with the kinetic trans effect,[19] with which one hopes there is some correlation.

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The Crystal and Molecular Structure of Tris(1,10-phenanthroline)nickel(II) Pentacarbonylmanganate(−I), $[Ni(1,10\text{-}phen)_3][Mn(CO)_5]_2$

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The crystal structure of tris(1,10-phenanthroline)nickel(II) pentacarbonylmanganate(−I), $[Ni(phen)_3][Mn(CO)_5]_2$, has been determined from X-ray counter data collected at $-123 \pm 2°$. Discrete $Ni(phen)_3^{2+}$ cations and $Mn(CO)_5^-$ anions crystallize in space group $P\bar{1}$ with lattice constants $a = 13.618$ (5), $b = 14.325$ (5), $c = 12.399$ (8) Å, $\alpha = 102.16$ (4), $\beta = 113.22$ (4), $\gamma = 98.46$ (3)° at −121°. The observed density of 1.535 (10) g/cm³ at 25° agrees well with that of 1.546 g/cm³ calculated for two formula units in the cell found at −123°. The $Ni(phen)_3^{2+}$ cations show approximate threefold symmetry. The N–Ni–N bite averages 79.4 (5)°; the variations in N–C and C–C bond distances in the ring system are consistent with previous structures. The $Mn(CO)_5^-$ anions are trigonal bipyramidal with a small distortion most noticeable in the equatorial plane, where the C–Mn–C bond angles range from 117.5 (3) to 125.0 (4)°. The average of the axial Mn–C bonds is slightly, but not significantly, longer than the average of the equatorial bonds. The Mn–C bond lengths range from 1.77 (1) to 1.82 (1) Å; the difference in axial and equatorial bond averages is 0.02 (2) Å. This difference is considered together with other d^8 complexes having five identical ligands about the central metal atom.

Introduction

Although almost 200 structures[1] of monomeric five-coordinate transition metal complexes have been studied by X-ray diffraction, only a dozen of these are compounds with five identical unidentate ligands. Multidentate ligands often impose steric restrictions on the geometry of the complexes and it is difficult to separate these restrictions from electronic effects. For complexes with several different unidentate ligands, the various effects of the ligands cannot be readily distinguished unless a series of similar structures is studied, *e.g.*, $Mn(NO)(CO)_{4-x}[P(C_6H_5)_3]_x$, $x = 0\text{–}2$,[2-4] or the twelve structures of the form $IrXYZ[P(C_6H_5)_3]_2$.[1] A comparison of structures with five identical ligands is desirable because only a few factors need to be considered for interpreting distortions in bond angles and bond distances.

Most of the ML_5 structures are regular trigonal bipyramids, *viz.*, $CuCl_5^{3-}$,[5] $Fe(CO)_5$,[6] $Fe(N_3)_5^{2-}$,[7] $Ni[P(OCH)_3(CH_2)_3]_5^{2+}$,[8] $Co(C_6H_7NO)_5^{2-}$,[9] and $Co(CNCH_3)_5^+$.[10] The structures of $Nb[N(CH_3)_2]_5$,[11] $Nb(NC_5H_{10})_5$,[11] and $MnCl_5^{2-}$ [12] are better described as tetragonal pyramidal. Both trigonal-bipyramidal and tetragonal-pyramidal forms of $Ni(CN)_5^{3-}$ have been reported.[13-15] The structure of $Ni(OAsMe_3)_5^{2+}$ [16] is a tetragonal pyramid and those of $CdCl_5^{3-}$ [17] and $Pt(SnCl_3)_5^{3-}$ [18] are trigonal bipyramids, although structural details have not been published for these three complexes.

In most of the trigonal-bipyramidal complexes the axial M–L bond distances differ from the equatorial bond lengths. Such distortions were predicted[19] by Gillespie for low-spin d^7, d^8, and d^9 systems. Because the d_{z^2} orbital is empty or only half-filled, the shape of the d-shell electron cloud will be oblate ellipsoidal. Thus repulsions between nonbonding d electrons and valency-shell electrons will be greater in the equatorial plane and cause the equatorial bonds to be longer than the axial bonds. Acting in the opposite direction are ligand–ligand electrostatic repulsion forces which always favor axial lengthening.

For each of the d^8 and d^9 ML_5 structures studied thus

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far, the equatorial bond distance is greater than the axial bond distance. In an investigation[2] of the structure of $\mathrm{Mn(NO)(CO)_4}$ we found the reverse to be true; the axial Mn–C bonds of 1.886 (8) Å were 0.035 (12) Å longer than the equatorial bonds of 1.851 (8) Å. It was reasoned that this should also be the case for $\mathrm{Mn(CO)_5^-}$ for which no structural data were available. In fact, in the isoelectronic series $\mathrm{Ni^{II}L_5}$, $\mathrm{Co^{I}L_5}$, $\mathrm{Fe^{0}L_5}$, the difference in equatorial and axial bond lengths diminishes with decreasing charge on the central metal atom. Thus $\mathrm{Mn^{-I}}$ may well be the turning point and $\mathrm{Mn(CO)_5^-}$ could be the first example of a $\mathrm{d^8}$ $\mathrm{ML_5}$ complex with longer axial than equatorial bond lengths. For these reasons, a structural investigation of $\mathrm{Mn(CO)_5^-}$ was undertaken and is reported here.

Collection and Reduction of Intensity Data

A solution of $\mathrm{NaMn(CO)_5}$ was prepared from manganese carbonyl and sodium amalgam in THF.[20] Attempts were made to precipitate the anion with a variety of cations (*e.g.*, $\mathrm{N(C_2H_5)_4^+}$, $\mathrm{P(CH_3)(C_6H_5)_3^+}$, $\mathrm{As(C_6H_5)_4^+}$, and $\mathrm{Co(C_5H_5)_2^+}$). However, only with a dilute methanol solution of $\mathrm{Ni(phen)_3{}^{2+}SO_4{}^{2-}}$,[21] prepared from $\mathrm{NiSO_4}$ and 1,10-phenanthroline, were crystals obtained suitable for X-ray studies.

Dark red crystals, some measuring up to 7 mm in length, were grown overnight, filtered, and dried on a vacuum line. A series of precession photographs using Mo Kα and Cu Kα radiation revealed no symmetry elements; hence the triclinic space group $P\bar{1}$ was assigned to the crystal. Data were collected at 22° for a crystal measuring approximately 0.58 × 0.29 × 0.20 mm on a Picker four-circle automatic X-ray diffractometer. Five reflections representing diverse regions of reciprocal space were used as standards and their intensities were measured every 200 reflections as a check on electronic and crystal stability. After the intensities of approximately 2600 reflections were recorded, four of these standards showed virtually no change in intensity. However, the fifth standard, the 203 reflection, dropped rapidly in intensity after 500 reflections were measured and showed almost no intensity when data collection was terminated after 2626 reflections in the range $0° \leq 2\theta(\mathrm{Mo\ K}\alpha_1) \leq 35°$ had been collected.

The structure was solved and refined as described in the following section, but because of the unsatisfactory nature of the one reference reflection, we decided to re-collect the data at low temperature where it was hoped decomposition would be less severe. The cooling system used was an AC-1-101A Cryo-Tip refrigerator manufactured by Air Products and Chemicals, Inc. High-pressure nitrogen gas expands in a chamber located above the arcs of a modified eucentric goniometer mount. Cooling occurs as a result of the Joule–Thompson cycle. The crystal is cooled by conduction through the copper pin on which it is mounted. The crystal and its mount are covered by a beryllium shroud and the chamber is evacuated.

