

Figure 4. Proton magnetic resonance shifts in  $\text{Mo}(\text{CO})_4$ -(*E*)-5'-Me-(paphy) and  $\text{Mo}(\text{CO})_4$ -(*E*)-paphy with respect to the free ligand; shifts in ppm positive for increasing  $\delta$ .

paphy, 5-Me(paphy), 5'-Me(paphy), and 5,5'-Me<sub>2</sub>paphy),<sup>26</sup> there is strong evidence to show that in solution the chelated ligand remains planar with the lone pair of N(4) directed toward the proton attached to C(10). The large downfield shift of the resonance of this proton on complex formation is consistent with electron drain to N(4) and the formation of a C-H...N hydrogen bond.

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**Registry No.** Tetraethylammonium chloropentacarbonylmolybdate(0), 14780-96-2; (*E*)-5-methylpyridine-2-carboxaldehyde-2'-pyridylhydrazonetetracarbonylmolybdenum(0), 50830-74-5.

**Supplementary Material Available.** A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W. Washington, D. C. 20036. Remit check or money order for \$5.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-1032.

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## Molecular Structure of Tri(cyclopentadienylmanganese) Tetranitrosyl

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The molecular structure of tri(cyclopentadienylmanganese) tetranitrosyl,  $(\eta^5\text{-C}_5\text{H}_5)_3\text{Mn}_3(\mu_3\text{-NO})(\mu_2\text{-NO})_3$ , has been determined using a Syntex PI X-ray diffractometer. The compound crystallizes in a monoclinic cell,  $a = 13.341$  (4),  $b = 7.951$  (2),  $c = 16.837$  (7) Å,  $\beta = 107.73$  (3)°; space group,  $P2_1/c$ ;  $Z = 4$ . Least-squares refinement using anisotropic thermal parameters and calculated hydrogen atom positions converged to  $wR = 0.012$  and  $R = 0.032$ . The molecular structure of  $C_{3v}$  symmetry consists of an equilateral triangle of metal atoms triply bridged by a nitrosyl above the metal plane and doubly bridged by three nitrosyls along the edges of the metal triangle below the plane. The cyclopentadienyl rings are located off the apices of the metal triangle. The average Mn-Mn bond length is 2.506 (3) Å. The NO bond length increases from doubly bridging,  $\mu_2\text{-NO}$ , 1.212 (6) to triply bridging nitrosyl,  $\mu_3\text{-NO}$ , 1.247 (5) Å.

### Introduction

Several years ago, a fragmentary account of the structure of tri(cyclopentadienylmanganese) tetranitrosyl,  $(\eta^5\text{-C}_5\text{H}_5)_3\text{Mn}_3(\mu_3\text{-NO})(\mu_2\text{-NO})_3$  was communicated,<sup>1</sup> describing a triangular metal atom cluster containing a triply bridging and three doubly bridging nitrosyl groups. The solution of the structure was complicated by an apparent disorder problem. Since that time, Professor Dahl and coworkers at the University of Wisconsin have investigated several analogous structures,<sup>2,3</sup> viz.,  $[(\eta^5\text{-C}_5\text{H}_5)_3\text{Mo}_3(\mu_3\text{-S})(\mu_2\text{-S})_3]^+ [\text{Sn}(\text{CH}_3)_3\text{Cl}_2]^-$ , in which the sulfur atoms of the cation replace the nitrosyl groups in the manganese compound, and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}]_2\text{Fe}(\text{CO})_3(\mu_3\text{-CO})_2$ , which contains two triply bridging carbonyl moieties, one above and one below the plane of the three metal atoms, and no doubly bridging carbonyls. In solving this structure using Patterson methods, Dr. Teo first found an apparent disorder analogous to that found for the manganese structure; however, a second, direct methods solution led to an ordered structure which was refined without subsequent difficulty. Therefore, Teo and Dahl suggested that perhaps the manganese structure was not truly dis-

ordered. On the basis of this suggestion, the data for the manganese compound have been recollected and the structure solved by direct methods without any evidence of disorder. Since no other triply bridging nitrosyl groups have been reported in the intervening period and due to the interesting nature of the compound its full structure is reported here.

### Experimental Section

**Preliminary Crystal Data.** Needle shaped crystals of  $(\eta^5\text{-C}_5\text{H}_5)_3\text{Mn}_3(\mu_3\text{-NO})(\mu_2\text{-NO})_3$  were selected from the material prepared by Dr. Schunn<sup>1</sup> of Du Pont and recrystallized several years ago. Most of these were twinned; however, one single crystal was obtained and used for both precession photographs and intensity measurements. This crystal which appeared black in reflected light was of approximate dimensions 0.1 × 0.1 × 0.3 mm. It was mounted on a glass fiber along the long dimension of the crystal. Preliminary precession photographs of  $hk0$ ,  $hk1$ ,  $hk2$ ,  $0kl$ , and  $1kl$  zones (using Cu K $\alpha$  radiation) showed systematic absences of  $h0l$  for  $l$  odd and  $0k0$  for  $k$  odd confirming the original choice of the space group as  $P2_1/c$ , No. 14.<sup>4</sup> The approximate cell constants were in agreement with those previously reported<sup>1</sup> ( $a = 13.34$ ,  $b = 7.95$ ,  $c = 16.82$  Å,  $\beta = 107.8^\circ$ ) and confirmed the identity of this crystal with the previously studied material. The crystal was placed on a Syntex PI automated diffractometer and optically centered for data collection. Fourteen reflections which were found on a rotation photograph were precisely centered using manufacturer supplied software.<sup>5</sup> Least-squares

(1) R. C. Elder, F. A. Cotton, and R. A. Schunn, *J. Amer. Chem. Soc.*, **89**, 3645 (1967).

