Contribution from the Department of Chemistry,
University of Nebraska, Lincoln, Nebraska 68508

Distortions of the Coordination Polyhedron in High-Spin Manganese(III) Complexes. I. Synthesis and Characterization of a Series of Five- and Six-Coordinate Bis(acetylacetonato)manganese(III) Complexes. Crystal Structure of Azidobis(acetylacetonato)manganese(III)[1]

B. RAY STULTS, ROBERT S. MARIANELLI,* and VICTOR W. DAY*

Received May 31, 1974 AIC403509

A new class of high-spin bis(acetylacetonato)manganese(III) complexes, having the general formulations Mn(acac)$_2$(X) and Mn(acac)$_2$(X)(B), where acac is the acetylacetonate anion, X is a mononegative anionic ligand such as N_3^-, NCS^-, Br^-, or Cl^-, and B is a neutral Lewis base such as methanol or pyridine, have been synthesized and characterized chemically and spectroscopically. Although the Mn(acac)$_2$(X) complexes may be five-coordinate in solutions of poorly coordinating solvents, the results of a three-dimensional crystal structure analysis for Mn(acac)$_2$(N$_3$) reveal the presence of bridging azide ligands to give octahedrally coordinated manganese(III) atoms in the solid state. The Mn(acac)$_2$(X)(B) complexes are believed to be six-coordinate in solution as well as in the solid state. Mn(acac)$_2$(N$_3$) crystallizes in the centrosymmetric monoclinic space group $C2/c$ (C_{2h}^6, No. 15) with $a = 11.527$ (4) Å, $b = 10.005$ (4) Å, $c = 11.263$ (3) Å, $\beta = 94.86$ (2)°, and $Z = 4$ (formula units) to give $\rho_{\mathrm{calcd}} = 1.514$ g/cm^3 ($\rho_{\mathrm{obsd}} = 1.499$ g/cm^3). Intensity measurements were made for the 2239 independent reflections having $2\theta_{\mathrm{Mo}K\bar{\alpha}} < 63.7°$ with Nb-filtered Mo Kα radiation utilizing the θ–2θ scan technique on a Syntex $P\bar{1}$ Autodiffractometer. The structure was solved using the heavy-atom technique and has been refined using full-matrix least-squares procedures to a final value of 0.042 for the conventional unweighted residual, R, using 1908 independent reflections having $I > \sigma(I)$. This refinement employed anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for the hydrogen atoms. The manganese atoms occupy crystallographic inversion centers and the middle nitrogen atoms of the azide ligands occupy crystallographic twofold axes. Each azide ligand bridges two adjacent Mn(acac)$_2^+$ groups in the three-dimensional lattice using the glide operator to generate infinite chains of octahedral Mn(III) subunits along the $\vec{c}$ axis of the unit cell. The octahedral coordination polyhedron is tetragonally elongated and approximates ideallized D_{4h} symmetry. The four "short" Mn–O bonds have average lengths of 1.910 (1) Å while the two "long" trans Mn–N bonds to the ends of the bridging azide ligands have lengths of 2.245 (2) Å.

Introduction

Octahedral complexes of high-spin Mn(III) are expected to be susceptible to Jahn–Teller distortions causing them to deviate from idealized O_h symmetry either by a trigonal distortion[2] or by a tetragonal elongation or compression.[3] Subtle electronic effects such as these are often critical in the vital roles played by metals in certain biological systems. For example, high-spin Mn(III) can incorporate into the plane of a porphine skeleton by distorting its coordination sphere,[4] whereas it appears Fe(II) and Fe(III) must go to the low-spin state before fitting into the size-restricting porphine skeleton.[5,6]

A series of high-spin Mn(III) complexes having formulations Mn(acac)$_2$(X) and Mn(acac)$_2$(X)(B), where acac is the acetylacetonate anion, X is a mononegative anionic ligand such as N_3^-, NCS^-, or Cl^-, and B is a neutral Lewis base such as pyridine or methanol, has been prepared in this laboratory as synthetic intermediates for manganese(III) porphyrins. Structural studies of selected members of this series have demonstrated several interesting facets of Mn(III) coordination chemistry.[4,7] The synthesis and characterization of the bis(acetylacetonato)manganese(III) complexes and the structure of Mn(acac)$_2$(N$_3$) are described in detail at this time.

Experimental Section

General Information. Infrared spectra were recorded on a Perkin-Elmer Model 621 grating spectrometer and calibrated against polystyrene. The solid-state spectra were measured as Nujol mulls between KBr plates, as potassium bromide pellets (4000–400 cm^{-1}), and as cesium iodide pellets (400–200 cm^{-1}). Solution infrared spectra were measured using 1.0-mm path length potassium bromide cells.

Mass spectra were measured using a Perkin-Elmer Hitachi RMU-6D double-focusing spectrometer with an electron energy of 70 eV and an ionizing current of 100 μA. All compounds were introduced into the ionizing chamber by direct insertion methods. Molar conductivities, Λ_m, were measured with an Industrial Instruments Conductivity Bridge, Model RC 16. The values reported for 10^{-3} M solutions were calculated using the method described by Geary.[8] Melting points were determined in sealed capillaries with a Mel-Temp melting point apparatus and are uncorrected. Carbon, hydrogen, and nitrogen microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill. Manganese analyses[9] were conducted in aqueous solution by titration with EDTA using Calmagite as an indicator, while the halogen content was measured using standard analytical techniques.[10] Magnetic susceptibility measurements were made at 24° on an Alpha Scientific Co. Gouy balance with a Model 7500 electromagnet and a 7500 R series current regulator. $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ was used for calibration, and diamagnetic corrections were made according to procedures outlined by Earnshaw.[11]