For the second data set a new batch of crystals was prepared as before. Because of imperfections in the smaller crystals, a large crystal was selected. Dimensions between parallel faces are as follows: 0.90, 0.88, 0.72, 0.69, 0.64, and 0.55 mm for faces $11\bar{1}$, $10\bar{1}$, $1\bar{1}0$, $01\bar{1}$, 010, and 100 and their corresponding Friedel pairs, respectively. The crystal was mounted with orange shellac in ethanol along its long direction. Using a narrow source and a wide-open counter, ω scans of several strong reflections showed a width at half-height of approximately 0.12°. At −121° nine reflections having 2θ values greater than 31.5° (Mo Kα) were centered on a Picker FACS-1 computer-controlled four-circle diffractometer equipped with a graphite crystal incident beam monochromator. Least-squares refinement of these setting angles gave the following unit cell parameters for λ 0.7093 Å: a = 13.618 (5), b = 14.325 (5), c = 12.399 (8) Å, α = 102.16 (4), β = 113.22 (4), γ = 98.46 (3)° at −121 ± 1°. As expected, these cell parameters are slightly smaller than those obtained for the first crystal at 22°: a = 13.66 (2), b = 14.39 (2), c = 12.44 (2) Å, α = 102.0 (1), β = 113.4 (1), γ = 98.5 (1)°. The calculated density at −121° is 1.546 g cm^{-1} for Z = 2, mol wt 989.32, and V = 2100.6 Å^3. This compares well with the density of 1.535 (10) g cm^{-3} measured by flotation in carbon tetrachloride–chloroform mixtures at room temperature. The calculated density at 22° is 1.53 g cm^{-3}.

The data were collected at −123 ± 2° by the θ–2θ scan technique at a scan rate of 2°/min using a symmetric scan range from $2\theta(\mathrm{Mo\ K}\alpha_1) - 1.0°$ to $2\theta(\mathrm{Mo\ K}\alpha_2) + 1.0°$. Stationary-crystal, stationary-counter background counts were taken for 4 sec at each end of the 2θ scan range. For the second shell of data, $30.01° \leq 2\theta \leq 36.10°$, the background time was increased to 10 sec. The counter was placed 31 cm from the crystal with the counter aperture wide open at 7 mm × 7 mm. The pulse height analyzer was adjusted to receive approximately 90% of the diffracted radiation. At the takeoff angle of 2.5° the peak intensity of a strong reflection was about 80% of the maximum value as a function of takeoff angle. Copper foil attenuators were inserted automatically if the diffracted beam intensity exceeded about 7000 counts/sec during the scan; the attenuator factors were approximately 2.2.

Five standard reflections were measured every 50 reflections. An increase of 2.8% in intensity of all the standards was observed after 970 reflections, possibly as a result of an electronic change of unknown origin. Intensities were constant both before and after the increase; therefore the intensities for the first 970 reflections were multiplied by 1.028. Without the correction the standard deviation of the intensity for each reference reflection was less than 3 times that expected on counting statistics alone.

A total of 2577 reflections were collected in the range $0° \leq 2\theta \leq 36.1°$. The number of reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$ was 2386. Data collection was terminated prematurely when the crystal fell from its mount and disappeared in the vacuum pump.

The data were processed in the usual manner.[22] The constant p used in the expression for $\sigma(F^2)$ was assigned a value of 0.04.

The linear absorption coefficient of the compound is 11.2 cm^{-1} for Mo Kα radiation. Because of this low value and because of the uniform shape of the crystal, the magnitude of the absorption correction[23] ranged only from 1.71 to 1.79 in preliminary calculations. Therefore an absorption correction was not applied to the data. The uniform cross section presented to the beam is presumably why a successful data set was obtained with such a large crystal.

Solution and Refinement

A sharpened three-dimensional Patterson function calculated[23] from the room-temperature data set revealed the positions of the nickel and the two manganese atoms. A cycle of least-squares refinement[23] of the scale factor and atomic coordinates was followed by a difference Fourier map.[23] Almost all of the remaining nonhydrogen atoms were located from this map. The positions of those few that were not observed were calculated by hand on the basis of the partial structure.

The least-squares refinements were carried out on F_o; the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and the weight w is $4F_o{}^2/\sigma^2(F_o{}^2)$. The atomic scattering factors for Mn and H were those calculated by Cromer and Waber[24] and by Stewart, Davidson, and Simpson,[25] respectively; scattering factors for Ni, O, N, and C were taken from the usual tabulation.[26] Anomalous dispersion effects for Ni and Mn were included in the calculation of F_c;[27] values calculated by Cromer[28] were used for $\Delta f'$ and $\Delta f''$.

In initial least-squares refinements the 1,10-phenanthroline (phen) ligands were refined as rigid groups with individual thermal

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[21] The following abbreviations are used: phen, 1,10-phenanthroline; Me$_2$phen, 2,9-dimethyl-1,10-phenanthroline.

[22] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

[23] In addition to various local programs, the following programs were used: Zalkin's FORDAP Fourier program; our local NUCLS least-squares program, which, in its nongroup form, closely resembles Busing and Levy's ORFLS program; Johnson's ORTEP plotting program; and Busing and Levy's ORFFE error function program. Our local absorption program, AGNOST, written by D. Cahen, is based on the numerical methods of Coppens, Leiserowitz, and Rabinovich and on the analytical methods of DeMeulenaer and Tompa.

[24] D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

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

[26] J. A. Ibers, "International Tables of X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, Table 3.3.1A.

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[28] D. T. Cromer, *ibid.*, **18**, 17 (1965).

TABLE I

POSITIONAL AND ANISOTROPIC THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS FOR Ni AND THE $Mn(CO)_5^-$ ANIONS

Atom	x	y	z	$10^4\beta_{11}$[a]	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ni	−0.12911 (7)	0.21060 (5)	0.18871 (7)	51.5 (11)	35.0 (7)	52.2 (11)	10.3 (6)	21.5 (7)	10.1 (6)
				Molecule 1					
Mn	0.79475 (10)	0.72646 (8)	0.12411 (10)	77.7 (14)	58.1 (9)	97.0 (15)	26.3 (8)	36.3 (11)	25.0 (8)
C(1)	0.6736 (9)	0.6653 (6)	−0.0235 (9)	101 (10)	72 (6)	118 (11)	37 (6)	63 (9)	29 (7)
C(2)	0.8432 (7)	0.6167 (7)	0.1144 (6)	86 (9)	63 (6)	73 (8)	24 (6)	36 (6)	22 (6)
C(3)	0.7059 (8)	0.7401 (6)	0.2008 (8)	72 (10)	67 (6)	100 (10)	29 (6)	33 (8)	22 (6)
C(4)	0.8383 (7)	0.8153 (7)	0.0578 (8)	76 (9)	83 (7)	157 (11)	42 (6)	32 (8)	55 (8)
C(5)	0.9128 (8)	0.7903 (6)	0.2690 (9)	79 (10)	58 (6)	142 (12)	18 (6)	49 (9)	31 (7)
O(1)	0.5976 (6)	0.6276 (5)	−0.1153 (6)	90 (7)	118 (5)	112 (7)	15 (5)	22 (6)	−7 (5)
O(2)	0.8742 (5)	0.5460 (4)	0.1084 (5)	110 (6)	65 (4)	133 (7)	48 (4)	58 (5)	29 (4)
O(3)	0.6489 (6)	0.7482 (4)	0.2488 (6)	98 (7)	106 (5)	135 (8)	38 (5)	70 (6)	20 (5)
O(4)	0.8696 (5)	0.8721 (6)	0.0172 (7)	115 (7)	139 (6)	283 (12)	61 (5)	100 (7)	152 (8)
O(5)	0.9884 (6)	0.8317 (4)	0.3627 (6)	118 (7)	83 (5)	132 (8)	−1 (5)	24 (6)	24 (5)
				Molecule 2					
Mn	0.35609 (9)	0.75076 (7)	0.39471 (9)	59.3 (12)	50.8 (13)	79.3 (14)	6.8 (7)	24.3 (10)	19.5 (8)
C(1)	0.4188 (7)	0.6531 (6)	0.3527 (7)	64 (9)	52 (6)	106 (9)	5 (6)	17 (7)	14 (6)
C(2)	0.4605 (8)	0.8426 (6)	0.3977 (7)	75 (9)	69 (6)	147 (10)	24 (6)	65 (8)	46 (7)
C(3)	0.3774 (6)	0.7194 (5)	0.5337 (8)	74 (8)	58 (5)	97 (10)	−3 (5)	23 (7)	27 (6)
C(4)	0.2310 (8)	0.6977 (5)	0.2534 (9)	66 (9)	52 (5)	121 (10)	8 (5)	28 (8)	30 (6)
C(5)	0.2922 (7)	0.8456 (7)	0.4376 (7)	68 (9)	70 (6)	72 (8)	12 (6)	29 (6)	19 (6)
O(1)	0.4568 (5)	0.5920 (5)	0.3270 (6)	109 (7)	67 (5)	205 (9)	40 (5)	45 (6)	0 (5)
O(2)	0.5287 (6)	0.9034 (5)	0.3998 (7)	127 (8)	95 (5)	296 (12)	29 (5)	136 (8)	81 (6)
O(3)	0.3922 (5)	0.7020 (4)	0.6254 (6)	102 (6)	100 (5)	102 (7)	−21 (4)	16 (5)	51 (5)
O(4)	0.1510 (5)	0.6665 (4)	0.1638 (6)	91 (7)	71 (4)	121 (7)	4 (4)	−15 (6)	20 (4)
O(5)	0.2508 (5)	0.9056 (5)	0.4636 (5)	110 (7)	96 (5)	120 (7)	53 (5)	58 (5)	33 (5)