(2) P. J. Vergamini, H. Vahrenkamp, and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 6327 (1971).

(3) B. K. Teo, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1973.

(4) "International Tables for X-Ray Crystallography," Vol. 1, 2nd ed, Kynoch Press, Birmingham, England, 1965.

(5) R. A. Sparks, et al., "Operations Manual Syntex PI Diffractometer," Syntex Analytical Instruments, Cupertino, Calif., 1970.

analysis of the  $2\theta$  values for these reflections gave the following cell constants and errors:  $a = 13.341$  (4),  $b = 7.951$  (2),  $c = 16.837$  (7) Å.  $\beta = 107.73$  (3)°. With  $Z = 4$ , the calculated density of  $1.87$  g cm $^{-3}$  agrees with the measured density of  $1.88$  (5) g cm $^{-3}$ .

**Collection and Reduction of Intensity Data.** These data were collected using Mo  $K\alpha$  radiation ( $\lambda$  0.71069 Å) with a graphite single crystal as monochromator. All measurements were made at  $21 \pm 2^\circ$ . A  $\theta$ - $2\theta$  scan mode was used with  $2\theta$  ranging from  $1^\circ$  below the calculated position for the  $K\alpha_1$  reflection to  $1^\circ$  above the calculated position for the  $K\alpha_2$  reflection. The scan rate was varied from 0.5 to  $24^\circ$  per minute depending on the intensity of the reflection. Backgrounds were measured in the normal fashion<sup>6</sup> and all other machine parameters have been previously described.<sup>6</sup> Four reflections were used as standards and remeasured periodically. They varied less than 2% throughout data collection. A total of 1520 reflections were measured with  $2\theta \leq 38^\circ$  from which the 1338 unique reflections were obtained by averaging.<sup>7</sup>

The linear absorption coefficient,  $\mu$ , of the compound for Mo  $K\alpha$  radiation is  $23.4$  cm $^{-1}$ . Minimum and maximum path lengths through the crystal were estimated to be 0.10 and 0.15 mm, respectively, under the conditions of data collection. Since the crystal was accidentally destroyed after the reflections were measured and before its accurate physical dimensions could be measured, no absorption corrections were possible. However, it appears that the maximum relative error in  $F_o$  due to absorption is less than 8%, and the error introduced by uncorrected absorption is expected to be insignificant.

The set of unique, normalized integrated intensities was processed<sup>8</sup> to give values of  $|F|$  and  $|E|$ .

**Structure Solution and Refinement.** An inspection of the  $\Sigma_2$  statistical relationships among the largest 100  $|E|$  values showed the signs of four reflections to be positive (0, 6, 0,  $E = 2.96$ , P6; 10, 0, 0,  $E = 2.80$ , P13; 0, 4, 0,  $E = 2.33$ , P40, and 2, 0, -14,  $E = 1.95$ , P92, where P6 indicates the reflection had the sixth largest  $|E|$  value) with a probability of greater than 0.99. Two reflections (2, 5, 7,  $E = 3.35$ , P2 and 1, 5, -1,  $E = 3.12$ , P3) could be given positive signs to determine the origin. At this point the program PHASE in the Stewart<sup>7</sup> package indicated that if two more reflections (4, 0, -14,  $E = 3.60$ , P1 and 3, 0, -12,  $E = 3.12$ , P4) were arbitrarily given signs, that the signs of the largest 40  $|E|$  values could all be determined. Three nontrivial combinations were used (No. 1, P1 = -, P4 = -; No. 2, P1 = -, P4 = +, and No. 3, P1 = +, P4 = -) to calculate signs for 153 of the 188 reflections with  $|E|$  values greater than 1.5 and to calculate  $E$  maps based on these possibilities. Map 1 contained an irregular triangular array composed of peaks 1, 2, and 4 in order of decreasing height. The distances were 2.85, 2.52, and 2.54 Å. Map 2 contained a nearly equilateral triangle using peaks 1, 2, and 3. The distances were 2.44, 2.55, and 2.55 Å. The lowest of the three peaks was approximately twice the height of the next peak. Map 3 contained no triangular array of strong peaks. Thus, the peak positions from map 2 were chosen as manganese atoms and used to calculate signs for a subsequent Fourier based on all reflections. The nitrogen and oxygen atom positions were evident from this map. A cycle of least-squares refinement of manganese atom positions with fixed isotropic temperature factors and fixed parameters for all nitrogen and oxygen atoms gave a conventional residual,  $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.28$ . The resulting Fourier indicated the positions of the 15 carbon atoms. Inclusion of these atoms and a cycle of positional refinement gave  $R_1 = 0.19$ . Refinement of positional and isotropic thermal parameters for all included atoms yielded  $R_1 = 0.12$ . Further refinement using anisotropic thermal parameters lead to  $R_1 = 0.063$ , using unit weights. The hydrogen atoms were included at their calculated<sup>9</sup> positions (C-H = 1.07 Å)<sup>9</sup> with arbitrarily assigned isotropic thermal parameters (4.0 Å<sup>2</sup>), and refinement continued using the weighting scheme of Corfield,

(6) R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *Inorg. Chem.*, **12**, 2690 (1973).

(7) All computations were carried out using a local version of XRAY67, J. M. Stewart, University of Maryland, crystallographic computer system.

(8) The subprogram LOADAT has been modified to include an atom positioning function. This is run after every cycle of least squares to reposition the fixed hydrogen atoms.

(9) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973), comments that the X-H distances used here were undoubtedly too long; note, however, that the spherically symmetric floated scattering curves [R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965)] used here attempt to compensate for the discrepancy between the position of the centroid of electron density about the hydrogen atom and the nuclear position, and the error introduced is likely to be insignificant.

