

Contribution from the Department of Chemistry, University of Natal, Durban 4001, Republic of South Africa, and the National Chemical Research Laboratory, C.S.I.R., Pretoria 0001, Republic of South Africa

Structures of Five-Coordinate Dinitrosyls of Manganese. 1. The Monoclinic Form of Dinitrosylbis(dimethyl phenylphosphonite)manganese(I) Chloride, $[\text{Mn}(\text{NO})_2\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2\text{Cl}]$

MICHAEL LAING,* ROLF H. REIMANN, and ERIC SINGLETON

Received July 20, 1978

The structure of dinitrosylbis(dimethyl phenylphosphonite)manganese(I) chloride, $[\text{Mn}(\text{NO})_2\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2\text{Cl}]$, has been determined by X-ray diffraction. The compound crystallizes from benzene in the monoclinic space group $C2/c$ with $a = 25.86$ (1) Å, $b = 11.863$ (5) Å, $c = 14.563$ (5) Å, $\beta = 90.96$ (5)°, $V = 4467.5$ Å³, $\rho(\text{obsd}) = 1.45$ g cm⁻³, and $Z = 8$. The structure was solved by conventional Patterson and Fourier methods and refined by block-diagonal least squares to a conventional $R = 0.041$ for 2265 reflections with $I > 1.65\sigma(I)$. The coordination geometry about the manganese is trigonal bipyramidal with the phosphonite ligands trans. The two NO groups are ordered, and the atoms of the $\{\text{Mn}(\text{NO})_2\text{Cl}\}$ group are coplanar with the NO groups bent in toward each other. Bond lengths and angles of interest are Mn–N = 1.665, 1.650 (10) Å, N–O = 1.18, 1.18 (1) Å, Mn–N–O = 163, 166 (1)°, Mn–P = 2.294, 2.291 (5) Å, Mn–Cl = 2.351 (5) Å, N–Mn–N = 111.5°, O–Mn–O = 99.0°, and Cl–Mn–N = 123.9, 124.6°. The phosphonite ligands bend toward the Cl atom, away from the NO groups: P–Mn–P = 166.9°, P–Mn–Cl = 83.4, 83.5°, P–Mn–N angles are between 91.3 and 95.6°; P···Cl = 3.09, 3.09 Å, and P···N distances are between 2.85 and 2.95 Å.

Introduction

As part of a study of the reactions of manganese and rhenium carbonyls, the compound $[\text{Mn}(\text{NO})_2\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2\text{Cl}]$ was prepared.¹ The frequencies of the nitrosyl stretching modes were 1723 and 1674 (± 3) cm⁻¹ in CHCl_3 , suggesting that the two nitrosyl groups were nearly identical in character with little or no distortion from linearity. Similar values for the analogous NO stretching frequencies had been observed² in related manganese compounds, e.g., in $[\text{Mn}(\text{NO})_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\text{Br}]$.

The structures of nitrosyl derivatives of transition metals and the problems of describing the bonding in them were discussed in two reviews in 1972.^{3,4} Both reviews emphasized the (then) lack of a suitable theory that would account for the various structures of the five-coordinate complexes; in particular, it was evident that the parameters associated with the NO group in the series $[\text{Mn}(\text{NO})(\text{CO})_{4-x}\{\text{P}(\text{C}_6\text{H}_5)_3\}_x]$ ($x = 0, 1, 2$) were suspect because of disorder in the crystal structures.

Enemark and Feltham subsequently presented⁵ a detailed discussion of the bonding in metal–nitrosyl complexes. Although the data for only two five-coordinate dinitrosyl complexes were available to them, they successfully rationalized the observed structures with the aid of the correlation diagrams for the molecular orbitals. They specifically noted that “there are no well-characterized examples of five-coordinate (bipyramidal) complexes” in which the two NO groups are diequatorial and the two phosphine ligands are trans diaxial.