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

parameters on the 14 atoms. In later refinements the phen atoms were refined individually with isotropic thermal parameters. The metal and carbonyl atoms were refined anisotropically. Because of the large number of variables (376) it was necessary to divide them into two blocks. One block, containing a scale factor, the nickel atom, and one $Mn(CO)_5$ molecule, was held constant while the second block, containing the scale factor, the second $Mn(CO)_5$ molecule, and the phen atoms, was refined. Then the process was reversed; block 2 was held constant while block 1 was refined. In a final set of refinements hydrogen atom contributions, based on their idealized positions on the phen rings, were added to the total structure factor. The final agreement factors for the room-temperature data set were

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.064$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.104$$

The second data set, collected at −123 ± 2°, was used in a least-squares refinement of all atoms (isotropic) with phen ligands refined as groups where the parameters were taken from the results of the first data set. Because of small errors in all of the atomic positions the structure would not refine and it was necessary to start with a smaller number of parameters. The initial least-squares refinement was on the Ni and Mn atomic positions; a second cycle included the carbonyl ligands; and finally the phen groups were added in succeeding refinements. with all nonhydrogen atoms included and the phen ligands refined as groups the R_1 and R_2 factors were 0.11 and 0.18, respectively.

Succeeding least-squares refinements were carried out by Professor K. N. Raymond and Mr. K. Hodgson at the University of California, Berkeley, Calif., on a CDC 7600. The larger capacity of this computer allowed full-matrix, least-squares refinement of 376 variables derived as follows: the nickel, manganese, and carbonyl atoms were refined anisotropically; the atoms of the phenanthroline ligands were refined individually with isotropic temperature factors; one scale factor was refined. The idealized positions of the hydrogen atoms on the phenanthroline ligands were included as fixed contributions to the structure factor. The C–H distance was taken as 1.0 Å, and each H atom was assigned an isotropic thermal parameter equal to that of the C atom to which it was attached. A secondary extinction correction was applied,[29] as suggested by an inspection of the data; the final coefficient was 1.5 (3) × 10^{-7} (in absolute units). The final discrepancy factors for 2387 data were $R_1 = 0.038$ and $R_2 = 0.065$. The error in an observation of unit weight is 2.99. Shifts on the final cycle were less than 1% of the estimated standard deviations.

Classes of reflections based on $|F_o|$, Miller indices, and $\lambda^{-1} \sin \theta$ were analyzed[23] for discrepancies in $\Sigma w(|F_o| - F_c|)^2$. No unexpected trends were shown; thus the weighting scheme is a reasonable one. A difference map based on the final parameters showed no significant features. The highest peak of 1.0 (1) e $Å^{-3}$ is *ca.* 25% of the height of the oxygen atoms in a previous map.

The positional and thermal parameters obtained from the last least-squares cycle are given in Tables I and II; standard deviations of the least significant figures are given in parentheses in the tables. Root-mean-square amplitudes of vibration for the atoms are given in Table III. The final values of $10|F_o|$ and $10|F_c|$ in electrons are available.[30] Not included in this table are the 190 reflections with $F_o^2 < 3\sigma(F_o^2)$. For these reflections, which were omitted from refinement, none had $|F_o^2 - F_c^2|/\sigma(F^2) > 3.6$.

Description and Discussion of the Structure

1. The Crystal Structure.—The crystal structure consists of well-separated $Ni(phen)_3^{2+}$ cations and $Mn(CO)_5^-$ anions. The closest approach between metal atoms is *ca.* 7 Å. There are no intermolecular distances less than 3.1 Å. The distance between the O(5) atoms of different $Mn(CO)_5^-$ anions is 3.203 (9) Å. Eleven O···C distances between carbonyl oxygen atoms and phen carbon atoms are in the range 3.176–3.461 Å. All other intermolecular distances are greater than 3.5 Å. A stereoscopic view of the contents of the unit cell is shown in Figure 1.

2. The Molecular Structure of $Ni(phen)_3^{2+}$.—The Λ isomer[31] of $Ni(phen)_3^{2+}$ is shown in Figure 2. Because of the crystallographic center of symmetry the Δ isomer is also in the unit cell (Figure 1). Bond

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[29] W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963).

[30] A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1109. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

[31] *Inorg. Chem.*, **9**, 1 (1970).

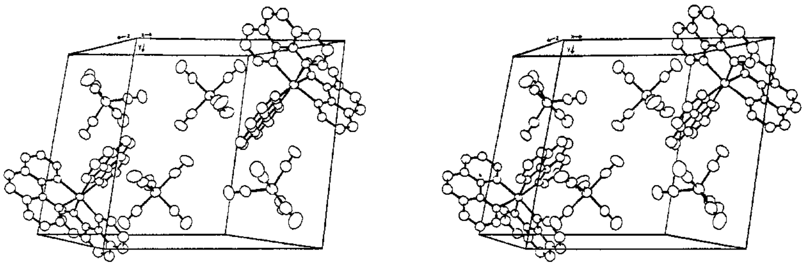

Figure 1.—A stereoscopic view of the unit cell of [Ni(phen)$_3$][Mn(CO)$_5$]$_2$.

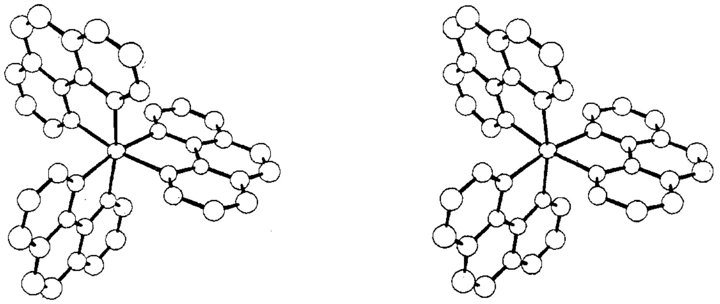

Figure 2.—A stereoscopic view of Ni(phen)$_3$$^{2+}$.