Materials. Tris(acetylacetonato)manganese(III), Mn(acac)$_3$, was prepared by published methods.[12] Manganese(II) sulfate tetrahydrate, $MnSO_4 \cdot 4H_2O$, and manganese(II) acetate tetrahydrate, $Mn(C_2H_3O_2)_2 \cdot 4H_2O$, were prepared by the reaction of the corresponding concentrated acid with manganese metal in an aqueous medium. The pink salts were recrystallized from water. Reagent grade acetylacetone was purchased from Matheson Coleman and Bell and purified using the method described by Cartledge.[13] All other materials used in the synthesis were obtained commercially as reagent grade chemicals and were used without further purification. The acetonitrile (CH_3CN) and dichloromethane (CH_2Cl_2) used for the conductivity measurements were treated as follows. CH_3CN was deoxygenated with N_2, dried over P_2O_5, and distilled under an N_2 atmosphere (measured resistance $R = 420 \times 10^3$ ohms); CH_2Cl_2 was similarly purified by drying with calcium chloride (measured resistance $R > 2300 \times 10^3$ ohms). The chloroform used for the spectral measurements was dried over barium oxide and fractionally distilled under N_2.

Thiocyanatobis(acetylacetonato)manganese(III), $\mathbf{Mn(O_2C_5H_7)_2(NCS)}$, and Azidobis(acetylacetonato)manganese(III), $\mathbf{Mn(O_2C_5H_7)_2(N_3)}$. Method I. A 3.52-g (10-mmol) sample of Mn(acac)$_3$ in 20 ml of H_2O was treated with 0.52 g (5 mmol) of concentrated sulfuric acid for 20 min with stirring. A 1.5-g sample of KSCN was added to the solution with an additional 10 min of stirring. A crude green product, obtained by filtering this solution, was then purified by redissolving in methanol, filtering, and removing the solvent with a Rotovap. The resulting product was dried under vacuum over P_2O_5; yield 2.65 g, 85%. Mn(acac)$_2$(N$_3$) was prepared in 70% yield by substituting KN_3 or NaN_3 for KSCN.

Method II. A 9.80-g (40-mmol) sample of $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ (or 40 mmol of $MnSO_4 \cdot 4H_2O$) was dissolved in 20 ml of H_2O. After addition of 10 g (100 mmol) of acetylacetone, 1.58 g (10 mmol) of $KMnO_4$ (which had been dissolved in ~50 ml of H_2O) was added to the aqueous layer. After approximately 15 min of stirring, 4.85

g (50 mmol) of KSCN was added to the solution followed by 30 min of stirring. The product was recrystallized as previously described and resulted in an 85% yield. Substituting KN_3 or NaN_3 for KSCN gives a 74% yield of the brown $Mn(acac)_2(N_3)$ complex.

$Mn(acac)_2(NCS)$ is an olive green material, mp 169–170°, molar conductivity Λ_m 10.9 (CH_3CN). *Anal.* Calcd for $MnSO_4NC_{11}H_{14}$: Mn, 17.65; N, 4.50; C, 42.45; H, 4.53. Found: Mn, 17.65; N, 4.46; C, 42.46; H, 4.52; $\mu_{eff} = 4.90$ BM.

Infrared spectrum (cm^{-1}): 2080 (vs), 1550 (vs), 1525 (vs), 1421 (m), 1375 (w), 1340 (vs, vb), 1286 (m), 1033 (m), 1015 (w), 950 (m), 937 (m), 798 (s, b), 687 (m), 656 (w), 629 (m), 488 (vs), 472 (sh), 429 (m), 344 (m), 235 (m, vb). Solution ir: 2060 (vs) (THF).

Prominent mass spectral peaks (*m/e*): 311 (0.2, parent ion),[14] 254 (8.0), 253 (51.0), 239 (5.0), 238 (32.6), 211 (6.1), 197 (1.5), 196 (1.0), 155 (10.2), 154 (base peak), 100 (>100).

$Mn(acac)_2(N_3)$ is a brown material, mp 200° dec, molar conductivity Λ_m 0.04 (CH_2Cl_2) and 13.9 (CH_3CN). *Anal.* Calcd for $MnO_4N_3C_{10}H_{14}$: Mn, 18.61; N, 14.24; C, 40.69; H, 4.78. Found: Mn, 18.65; N, 14.37; C, 40.35; H, 4.78, $\mu_{eff} = 4.40$ BM.

Infrared spectrum (cm^{-1}): 3385 (m), 2050 (vs), 1546 (vs), 1524 (vs), 1420 (m), 1360 (s), 1339 (s), 1282 (m), 1025 (m), 1015 (m), 938 (m), 975 (m), 685 (m), 658 (w), 615 (w), 480 (s), 425 (m), 345 (m, b), 275 (m, b).

Prominent mass spectral peaks (*m/e*): 253 (50.0), 239 (6.0), 238 (34.0), 211 (5.6), 155 (11.3), 154 (base peak), 100 (75.0).

Chlorobis(acetylacetonato)manganese(III), $Mn(O_2C_5H_7)_2Cl$, and Bromobis(acetylacetonato)manganese(III), $Mn(O_2C_5H_7)_2Br$. A 3.11-g (10-mmol) sample of $Mn(acac)_2(SCN)$ was treated with $AgClO_4$ in methanol for 15 min with stirring, followed by filtration to remove the white AgSCN precipitate. The filtrate was combined with 0.75 g (10 mmol) of KCl and stirred for 12 hr. The solid brown material was isolated by filtering off the $KClO_4$ precipitate and by vacuum removal of the solvent. The crude material was purified by redissolving in a 1:1 $CHCl_3$–heptane solution, followed by filtration and solvent removal to near dryness with a Rotovap. The crystalline complex was isolated by filtration and dried under vacuum over P_2O_5 with a 45% yield. Substituting KBr for KCl gives $Mn(acac)_2Br$ in 69% yield.