Table I. Fractional Atomic Positional Parameters<sup>a,b</sup>

Atom	x	y	z
Mn(1)	0.19407 (5)	0.01021 (8)	0.22466 (4)
Mn(2)	0.18938 (5)	0.00899 (8)	0.37210 (4)
Mn(3)	0.31776 (5)	0.19423 (8)	0.33147 (4)
O(1)	0.1935 (2)	0.3531 (4)	0.4208 (2)
O(2)	0.2016 (3)	0.3549 (4)	0.1789 (2)
O(3)	-0.0079 (3)	0.0590 (4)	0.2469 (2)
O(4)	0.3681 (3)	-0.1625 (4)	0.3441 (2)
N(1)	0.2184 (3)	0.2369 (5)	0.3844 (2)
N(2)	0.2227 (3)	0.2388 (4)	0.2274 (2)
N(3)	0.0874 (3)	0.0429 (4)	0.2714 (2)
N(4)	0.3010 (3)	-0.0481 (5)	0.3273 (2)
C(11)	0.1694 (9)	-0.2339 (7)	0.1661 (4)
C(12)	0.0868 (5)	-0.1333 (14)	0.1270 (5)
C(13)	0.1216 (10)	-0.0060 (10)	0.0919 (4)
C(14)	0.2279 (10)	-0.0208 (13)	0.1088 (6)
C(15)	0.2582 (6)	-0.1669 (13)	0.1570 (4)
C(21)	0.1584 (6)	-0.2381 (7)	0.4147 (3)
C(22)	0.2494 (5)	-0.1756 (8)	0.4707 (3)
C(23)	0.2255 (6)	-0.0343 (9)	0.5038 (3)
C(24)	0.1186 (7)	0.0008 (7)	0.4715 (5)
C(25)	0.0753 (4)	-0.1290 (9)	0.4132 (4)
C(31)	0.4856 (4)	0.1629 (8)	0.3642 (9)
C(32)	0.4515 (7)	0.2774 (21)	0.2975 (5)
C(33)	0.4117 (7)	0.4106 (15)	0.3311 (11)
C(34)	0.4197 (7)	0.3803 (18)	0.4070 (11)
C(35)	0.4634 (7)	0.2339 (18)	0.4294 (4)
H(11)	0.1648 <sup>c</sup>	-0.3486	0.1992
H(12)	0.0060	-0.1537	0.1248
H(13)	0.0735	0.0932	0.0557
H(14)	0.2791	0.0637	0.0890
H(15)	0.3370	-0.2161	0.1818
H(21)	0.1524	-0.3517	0.3783
H(22)	0.3266	-0.2315	0.4851
H(23)	0.2814	0.0422	0.5495
H(24)	0.0769	0.1056	0.4874
H(25)	-0.0057	-0.1413	0.3751
H(31)	0.5223	0.0421	0.3632
H(32)	0.4554	0.2640	0.2347
H(33)	0.3788	0.5239	0.2979
H(34)	0.3938	0.4641	0.4473
H(35)	0.4793	0.1786	0.4906

<sup>a</sup> The estimated errors in the last digit are given in parentheses. This form is used throughout. <sup>b</sup> The numbering scheme for non-hydrogen atoms is given in Figure 1. The hydrogen atoms are given the number of the carbon atom to which they are bound. <sup>c</sup> These are calculated positions and thus have no errors.

*et al.*<sup>10</sup> Convergence was reached with  $wR = R_2 = \{\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2\}^{1/2} = 0.012$  and  $R_1 = 0.032$ . All parameter shifts were less than two-tenths of their estimated errors in the final cycle of refinement. The scattering curves were those of Cromer<sup>11</sup> for Mn, O, N and C and those of Stewart<sup>9</sup> for H. The Mn curve was corrected for anomalous dispersion<sup>12</sup> using  $\Delta f' = 0.4$  and  $\Delta f'' = 0.9$ .

## Results and Discussion

**Refinement and Disorder Problems.** Although the successful refinement of these data to  $R_2 = 0.012$  and  $R_1 = 0.032$  indicated no serious disorder was present in the sample crystal, two comments are necessary. First, the structure is of more limited accuracy than might be expected (see below) since only 1338 unique reflections were obtained before loss of the crystal and 234 parameters were varied in the final cycle of refinement for a low ratio of data points to variables of 4. Second, none of the three maps computed here showed any evidence of the previously found disorder. Since the original data<sup>1</sup> which indicate the disorder had been inadvertently discarded, a detailed comparison of data is not

(10) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967); the value of  $p$  was set to 0.02.

(11) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(12) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 215.

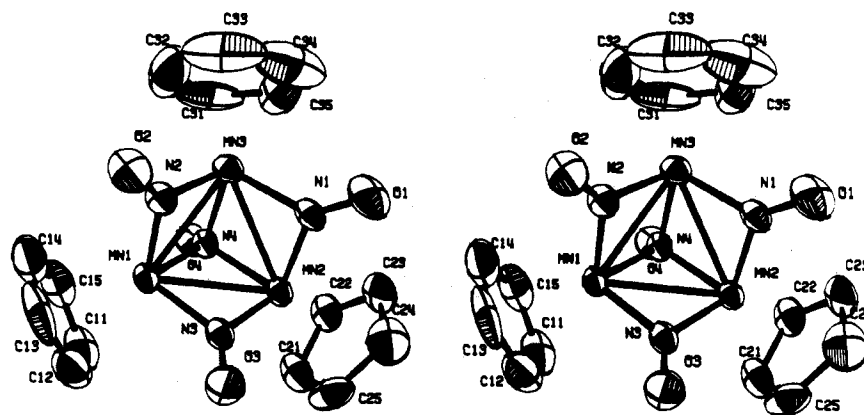


Figure 1. Stereoscopic view of tri(cyclopentadienylmanganese) tetranitrosyl with 50% probability ellipsoids.