TABLE II
POSITIONAL AND ISOTROPIC THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS FOR 1,10-PHENANTHROLINE LIGANDS

Atom	*x*	*y*	*z*	*B*, Å^2
		phen 1		
N(1)	−0.2511 (4)	0.0974 (3)	0.1767 (4)	3.0 (1)
C(2)	−0.2870 (6)	0.0866 (5)	0.2603 (6)	4.0 (2)
C(3)	−0.3701 (6)	0.0036 (5)	0.2379 (7)	4.8 (2)
C(4)	−0.4178 (6)	−0.0651 (5)	0.1269 (7)	4.8 (2)
C(5)	−0.4318 (6)	−0.1240 (5)	−0.0853 (7)	4.9 (2)
C(6)	−0.3981 (7)	−0.1088 (5)	−0.1676 (7)	5.0 (2)
C(7)	−0.2643 (6)	−0.0079 (5)	−0.2211 (7)	4.9 (2)
C(8)	−0.1763 (7)	0.0655 (5)	−0.1851 (7)	4.9 (2)
C(9)	−0.1276 (6)	0.1288 (5)	−0.0622 (6)	3.5 (2)
N(10)	−0.1699 (4)	0.1162 (3)	0.0154 (4)	2.9 (1)
C(11)	−0.2580 (5)	0.0400 (4)	−0.0197 (6)	2.9 (1)
C(12)	−0.2984 (5)	0.0276 (4)	0.0660 (6)	2.9 (1)
C(13)	−0.3846 (6)	−0.0563 (5)	0.0359 (6)	3.9 (2)
C(14)	−0.3090 (6)	−0.0277 (5)	−0.1420 (6)	4.2 (2)
		phen 2		
N(1)	−0.1160 (4)	0.3094 (3)	0.3488 (4)	2.8 (1)
C(2)	−0.0515 (6)	0.3169 (5)	0.4655 (6)	3.9 (2)
C(3)	−0.0495 (6)	0.3896 (5)	0.5647 (7)	4.5 (2)
C(4)	−0.1138 (6)	0.4518 (5)	0.5405 (6)	4.5 (2)
C(5)	−0.2516 (6)	0.5089 (5)	0.3850 (7)	4.7 (2)
C(6)	−0.3164 (6)	0.4993 (5)	0.2689 (7)	5.0 (2)
C(7)	−0.3842 (6)	0.4099 (5)	0.0456 (7)	4.7 (2)
C(8)	−0.3794 (6)	0.3378 (5)	−0.0406 (6)	4.2 (2)
C(9)	−0.3075 (6)	0.2785 (5)	−0.0034 (6)	3.3 (1)
N(10)	−0.2434 (4)	0.2897 (3)	0.1140 (4)	2.8 (1)
C(11)	−0.2483 (5)	0.3621 (4)	0.2020 (5)	2.8 (1)
C(12)	−0.1798 (5)	0.3728 (4)	0.3252 (6)	2.9 (1)
C(13)	−0.1811 (6)	0.4468 (5)	0.4200 (6)	3.5 (2)
C(14)	−0.3187 (6)	0.4252 (5)	0.1691 (6)	3.8 (2)
		phen 3		
N(1)	0.0024 (4)	0.3051 (3)	0.1891 (4)	2.7 (1)
C(2)	−0.0015 (5)	0.3745 (4)	0.1324 (6)	3.0 (1)
C(3)	0.0964 (6)	0.4329 (5)	0.1415 (6)	3.7 (2)
C(4)	0.1954 (6)	0.4194 (5)	0.2084 (6)	4.0 (2)
C(5)	0.3026 (6)	0.3294 (5)	0.3480 (6)	4.4 (2)
C(6)	0.3024 (6)	0.2621 (5)	0.4069 (6)	4.5 (2)
C(7)	0.1978 (6)	0.1268 (5)	0.4489 (6)	4.1 (2)
C(8)	0.1002 (6)	0.0694 (5)	0.4230 (6)	3.9 (2)
C(9)	0.0016 (6)	0.0854 (5)	0.3421 (6)	3.4 (1)
N(10)	0.0026 (4)	0.1577 (3)	0.2893 (4)	2.9 (1)
C(11)	0.1021 (5)	0.2141 (4)	0.3139 (5)	2.7 (1)
C(12)	0.1024 (5)	0.2910 (4)	0.2562 (5)	2.5 (1)
C(13)	0.2015 (6)	0.3481 (5)	0.2695 (6)	3.4 (2)
C(14)	0.2039 (6)	0.2016 (5)	0.3944 (6)	3.4 (1)

TABLE III
ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	Min	Intermed	Max
Ni	0.174 (2)	0.186 (2)	0.198 (2)
		Molecule 1	
Mn	0.213 (2)	0.242 (2)	0.252 (2)
C(1)	0.218 (14)	0.260 (11)	0.287 (13)
C(2)	0.206 (12)	0.234 (13)	0.258 (12)
C(3)	0.211 (17)	0.244 (12)	0.269 (13)
C(4)	0.190 (15)	0.284 (12)	0.329 (12)
C(5)	0.228 (12)	0.239 (15)	0.294 (12)
O(1)	0.231 (9)	0.291 (9)	0.374 (8)
O(2)	0.195 (10)	0.282 (7)	0.303 (8)
O(3)	0.215 (13)	0.293 (8)	0.331 (7)
O(4)	0.221 (9)	0.269 (10)	0.457 (9)
O(5)	0.249 (9)	0.293 (7)	0.358 (9)
		Molecule 2	
Mn	0.201 (2)	0.216 (2)	0.239 (2)
C(1)	0.200 (1)	0.239 (13)	0.284 (12)
C(2)	0.203 (17)	0.237 (12)	0.301 (11)
C(3)	0.200 (12)	0.232 (12)	0.295 (12)
C(4)	0.207 (12)	0.229 (13)	0.288 (12)
C(5)	0.207 (12)	0.226 (15)	0.261 (12)
O(1)	0.210 (10)	0.287 (8)	0.405 (8)
O(2)	0.221 (11)	0.299 (9)	0.424 (8)
O(3)	0.214 (9)	0.233 (8)	0.395 (8)
O(4)	0.204 (9)	0.266 (7)	0.378 (8)
O(5)	0.231 (10)	0.267 (7)	0.325 (8)

distances and angles for Ni(phen)$_3$$^{2+}$ are given in Tables IV–VI.

Although many structural studies of 1,10-phenanthroline (phen) or 2,9-dimethyl-1,10-phenanthroline (Me$_2$phen) bound to a transition metal have been reported, few authors have correlated their work with previous studies. Therefore a detailed comparison of these structures will be given here.[32–35]

A plot of metal (M)–nitrogen distances *vs.* N–M–N angles for a series of phen complexes is shown in Figure

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(32) The structures of CoCl$_2$(phen)$_2$$^+$,[33] Fe(phen)$_3$$^{2+}$,[34] and Ni(phen)$_3$-[S$_2$P(OCH$_3$)$_2$]$_2$[35] also have been studied, but these are not included in the discussion because of insufficient available information.

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TABLE IV

BOND DISTANCES (Å) AND ANGLES (DEG) IN THE Ni COORDINATION SPHERE OF Ni(phen)$_3$$^{2+}$

Atoms	phen 1	phen 2	phen 3
Ni–N(1)	2.078 (5)	2.106 (5)	2.078 (5)
Ni–N(10)	2.090 (5)	2.095 (5)	2.093 (5)
N(1)–Ni–N(10)	80.0 (3)	78.7 (3)	79.4 (3)

Atoms[a]	Angle	Atoms[a]	Angle
1N(1)–Ni–2N(1)	96.1 (3)	1N(10)–Ni–2N(1)	170.0 (3)
1N(1)–Ni–2N(10)	92.5 (3)	1N(10)–Ni–2N(10)	92.2 (3)
1N(1)–Ni–3N(1)	170.5 (3)	1N(10)–Ni–3N(1)	93.1 (3)
1N(1)–Ni–3N(10)	94.9 (3)	1N(10)–Ni–3N(10)	97.2 (3)
2N(1)–Ni–3N(1)	91.7 (3)	2N(10)–Ni–3N(1)	94.3 (3)
2N(1)–Ni–3N(10)	92.3 (3)	2N(10)–Ni–3N(10)	168.9 (3)

[a] The prefixed numbers for the atom designators refer to the respective phen ligand.