$Mn(acac)_2Cl$ is a brown material, mp 160° dec, molar conductivity Λ_m 1.57 (CH_2Cl_2) and 13.0 (CH_3CN). *Anal.* Calcd for $MnClO_4C_{10}H_{14}$: Mn, 19.04; Cl, 12.28; C, 41.62; H, 4.89. Found: Mn, 19.03; Cl, 12.40; C, 41.33; H, 4.80.

Infrared spectrum (cm^{-1}): 1540 (vs), 1518 (vs), 1415 (m), 1348 (s), 1335 (s), 1285 (m), 1030 (m), 1015 (m), 940 (m), 815 (m), 688 (m), 655 (w), 625 (w), 480 (s), 425 (m), 338 (m), 290 (m, vb).

Prominent mass spectral peaks (*m/e*): 290 (0.1) and 288 (0.5) (parent ions), 254 (9.0), 253 (14.3), 211 (5.0), 191 (0.3), 189 (0.8), 176 (0.5), 174 (1.3), 154 (base peak), 100 (39.0).

$Mn(acac)_2Br$ is a green material, mp 158° dec, molar conductivity Λ_m 0.04 (CH_2Cl_2) and 14.8 (CH_3CN). *Anal.* Calcd for $MnBrO_4C_{10}H_{14}$: Mn, 16.49; Br, 23.99; C, 36.06; H, 4.24. Found: Mn, 16.50; Br, 23.94; C, 35.08; H, 4.24.

Infrared spectrum (cm^{-1}): 1540 (vs), 1516 (vs), 1413 (m), 1350 (s), 1332 (s), 1285 (m), 1036 (m), 1028 (m), 1018 (m), 1010 (w), 941 (m), 800 (m), 693 (m), 658 (w), 635 (m), 495 (s), 430 (m), 340 (m), 255 (m), 225 (m, b).

Prominent mass spectral peaks (*m/e*): 334 (0.6) and 332 (0.6) (parent ions), 254 (10.4), 253 (58.3), 238 (37.0), 235 (0.7), 233 (0.6), 220 (1.3), 218 (1.4), 211 (6.3), 155 (10.0), 154 (base peak), 100 (>100).

Thiocyanatobis(acetylacetonato)manganese(III) Pyridine, $Mn(O_2C_5H_7)_2(NCS)(C_5NH_5)$. An excess (2.0 g) of pyridine (py) was stirred for 1 hr with 6.22 g (20 mmol) of $Mn(acac)_2NCS$ in CH_3OH followed by filtration to isolate the red-brown solid which was washed with methanol. A pure product was obtained in 53% yield by washing this solid with *n*-pentane followed by drying under vacuum over P_2O_5.

$Mn(acac)_2(NCS)(py)$ is a red-brown material, mp 142–143°, molar conductivity Λ_m 0.19 (CH_2Cl_2) and 8.0 (CH_3CN). *Anal.* Calcd for $MnSO_4N_2C_{16}H_{19}$: Mn, 14.07; N, 7.18; C, 49.23; H, 4.91. Found: Mn, 14.15; N, 7.06; C, 49.21; H, 4.91.

Infrared spectrum (cm^{-1}): 2067 (vs), 1594 (sh), 1550 (vs), 1523 (vs), 1423 (s), 1368 (s), 1352 (s), 1282 (m), 1218 (w), 1068 (m), 1030 (m), 1003 (m), 947 (m), 931 (m), 797 (s), 768 (m), 709 (m), 681 (m), 655 (m), 618 (m), 472 (s), 412 (m), 336 (w, b), 250 (s, b).

Prominent mass spectral peaks (*m/e*): 311 (0.1), 254 (7.2), 253 (45.0), 239 (4.4), 238 (31.1), 211 (0.6), 154 (base peak), 100 (>100).

Crystallographic Work. Although $Mn(O_2C_5H_7)_2(N_3)$ is soluble in a wide range of polar solvents including methyl acetate, methanol, chloroform, dichloromethane, and acetonitrile, initial attempts to grow single crystals suitable for X-ray analysis resulted in microcrystalline samples for all solvents except methyl acetate. After repeated attempts to crystallize the compound from a saturated methyl acetate solution had resulted in the formation of crystal clusters, it was decided to try cutting a single crystal from one of the clusters. Several multiple crystalline samples were examined photographically before an irregularly shaped specimen with dimensions ranging from 0.25 to 0.40 mm was finally obtained which contained only a very small fragment of a second crystal. Precession photographs used to determine the probable space group and a preliminary set of lattice constants indicated monoclinic, $2/m$, symmetry. The systematically absent reflections were those required by space group Cc-C_s^4 (No. 9) or $C2/c$-C_{2h}^6 (No. 15).[15] Use of the accurate lattice constants given below for a unit cell containing four $Mn(O_2C_5H_7)_2(N_3)$ formula units gave a calculated density of 1.514 g/cm^3, in good agreement with the observed density of 1.499 g/cm^3 measured by flotation in a solution of carbon tetrachloride and hexane.

A unit cell containing four formula units and an anticipated five-coordinate geometry for the Mn atom seemed to preclude the choice of the centrosymmetric space group, $C2/c$, since this would require the Mn atom and azide ligand to occupy special positions in the unit cell, *i.e.*, crystallographic inversion centers or twofold axes in the case of $C2/c$.[15] Only the twofold axes would be compatible with five-coordination but would require the azide ligand to bond linearly to the Mn atom—a highly improbable circumstance. With the negative results of sensitive tests for piezoelectricity made with a Geibe–Schiebe detector not available at this time (nor an operational Wilson plot computer program) and an anticipated five-coordinate species, the most probable space group seemed to be Cc.