Table II. Anisotropic<sup>a</sup> Thermal Parameters

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
			$\times 10^4$			
Mn(1)	358 (5)	234 (5)	183 (4)	6 (3)	100 (4)	-13 (3)
Mn(2)	328 (5)	237 (5)	184 (4)	-16 (3)	93 (4)	13 (3)
Mn(3)	332 (5)	233 (5)	292 (4)	-32 (4)	100 (3)	1 (3)
O(1)	795 (27)	263 (23)	548 (23)	31 (20)	322 (20)	-182 (18)
O(2)	799 (27)	272 (22)	418 (22)	54 (21)	96 (20)	262 (18)
O(3)	311 (23)	767 (30)	406 (21)	97 (21)	65 (18)	36 (20)
O(4)	443 (21)	300 (20)	428 (20)	141 (19)	142 (17)	16 (18)
N(1)	413 (25)	204 (23)	246 (22)	-9 (21)	67 (19)	-37 (19)
N(2)	378 (25)	306 (25)	309 (25)	-3 (22)	152 (21)	-59 (21)
N(3)	340 (27)	275 (26)	229 (23)	25 (22)	76 (22)	14 (18)
N(4)	377 (25)	204 (24)	210 (23)	42 (23)	114 (20)	51 (19)
			$\times 10^3$			
C(11)	122 (7)	26 (4)	45 (4)	-20 (5)	46 (5)	-138 (3)
C(12)	45 (4)	94 (6)	55 (5)	-10 (5)	11 (4)	-53 (4)
C(13)	158 (10)	57 (6)	18 (4)	26 (6)	-6 (5)	-6 (3)
C(14)	146 (8)	88 (7)	48 (5)	-79 (7)	72 (6)	-46 (5)
C(15)	59 (5)	90 (6)	46 (4)	30 (5)	13 (4)	-45 (4)
C(21)	84 (5)	33 (3)	26 (3)	-17 (4)	16 (4)	10 (3)
C(22)	63 (5)	36 (4)	26 (3)	8 (3)	14 (3)	16 (3)
C(23)	82 (6)	76 (6)	16 (3)	-40 (4)	10 (4)	4 (3)
C(24)	104 (6)	41 (4)	61 (5)	0 (4)	65 (5)	8 (4)
C(25)	33 (4)	75 (5)	53 (4)	-11 (4)	14 (3)	40 (4)
C(31)	21 (4)	42 (4)	166 (8)	-5 (3)	10 (5)	-11 (6)
C(32)	69 (6)	191 (11)	50 (5)	-77 (7)	31 (4)	-17 (7)
C(33)	68 (6)	67 (7)	183 (12)	-36 (6)	-18 (8)	75 (9)
C(34)	66 (7)	91 (9)	192 (12)	-32 (6)	34 (8)	-98 (8)
C(35)	61 (6)	158 (10)	36 (4)	-55 (6)	1 (4)	8 (6)

<sup>a</sup> The thermal parameters are of the form  $\exp[-2\pi^2(a^*U_{11}h^2 + b^*U_{22}k^2 + c^*U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$ .

possible. However, the disordered solution contained a pseudomirror plane perpendicular to  $x$  at  $a = 1/4$ , with the double weighted atom at  $a = 1/4$ . No possible manganese atom in any of the three maps was at  $a = 1/4$ . Two possibilities for the discrepancy are obvious, either the direct methods used<sup>13</sup> in the previous study resulted in such a different choice of signs for the reflections that there is no correspondence between the previous  $E$  map and those calculated here, or the crystal used in the first study was indeed disordered<sup>14</sup> and that used here was not. It may be useful to note that Patterson, superposition, and (in a sense) direct methods are an attempt to seek a vector solution to the structure and as such may lead to a partial solution in which fragments of the structure may appear quite reasonable.

**Description of Molecular Structure.** This is shown in a

(13) E. B. Fleischer, A. L. Stone, and R. B. K. Dewar, "MAGIC, Multiphase Automatic Generation of Intensities in Centric Crystals," program for the IBM7094 computer, University of Chicago, 1966.

(14) The possibility that the original crystal was an unrecognized twin seems unlikely as the normal twinning phenomena had been recognized and are clearly apparent on a first layer precession photograph.

Table III. Root Mean Square Amplitudes of Vibration, Å ( $\times 10^3$ )

Atom	Min	Mean	Max	Atom	Min	Mean	Max
Mn(1)	135	153	195	C(13)	130	237	424
Mn(2)	135	154	187	C(14)	192	274	407
Mn(3)	152	166	196	C(15)	190	230	335
O(1)	153	239	288	C(21)	152	184	303
O(2)	139	219	301	C(22)	146	201	259
O(3)	168	219	278	C(23)	126	244	323
O(4)	164	201	232	C(24)	199	239	322
N(1)	140	157	216	C(25)	180	204	303
N(2)	166	182	201	C(31)	143	206	426
N(3)	148	166	195	C(32)	222	246	450
N(4)	134	153	200	C(33)	218	259	484
C(11)	154	213	354	C(34)	232	295	472
C(12)	190	237	330	C(35)	180	252	409

stereodiagram<sup>15</sup> (Figure 1). The final atomic positional parameters and their estimated standard deviations are listed in Table I. The anisotropic thermal parameters for the non-hydrogen atoms are given in Table II. The root mean square

(15) C. K. Johnson, "A FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustration," ORTEPII, Report ORNL-3794, 2nd Revision, Oak Ridge National Laboratory, Oak Ridge Tenn., 1970. The ellipsoids are plotted at 50% probability.