TABLE V

BOND DISTANCES (Å) IN THE 1,10-PHENANTHROLINE LIGANDS OF Ni(phen)$_3$$^{2+}$

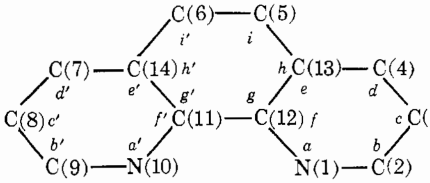
Atoms	phen 1	phen 2	phen 3
N(1)–C(2)	1.335 (8)	1.335 (8)	1.329 (7)
C(2)–C(3)	1.410 (10)	1.423 (9)	1.416 (9)
C(3)–C(4)	1.349 (9)	1.336 (9)	1.344 (9)
C(4)–C(13)	1.393 (9)	1.391 (9)	1.389 (9)
C(13)–C(5)	1.433 (10)	1.410 (9)	1.440 (9)
C(5)–C(6)	1.317 (9)	1.323 (9)	1.327 (9)
C(6)–C(14)	1.431 (10)	1.437 (10)	1.419 (10)
C(14)–C(7)	1.396 (9)	1.384 (9)	1.391 (9)
C(7)–C(8)	1.323 (9)	1.350 (9)	1.333 (9)
C(8)–C(9)	1.424 (9)	1.395 (9)	1.410 (9)
C(9)–N(10)	1.330 (8)	1.328 (7)	1.339 (7)
N(10)–C(11)	1.350 (7)	1.369 (7)	1.353 (7)
C(11)–C(12)	1.405 (8)	1.401 (8)	1.434 (8)
C(12)–N(1)	1.356 (7)	1.345 (7)	1.358 (7)
C(12)–C(13)	1.418 (9)	1.415 (9)	1.401 (8)
C(11)–C(14)	1.441 (9)	1.415 (9)	1.417 (8)

3.[36–48] A correlation between increasing M–N distances and decreasing N–M–N angles is discernible, although exceptions are noted. The nonbonded N···N bite has been calculated for the series of complexes and, as tabulated in the figure, is relatively constant. It appears that as the M–N distance varies, because of changing metallic radii, the N–M–N angle must alter in order to compensate for the inflexibility of the phen bite.

A detailed tabulation of bond distances from structural investigations of the phen ring system is given in Table VII.[36–52] Bond distances from Me$_2$phen com-

TABLE VI

BOND ANGLES IN THE 1,10-PHENANTHROLINE LIGANDS OF Ni(phen)$_3$$^{2+}$



Bond angle	phen 1	phen 2	phen 3	Av
a	118.6 (5)	118.8 (5)	118.8 (5)	118.8 (8)[a]
a'	120.3 (5)	118.7 (5)	117.7 (5)	
b	122.0 (6)	121.6 (6)	120.9 (6)	121.7 (5)
b'	121.3 (6)	122.7 (6)	121.6 (6)	
c	119.0 (7)	119.2 (7)	120.4 (6)	119.5 (7)
c'	118.8 (7)	119.1 (7)	120.3 (6)	
d	121.1 (7)	120.8 (7)	119.7 (7)	120.9 (9)
d'	122.5 (7)	120.6 (7)	120.6 (7)	
e	116.9 (6)	117.4 (6)	117.9 (6)	117.2 (7)
e'	116.3 (6)	118.0 (6)	116.6 (6)	
f	122.3 (6)	122.2 (6)	122.3 (5)	122.0 (9)
f'	120.8 (6)	120.9 (5)	123.2 (5)	
g	120.2 (6)	120.1 (6)	121.0 (6)	120.5 (7)
g'	120.6 (6)	121.4 (6)	119.5 (6)	
h	117.9 (6)	117.6 (6)	117.2 (6)	117.1 (7)
h'	116.2 (6)	116.2 (6)	117.5 (6)	
i	121.5 (7)	122.6 (7)	121.7 (7)	122.4 (7)
i'	123.3 (7)	122.2 (7)	122.9 (7)	

[a] The standard deviation in parentheses is the larger of that obtained from the individual estimates, derived from the least-squares procedure, and that obtained from the deviation from the mean on the assumption that the angles being averaged are equivalent. The good agreement between the two estimates indicates that the angles are equivalent and that the standard deviations of the parameters derived from the least-squares procedure are reasonable.

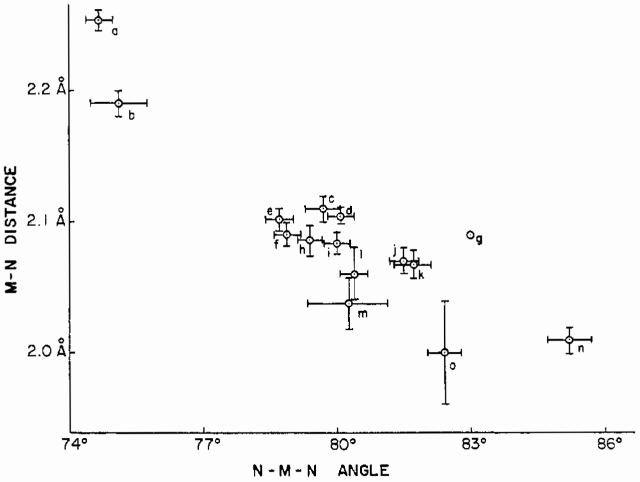


Figure 3.—Plot of average metal–nitrogen bond distance *vs.* nitrogen–metal–nitrogen bond angle for 1,10-phenanthroline and 2,9-dimethyl-1,10-phenanthroline complexes. The labeled points on the graph refer to the following compounds: a, Mo(NCS)(C$_4$H$_7$)(CO$_2$)(phen) (2.73 Å);[36] b, CrO(O$_2$)$_2$(phen) (2.67 Å);[37] c, CuCl$_2$(H$_2$O)(Me$_2$phen) (2.71 Å);[38] d, Ni[S$_2$P(OC$_2$H$_5$)$_2$](phen) (2.72 Å);[39] e, compound of this work (2.66 Å); f, Ni[S$_2$P(OCH$_3$)$_2$](phen) (2.65 Å);[40] g, Pd(NO$_3$)$_2$(Me$_2$phen) (2.78 Å);[41] h, compound of this work (2.66 Å); i, compound of this work (2.68 Å); j, ZnCl$_2$(Me$_2$phen) (2.70 Å);[42] k, [NiCl$_2$(Me$_2$phen)]$_2$ (2.70 Å);[43] l, ZnCl$_2$(phen) (2.66 Å);[44] m, Co[S$_2$C$_6$H$_3$(CH$_3$)]$_2$(phen)$^-$ (2.63 Å);[45,46] n, Co[S$_2$C$_2$(CN)$_2$]$_2$(phen)$^-$ (2.72 Å);[45,47] o, Ni[S$_2$P(OCH$_3$)$_2$]$_2$(Me$_2$phen) (2.64 Å);[39,48] where the N···N distances are given in parentheses.