A crystallographic study of $[\text{Mn}(\text{NO})_2\{\text{P}(\text{OCH}_3)_2\text{C}_6\text{H}_5\}_2\text{Cl}]$ was therefore undertaken in the hope of obtaining precise values for the bond lengths and angles in the Mn–N–O system and to compare the structure with that of the formally isoelectronic square-pyramidal complex $[\text{Ru}(\text{NO})_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\text{Cl}]^+$ in which the two NO groups differ dramatically in character.⁶ Preliminary results have been published.⁷

Experimental Section

The compound was prepared by the published method,¹ and after much effort good crystals were obtained from benzene. Preliminary Weissenberg and precession photographs showed the crystals to be monoclinic, probably space group $C2/c$ (subsequently confirmed by satisfactory elucidation of the structure).

Crystal Data: $\text{C}_{16}\text{H}_{22}\text{MnClN}_2\text{O}_6\text{P}_2$, mol wt 490.4, monoclinic space group $C2/c$, $a = 25.86$ (1) Å, $b = 11.863$ (5) Å, $c = 14.563$ (5) Å,

* To whom correspondence should be addressed at the University of Natal.

$\beta = 90.96$ (5)°, $V = 4467.5$ Å³, $\rho(\text{obsd}) = 1.45$ (3) g cm⁻³, $Z = 8$, $\mu(\text{Mo K}\alpha) = 9.15$ cm⁻¹.

Intensity data were collected on a Philips PW1100 four-circle diffractometer (C.S.I.R., Pretoria) with graphite-monochromated Mo K α radiation (λ 0.7107 Å) for θ between 3 and 22°. Accurate unit cell dimensions were determined by least-squares refinement of the 2θ , χ , and ϕ angles of 25 reflections. Three reflections were used as intensity standards and remeasured after every 60 reflections: no crystal decomposition was detectable. The diffractometer was operated in the standard mode, the ω - 2θ scan technique was used, and the scan width was 1.2°, with each peak scanned over 30 s and the background counted for 30 s. Of 2757 reflections measured (including space group extinctions of the class $h0\text{odd}$), 2265 data were classed as observed: $I > 1.65\sigma(I)$. Lorentz–polarization corrections were applied; corrections for absorption were considered unnecessary as the crystal's dimensions were $0.3 \times 0.3 \times 0.3$ mm.

The coordinates of the Mn atom were readily obtained from a three-dimensional Patterson map, and the remaining atoms were located in the subsequent Fourier maps. The structure was refined by block-diagonal least squares, first isotropically, and then anisotropically. Weighting was proportional to $1/\sigma(F)$. At convergence, the conventional R was 0.041 for the 2265 observed data. (H atoms were not included in the structure factor calculations; no attempt was made to locate them in the Fourier maps.)

All calculations were done with a local set of programs⁸ on a Burroughs 5700 computer. Scattering factors were taken from ref 9; that of manganese was corrected for the real part of anomalous dispersion. A list of observed and calculated structure factors is available.¹⁰

The fractional atomic coordinates are given in Table I, and the anisotropic thermal parameters are in Table II; estimated standard deviations in the last significant figure are given in parentheses.

Results and Discussion

The coordination about the manganese atom is trigonal bipyramidal with the two phosphonite ligands trans diaxial (see Figure 1). The compound is thus one of the very few trigonal-bipyramidal nitrosyls—possibly the only dinitrosyl—whose structure has been determined; therefore the bonding parameters are of interest.

The molecule has approximate symmetry 2, with the twofold axis coincident with the Mn–Cl bond. The Cl–Mn–P angles (Table IV) show that the two phosphonite ligands are bent toward the chlorine atom, away from the NO groups (see Figure 1). The two phosphonite ligands are identical in geometry. One O–CH₃ group is bent in toward the equatorial plane and between the Cl and one NO group, while the other O–CH₃ group is bent away from the equatorial plane. (See Tables VI and VII.) The difference in the environments of