Table IV. Bond Distances, Å

Mn(1)-Mn(2) 2.502 (1)	Metal-Metal Mn(1)-Mn(3) 2.508 (1) Av 2.506 (3) <sup>a</sup>	Mn(2)-Mn(3) 2.507 (1)
Mn(1)-N(4) 1.932 (3)	Metal-Nitrogen (Triple Bridge) Mn(2)-N(4) 1.917 (4) Av 1.929 (11)	Mn(3)-N(4) 1.938 (4)
Mn(1)-N(2) 1.855 (4) Mn(1)-N(3) 1.842 (4)	(Double Bridge) Mn(2)-N(3) 1.841 (3) Mn(2)-N(1) 1.851 (4) Av 1.848 (8)	Mn(3)-N(1) 1.840 (4) Mn(3)-N(2) 1.857 (3)
Mn(1)-RC(1) 1.812 <sup>b</sup>	Metal-Ring Mn(2)-RC(2) 1.812	Mn(3)-RC(3) 1.814
Mn(1)-C(11) 2.155 (6) Mn(1)-C(12) 2.149 (8) Mn(1)-C(13) 2.152 (6) Mn(1)-C(14) 2.145 (11) Mn(1)-C(15) 2.146 (9)	Metal-Carbon Mn(2)-C(21) 2.173 (6) Mn(2)-C(22) 2.176 (6) Mn(2)-C(23) 2.149 (6) Mn(2)-C(24) 2.158 (9) Mn(2)-C(25) 2.153 (7) Av 2.151 (12)	Mn(3)-C(31) 2.151 (5) Mn(3)-C(32) 2.137 (11) Mn(3)-C(33) 2.129 (12) Mn(3)-C(34) 2.145 (13) Mn(3)-C(35) 2.154 (7)
C(11)-C(12) 1.359 (12) C(12)-C(13) 1.324 (14) C(13)-C(14) 1.365 (19) C(14)-C(15) 1.403 (14) C(15)-C(11) 1.349 (14)	Carbon-Carbon C(21)-C(22) 1.382 (8) C(22)-C(23) 1.336 (10) C(23)-C(24) 1.391 (11) C(24)-C(25) 1.420 (9) C(25)-C(21) 1.401 (9) Av 1.363 (41)	C(31)-C(32) 1.409 (17) C(32)-C(33) 1.381 (20) C(33)-C(34) 1.273 (26) C(34)-C(35) 1.305 (18) C(35)-C(31) 1.346 (17)
N(1)-O(1) 1.210 (5)	Nitrogen-Oxygen (Double Bridge) N(2)-O(2) 1.207 (5) Av 1.212 (6)	N(3)-O(3) 1.218 (5)
	(Triple Bridge) N(4)-O(4) 1.247 (5)	

<sup>a</sup> See ref 17. <sup>b</sup> The symbol RC(1) refers to the centroid of ring 1.

amplitudes of vibration for these atoms are to be found in Table III, and their directions are shown in the figure. A table of observed and calculated structure factors is available.<sup>16</sup>

The structure consists of isolated molecules separated by normal van der Waals contacts. The five shortest intermolecular O-H distances are in the range 2.4-2.6 Å; three C-H contacts fall between 2.7 and 3.0 Å; one C-C contact (3.46 Å) is less than 3.5 Å; no H-H contacts are below 2.4 Å; and no N-H contacts are below 2.7 Å.

The molecules themselves have essentially  $C_{3v}$  symmetry as was originally proposed. They are based on an equilateral triangle of manganese atoms doubly bridged along the edges by three nitrosyl groups bent below the metal plane and a triply bridging NO group centered above the plane. The cyclopentadienyl groups are located off the apices of the metal triangle and inclined to accommodate the positions of the nitrosyls. The bond lengths appear in Table IV and the bond angles in Table V.

Dahl and coworkers<sup>2</sup> have commented that the metal-metal distances in this compound are expected to correspond nearly to single bond lengths. If each NO contributes three electrons, and each cyclopentadienyl ring donates five electrons, then the noble gas rule is satisfied by the formation of a single bond to each of the two adjacent manganese atoms. From a qualitative molecular orbital viewpoint, the three metal atoms in this  $C_{3v}$  molecule form 27 group orbitals ( $6a_1 + 3a_2 + 9e$ ) of which 18 ( $4a_1 + 2a_2 + 6e$ ) are used to bind the nitrosyl and cyclopentadienyl groups leaving nine metal group orbitals ( $2a_1 + a_2 + 3e$ ) for metal-metal inter-

actions and possible  $\pi$  bonding to the ligands. Four of the nine ( $2a_1 + e$ ) are expected to be bonding and five ( $a_2 + 2e$ ) to be antibonding. The 12 electrons available are expected to fill all four bonding orbitals and a doubly degenerate antibonding ( $e$ ) orbital. This gives a net of two bonding orbitals to bind the three manganese atoms (bond order, *i.e.*,  $2/3$ ) and predicts a somewhat longer than single bond distance between manganese atoms. The average<sup>17</sup> Mn-Mn distance found here is 2.506 (3) Å. The distance found in the  $[\text{Mo}_3(\eta^5\text{-C}_5\text{H}_5)_3(\mu_3\text{-S})(\mu_2\text{-S})_3]^+$  cation in several structures<sup>2,18</sup> for the Mo-Mo single bond is 2.81 Å. The difference in Mo and Mn radii in these compounds may be obtained from the metal-ring centroid distances of Mo 2.03 and Mn 1.81 Å, or  $\Delta = 0.22$  Å, which leads to a prediction of 2.37 Å for the Mn-Mn single bond. The increase found over the predicted value is in agreement with a bond order of less than one. The value of 2.506 (3) Å found here agrees much more closely with the Mn-Mn distance (2.526 ( $<10$ ) Å) found<sup>19</sup> in  $(\eta^5\text{-C}_5\text{H}_5)(\text{NO}_2)\text{Mn}(\mu\text{-NO})_2\text{Mn}(\text{NO})(\eta^5\text{-C}_5\text{H}_5)$  which by the noble gas rule is also expected to have a Mn-Mn single bond.