The crystal was glued to a thin glass fiber, mounted on a goniometer head, and accurately centered on a computer-controlled four-circle Syntex $P\bar{1}$ Autodiffractometer using 15 high-angle reflections. A complete set of θ–2θ scan data having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 43°$ was collected using Nb-filtered Mo K$\bar{\alpha}$ radiation and a scan rate of 3.00°/min before the intensities of the six standard reflections (measured every 100 reflections) had decreased uniformly by 15%. At this point it was decided to terminate data collection on this crystal and to proceed with the structure determination while continuing the attempts to grow better single crystals from methyl acetate and other solvents.

The 683 independent reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 43°$ and $I > \sigma(I)$ were used to calculate a three-dimensional Patterson synthesis which contained peaks that were consistent with a Mn atom positioned at the origin of the unit cell in Cc or $C2/c$ or with a Mn atom positioned on the crystallographic twofold axis of $C2/c$ with $y \approx 0.000$. When the difference Fourier syntheses using phases derived from the Mn atom positioned on the twofold axis of $C2/c$ failed to reveal the remaining atoms of the molecule, the structure was assumed to be acentric. Solution of the structure in the acentric space group, Cc, proceeded in a straightforward manner. When all nonhydrogen atoms of the asymmetric unit had been located from difference Fourier syntheses, the complex was seen to be octahedral with an (approximate) inversion center at the Mn atom. The azide ligand symmetrically bridged adjacent Mn(III) atoms in the three-dimensional lattice. Transformation to the centric space group, $C2/c$, was accomplished by placing the Mn atom at the crystallographic inversion center coincident with the origin of the unit cell and the middle nitrogen atom of the azide ligand on the crystallographic twofold axis at $(0, y, {}^1/_4)$. Unit-weighted full-matrix least-squares refinement of the properly transformed positional and isotropic thermal parameters for each atom resulted in a conventional unweighted residual, $R = \sum||F_o| - |F_c||/\sum|F_o|$, of 0.090 and a conventional weighted residual, $r = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, of 0.082 for 683 independent reflections having $2\theta_{\mathrm{MoK}\bar{\alpha}} < 43°$ and $I > \sigma(I)$. Further unit-weighted least-squares minimization of the function $\sum w(|F_o| - k^{-1}|F_c|)^2$ (where k is the scale factor which puts F_o on an absolute basis), which employed anisotropic thermal parameters, resulted in $R = 0.050$ and $r = 0.053$. A single difference Fourier synthesis at this point permitted the location of all seven hydrogen atoms of the asymmetric unit in chemically anticipated positions. Further cycles of unit-weighted full-matrix least-squares refinement which employed isotropic thermal parameters for hydrogen atoms but was otherwise anisotropic, gave $R = 0.033$ and $r = 0.034$.

Large well-shaped single crystals of $Mn(acac)_2(N_3)$ were eventually obtained by recrystallizing from acetonitrile. A cube-shaped specimen was cut from one of these large single crystals, ground to a sphere 0.50 mm in diameter, and glued to the inside of a sealed glass capillary before mounting on a goniometer head. This crystal was then carefully centered optically on a Syntex $P\bar{1}$ Autodiffractometer, and a total of 15 high-angle ($2\theta_{\mathrm{Mo}K\bar{\alpha}} > 25°$) reflections, chosen to give a good sampling of reciprocal space and diffractometer settings, were used to align the crystal and calculate angular settings for each reflection. A least-squares refinement of the diffraction geometry for these 15 reflections, recorded at the ambient laboratory temperature of 20 ± 1° with Nb-filtered Mo K$\bar{\alpha}$ radiation (λ 0.71069 Å) gave the lattice constants a = 11.527 (4) Å, b = 10.005 (4) Å, c = 11.263 (3) Å, and β = 94.86 (2)°.

Intensity measurements utilized Nb-filtered Mo K$\bar{\alpha}$ radiation and the θ–2θ scanning technique with a 4° takeoff angle and a normal-focus X-ray tube. A scanning rate of 2°/min was employed for the scan between 2θ settings 1.0° above and below the calculated Kα doublet values ($\lambda_{K\bar{\alpha}_1}$ 0.70926 Å and $\lambda_{K\bar{\alpha}_2}$ 0.71354 Å) of each reflection. Background counts, each lasting for half the total scan time, were taken at both ends of the scan range. A total of 2239 independent reflections having $2\theta_{\mathrm{Mo}K\bar{\alpha}} < 63.70°$ (1.5 times the number of data in the limiting Cu K$\bar{\alpha}$ sphere) were measured in concentric shells of increasing 2θ containing approximately 750 reflections each. The six standard reflections, measured every 300 reflections as a monitor for possible disalignment and/or deterioration of the crystal, gave no indication of either.

The linear absorption coefficient of the crystal for Mo K$\bar{\alpha}$ is 1.074 mm^{-1},[16] yielding a μr of 0.27 for the spherical specimen used for data collection. Since the absorption of X-rays by a spherical crystal having μr = 0.27 is virtually independent of scattering angle, no absorption corrections were made, and the intensities were reduced to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

Of the 2239 reflections examined, 331 were rejected as objectively unobserved by applying the rejection criterion, $I < \sigma(I)$, where $\sigma(I)$ is the standard deviation in the intensity computed from

$$\sigma^2(I) = (\mathrm{Ct} + K^2 B) \tag{1}$$

Ct being the total count from scanning, K the ratio of scanning time to total background time (in this case, K = 1), and B the total background count.