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TABLE VII

BOND DISTANCES (Å) in 1,10-PHENANTHROLINE COMPLEXES

Compound	N(1)–C(2) N(10)–C(9)	N(1)–C(12) N(10)–C(11)	C(2)–C(3) C(8)–C(9)	C(3)–C(4) C(7)–C(8)	C(4)–C(13) C(7)–C(14)	C(13)–C(5) C(6)–C(14)	C(5)–C(6)	C(11)–C(12)	C(12)–C(13) C(11)–C(14)	Ref
$CrO(O_2)_2$(phen)	1.43 (3)	1.35 (3)	1.33 (3)	1.30 (4)	1.44 (4)	1.45 (3)	1.36 (3)	1.40 (3)	1.39 (3)	*a*
	1.36 (3)	1.42 (2)	1.38 (3)	1.37 (3)	1.41 (3)	1.43 (3)			1.41 (3)	
$ZnCl_2$(phen)	1.32 (1)	1.34 (1)	1.41 (1)	1.36 (1)	1.42 (1)	1.42 (1)	1.36 (1)	1.46 (1)	1.40 (1)	*b*
	1.36 (1)	1.35 (1)	1.41 (1)	1.36 (1)	1.42 (1)	1.43 (1)			1.38 (1)	
$Hg_2(phen)^{2+}$	1.34 (6)	1.40 (5)	1.52 (7)	1.36 (7)	1.40 (6)	1.47 (6)	1.31 (6)	1.50 (6)	1.44 (6)	*c*
	1.24 (6)	1.53 (6)	1.39 (7)	1.36 (8)	1.44 (8)	1.48 (8)			1.53 (7)	
$Co[S_2C_2(CN)_2]_2(phen)^-$	1.31 (2)	1.35 (2)	1.47 (2)	1.39 (2)	1.39 (2)	1.46 (2)	1.34 (2)	1.45 (2)	1.47 (2)	*d*
	1.34 (2)	1.39 (2)	1.42 (2)	1.40 (2)	1.45 (2)	1.48 (2)			1.45 (2)	
$Co[S_2C_6H_3(CH_3)]_2(phen)^-$	1.39 (2)	1.39 (2)	1.46 (3)	1.40 (3)	1.38 (3)	1.44 (3)	1.39 (3)	1.36 (3)	1.43 (3)	*e*
	1.34 (3)	1.36 (3)	1.49 (3)	1.39 (3)	1.37 (3)	1.41 (3)			1.45 (3)	
$Mo(CO)_2(NCS)(C_4H_7)$(phen)	1.35 (1)	1.34 (1)	1.35 (2)	1.35 (2)	1.37 (2)	1.42 (2)	1.36 (2)	1.41 (2)	1.45 (1)	*f*
	1.32 (1)	1.37 (1)	1.42 (2)	1.38 (2)	1.43 (2)	1.44 (2)			1.43 (1)	
$Ni[S_2P(OC_2H_5)_2]$(phen)	1.354 (6)	1.362 (5)	1.420 (7)	1.395 (8)	1.467 (7)	1.428 (7)	1.37 (1)	1.433 (9)		*g*
$Ni[S_2P(OCH_3)_2]$(phen)	1.36 (1)	1.34 (1)	1.41 (1)	1.39 (2)	1.38 (2)	1.45 (2)	1.37 (2)	1.40 (1)	1.43 (1)	*h*
	1.35 (1)	1.36 (1)	1.44 (2)	1.35 (2)	1.42 (2)	1.44 (2)			1.45 (2)	
$Nb(O_2)_3(phen)^-$	1.35 (2)	1.37 (2)	1.42 (2)	1.37 (2)	1.42 (2)	1.43 (2)	1.35 (2)	1.44 (2)	1.39 (2)	*i*
	1.35 (2)	1.37 (2)	1.42 (2)	1.35 (2)	1.44 (2)	1.44 (2)			1.41 (2)	
$[NiCl_2(Me_2phen)]_2$	1.30 (2)	1.38 (1)	1.43 (2)	1.32 (2)	1.45 (2)	1.45 (2)	1.34 (2)	1.46 (2)	1.38 (2)	*j*
	1.35 (2)	1.37 (1)	1.41 (2)	1.35 (2)	1.40 (2)	1.41 (2)			1.39 (1)	
$Ni[S_2P(OCH_3)_2]_2(Me_2phen)$	1.28 (2)	1.45 (2)	1.51 (2)	1.43 (2)	1.33 (2)	1.39 (2)	1.37 (2)	1.31 (2)	1.50 (2)	*k*
	1.38 (2)	1.29 (2)	1.43 (2)	1.31 (2)	1.36 (2)	1.37 (2)			1.48 (2)	
$ZnCl_2(Me_2phen)$	1.34 (1)	1.34 (1)	1.42 (2)	1.39 (2)	1.39 (2)	1.46 (2)	1.30 (2)	1.44 (2)	1.37 (2)	*l*
	1.32 (1)	1.39 (1)	1.45 (2)	1.38 (2)	1.41 (2)	1.45 (2)			1.41 (2)	
$CuCl_2(Me_2phen)(H_2O)$	1.33 (1)	1.39 (1)	1.41 (2)	1.36 (2)	1.40 (2)	1.45 (2)	1.35 (2)	1.42 (2)	1.40 (2)	*m*
	1.33 (2)	1.36 (2)	1.40 (2)	1.39 (2)	1.42 (2)	1.40 (2)			1.40 (2)	
$Pd(NO_3)_2(Me_2phen)$	1.33	1.34	1.43	1.36	1.44	1.43	1.32	1.43	1.46	*n*
	1.34	1.37	1.38	1.44	1.42	1.43			1.40	
$Ni(phen)_3^{2+}$	1.35 (5)	1.35 (4)	1.45 (6)	1.37 (6)	1.37 (5)	1.51 (5)	1.37 (5)	1.40 (4)	1.52 (5)	*o*
	1.43 (5)	1.29 (4)	1.50 (5)	1.36 (5)	1.41 (5)	1.47 (5)			1.50 (5)	
$Ni(phen)_3^{2+}$ (av)	1.333 (8)	1.355 (8)	1.413 (10)	1.339 (10)	1.391 (9)	1.428 (10)	1.322 (9)	1.413 (18)	1.418 (10)	*p*
Av	1.34 (3)	1.37 (4)	1.42 (4)	1.36 (3)	1.41 (3)	1.44 (3)	1.34 (3)	1.42 (4)	1.43 (4)	
Double-bond character	$^3/_5$	$^2/_5$	$^2/_5$	$^3/_5$	$^2/_5$	$^1/_5$	$^4/_5$	$^1/_5$	$^2/_5$	*q*

[a] Reference 37. [b] Reference 44. [c] Reference 49. [d] References 45 and 47. [e] References 45 and 46. [f] Reference 36. [g] Reference 39. [h] Reference 40. [i] Reference 50. [j] Reference 43. [k] References 39 and 48. [l] Reference 42. [m] Reference 38. [n] Reference 41. [o] Reference 51. [p] This work. [q] Reference 52.

plexes are also listed; these do not differ significantly from the parent ligand. The majority of these distances are relatively inexact, having high standard deviations, and the individual values vary widely among presumably equivalent bonds. However the average distances are in good agreement with the corresponding values found in the present $Ni(phen)_3^{2+}$ structure (Tables V and VII).

The variations in C–N and C–C bond lengths within the ring system have been correlated[47] with the π-bond orders[52] of the analogous phenanthrene molecule. These fractions of double-bond character, calculated by averaging the stable resonating structures, agree well with observed average bond distances (Table VII).

Bond angles in the phen ligands of $Ni(phen)_3^{2+}$ are given in Table VI. Most of these angles deviate from the ideal 120°. In the rings designated by angles *a* through *f* in the table, small and large angles alternate around the ring in the order: 119, 122, 119, 121, 117, 122°. This contrasts with the opposite pattern of bond angles found[53] in phenanthrene ($C_{14}H_{10}$) where the corresponding values are 122, 120, 123, 117, 122, and 118°. In other phen and Me_2phen complexes for which angles have been reported[36–40,42–44,49,51] the values vary widely for presumably equivalent angles. The average values for angles *a*–*i* are 120, 121, 120, 120, 117, 122, 120, 119, and 122° where the average deviation from the mean is 2°. Only angles *a* and *e* are consistent in all of the structures; and these values of 120 (1) and 117 (1)° are in good agreement with those of $Ni(phen)_3^{2+}$.

Calculations of least-squares planes indicate deviations from planarity in the phen ligands (Table VIII). phen 1 and phen 2 are similar in their deviations and roughly show a twofold symmetry axis passing through C(5)–C(6) and C(11)–C(12); *i.e.*, atoms related by the pseudo twofold symmetry have deviations similar in magnitude but opposite in sign. phen 2 is considerably more planar and the deviations more closely reflect mirror symmetry than twofold symmetry. Calculations of least-squares planes for other phen complexes[36,38,43,44,46,47,49,51] also show deviations from planarity but no consistent trend is apparent to us.