The cyclopentadienyl rings show considerable librational motion. This is evident in Figure 1 and also may be noted in the listing of their highly anisotropic vibrational amplitudes in Table III. The average C-C distances for each of the cyclo-

(17) The error in a mean value has been calculated to be either the largest of the individual esd or  $\sigma_{\bar{d}} = [\sum_{i=1}^n (d_i - \bar{d})^2 / (n-1)]^{1/2}$ , whichever is larger.

(18) The structure of this cation has been determined with several different anions and all show the same metal-metal distance, L. F. Dahl, private communication.

(19) J. L. Calderon, F. A. Cotton, B. G. DeBoer, and N. Martinez, *Chem. Commun.*, 1476 (1971).

(16) See paragraph on Supplementary Material Available.

Table V. Selected<sup>a,b</sup> Bond Angles, Degrees

Metal Angles		
Mn(1)-Mn(2)-Mn(3) 60.09 (3)	Mn(2)-Mn(3)-Mn(1) 59.86 (3)	Mn(3)-Mn(1)-Mn(2) 60.05 (3)
N(2)-Mn(1)-N(3) 91.8 (2)	N(1)-Mn(2)-N(3) 91.7 (2)	N(1)-Mn(3)-N(2) 92.1 (2)
N(2)-Mn(1)-N(4) 97.0 (1)	N(1)-Mn(2)-N(4) 96.6 (2)	N(1)-Mn(3)-N(4) 96.2 (2)
N(3)-Mn(1)-N(4) 96.2 (2)	N(3)-Mn(2)-N(4) 96.7 (2)	N(2)-Mn(3)-N(4) 96.7 (2)
RC(1)-Mn(1)-N(2) 121.6	RC(2)-Mn(2)-N(3) 122.2	RC(3)-Mn(3)-N(1) 121.1
RC(1)-Mn(1)-N(3) 121.1	RC(2)-Mn(2)-N(1) 121.8	RC(3)-Mn(3)-N(2) 121.7
RC(1)-Mn(1)-N(4) 122.1	RC(2)-Mn(2)-N(4) 120.8	RC(3)-Mn(3)-N(4) 122.0
Nitrogen Angles		
Mn(1)-N(2)-Mn(3) 85.0 (1)	Mn(2)-N(1)-Mn(3) 85.6 (2)	Mn(1)-N(3)-Mn(2) 85.6 (2)
Mn(1)-N(4)-Mn(2) 81.1 (1)	Mn(2)-N(4)-Mn(3) 81.1 (2)	Mn(1)-N(4)-Mn(3) 80.8 (2)
Mn(1)-N(4)-O(4) 131.4 (3)	Mn(2)-N(4)-O(4) 132.3 (3)	Mn(3)-N(4)-O(4) 130.5 (3)
Mn(1)-N(2)-O(2) 136.7 (3)	Mn(2)-N(3)-O(3) 136.9 (3)	Mn(3)-N(1)-O(1) 137.3 (3)
Mn(1)-N(3)-O(3) 137.1 (3)	Mn(2)-N(1)-O(1) 136.4 (3)	Mn(3)-N(2)-O(2) 137.4 (3)
Carbon Angles		
C(11)-C(12)-C(13) 108.9 (8)	C(21)-C(22)-C(23) 108.4 (6)	C(31)-C(32)-C(33) 103.9 (10)
C(12)-C(13)-C(14) 108.9 (8)	C(22)-C(23)-C(24) 110.6 (6)	C(32)-C(33)-C(34) 110.0 (11)
C(13)-C(14)-C(15) 106.9 (10)	C(23)-C(24)-C(25) 106.1 (6)	C(33)-C(34)-C(35) 110.6 (14)
C(14)-C(15)-C(11) 106.6 (8)	C(24)-C(25)-C(21) 106.5 (5)	C(34)-C(35)-C(31) 109.2 (11)
C(15)-C(11)-C(12) 108.8 (7)	C(25)-C(21)-C(22) 108.4 (5)	C(35)-C(31)-C(32) 106.3 (8)
Av 108.0 (12)	Av 108.0 (18)	Av 108.0 (28)

<sup>a</sup> No bond angles involving C-Mn-X are given. <sup>b</sup> The symbol RC(1) is used to designate the centroid of ring 1.

pentadienyl rings (R(1) 1.360 (29), R(2) 1.386 (31), R(3) 1.343 (55) Å) are far less than the accepted C-C value of 1.431 (5) found from an electron diffraction study of ferrocene.<sup>20</sup> This apparent contraction has been ascribed to the effect of librational motion by Wheatley.<sup>21</sup> This explanation is further reinforced by a comparison of the average maximum rms displacement for each of the rings with the average bond lengths (R3, av C-C, 1.34 Å, av max rms displacement, 0.44 Å; R1, 1.36, 0.37 Å; R2, 1.39, 0.30 Å), where the greatest shortening corresponds to the largest average vibrational amplitude. It should be noted that such a contraction may also result<sup>22</sup> from the refinement of a limited sphere of data, such as that used here. However, it appears that the librational motion is principally responsible for the contraction. The rings are found to be planar within experimental error as expected.<sup>21</sup> The equations of the least-squares planes through the rings and deviations of the atoms from these planes are given in Table VI. The ring angles for each ring average to 108.0°, the expected value for a plane pentagon. The distances of the ring centroids from the manganese atoms are RC(1)-Mn(1), 1.812 Å; RC(2)-Mn(2), 1.812 Å; RC(3)-Mn(3), 1.814 Å. These values fall in the range 1.794-1.820 Å found by other investigators<sup>23-27</sup> for RC-Mn distances. Each ring is essentially perpendicular to the line between the ring centroid and the bound manganese atom. Thus, RC(1)-Mn(1)-RN(1), 0.7°; RC(2)-Mn(2)-RN(2), 1.1°; RC(3)-Mn(3)-RN(3), 1.4°, where RN(1) indicates the normal to ring 1. The rings are, however, inclined with respect to the plane of the manganese atoms rather than perpendicular to it. Thus, the angles between the ring normals and their projections on the metal plane are 16.5, 17.4, and 16.8° for rings 1, 2, and 3, respectively.