The remaining 1908 observed intensities were used in the final cycles of full-matrix least-squares refinement of the structural parameters for $\mathrm{Mn(acac)_2(N_3)}$. Unit-weighted refinement cycles which employed isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for all other atoms converged to R = 0.042 and r = 0.040. These and all subsequent structure factor calculations employed the atomic form factors compiled by Cromer and Mann[17] and an anomalous dispersion correction to the scattering factor of the Mn atom.[18]

Empirical weights ($w = 1/\sigma^2$) were then calculated from

$$\sigma = \sum_0^2 a_n |F_o|^n = 0.731 - 2.436 \times 10^{-3} F_o + 1.825 \times 10^{-5} F_o^2 \tag{2}$$

the a_n being coefficients derived from the least-squares fitting of the curve

$$||F_o| - |F_c|| = \sum_0^2 a_n |F_o|^n \tag{3}$$

where the F_c values were calculated from the fully refined model using unit weighting. The final cycles of full-matrix least-squares refinement utilized these weights to refine hydrogen atoms isotropically and all other atoms anisotropically together with the scale factor to give final values of 0.040 and 0.046 for R and r, respectively, for 1908 independent reflections.[19] During the final cycle of refinement, no parameter shifted by more than $0.30\sigma_p$ with the average shift (including those for hydrogen atoms) being $0.05\sigma_p$, where σ_p is the estimated standard deviation of that parameter. No significant differences were observed between the final parameters from least-squares refinement cycles which utilized the empirical weights and those which utilized unit weights. A close examination of the agreement between observed and calculated structure factors gave no indication of the presence of extinction effects.

The following programs were used on an IBM 360/65 computer for this work: MAGTAPE, SCALEUP, and SCTFT2, data reduction programs written by V. W. Day; FORDAP, Fourier and Patterson synthesis program, a modified version of A. Zalkin's program; ORFLSE, full-matrix least-squares refinement program, a highly modified version of Busing, Martin, and Levy's original ORFLS; ORFFE, bond lengths and angles with standard deviations by Busing, Martin, and Levy; ORTEP2, thermal ellipsoid plotting program by C. K. Johnson; MPLANE, least-squares mean-plane calculation program from L. Dahl's laboratory; PRTOUT, structure factor table program written by V. W. Day.

Results and Discussion

The described synthetic procedures offer convenient routes for the preparation of the pure bis(acetylacetonato)manganese(III) complexes in high yields utilizing the $\mathrm{Mn(acac)_2(H_2O)_2^+}$ ion as a precursor.[13] The complexes are stable and capable of being stored for long periods of time with no apparent decomposition and, with the exception of the chloride and bromide derivatives which are hygroscopic, can be handled in the atmosphere with no special precautions. Although good manganese and halogen analyses were obtained for the chloro and bromo complexes, initial carbon analyses were from 1 to 2% low, while the hydrogen analyses were in good agreement with the theoretical values. When the manganese and halogen analyses were repeated after exposure to the atmosphere for several hours (initial analyses used freshly dried samples), low values were obtained for the metal and halogen content. Further controlled tests showed light and oxygen were not affecting the analyses. After realizing the hygroscopic nature of the two halogen complexes, the carbon and hydrogen analyses were repeated, with appropriate precautions taken, for the $\mathrm{Mn(acac)_2\,Cl}$ complex and are reported in the Experimental Section (initial carbon and hydrogen analyses are reported for $\mathrm{Mn(acac)_2Br}$).

Infrared and Mass Spectra. The infrared spectra for all complexes were recorded in the solid state as both CsI or KBr pellets and Nujol mulls. Since essentially identical spectra were recorded in the solid state by the various techniques, with only minor shifts for peaks recorded as mulls relative to those for pellets, only the spectra recorded as pressed pellets are reported (prominent peaks are listed in the Experimental Section). A majority of the observed peaks are found in the same regions for all five complexes and as such are assignable to the $\mathrm{Mn(acac)_2^+}$ group from literature references for acetylacetonate-containing complexes.[20–23] The two peaks in the region 1600–1500 cm^{-1} most characteristic of the bidentate acetylacetonate ligand are assigned to the ν(C=O) (the peak at the higher wave number value) and ν(C=C) stretching frequencies. Peaks not common to all complexes can be assigned to the coordinated X or B groups by comparison to literature reports.

Additional peaks at 290 and 225 cm^{-1} in the spectra for the halogen complexes are assigned to the ν(Mn–Cl) and ν(Mn–Br) stretching modes, respectively. The precise assignment of the Mn–Cl stretch may be questioned since the peak is very broad, having significant Mn–O contribution; however, the assigned frequencies are in a ratio of 0.78 (ν(Mn–Br)/ν(Mn–Cl)) which is consistent with the expected ratio reported by Nakamoto.[20] The two infrared peaks most characteristic of the coordinated azide group are the strong absorption at 2050 cm^{-1} (ν_{as}(N–N)) and the weaker band at 3385 cm^{-1} (combination band $\nu_2 + \nu_3$) observed in other azide complexes.[20,24–27] The value for the asymmetric stretching frequency compares quite favorably with the reported value of 2045 cm^{-1} for $\mathrm{[Cu(\mu\text{-}N_3)(P(C_6H_5)_3)_2]_2}$[28] and differs only slightly from the value of 2080 cm^{-1} for $\mathrm{[Co(acac)_2(\mu\text{-}N_3)]_2}$.[29]

$\mathrm{Mn(acac)_2(NCS)}$ also has two bands in its infrared spectra characteristic of a coordinated $\mathrm{NCS^-}$ ligand, namely, ν(C–N) at 2080 cm^{-1} and ν(C–S) at 798 cm^{-1}.[20,30–32] The ν(C–S) stretching frequency is described as the more useful in distinguishing N- or S-bonded NCS,[30] and the observed value