TABLE VIII

WEIGHTED LEAST-SQUARES PLANES AND THE DISTANCES (Å) OF THE ATOMS FROM THEIR RESPECTIVE PLANES FOR 1,10-PHENANTHROLINE[a]

phen 1: $9.022x - 10.929y + 2.611z + 2.806 = 0$
phen 2: $10.038x + 8.014y - 6.159z + 0.835 = 0$
phen 3: $-5.814x + 7.067y + 9.250z - 3.827 = 0$

Atom	phen 1	phen 2	phen 3
N(1)	−0.063 (5)	0.002 (5)	0.064 (5)
C(2)	−0.051 (7)	−0.009 (7)	0.054 (6)
C(3)	0.049 (7)	−0.019 (7)	−0.019 (7)
C(4)	0.079 (8)	−0.016 (7)	−0.072 (7)
C(5)	0.044 (8)	0.016 (7)	−0.039 (7)
C(6)	−0.034 (8)	0.004 (8)	0.031 (7)
C(7)	−0.070 (8)	−0.018 (7)	0.072 (7)
C(8)	0.016 (8)	−0.017 (7)	−0.005 (7)
C(9)	0.085 (7)	0.002 (6)	−0.068 (7)
N(10)	0.044 (5)	0.010 (5)	−0.051 (5)
C(11)	−0.011 (6)	0.000 (6)	−0.003 (6)
C(12)	−0.016 (6)	0.014 (6)	0.004 (6)
C(13)	0.045 (7)	0.011 (7)	−0.045 (6)
C(14)	−0.050 (7)	0.001 (7)	0.061 (6)

[a] *x*, *y*, and *z* are triclinic fractional coordinates.

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TABLE IX
BOND ANGLES (DEG) FOR $Mn(CO)_5^-$

Atoms	Angle		Atoms	Angle	
	Molecule 1	Molecule 2		Molecule 1	Molecule 2
C(1)-Mn-C(2)	90.3 (3)	91.5 (4)	C(2)-Mn-C(3)	117.5 (3)	118.5 (3)
C(1)-Mn-C(3)	90.5 (4)	89.4 (4)	C(2)-Mn-C(4)	117.6 (4)	118.0 (4)
C(1)-Mn-C(4)	89.5 (4)	91.6 (3)	C(3)-Mn-C(4)	125.0 (4)	123.4 (3)
C(5)-Mn-C(2)	91.5 (3)	89.8 (4)			
C(5)-Mn-C(3)	89.0 (4)	89.6 (4)	Mn-C(1)-O(1)	179.5 (8)	179.2 (7)
C(5)-Mn-C(4)	89.4 (4)	88.2 (4)	Mn-C(2)-O(2)	179.8 (7)	179.6 (8)
			Mn-C(3)-O(3)	179.5 (8)	178.1 (7)
C(1)-Mn-C(5)	178.2 (3)	178.6 (4)	Mn-C(4)-O(4)	177.8 (8)	178.0 (7)
			Mn-C(5)-O(5)	179.5 (8)	179.3 (7)

The Ni atom, which was not included in the calculation of the least-squares planes, lies out of the plane by 0.17 and 0.20 Å for phen 1 and phen 3 and lies approximately in the plane (0.02 Å) for phen 2.

3. The Molecular Structure of $Mn(CO)_5^-$.—The two independent molecules of $Mn(CO)_5^-$ are depicted in Figure 4. A slight distortion from trigonal-bipyramidal geometry is evident in the bond angles listed in Table IX for $Mn(CO)_5^-$. This is particularly evident in the equatorial bond angles where two angles are significantly less than the ideal 120° and the third angle is significantly greater than 120° for each $Mn(CO)_5^-$ molecule. The Mn–C distance opposite the enlarged equatorial angle is slightly shorter than the other two equatorial bonds in each molecule. Similar small distortions have been observed for $Ni[P(OCH)_3(CH_2)_3]_5^{2+}$ [8] and $Fe(N_3)_5^{2-}$.[7] In $Co(CNCH_3)_5^+$, although the angular distortions are greater, the equatorial Co–C distances of 1.88 (2) Å are the same.[10] In $Co(C_6H_7NO)_5^{2+}$ the angular distortions are still greater and the bond distance of 1.99 (1) Å opposite the enlarged angle is longer than the other distances of 1.97 (1) Å.[9] The geometries of other ML_5 complexes—$Ni(CN)_5^{3-}$,[13] $Nb(NC_5H_{10})_5$,[11] $Nb[N(CH_3)_2]_5$,[11] and $MnCl_5^{2-}$ [12]—are greatly distorted and approach tetragonal-pyramidal structures. In the Nb complexes the bond opposite the enlarged angle (or the apical bond in a tetragonal-pyramidal description) is shorter than the other bonds; in the Ni and Mn structures and in a series of $Ni(CN)_2L_3$ structures[1] the bond is longer. Explanations for these distortions can be found in the opposing effects of π bonding[54] and valency-shell electron-pair repulsion.[19] Electrostatic ligand–ligand repulsions favor an increase in apical bonds and this has been observed in most of the structures that are greatly distorted toward the tetragonal-pyramidal geometry. On the other hand, the shortened apical Nb–N bond has been interpreted[11] in terms of pπ–dπ bonding. Similar arguments may apply to $Mn(CO)_5^-$; however the difference in the bond lengths is small and probably not significant.

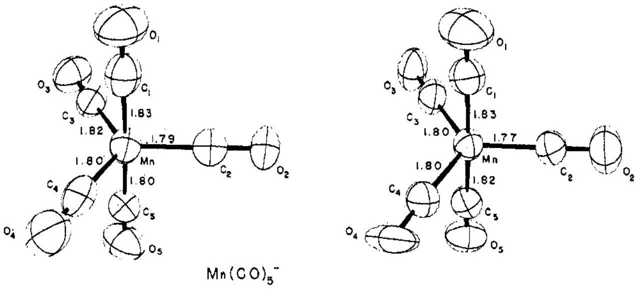

Figure 4.—View of the two independent molecules of $Mn(CO)_5^-$ in the asymmetric unit.

Least-squares planes through the equatorial atoms of the $Mn(CO)_5^-$ molecules are given in Table X.

TABLE X
WEIGHTED LEAST-SQUARES PLANES AND THE DISTANCES OF THE ATOMS FROM THEIR RESPECTIVE EQUATORIAL PLANES FOR $Mn(CO)_5^-$

Plane through Mn and C(2)–C(4)
Molecule 1: $6.009x + 2.045y + 6.635z + 0.969 = 0$ (eq 1)
Molecule 2: $9.462x - 10.899y - 4.112z - 4.461 = 0$ (eq 2)

Plane through Mn, C(2)–C(4) and O(2)–O(4)
Molecule 1: $5.962x + 1.998y + 6.693z + 0.938 = 0$ (eq 3)
Molecule 2: $9.417x - 10.928y - 4.111z - 4.448 = 0$ (eq 4)

Atom	Deviations, Å			
	Eq 1	Eq 2	Eq 3	Eq 4
Mn	−0.000 (1)	0.001 (1)	−0.001 (1)	0.006 (1)
C(2)	0.002 (7)	−0.025 (8)	0.003 (7)	−0.027 (8)
C(3)	0.003 (8)	−0.027 (8)	0.010 (8)	−0.021 (8)
C(4)	0.003 (8)	−0.023 (8)	−0.008 (8)	−0.011 (8)
O(2)	. . .	. . .	0.007 (5)	−0.057 (7)
O(3)	. . .	. . .	0.006 (6)	−0.055 (6)
O(4)	. . .	. . .	0.021 (7)	−0.069 (7)

The deviations from planarity for molecule 1 are negligible. For molecule 2 the Mn atom is significantly out of the plane of the carbonyl atoms. Interatomic distances for $Mn(CO)_5^-$ are given in Table XI. The average Mn–C bond length of 1.81 (2) Å compares well with the median value of 1.81 Å for previously reported (average) distances: $(C_6H_5)_3SnMn(CO)_5$ (1.76 Å),[55] $Mn(NO)(CO)_2[P(C_6H_5)_3]_2$ (1.77 Å),[4] $(C_6H_5)_3PAuMn(CO)_5$ (1.78 Å),[56] $Mn(\pi\text{-}C_5H_5)(COC_6H_5)(CO)_2^-$ (1.78 Å),[57] $Mn(CF_2CFH)(CO)_5$ (1.79 Å),[58]