Similarly, the doubly bridging nitrosyl groups are inclined on the opposite side of the metal plane. The angles between

Table VI. Least-Squares Planes

Atom	Dev <sup>a</sup>	Atom	Dev	Atom	Dev
Ring 1					
C(11)	-0.006	C(12)	0.006	C(13)	-0.003
C(14)	-0.001	C(15)	0.005		
Ring 2					
C(21)	0.005	C(22)	-0.001	C(23)	-0.004
C(24)	0.006	C(25)	-0.007		
Ring 3					
C(31)	0.002	C(32)	-0.003	C(33)	0.003
C(34)	-0.002	C(35)	-0.001		
Equations of Planes					
Ring 1: $-1.630x + 4.249y + 14.04z = 1.069$					
Ring 2: $-5.691x - 4.245y + 13.89z = 5.866$					
Ring 3: $11.44x + 3.428y + 0.1106z = 6.150$					

<sup>a</sup> These are the deviations of the atoms in angstroms from the calculated plane.

the line through the nitrosyl and its projection on the metal plane are 47.0, 46.2, and 48.5° for groups 1, 2, and 3, respectively. This results in a remarkably symmetric disposition of all the nitrosyls (both doubly and triply bridging) with respect to the cyclopentadienyl rings. Thus, the RC-Mn-N( $\mu_2$ ) angles average 121.6° (range 121.1-121.8°), the same value as the RC-Mn-N( $\mu_3$ ) angles, 121.6° (range 120.8-122.1°).

In their original report<sup>28</sup> of the synthesis of ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>-Mn<sub>3</sub>(NO)<sub>4</sub>, King and Bisnette were led to postulate the presence of doubly and triply bridging nitrosyl groups due to the appearance of three NO stretching bands at ~1530, ~1480, and ~1320 cm<sup>-1</sup>. These bands can be assigned to the A<sub>1</sub> and E modes of the doubly bridging NO (1480 and 1530 cm<sup>-1</sup>) and to the A<sub>1</sub> mode of the triply bridging NO (1320 cm<sup>-1</sup>). It might be expected that the lowering of stretching frequency on going from terminal to doubly bridging to triply bridging nitrosyls would be reflected in inverse changes in the NO bond length and indeed it is (see Table VII). It is difficult to assign a normal NO terminal bond length, since NO is known to bond<sup>29,30</sup> as NO<sup>-</sup> and NO<sup>+</sup>, and a cursory

- (20) R. K. Bohn and A. Hoaland, *J. Organometal. Chem.*, **5**, 470 (1966).  
 (21) P. J. Wheatley, *Perspect. Struct. Chem.*, **1**, 1 (1967).  
 (22) (a) D. M. Collins and J. L. Hoard, *J. Amer. Chem. Soc.*, **92**, 3761 (1970); (b) W. R. Scheidt, R. Countryman, and J. L. Hoard, *ibid.*, **93**, 3878 (1971).  
 (23) B. Granoff and R. A. Jacobson, *Inorg. Chem.*, **7**, 2328 (1968).  
 (24) M. R. Churchill and P. H. Bird, *Inorg. Chem.*, **7**, 1793 (1968).  
 (25) A. F. Bennet and R. E. Marsh, *Acta Crystallogr.*, **16**, 118 (1963).  
 (26) E. Hadicke and W. Hoppe, *Acta Crystallogr., Sect. B*, **27**, 760 (1971).  
 (27) R. F. Bryan and H. P. Weber, *J. Chem. Soc. A*, 843 (1968).  
 (28) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964).  
 (29) D. A. Snyder and D. L. Weaver, *Inorg. Chem.*, **9**, 2760 (1970).  
 (30) C. G. Pierpoint and R. Eisenberg, *Inorg. Chem.*, **11**, 1088 (1972).

Table VII

Bond type	$\bar{\nu}$ , cm <sup>-1</sup>	Bond length, Å	
		$\bar{A}_v$	Range
Linear terminal	1850–1650 <sup>a</sup>	1.19	1.12–1.23 <sup>b</sup>
Doubly bridging			
Ru <sub>3</sub> (CO) <sub>10</sub> (NO) <sub>2</sub>	1503–1475 <sup>c</sup>	1.22	1.20–1.24
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Mn <sub>2</sub> (NO <sub>2</sub> )(NO) <sub>3</sub>		1.205 <sup>d</sup>	
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> Mn <sub>3</sub> (NO) <sub>4</sub>	1530–1480 <sup>e</sup>	1.212	1.207–1.218
Triply bridging			
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> Mn <sub>3</sub> (NO) <sub>4</sub>	1320 <sup>e</sup>	1.247	

<sup>a</sup> B. F. G. Johnson and J. A. McCleverty, *Progr. Inorg. Chem.*, **7**, 277 (1966). <sup>b</sup> See ref 19, 30–37. <sup>c</sup> See ref 40. <sup>d</sup> See ref 19. <sup>e</sup> This work.

survey<sup>19,30–37</sup> of the literature shows a wide range of NO distances. However, the average, 1.19 Å, appears to be a reasonable value.<sup>38</sup> At least four crystal structures<sup>19,39,40</sup>

(31) M. A. Busch, G. Sim, G. A. Knox, and C. G. Robertson, *Chem. Commun.*, **74** (1969).