Table I. Solution Infrared Spectral Peaks in the Region 2200–2000 cm^{-1}

Complex	Solvent	Base added	Peaks		
$Mn(O_2C_5H_7)_2(N_3)$	$CHCl_3$	Pyridine			2050 (vs)
$Mn(O_2C_5H_7)_2(N_3)$	$CHCl_3$	DMSO	2138 (w)		2058 (vs)
$Mn(O_2C_5H_7)_2(N_3)$	$CHCl_3$	CH_3OH	2138 (w)		2058 (vs)
$Mn(O_2C_5H_7)_2(N_3)$	$CHCl_3$	THF	2138 (m)	2090 (sh)	2058 (vs)
$Mn(O_2C_5H_7)_2(N_3)$	$CHCl_3$	Acetone	2138 (m)	2090 (m)	2058 (s)
$Mn(O_2C_5H_7)_2(N_3)$	$CHCl_3$	Acetonitrile	2138 (m)	2090 (m)	2058 (s)
$Mn(O_2C_5H_7)_2(N_3)$ (fresh)	$CHCl_3$		2138 (m)	2090 (sh)	2058 (vs)
$Mn(O_2C_5H_7)_2(N_3)$ (12 hr)	$CHCl_3$		2138 (m)	2095 (m)	2058 (s)
$Mn(O_2C_5H_7)_2(N_3)$ (36 hr)	$CHCl_3$		2138 (m)	2100 (s)	2060 (s)
$Mn(O_2C_5H_7)_2(N_3)$	THF	Pyridine			2050 (vs)
$Mn(O_2C_5H_7)_2(N_3)$	THF	DMSO			2050 (vs)
$Mn(O_2C_5H_7)_2(N_3)$	THF				2050 (vs)
$Mn(O_2C_5H_7)(NCS)$	THF				2060 (vs)

of 798 cm^{-1} falls in the region expected for an N-bonded NCS group (780–860 cm^{-1}) while the value of the ν(C–N) stretching frequency is perhaps higher than one might expect. A crystal structure analysis of Mn(acac)$_2$(NCS) shows the presence of bridging thiocyanate groups in the solid state.[4] The spectra of Mn(acac)$_2$(NCS)(py) closely resemble the spectra for Mn(acac)$_2$(NCS) with no observed shift occurring for the ν(C–S) stretching frequency while the ν(C–N) frequency drops to 2067 cm^{-1}, a value more consistent with a nonbridging, N-bonded thiocyanate ligand. Additional peaks in the spectra for Mn(acac)$_2$(NCS)(py) are easily assigned to the coordinated pyridine group from appropriate literature references.[20,33] Although several infrared peaks found in the solid state for the azido, thiocyanato, and thiocyanato-pyridine complexes could be assigned to both the acetylacetonate and the coordinated X group, no attempt was made to distinguish between the assignments.

Solution infrared spectra were recorded in the region 2200–2000 cm^{-1} for the Mn(acac)$_2$(N$_3$) and Mn(acac)$_2$(NCS) complexes, both shown by crystal structure analysis to contain bridging X groups in the solid state, to obtain information concerning the nature of the species present in solution (Table I). The azido complex exhibits three bands at 2138 (m), 2090 (sh), and 2058 (vs) cm^{-1} in $CHCl_3$ or CH_2Cl_2 but has only one band at 2050 (vs) cm^{-1} in THF. The spectra for $CHCl_3$ solutions of the azide complex containing approximately 1–2% of the various donor solvents listed in Table I show a gradual shift in the observed absorption until a single band at 2050 cm^{-1} is observed when pyridine is added. The observed shifts correlate well with the donor strength of the added solvent: py > DMSO ≥ CH_3OH > THF ≥ acetone, CH_3CN. These observations suggest the presence of a mixture of species in solutions of weakly coordinating solvents such as $CHCl_3$ or CH_2Cl_2 and a single species (probably nonbridged with a solvent molecule occupying the sixth coordination site) in strongly coordinating solvents. The low solubility of Mn(acac)$_2$(NCS) in weakly coordinating solvents such as $CHCl_3$ or CH_2Cl_2 prevented similar infrared studies of the effect of stronger coordinating solvents. The observed change in the ν(C–N) stretching frequency for Mn(acac)$_2$(NCS) from 2087 cm^{-1} in the solid state to 2060 cm^{-1} in THF is consistent with a transformation from a bridged to a nonbridged, N-coordinated thiocyanato ligand. The latter frequency is similar to that observed in the solid-state spectra for Mn(acac)$_2$(NCS)(py), also indicating the probable formation of a nonbridged species in solution with a solvent molecule occupying the sixth site.

Mass spectra for all five complexes gave the expected fragmentation patterns (prominent peaks (*m/e*) for each complex are given in the Experimental Section). The primary fragmentation sequence consists of the loss of the more weakly coordinated X group to give the Mn(acac)$_2^+$ ion (*m/e* 253) followed by fragment ions with *m/e* values the same as those observed by McDonald and Shannon.[34] The chloro and bromo complexes have additional peaks corresponding to the loss of one acetylacetonate group to give Mn(acac)Cl$^+$ and Mn(acac)Br$^+$ ions, followed by peaks corresponding to the loss of $\cdot CH_3$ (15) to give the corresponding $MnX(CH_3COCHCO)^+$ ions. These were identified from the isotopic ratios of the doublet peaks for the chloro and bromo derivatives. Similar peaks for the azido and thiocyanato complexes were observed although the necessary metastable measurements required for positive identification were not conducted. The chloro, bromo, and thiocyanato complexes have peaks corresponding to the monomeric parent ions but no peaks at masses corresponding to dimeric species. The fragmentation pattern observed for the Mn(acac)$_2$(NCS)(py) complex gives initially the spectrum for pyridine, corresponding to the loss of pyridine under the high vacuum of the mass spectrometer, followed by a spectrum identical with that for the Mn(acac)$_2$(NCS) complex.