TABLE XI
INTERATOMIC DISTANCES (Å) FOR $Mn(CO)_5^-$

Atoms	Distance		Atoms	Distance	
	Molecule 1	Molecule 2		Molecule 1	Molecule 2
Mn–C(1)	1.832 (11)	1.831 (11)	C(1)–O(1)	1.143 (9)	1.132 (9)
Mn–C(2)	1.791 (10)	1.772 (10)	C(2)–O(2)	1.153 (8)	1.164 (9)
Mn–C(3)	1.818 (12)	1.796 (10)	C(3)–O(3)	1.154 (9)	1.161 (8)
Mn–C(4)	1.804 (11)	1.804 (10)	C(4)–O(4)	1.155 (9)	1.147 (8)
Mn–C(5)	1.802 (11)	1.815 (11)	C(5)–O(5)	1.162 (9)	1.153 (9)
C(1)–C(2)	2.57 (1)	2.58 (1)	O(1)–O(2)	4.204 (9)	4.163 (10)
C(1)–C(3)	2.59 (1)	2.55 (1)	O(1)–O(3)	4.210 (10)	4.085 (9)
C(1)–C(4)	2.56 (1)	2.61 (1)	O(1)–O(4)	4.200 (10)	4.161 (9)
C(1)–C(5)	3.63 (2)	3.65 (2)	O(1)–O(5)	5.938 (11)	5.931 (10)
C(2)–C(3)	3.08 (1)	3.07 (1)	O(2)–O(3)	5.054 (9)	5.035 (10)
C(2)–C(4)	3.07 (1)	3.07 (1)	O(2)–O(4)	5.035 (9)	5.051 (9)
C(2)–C(5)	2.57 (1)	2.53 (1)	O(2)–O(5)	4.235 (9)	4.242 (9)
C(3)–C(4)	3.21 (1)	3.17 (1)	O(3)–O(4)	5.273 (11)	5.222 (9)
C(3)–C(5)	2.54 (1)	2.54 (1)	O(3)–O(5)	4.162 (10)	4.261 (9)
C(4)–C(5)	2.53 (1)	2.52 (1)	O(4)–O(5)	4.142 (10)	4.179 (10)

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$(C_6H_5)_3SnMn(CO)_4P(C_6H_5)_3$ (1.79 Å),[59] monoclinic $Mn(CONHCH_3)(CO)_4(NH_2CH_3)$ (1.79 Å),[60] $Mn(\pi\text{-}C_5H_5)(CO)_3$ (1.80 Å),[61] $Mn_2(CO)_6(C_{10}H_8)$ (1.80 Å),[62] $(CH_3)_5SnMn(CO)_5$ (1.80 Å),[63] $Mn_2(CO)_8Br_2$ (1.81 Å),[64] $Fe(\pi\text{-}C_5H_5)(CO)_2Mn(CO)_5$ (1.81 Å),[65] $Mn_2H(CO)_8[P(C_6H_5)_2]$ (1.81 Å),[66] $ClSn[Mn(CO)_5]_3$ (1.81 Å),[67] $Mn_2(CO)_8[P(C_2H_5)_3]_2$ (1.81 Å),[68] $Mn_2(CO)_{10}$ (1.82 Å),[69] $Mn_2Fe(CO)_{14}$ (1.82 Å),[70] $Re_2MnH(CO)_{14}$ (1.82 Å),[71] tetragonal $Mn(CONHCH_3)(CO)_4(NH_2CH_3)$ (1.83 Å),[60] $Mn(CO)_5Sn(C_6H_5)_2Co(CO)_4$ (1.83 Å),[72] $MnH(CO)_5$ (1.85 Å),[73] $MnCl(CO)_5$ (1.87 Å),[74] and $Mn(NO)(CO)_4$ (1.87 Å).[2] (Standard deviations for the average bond distances are not included in the preceding tabulation because, in most cases, the bonds are not equivalent.) The average C–O distance of 1.15 (1) Å is in good agreement with the many other determinations of this bond length.

Although the Mn–C distances in $Mn(CO)_5^-$ fluctuate, the average axial bond length of 1.820 (14) Å is slightly longer than the equatorial average of 1.798 (15) Å. This small difference of 0.02 (2) Å is not significant in itself and on the basis of this structural determination alone it would appear that the Mn–C bonds have equivalent lengths. However, when $Mn(CO)_5^-$ is compared with other trigonal-bipyramidal d^8 ML_5 complexes, a structural trend is apparent. Table XII summarizes the data available for these structures. In the last column the difference in equatorial and axial bond lengths is tabulated; there appears to be an increase in equatorial bond lengths relative to axial distances as the atomic number of the metal increases.

TABLE XII

AXIAL AND EQUATORIAL BOND LENGTHS (Å) OF d^8 TRIGONAL-BIPYRAMIDAL COMPLEXES WITH FIVE IDENTICAL LIGANDS

Compound	Equatorial	Axial	Equatorial minus axial	Ref
$Mn(CO)_5^-$	1.798 (15)	1.820 (14)	−0.022 (21)	*b*
$Fe(CO)_5$				
X-Ray	1.795 (20)	1.795 (20)	0.00 (3)	*c*
ED[a]	1.832 (5)	1.820 (6)	0.012 (8)	*d*
ED[a]	1.833 (4)	1.806 (5)	0.027 (7)	*e*
$Co(CNCH_3)_5^+$	1.88 (2)	1.84 (2)	0.04 (3)	*f*
$Ni[P(OCH)_3(CH_2)_3]_5^{2+}$	2.190 (10)	2.144 (15)	0.046 (18)	*g*
$Ni(CN)_5^{3-}$	1.94	1.839 (9)	0.10	*h*

[a] Electron diffraction; trigonal-bipyramidal geometry assumed. [b] This work. [c] A. W. Hanson, *Acta Crystallogr.*, **18,** 502 (1962). [d] A. Almenningen, A. Haaland, and K. Wahl, quoted in ref 6. [e] Reference 6. [f] Reference 10. [g] Reference 8. [h] Reference 13.

As has been discussed previously[45] the differences in axial and equatorial bond lengths can be attributed to two factors. First, valency-shell electron-pair repulsions will cause axial bonds to be longer than equatorial bonds.[75] This is observed in compounds such as PF_5 (axial, 1.577 Å; equatorial, 1.534 Å).[76] For transition metal complexes a second factor needs to be considered.[19] The effect of the interaction of nonbonding d electrons and valency-shell electrons will depend on the shape of the d-electron cloud. For d^0, d^5, and d^{10} systems the d shell is spherical and no differentiating effect on axial and equatorial bond lengths is expected as a result of this interaction. However for a d^8 system the d_{z^2} orbital is empty giving rise to an oblate ellipsoidal shape for the d-electron cloud;[77] *i.e.*, the cloud is flattened in the *z* direction. As a result the d-electron–ligand repulsion is greater in the equatorial direction than in the axial. Thus two opposing effects are operative in trigonal-bipyramidal d^8 complexes: ligand–ligand repulsions favor axial bond lengthening, while d-electron–ligand repulsions favor equatorial bond lengthening. The determination of the relative importance of each of these effects has depended on diffraction studies such as those listed in Table XII.

One possible explanation for the trend observed in the table is the following. In this isoelectronic series the charge on the metal increases from Mn^{-I} to Ni^{II}. Increased nuclear charge causes a decrease in metallic radius and an accompanying shortening of the metal–ligand distance. This, in turn, causes an increase in d-electron–ligand repulsion. Because of the nonspherical shape of the d-electron cloud these repulsions are greater in the equatorial direction than the axial. Hence a greater difference (equatorial minus axial) in the bond lengths is expected for the Ni^{II} end of the isoelectronic series than for the Mn^{-I} end. In fact, in $Mn(CO)_5^-$ it appears that the d-electron–ligand repulsions play a minor role compared with the ligand–ligand repulsions in determining the relative bond lengths. Presumably a similar argument, suitably modified, could have been found to explain the opposite trend, had it been found experimentally.

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