(32) D. M. P. Mingos and J. A. Ibers, *Inorg. Chem.*, **10**, 1479 (1971).

(33) C. P. Brock and J. A. Ibers, *Inorg. Chem.*, **11**, 2812 (1972).

(34) J. H. Enemark, *Inorg. Chem.*, **10**, 1952 (1971).

(35) J. H. Enemark, M. S. Quimby, L. L. Reed, M. J. Steuck, and K. K. Walthers, *Inorg. Chem.*, **9**, 2397 (1970).

(36) R. Eisenberg, A. P. Gaughan, Jr., C. G. Pierpoint, J. Reed, and A. J. Schultz, *J. Amer. Chem. Soc.*, **94**, 6240 (1972).

(37) J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **7**, 2339 (1968).

(38) A referee has kindly pointed out a recent review (B. A. Frenz and J. A. Ibers in "MTP International Review of Science, Physical Chemistry Series One," Vol. 11, J. M. Robertson, Ed., Butterworths, London, 1972, Chapter 2) in which the average NO distance is given as 1.17 Å.

(39) L. Y. Y. Chan and F. W. B. Einstein, *Acta Crystallogr., Sect. B*, **26**, 1899 (1970). This structure suffers from at least two kinds of disorder and shows an extremely short doubly bridging NO distance of 1.121 (22) Å. This somewhat suspicious value has been omitted from Table VII.

(40) J. R. Norton, J. P. Collman, G. Dolcetti, and W. T. Robinson, *Inorg. Chem.*, **11**, 382 (1972).

are known to contain doubly bridging nitrosyls. The average value found here of 1.212 (6) Å for the doubly bridging NO bond falls in the range of those previously determined. The triply bridging nitrosyl (1.247 (5) Å) appears to be the only one reported and it has both the lowest infrared stretching frequency (1320 cm<sup>-1</sup>) and the longest NO bond length so far observed.

Fackler and Coucouvanis<sup>41</sup> have attempted to show a linear relationship between bond orders and the square of the associated stretching frequency for CO, CN, and NO, with considerable success in the first two cases. Following their methods, the doubly bridging bond order for NO is calculated to be 1.72 and that for triply bridging NO is 1.56. However, the predicted stretching frequencies (1675 and 1575 cm<sup>-1</sup>) are much too high<sup>42</sup> and the method fails for NO.

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**Registry No.** ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Mn<sub>3</sub>( $\mu_3$ -NO)( $\mu_2$ -NO)<sub>3</sub>, 12312-71-9.

**Supplementary Material Available.** A listing of the structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th 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-74-1037.

(41) J. P. Fackler and D. Coucouvanis, *Inorg. Chem.*, **7**, 181 (1968).

(42) Indeed, the two points generated here fall on the same line as two other cases [Fe(CO)<sub>2</sub>(NO)<sub>2</sub> and Co(NO)(CO)<sub>3</sub>] which were considered anomalous.

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## Structure of the Dimetallic Complex *catena*- $\mu$ -Chloro-dichloro- $\mu$ -[*N,N'*-bis[2-(2-pyridyl)ethyl]-2,3-pyrazinedicarboxamidato-*N,N,N',N',N',N'*]-dicopper

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The crystal structure of the complex Cu<sub>2</sub>LCl<sub>3</sub>, *catena*- $\mu$ -chloro-dichloro- $\mu$ -[*N,N'*-bis[2-(2-pyridyl)ethyl]-2,3-pyrazinedicarboxamidato-*N,N,N',N',N',N'*]-dicopper, was determined by a complete three-dimensional X-ray analysis. The structure of the compound is that of a bimetallic (two cupric ions) complex with both copper ions similarly bound by one of the pyrazine nitrogens, a deprotonated amide nitrogen, a pyridine nitrogen, and two chloride ions. The pseudo-trigonal-bipyramidal geometry is accomplished in the crystal by a chloride ion bridging between the complexes forming an infinite-chain structure in the solid. The crystal is in the space group *P2<sub>1</sub>/c* with four molecules per cell. The cell constants for the monoclinic system are *a* = 7.95 (1) Å, *b* = 27.00 (3) Å, *c* = 10.25 (1) Å, and  $\beta$  = 92.1 (1)<sup>o</sup>, and the observed density of 1.86 g/cm<sup>3</sup> agrees well with the calculated density of 1.85 g/cm<sup>3</sup>. The structure was refined by a least-squares technique with 1941 structure factor amplitudes collected on a diffractometer to an *R* factor of 4.2%. The temperature-dependent magnetic susceptibility was measured for the complex and is suggestive of a weak antiferromagnetic interaction in the system.

We have previously synthesized<sup>1</sup> the ligand *N,N'*-bis[2-(2-pyridyl)ethyl]-2,3-pyrazinedicarboxamide, Figure 1

(1) E. B. Fleischer and M. B. Lawson, *Inorg. Chem.*, **11**, 2772 (1972).

(hereafter abbreviated in the paper as L), and prepared some transition metal complexes of it. One of the complexes of interest is with cupric ion and has the formulation of Cu<sub>2</sub>LCl<sub>3</sub>. The stoichiometry with the three chlorides was interesting because it implied that one of the amide protons was lost