes tabulated.

The N-O distance of 1.152 (15) Å compares well with 19 other N-O distances²³ (the Co complex is omitted) ranging from 1.1 to 1.26 Å with an average of 1.165 Å. The average C-O distance of 1.15 Å is in the range of the many other carbonyl distances reported.

The axial Mn-C bond distance of 1.886 (8) Å is 0.035 Å (>3σ) longer than the equatorial Mn-C distance of 1.851 (8) Å. This same trend has been observed in the five-coordinate carbonyl complex Co(SiCl₃)(CO)₄.²⁷ However, several trigonal-bipyramidal complexes with ligands other than CO have been reported²⁸ to have axial M-L bond lengths shorter than equatorial bond lengths. These axial-equatorial differences are discussed below.

In addition to Mn(NO)(CO)₄, the structures are known for two other compounds containing only NO and CO as ligands on a single metal atom (Table VI).

TABLE VI
COMPARISON OF METAL-CARBON AND METAL-NITROGEN BOND DISTANCES (Å) IN MIXED CARBONYL-NITROSYL COMPLEXES

Complex	Coordn no.	Av M-C	M-N	(M-C) - (M-N)
Co(NO)(CO) ₅ ^a	4	1.83 (2)	1.76 (3)	0.07
Fe(NO) ₂ (CO) ₂ ^a	4	1.84 (2)	1.77 (2)	0.07
Mn(NO)(CO) ₄ ^b	5	1.87 (1)	1.80 (1)	0.07

^a L. O. Brockway and J. S. Anderson, *Trans. Faraday Soc.*, **33**, 1233 (1937). ^b This work.

A trend toward longer M-C and M-N distances is apparent as atomic number decreases and coordination number increases. In all three cases the M-C bond distance is longer than the M-N distance by 0.07 Å, approximately that suggested by the usual values of double-bond radii.²⁹

All intermolecular distances are normal. The shortest interaction (3.2 Å) is between O atoms. A stereoscopic view of the unit cell is shown in Figure 2.

(14) D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 2734 (1964).
 (15) S. J. La Placa, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1491 (1964).
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 (17) R. F. Bryan, *J. Chem. Soc., A*, 172 (1967).
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 (21) L. F. Dahl and R. E. Rundle, *ibid.*, **16**, 419 (1963).
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 (23) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968).

(24) D. Hall and A. A. Taggart, *J. Chem. Soc.*, 1359 (1965).
 (25) D. Dale and D. C. Hodgkin, *ibid.*, 1364 (1964).
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 (28) K. N. Raymond, D. W. Meek, and J. A. Ibers, *ibid.*, **7**, 1111 (1968), and references therein.
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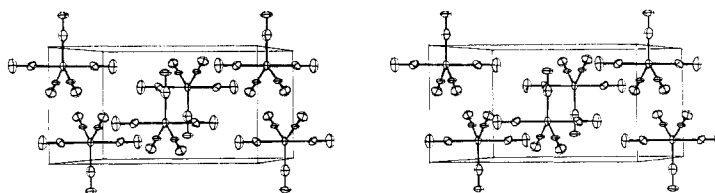
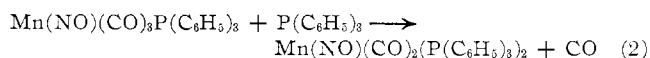
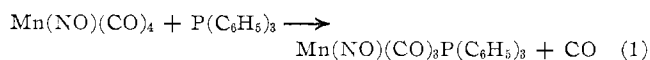


Figure 2.—Stereoscopic view of the unit cell of $\text{Mn}(\text{NO})(\text{CO})_4$, with the a axis horizontal from left to right, the b axis vertical from bottom to top, and the c axis pointing out of the plane of the paper.

**Discussion of $\text{Mn}(\text{NO})(\text{CO})_4$,
 $\text{Mn}(\text{NO})(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$, and
 $\text{Mn}(\text{NO})(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$**

The kinetic studies for the substitution reactions of $\text{Mn}(\text{NO})(\text{CO})_4$ have been reported.³⁰ The replacement of CO from $\text{Mn}(\text{NO})(\text{CO})_4$ by $\text{P}(\text{C}_6\text{H}_5)_3$ proceeds by an $\text{S}_\text{N}2$ displacement process, while the reaction of $\text{Mn}(\text{NO})(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ takes place largely by a dissociative process. (See eq 1 and 2.) The rate of reaction 2



is much slower than that of reaction 1.

$\text{Mn}(\text{NO})(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ and $\text{Mn}(\text{NO})(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$ were both shown to be trigonal bipyramids with the nitrosyl group in the basal plane. In the first compound the nitrogen atom was disordered with respect to the two carbon atoms in the basal plane and the structure was refined with each of the three atoms considered as $2/3\text{C}$ and $1/3\text{N}$. In the second compound the nitrosyl group was distinguished from the carbonyl groups on the basis of directions and magnitudes of atomic vibrations.