Conductivity and Magnetic Susceptibilities. Values for the molar conductivities (Λ_m) range from 8.0 to 14.8 ohm^{-1} cm^{-2} mol^{-1} in CH_3CN and from 0.04 to 1.57 ohm^{-1} cm^{-2} mol^{-1} in CH_2Cl_2 indicating at most only slight ionic character for the complexes in solution. A 1:1 electrolyte will typically have Λ_m values of 120–160 ohm^{-1} cm^{-2} mol^{-1} in CH_3CN and of 20–30 ohm^{-1} cm^{-2} mol^{-1} in CH_2Cl_2.[8] As expected the complexes show more ionic character in CH_3CN, the more polar solvent.

Magnetic susceptibility measurements for the Mn(acac)$_2$(N$_3$) and Mn(acac)$_2$(NCS) complexes measured at 24° show both complexes to be high-spin Mn(III) complexes. The observed value of μ_{eff} = 4.90 BM for Mn(acac)$_2$(NCS) corresponds to the value expected for high-spin manganese(III) complexes having four unpaired electrons. The value of μ_{eff} = 4.40 BM for Mn(acac)$_2$(N$_3$) is significantly lower than the expected value of 4.90 BM but is consistent with a value of 4.68 BM for Mn(salen)(AcO) (salen = *N,N'*-ethylenebis(salicylaldiminato); AcO = acetate), a complex having bridging acetate groups, and is indicative of the presence of magnetic interactions between adjacent Mn(III) ions.[35,36] Since the most probable mechanism for exchange coupling involves an exchange pathway using the π orbitals of the bridging ligands,[37,38] the lower value of μ_{eff} found in the azide complex relative to Mn(salen)(AcO) is to be expected considering the symmetrically bridging azide groups as having symmetric, uniform orbital systems which in addition to the close distance between the Mn(III) centers of 5.632 Å, compared to 6.536 Å in Mn(salen)(AcO), should offer a stronger coupling between the Mn(III) centers. The normal value of μ_{eff} for Mn(acac)$_2$(NCS) might be expected since the NCS ligand would possess a more localized π-orbital system, less favorable to exchange coupling, and the Mn(III) separation (6.838 Å) is also longer than the separation in either of the other two complexes.

Solid-State Structure of Mn(acac)$_2$(N$_3$). The final coordinates and anisotropic thermal parameters for all nonhydrogen atoms of Mn(acac)$_2$(N$_3$) are listed in Tables II and III, re-

Table II. Atomic Coordinates in Crystalline $Mn(O_2C_5H_7)_2N_3$[a]

	Fractional coordinates		
Atom type[b]	10^4x	10^4y	10^4z
Mn	0	0	0
N_1	313 (2)	1412 (2)	1542 (2)
N_2	0	1387 (2)	2500
O_1	1545 (1)	−671 (1)	328 (1)
O_2	530 (1)	1349 (1)	−1025 (1)
C_1	3560 (2)	−948 (3)	404 (4)
C_2	2479 (2)	−223 (2)	−54 (2)
C_3	2529 (2)	843 (2)	−823 (2)
C_4	1569 (2)	1567 (2)	−1282 (2)
C_5	1702 (3)	2680 (3)	−2138 (2)

[a] Figures in parentheses are the estimated standard deviations. Coordinates given without estimated standard deviations are symmetry required. [b] Atoms labeled in agreement with Figures 1–3.

Table III. Anisotropic Thermal Parameters in Crystalline $Mn(O_2C_5H_7)_2N_3$[a]

	Anisotropic parameters, Å^2						
Atom type[b]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B,[c] Å^2
Mn	2.56 (1)	3.65 (2)	3.23 (2)	0.20 (1)	0.60 (1)	1.15 (1)	2.96
N_1	5.6 (1)	4.9 (1)	3.9 (1)	−0.7 (1)	0.7 (1)	0.3 (1)	4.6
N_2	3.1 (1)	3.2 (1)	3.7 (1)	0.0 (1)	−0.2 (1)	0.0 (1)	3.3
O_1	2.8 (1)	4.0 (1)	4.8 (1)	0.4 (1)	0.6 (1)	1.3 (1)	3.7
O_2	3.5 (1)	4.2 (1)	3.6 (1)	0.1 (1)	0.7 (1)	1.4 (1)	3.5
C_1	2.9 (1)	4.7 (1)	8.0 (1)	0.4 (1)	−0.1 (1)	0.1 (1)	4.8
C_2	2.7 (1)	3.5 (1)	4.1 (1)	−0.1 (1)	0.3 (1)	−0.6 (1)	3.3
C_3	3.1 (1)	4.4 (1)	4.6 (1)	−0.9 (1)	0.9 (1)	0.2 (1)	3.8
C_4	3.9 (1)	3.3 (1)	2.6 (1)	−1.0 (1)	0.4 (1)	−0.2 (1)	3.1
C_5	5.4 (1)	4.6 (1)	3.4 (1)	−2.1 (1)	0.2 (1)	0.6 (1)	4.1

[a] Numbers in parentheses following each B_{ij} value are the estimated standard deviations in the last significant figure. The B_{ij} in Å^2 is related to the dimensionless β_{ij} employed during refinement as: $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$. [b] Atoms labeled in agreement with Table II and Figures 1–3. [c] Isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$.