Table I. Fractional Atomic Coordinates^a

atom	x	y	z	atom	x	y	z
Mn	0.62340 (3)	0.32629 (7)	0.11509 (6)	C(13)	0.6086 (3)	0.0862 (7)	-0.2118 (5)
Cl	0.65201 (6)	0.13875 (12)	0.10415 (11)	C(14)	0.6211 (3)	0.1672 (8)	-0.2719 (5)
P(1)	0.56231 (5)	0.26841 (13)	0.00927 (11)	C(15)	0.6167 (3)	0.2802 (7)	-0.2504 (5)
P(2)	0.69018 (5)	0.34179 (12)	0.21965 (10)	C(16)	0.5986 (2)	0.3100 (5)	-0.1645 (4)
N(1)	0.5816 (2)	0.3721 (4)	0.1909 (3)	C(21)	0.6873 (2)	0.2577 (4)	0.3230 (3)
N(2)	0.6438 (2)	0.4301 (4)	0.0478 (3)	C(22)	0.7302 (2)	0.2021 (5)	0.3574 (4)
O(1)	0.5547 (2)	0.4263 (5)	0.2389 (3)	C(23)	0.7271 (3)	0.1371 (6)	0.4363 (5)
O(2)	0.6497 (2)	0.5190 (4)	0.0128 (3)	C(24)	0.6814 (3)	0.1262 (5)	0.4792 (5)
O(11)	0.5278 (2)	0.1618 (4)	0.0333 (3)	C(25)	0.6391 (3)	0.1826 (6)	0.4472 (5)
O(12)	0.5236 (2)	0.3699 (3)	-0.0091 (3)	C(26)	0.6417 (2)	0.2499 (6)	0.3680 (4)
O(21)	0.7471 (1)	0.3099 (3)	0.1885 (3)	C(110)	0.5137 (3)	0.1370 (7)	0.1280 (5)
O(22)	0.6924 (1)	0.4694 (3)	0.2526 (3)	C(120)	0.4797 (3)	0.3623 (6)	-0.0750 (5)
C(11)	0.5841 (2)	0.2270 (5)	-0.1021 (4)	C(210)	0.7683 (2)	0.3394 (6)	0.1003 (4)
C(12)	0.5904 (2)	0.1151 (5)	-0.1261 (4)	C(220)	0.7303 (3)	0.5079 (5)	0.3211 (4)

^a Estimated standard deviations in the last significant figure are shown in parentheses.

Table II. Anisotropic Thermal Parameters $\times 10^5$ for Mn, Cl, and P Atoms and $\times 10^4$ for N, O, and C Atoms^a

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	66 (1)	470 (7)	251 (5)	12 (5)	-64 (4)	-9 (9)
Cl	147 (3)	428 (12)	451 (10)	107 (9)	-120 (8)	-89 (17)
P(1)	72 (2)	549 (13)	308 (9)	-21 (9)	-84 (7)	-30 (18)
P(2)	67 (2)	449 (12)	239 (9)	-2 (9)	-56 (7)	44 (16)
N(1)	9 (1)	91 (5)	38 (3)	15 (3)	-4 (2)	-23 (6)
N(2)	10 (1)	64 (4)	44 (3)	-6 (3)	-17 (2)	13 (6)
O(1)	15 (1)	169 (6)	68 (3)	46 (4)	6 (3)	-65 (7)
O(2)	22 (1)	77 (4)	85 (4)	-18 (3)	-16 (3)	76 (6)
O(11)	14 (1)	91 (4)	47 (3)	-32 (3)	-4 (2)	6 (5)
O(12)	13 (1)	83 (4)	52 (3)	22 (3)	-20 (2)	-29 (5)
O(21)	7 (1)	94 (4)	41 (3)	9 (3)	-2 (4)	17 (5)
O(22)	14 (1)	42 (3)	38 (2)	-7 (2)	-13 (2)	5 (4)
C(11)	9 (1)	60 (5)	28 (3)	-7 (4)	-12 (3)	-4 (6)
C(12)	16 (1)	71 (6)	50 (4)	-8 (4)	-6 (4)	-21 (8)
C(13)	22 (2)	122 (8)	61 (5)	-3 (6)	4 (4)	-87 (10)
C(14)	18 (1)	203 (11)	38 (4)	-1 (6)	3 (4)	-66 (11)
C(15)	18 (1)	168 (9)	33 (4)	-16 (6)	4 (4)	25 (10)
C(16)	16 (1)	84 (6)	39 (4)	-6 (5)	-10 (4)	10 (8)
C(21)	10 (1)	40 (5)	24 (3)	2 (3)	-1 (3)	2 (6)
C(22)	14 (1)	72 (6)	34 (4)	11 (4)	-3 (3)	15 (7)
C(23)	24 (2)	90 (7)	48 (4)	30 (5)	0 (4)	54 (9)
C(24)	28 (2)	62 (6)	39 (4)	0 (5)	2 (4)	27 (8)
C(25)	20 (1)	120 (8)	45 (4)	-10 (5)	15 (4)	30 (9)
C(26)	14 (1)	111 (7)	37 (4)	10 (5)	5 (3)	60 (9)
C(110)	25 (2)	186 (11)	41 (5)	-65 (7)	11 (4)	53 (11)
C(120)	14 (1)	132 (8)	79 (5)	28 (5)	-52 (4)	-30 (11)
C(210)	16 (1)	130 (8)	25 (4)	8 (5)	20 (3)	44 (9)
C(220)	21 (1)	74 (6)	49 (4)	-30 (5)	-36 (4)	-18 (8)