Table VII compares the interatomic distances observed in the series of complexes $\text{Mn}(\text{NO})(\text{CO})_4$, $\text{Mn}(\text{NO})(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$, and $\text{Mn}(\text{NO})(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$. In this series Mn remains in the same formal oxidation state while the ligands are systematically varied.

TABLE VII
COMPARISON OF INTERATOMIC DISTANCES (Å)

Atoms	$\text{Mn}(\text{NO})(\text{CO})_4$	$\text{Mn}(\text{NO})(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ ^a	$\text{Mn}(\text{NO})(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$ ^a
Mn-C (apical)	1.886 (8)	1.833 (11)	...
Mn-C (basal)	1.851 (8)	1.798 (10) ^a 1.782 (11) ^a 1.756 (10) ^a	1.78 (2) 1.75 (2)
Mn-N	1.797 (13)	...	1.73 (1)
Mn-P	...	2.305 (4)	2.278 (5) 2.279 (5)

^a Refined as $2/3\text{C}$ and $1/3\text{N}$.

The data in Table VII show that the first substitution of a $\text{P}(\text{C}_6\text{H}_5)_3$ group causes a significant decrease in Mn-N and Mn-C bond distances. Generally $\text{P}(\text{C}_6\text{H}_5)_3$ is considered to be a poorer π -bonding ligand than CO, and consequently the $\text{P}(\text{C}_6\text{H}_5)_3$ does not compete for electrons as well as the CO group it replaced. Thus more electrons are available for metal-carbon and metal-nitrogen π bonding, and the CO groups in Mn-

(30) H. Wawersik and F. Basoio, *J. Am. Chem. Soc.*, **89**, 4626 (1967).

$(\text{NO})(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ are more firmly held to the metal than those in $\text{Mn}(\text{NO})(\text{CO})_4$. As a result it is more difficult to replace a second group.

The product of reaction 2 shows a shortening of all of the metal-ligand distances (including the Mn-P distance) as additional electrons are made available for π bonding and as the competition for them is further decreased by replacement of a second CO group. However, the shortening of the Mn-N and Mn-C distances is much less significant than for reaction 1. It may be that with the substitution of two phosphine groups into axial positions, the π -bonding requirements of the carbonyl groups are nearly satisfied. Indeed, $\text{Mn}(\text{NO})(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$ is much more stable than $\text{Mn}(\text{NO})(\text{CO})_4$ and $\text{Mn}(\text{NO})(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$, and preliminary attempts³¹ to prepare the compound $\text{Mn}(\text{NO})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_3$ by further replacement of CO by $\text{P}(\text{C}_6\text{H}_5)_3$ have been unsuccessful. Steric factors would not seem to be responsible for the failure of the tris-phosphine complex to form, as several five-coordinate trigonal-bipyramidal complexes are known which contain three triphenylphosphine groups as adjacent ligands, *e.g.*, $\text{Rh}(\text{H})(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_3$ ³² and $\text{Co}(\text{H})(\text{N}_2)(\text{P}(\text{C}_6\text{H}_5)_3)_3$.³³

The structures of the reactants and products indicate that both reactions 1 and 2 result in axial substitution of carbonyls by phosphine. It is not possible to say whether this substitution pattern is due to steric factors, to the relative π -bonding possibilities for the ligands in axial and equatorial positions, or to a combination of these effects.

It is also apparent from Table VII that the Mn-N bond distance in $\text{Mn}(\text{NO})(\text{CO})_4$ is significantly less (0.05 Å, 4σ) than the equatorial Mn-C bond distance. A similar difference is observed for $\text{Mn}(\text{NO})(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_3)_2$, where the Mn-N bond distance is 0.04 Å (2σ) shorter than the average Mn-C bond distance.³⁴ These differences are similar to the differences in the double- (or triple-) bond radii of N and C of ~ 0.05 Å given by Pauling.²⁹ Consequently, we conclude that the differences in the Mn-N and Mn-C bond lengths shown in Table VII do not constitute experimental evidence that NO is a more effective π -bonding ligand than CO.

Comparison with $\text{Fe}(\text{CO})_5$

We have previously tabulated²⁸ axial and equatorial metal-ligand bond lengths in a series of ML_5 complexes

(31) H. Wawersik, unpublished work.

(32) S. J. La Placa and J. A. Ibers, *Acta Cryst.*, **18**, 511 (1965).

(33) J. H. Enemark, B. R. Davis, J. A. McGinney, and J. A. Ibers, *Chem. Commun.*, 96 (1968).