^a The form of the expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table III. Bond Lengths (Å)

Mn-Cl	2.351 (5)	P(2)-O(21)	1.59 (1)
Mn-P(1)	2.294 (5)	P(2)-O(22)	1.59 (1)
Mn-P(2)	2.291 (5)	P(2)-C(21)	1.81 (1)
Mn-N(1)	1.650 (10)	O(11)-C(110)	1.46 (2)
Mn-N(2)	1.665 (10)	O(12)-C(120)	1.48 (2)
N(1)-O(1)	1.18 (1)	O(21)-C(210)	1.45 (2)
N(2)-O(2)	1.18 (1)	O(22)-C(220)	1.46 (2)
P(1)-O(11)	1.59 (1)	C-C	1.34-1.40
P(1)-O(12)	1.59 (1)	mean	1.38
P(1)-C(11)	1.80 (1)		

the two CH_3 groups is reflected in their associated bond angles: e.g., $\text{Mn-P(1)-O(11)} \approx \text{Mn-P(2)-O(21)} = 119^\circ$ —large due to strain caused by the proximity of the CH_3 to Cl and NO; $\text{Mn-P(1)-O(12)} = \text{Mn-P(2)-O(22)} = 108^\circ$ —small because the CH_3 suffers no compression strain. $\text{O(11)-P(1)-C(11)} \approx \text{O(21)-P(2)-C(21)} = 99^\circ$ —small because the CH_3 is bent away from the phenyl ring; $\text{O(12)-P(1)-C(11)} \approx \text{O(22)-P(2)-C(21)} = 106^\circ$ —large because of the proximity of the CH_3 to the phenyl ring. The deviations from ideality of the angles around the P atoms are caused by the various nonbonded repulsions between the atoms involved, and the ge-

Table IV. Bond Angles (deg)

P(1)-Mn-P(2)	166.9 (5)	Mn-P(1)-C(11)	118 (1)
N(1)-Mn-N(2)	111.5 (5)	Mn-P(2)-O(21)	119 (1)
O(1)-Mn-O(2)	99.0 (5)	Mn-P(2)-O(22)	108 (1)
Cl-Mn-P(1)	83.4 (5)	Mn-P(2)-C(21)	118 (1)
Cl-Mn-P(2)	83.5 (5)	P(1)-O(11)-C(110)	121 (1)
Cl-Mn-N(1)	124.6 (5)	P(1)-O(12)-C(120)	123 (1)
Cl-Mn-N(2)	123.9 (5)	P(2)-O(21)-C(210)	124 (1)
P(1)-Mn-N(1)	95.6 (5)	P(2)-O(22)-C(220)	122 (1)
P(1)-Mn-N(2)	92.7 (5)	O(11)-P(1)-O(12)	107 (1)
P(2)-Mn-N(1)	91.3 (5)	O(11)-P(1)-C(11)	100 (1)
P(2)-Mn-N(2)	95.1 (5)	O(12)-P(1)-C(11)	105 (1)
Mn-N(1)-O(1)	166 (1)	O(21)-P(2)-O(22)	107 (1)
Mn-N(2)-O(2)	163 (1)	O(21)-P(2)-C(21)	99 (1)
Mn-P(1)-O(11)	118 (1)	O(22)-P(2)-C(21)	106 (1)
Mn-P(1)-O(12)	108 (1)		

Table V. Intramolecular Nonbonded Separations (Å)

N(1)···N(2)	2.74	Cl···P(2)	3.09
O(1)···O(2)	4.28	Cl···N(1)	3.56
N(1)···P(1)	2.95	Cl···N(2)	3.56
N(2)···P(1)	2.90	N(1)···O(12)	3.26
N(1)···P(2)	2.85	N(1)···O(22)	3.20
N(2)···P(2)	2.95	N(2)···O(12)	3.28
Cl···P(1)	3.09	N(2)···O(22)	3.25

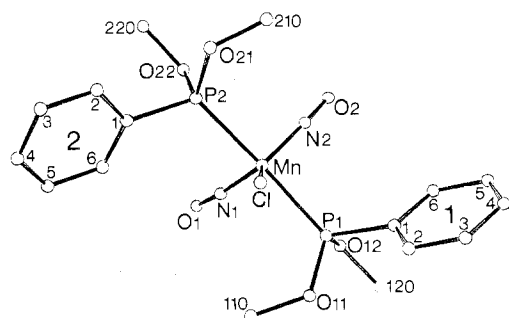


Figure 1. Projection of the molecule showing the numbering system. C atoms are identified by number only, e.g., atom 3 in phenyl ring 2 is C(23); parentheses have been omitted to improve clarity. The near-coplanarity of the atoms Mn, Cl, P(1), P(2), O(12), O(22), C(120), C(220) is clearly seen.

Table VI. Least-Squares Planes^a

(i) The {Mn(NO) ₂ Cl} Group							
A		B		C		D	
-0.746		-0.193		-0.638		-13.83	
Deviations (Å)							
Mn	Cl	N(1)	O(1)	N(2)	O(2)	P(1)	P(2)
0.01	-0.01	0.02	-0.02	0.00	0.00	2.29	-2.26
(ii) The {Mn(P) ₂ Cl} Group							
A		B		C		D	
0.623		0.264		-0.737		9.80	
Deviations (Å)							
Mn	Cl	P(1)	P(2)	O(12)	O(22)	C(120)	C(220)
0.01	0.00	0.00	0.00	-0.11	0.07	-0.13	0.06

^a The equation of the plane is of the form $Ax + By + Cz = D$, where A , B , and C are direction cosines, x , y , and z are orthogonalized coordinates, and D is in Å.

Table VII. Torsion Angles (deg)

Cl-Mn-P(1)-O(12)	176	C(11)-P(1)-P(2)-C(21)	-123
Cl-Mn-P(2)-O(22)	177	P(2)-P(1)-O(12)-C(120)	180
O(12)-P(1)-P(2)-O(22)	-7	P(1)-P(2)-O(22)-C(220)	179

ometry arrived at represents the compromise of lowest energy. Similar effects have been found in $P(CH_3)_2C_6H_5$ ligands.¹¹

The atoms of the $\{Mn(NO)_2Cl\}$ grouping are coplanar within 0.02 Å (see Table VI) and the NO groups are bent toward each other. The N-Mn-N angle is 111.5° and the two N-Mn-Cl angles are similar: 123.9, 124.6°. The geometry in the equatorial plane thus differs significantly from that in the trigonal-bipyramidal compound $[CoCl_2(NO)\{PCH_3(C_6H_5)_2\}_2]$ ¹² where the analogous angles are Cl-Co-Cl = 108.4° and Cl-Co-N = 134.3, 117.3°—a difference of 17°.

The two Mn-P bond lengths are effectively identical (2.291, 2.294 Å) and considerably shorter than the Mn-Cl bond length of 2.351 Å. A similar but smaller difference was also found in $[CoCl_2(NO)\{PCH_3(C_6H_5)_2\}_2]$ ¹² where the Co-P distances (2.254, 2.257 Å) were shorter than the Co-Cl distances (2.289, 2.264 Å). The Mn-P distances for the trans pair of $P(C_6H_5)_3$ ligands in $[Mn(NO)(CO)_2\{P(C_6H_5)_3\}_2]$ ¹³ were 2.278 and 2.279 Å, significantly shorter than the bond lengths now found for the phosphonite ligands. This difference is caused by the differences between the electronic character of the groups attached to the P atoms.