(34) In $\text{Mn}(\text{NO})(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ the disorder of the NO and CO groups in the equatorial plane precludes a comparison of the Mn-N and Mn-C bond distances.

and have discussed the trends in terms of ligand–ligand and d-electron–ligand repulsions. New electron diffraction data³⁵ are now available on Fe(CO)₅: the Fe–C (equatorial) bond length is 1.833 (4) Å and the Fe–C (axial) bond length is 1.806 (5) Å. This significant axial shortening in Fe(CO)₅ differs from the axial lengthening in Mn(NO)(CO)₄. If one assumes that π -bonding properties of NO and CO differ but little, then one can look upon Mn(NO)(CO)₄ as completely analogous to the Mn(CO)₅⁻ ion, with the charge residing on the metal. (No structural data are available for this ion.) Then axial shortening in Fe(CO)₅ and

(35) B. Beagley, D. W. J. Cruickshank, P. M. Pinder, A. G. Robiette, and G. M. Sheldrick, *Acta Cryst.*, in press, and references therein.

axial lengthening in Mn(NO)(CO)₄ are consistent with the idea that the d-electron–ligand repulsions should increase as the negative charge on the central metal increases. The fact that the average Fe–C distance of 1.822 Å is less than the average Mn–C distance of 1.868 Å is also consistent with this view.

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The Crystal and Molecular Structure of Racemic *cis*- β -(Chloroaquotriethylenetetramine)cobalt(III) Perchlorate

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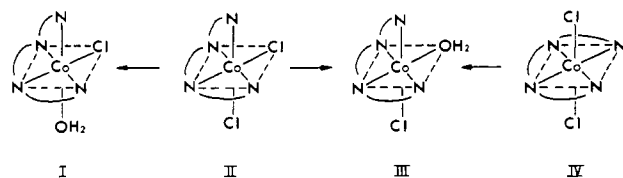
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The crystal and molecular structure of *cis*- β -(chloroaquotriethylenetetramine)cobalt(III) perchlorate, [CoClOH₂(NH₂CH₂CH₂NHCH₂CH₂NHCH₂CH₂NH₂)](ClO₄)₂, has been determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in space group Pna2₁ (C_{2v}⁹, no. 33) of the orthorhombic system, with $a = 12.09$ (1) Å, $b = 8.34$ (1) Å, $c = 15.74$ (2) Å, and $Z = 4$. Measured and calculated densities are, respectively, 1.90 and 1.91 g cm⁻³. The structure has been refined by full-matrix least-squares techniques to a final residual $R = 0.070$ for 1125 independent nonzero reflections. The crystal is composed of β -Co(trien)ClOH₂²⁺ cations and ClO₄⁻ anions held together by hydrogen bonds and electrostatic forces. The coordination around Co is octahedral with the coordinated water molecule *trans* to those two chelate rings of β -trien which have a common coordination plane. Important bond distances are as follows: mean Co–N, 1.93 \pm 0.01 Å; Co–OH₂, 1.98 \pm 0.01 Å; Co–Cl, 2.237 \pm 0.004 Å. The X-ray analysis confirms the structure of the complex cation as deduced from kinetic data.

Introduction

It has been shown by Sargeson, *et al.*,^{1,2} that β -Co(trien)Cl₂⁺ (II, trien = triethylenetetramine) aquates to form two chloroaquo species (I and III) which can further aquate to form a common diaquo product. From a similar study on the aquation of *trans*-Co(trien)Cl₂⁺ (IV) it could be reasoned¹ that isomer I was the only chloroaquo intermediate obtained in this case, and that this was the major chloroaquo isomer formed in the hydrolysis of β -Co(trien)Cl₂⁺. Correct structural assignments to the β -Co(trien)ClOH₂²⁺ isomers are particularly important as these structures are the basis of a number of further studies on triethylenetetramine–cobalt(III) complexes.^{3–5} A detailed knowledge of the stereochemistry of trien coordinated in the β geometry will also be of interest, particularly with respect to the configuration around that asymmetric secondary amine

nitrogen which connects the two chelate rings sharing a common coordination plane. (The nomenclature follows that of ref 1–3.) An X-ray crystal structure



analysis now removes the uncertainty hitherto attached to the structural assignment for isomer III. A brief report about the crystal structures of this compound and the related compound β -(triethylenetetramine-O-ethylglycylglycine)cobalt(III) perchlorate hydrate has been published.⁶

Experimental Section

Crystal Data.—Racemic *cis*- β -[Co(trien)ClOH]₂(ClO₄)₂ forms dark red crystals. The unit cell is orthorhombic with $a = 12.09$ (1) Å, $b = 8.34$ (1) Å, $c = 15.74$ (2) Å, $V = 1586.9$ Å³, $D_m =$

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