Exactly analogous differences have been found in the six-coordinate compounds $[Cr(CO)_5PR_3]$, where $R = C_6H_5$ and OC_6H_5 ,¹⁴ Cr-P was 2.422 Å for $R = C_6H_5$ and 2.309 Å for $R = OC_6H_5$. It is not clear whether the M-P bond lengths for a trans pair of phosphine ligands should be shorter than, equal to, or longer than the M-P distance when only one phosphine is bonded to the metal. Both extremes have been

Table VIII. Amplitudes of Vibration (Å) for Thermal Ellipsoids

	min	intermed	max
Mn	0.12	0.17	0.17
Cl	0.17	0.20	0.25
P(1)	0.15	0.20	0.20
P(2)	0.14	0.18	0.18
N(1)	0.17	0.20	0.28
N(2)	0.18	0.20	0.26
O(1)	0.18	0.26	0.37
O(2)	0.20	0.25	0.34

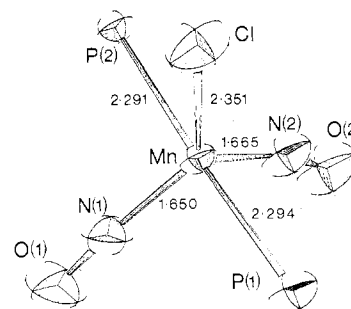


Figure 2. The $\{MnClP_2(NO)_2\}$ unit, oriented to show the relative size and orientation of the thermal ellipsoids. Note that the maximum amplitude of vibration of the Cl atom is in the plane $\{Mn(NO)_2Cl\}$.

found. In the five-coordinate complex $[Mn(NO)(CO)_3P(C_6H_5)_3]$,¹⁵ Mn-P is 2.305 Å, longer than in the trans diaxial compound.¹³ Similarly Cr-P in *trans*- $[Cr(CO)_4\{P(OC_6H_5)_3\}_2]$ ¹⁶ is 2.252 Å, shorter than Cr-P in the mono-substituted analogue.¹⁴ On the other hand, the trans pair of Ru-P bonds in both $[Ru(O_2CCH_3)\{P(CH_3)_2C_6H_5\}_4]^+$ ¹⁷ and $[Ru(S_2CH)\{P(CH_3)_2C_6H_5\}_4]^+$ ¹⁸ are considerably longer than the cis equatorial pair (2.42, 2.43 and 2.30, 2.31 Å; 2.42, 2.43 and 2.34, 2.36 Å, respectively) and the unique Ru-P bond length in $[Ru\{S_2C(H)P(CH_3)_2C_6H_5\}\{P(CH_3)_2C_6H_5\}_3]^+$ ¹⁸ is shorter than the two cis equatorial bonds (2.20 vs. 2.28, 2.31 Å).

The Mn-N lengths of 1.650 and 1.665 Å and the Mn-N-O angles of 163 and 166° are alike and similar to the analogous dimensions not only in $[CoCl_2(NO)\{P(CH_3)_2C_6H_5\}_2]$ but also in the tetrahedral compound $[Co(NO)_2(SacSac)]$.¹⁹ The O-Mn-O angle of 99.0° and the N-M-N angle fit nicely the correlation reported by Martin and Taylor.¹⁹ The NO bond lengths lie between the extremes of 1.12 and 1.23 Å found previously in nitrosyl complexes. It is important to note that the bond lengths have not been "corrected" for thermal motion, with the result that apparently large differences between these NO bond lengths and those reported for various other compounds can be meaningless. In fact, Brock et al.¹² state that their N-O distance "can be lengthened to 1.147 (7) Å by applying the correction for "riding motion" of Busing and Levy". Martin and Taylor¹⁹ find "the resulting, corrected N-O bond length is 1.208 Å". The increase in apparent bond length is close to 0.1 Å in both cases.

In their review,⁵ Enemark and Feltham discussed the case of five-coordinate dinitrosyl complexes and predicted correctly that the geometry here observed for the $\{Mn(NO)_2\}$ moiety should be found for 3d transition metals and good π -accepting ligands.

The deviation of the Mn-N-O groups from linearity is large, but they cannot be classed as "bent" in the generally accepted sense.^{3,4} Similar values for M-N-O angles have been found in several other cases: in $[Ir(NO)_2P(C_6H_5)_3]_2$,²⁰ Ir-N-O = 167°; in $[Ir(NO)_2\{P(C_6H_5)_3\}_2]^+$,²¹ Ir-N-O = 164°; in $[CoCl_2(NO)\{PCH_3(C_6H_5)_2\}_2]$,¹² Co-N-O = 164.5°; in $[Co(NO)_2(SacSac)]$,¹⁹ Co-N-O = 169°; in the series $[M(NO)(np_3)]^+$,²² M-N-O = 164, 165, and 168° for M = Fe, Co, and Ni, respectively. If meaningful comparisons are to

be made, it is essential that one has a measure of the accuracy of the Mn-N-O angles found in [Mn(NO)₂(P(OCH₃)₂C₆H₅)₂Cl]. The relative size, shape, and orientation of the thermal ellipsoids of the N and O atoms (Table VIII, Figure 2) show that the atoms are not disordered and that the thermal motion is physically reasonable; i.e., the ellipsoids of the O atoms are consistently larger than those of the N atoms, and the longest axes of the ellipsoids are perpendicular to the bonds while the shortest axes are parallel to the bonds. One may thus conclude that this particular deviation from linearity is real and not an artifact caused by either disorder or large thermal motion. However, the Mn-N-O groups in [Mn(NO)(CO)₃P(C₆H₅)₃], $\nu = 1712 \text{ cm}^{-1}$,^{2,4,15} and [Mn(NO)(CO)₂(P(C₆H₅)₃)₂], $\nu = 1662 \text{ cm}^{-1}$,^{2,4,13} were reported to be linear (between 178 and 180°). A close examination shows that the NO groups of these molecules are almost certainly disordered in the crystals. We suggest that the disorder in these two mononitrosyl complexes obscures the true Mn-N-O geometry and that the Mn-N-O groups in all of these compounds are similar in nature, i.e., nonlinear, with a Mn-N-O angle of about 165°.

The molecular parameters reported here for [Mn(N-O)₂(P(OCH₃)₂C₆H₅)₂Cl], while being generally similar to those found in the triclinic form,⁷ differ significantly in detail. A full paper describing the structure of this second polymorph has been submitted for publication in *Inorganic Chemistry*.

Acknowledgment. We thank Dr. G. Gafner (National Physical Research Laboratory, C.S.I.R.) for collecting the intensity data. Michael Laing thanks the South African Council for Scientific and Industrial Research for generous financial support.

Registry No. Mn(NO)₂(P(OCH₃)₂C₆H₅)₂Cl, 68366-07-4.

Supplementary Material Available: A listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) R. H. Reimann, Ph.D. Thesis, University of Natal, Durban, 1973; R. G. Copperthwaite, R. H. Reimann, and E. Singleton, *Inorg. Chim. Acta*, **28**, 107 (1978).
- (2) W. Beck and K. Lottes, *Chem. Ber.*, **98**, 2657 (1965).
- (3) B. A. Frenz and J. A. Ibers, *MTP Int. Rev. Sci.: Phys. Chem., Ser. One*, **1972**, **11**, 57-67 (1972).
- (4) J. A. McGinnety, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One*, **1972**, **5**, 245-259 (1972).
- (5) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974).
- (6) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **11**, 1088 (1972).
- (7) M. Laing, R. Reimann, and E. Singleton, *Inorg. Nucl. Chem. Lett.*, **10**, 557 (1974). The values of a , $\sigma(a)$, and $\sigma(\beta)$ quoted in this note must be revised to the values given above.
- (8) M. Laing, *Acta Crystallogr., Sect. B*, **28**, 986 (1972).
- (9) "International Tables for X-ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, pp 202, 203, 210, 215.
- (10) Supplementary material.
- (11) (a) M. Laing, *Acta Crystallogr., Sect. B*, **34**, 2100 (1978). (b) T. V. Ashworth, M. J. Nolte, E. Singleton, and M. Laing, *J. Chem. Soc., Dalton Trans.*, 1816 (1977).
- (12) C. P. Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester, and C. A. Reed, *Inorg. Chem.*, **12**, 1304 (1973).
- (13) J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **6**, 1575 (1967).
- (14) H. J. Plastas, J. M. Stewart, and S. O. Grim, *Inorg. Chem.*, **12**, 265 (1973).
- (15) J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **7**, 2339 (1968).
- (16) H. S. Preston, J. M. Stewart, H. J. Plastas, and S. O. Grim, *Inorg. Chem.*, **11**, 161 (1972).
- (17) T. V. Ashworth, M. J. Nolte, and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 2184 (1976).
- (18) T. V. Ashworth, E. Singleton, and M. Laing, *J. Chem. Soc., Chem. Commun.*, 875 (1976).
- (19) R. L. Martin and D. Taylor, *Inorg. Chem.*, **15**, 2970 (1976).
- (20) M. Angoletta, G. Ciano, M. Manassero, and M. Sansoni, *J. Chem. Soc., Chem. Commun.*, 789 (1973).
- (21) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **9**, 1105 (1970).
- (22) M. DiVaira, C. A. Ghilardi, and L. Sacconi, *Inorg. Chem.*, **15**, 1555 (1976).

Contribution from the Departments of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, and Rutgers, The State University of New Jersey, Newark, New Jersey 07102

Molecular Structures of the Copper-Amino Acid Complexes Bis(L-leucinato)copper(II) and Bis(D,L-2-aminobutyrate)copper(II)

TIMOTHY G. FAWCETT,^{1a} MICHAEL USHAY,^{1a} JOHN P. ROSE,^{1b} ROGER A. LALANCETTE,^{1b} JOSEPH A. POTENZA,^{*1a} and HARVEY J. SCHUGAR^{*1a}

Received August 18, 1978

The crystal structures of the title complexes, Cu(L-leu)₂ and Cu(D,L-but)₂, have been determined by single-crystal three-dimensional X-ray techniques. Crystal data for the two complexes are as follows. Cu(L-leu)₂, Cu(H₂NCH(CO₂)CH₂CH(CH₃)₂)₂: space group *P2*₁; $a = 9.725$ (4), $b = 5.127$ (1), $c = 14.689$ (6) Å; $\beta = 105.79$ (3)°; $d_{\text{obsd}} = 1.532$ (5), $d_{\text{calcd}} = 1.525 \text{ g/cm}^3$; $Z = 2$. Cu(D,L-but)₂, Cu(H₂NCH(CO₂)CH₂CH₃)₂: space group *P2*₁/*c*; $a = 11.138$ (6), $b = 5.066$ (1), $c = 9.487$ (6) Å; $\beta = 92.15$ (6)°; $d_{\text{obsd}} = 1.66$ (2), $d_{\text{calcd}} = 1.662 \text{ g/cm}^3$; $Z = 2$. Full-matrix least-squares refinement of 1683 and 1552 reflections with $F^2 \geq 3\sigma(F^2)$ gave final values for R_F of 0.032 and 0.037 for Cu(L-leu)₂ and Cu(D,L-but)₂, respectively. Both structures consist of tetragonally coordinated Cu(II) ions arranged in isolated sheets. Equatorial N₂O₂ ligation is provided by trans coordination of two amino acids, while axial Cu-O ligation by two neighboring amino acids completes the metal coordination and links the CuL₂ units to form carboxylate-bridged sheets of Cu(II) ions. Intermolecular N-H...O hydrogen bonds further link the CuL₂ units within each sheet. Coordination of the polar ends of the amino acids with Cu(II) allows the nonpolar side chains to align, creating hydrophobic regions which are slightly different in both structures. Bond distances and angles within the coordination spheres are typical, while C-C-C bond angles at the hydrophilic-hydrophobic juncture are ~6° larger than the remaining C-C-C angles. These large angles are attributed to modest steric strain between the carboxylate, amino, and alkyl groups attached to the α carbon atom. The structures are compared with those of their free amino acids and those of other Cu(II) amino acid complexes.

Introduction

For some time, we have been interested in the structural, spectroscopic, and magnetic properties of Cu(II) and Co(II) complexes,²⁻¹⁰ particularly those with sulfur-containing amino acid and amino acid derivative ligands. One goal of these studies has been to provide a series of well-characterized model

compounds which would lead to a better understanding of the absorption spectra of type 1 Cu(II) proteins such as stellacyanin and plastocyanin and their Co(II)-substituted counterparts.

While examining the structure⁹ of bis(L-methioninato)-copper(II), a strong similarity was noted between the structure