Table IV. Refined Parameters for Hydrogen Atoms in Crystalline $Mn(O_2C_5H_7)_2(N_3)$[a]

	Fractional coordinates			Isotropic thermal parameter,
Atom type[b]	10^3x	10^3y	10^3z	B, Å^2
H_{11}	368 (4)	−93 (4)	122 (4)	7 (1)
H_{12}	423 (5)	−59 (5)	32 (4)	8 (1)
H_{13}	352 (3)	−178 (5)	19 (4)	6 (1)
H_{31}	328 (2)	110 (3)	−105 (2)	2 (1)
H_{51}	234 (3)	298 (4)	−203 (3)	5 (1)
H_{52}	115 (3)	340 (4)	−195 (3)	3 (1)
H_{53}	152 (3)	238 (3)	−282 (3)	5 (1)

[a] Figures in parentheses are the estimated standard deviations. [b] Atoms labeled in agreement with Figures 1–3.

spectively; the refined positional and isotropic thermal parameters of the hydrogen atoms are listed in Table IV. Each atom is uniquely designated according to the following scheme. A numerical subscript is used to differentiate atoms of the same nonhydrogen element. For each hydrogen atom, the first subscripted number is the same as the subscript of the carbon atom to which it is covalently bonded, while the second subscripted number distinguishes among hydrogen atoms attached to the same carbon atom. Symmetry-related atoms of other asymmetric units are designated by primes.

A model seen in perspective showing the octahedral environment of the Mn atom is shown in Figure 1. All atoms except hydrogen atoms are represented by an ellipsoid having the shape, orientation, and relative size consistent with the thermal parameters listed in Table III. Hydrogen atoms are represented by arbitrarily small spheres for purposes of clarity.

Both the manganese atom and middle nitrogen atom of the azide group occupy special positions in the unit cell. Manganese atoms occupy crystallographic inversion centers at positions 4a[15] (0, 0, 0; 0, 0, 1/2; 1/2, 1/2, 0; 1/2, 1/2, 1/2) of space group $C2/c$, whereas the middle nitrogen atoms of the azide ligands are positioned on twofold axes at positions 4e[15] [±(0, y, 1/4); ±(1/2, 1/2 + y, 1/4)]. All other atoms occupy eightfold general positions 8f[15] [±(x, y, z); ±(x, $\bar{y}$, 1/2 + z); ±(1/2 + x, 1/2 + y, z); ±(1/2 + x, 1/2 − y, 1/2 + z)]. Atoms related to those specified by the coordinates in Tables II and IV by inversion through the manganese atom at the origin of the unit cell are designated by a single prime. Atoms related by the twofold axis at (0, y, 1/4) are designated by double primes.

Each azide ligand bridges two adjacent $Mn(acac)_2^+$ groups in the three-dimensional lattice, using the glide operator to generate infinite chains of octahedral Mn(III) subunits along the $\vec{c}$ axis of the unit cell. A section of one such chain, containing two octahedral Mn(III) groupings, is shown in Figure 2.

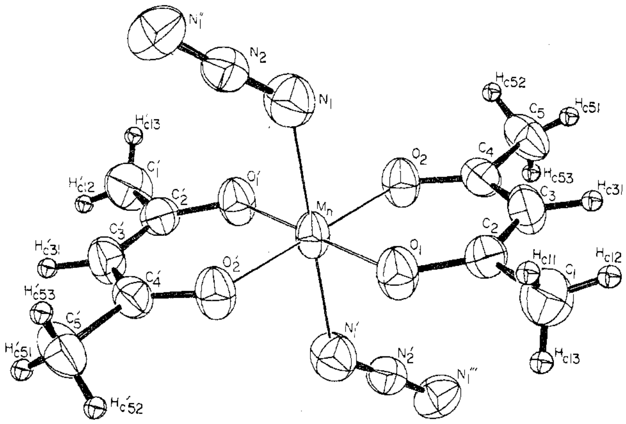


Figure 1. Model in perspective of one octahedral Mn(III) submit of the infinite chains generated along the c axis of the unit cell by the bridging azide ligands. This drawing contains one formula unit plus an additional coordinated azide ligand. All nonhydrogen atoms are represented by ellipsoids which reflect the refined anisotropic thermal parameters. Hydrogen atoms are represented by arbitrarily small spheres which are in no way representative of their true thermal motion.

Values for the bond lengths and angles within the coordination polyhedron and the polyhedral edge lengths are shown in Figure 3 and given along with their estimated standard deviations in Table V. Whereas orthorhombic and tetragonal distortions of the idealized octahedral coordination polyhedron of O_h symmetry are known for high-spin Mn(III) complexes, the majority of those listed in Table VI approximate a tetragonally elongated octahedron. Such a coordination polyhedron would have four short and two long complexing bonds and would ideally possess D_{4h} symmetry. The distortion in $Mn(acac)_2(N_3)$ is clearly of this type with four short Mn–O bonds of average length 1.910 (1, 0, 0) Å[39] and two long trans Mn–N bonds of length 2.245 (2) Å to the ends of the bridging azide ligand. All complexing bond angles are within 1.4° of

Table V. Bond Distances, Polyhedral Edge Lengths, and Bond Angles Subtended at the Mn(III) Atom in the Coordination Group of Crystalline Mn(O$_2$C$_5$H$_7$)$_2$(N$_3$)[a]

Type[b]	Length, Å	Type[b]	Length, Å
Mn–O$_1$	1.910 (1)	O$_1$···N$_1$	2.926 (3)
Mn–O$_2$	1.910 (1)		
		O$_2$···N$_1$	2.924 (3)
Mn–N$_1$	2.245 (2)		
		O$_1$'···N$_1$	2.968 (3)
O$_1$···O$_2$[c]	2.733 (2)		
		O$_2$'···N$_1$	2.970 (3)
O$_1$···O$_2$'	2.668 (2)		
Type[b]	**Angle, deg**	**Type[b]**	**Angle, deg**
O$_1$MnO$_2$	91.39 (6)	O$_1$MnN$_1$	89.16 (8)
O$_1$MnO$_2$'	88.61 (6)	O$_2$MnN$_1$	89.10 (7)

[a] Figures in parentheses are the estimated standard deviations. [b] Atoms labeled in agreement with Tables II–IV and Figures 1–3. Atoms labeled with a prime are related to those in Tables II–IV by the inversion center at the origin of the unit cell. [c] The "bite" of the ligand.

the idealized 90° value. With the exception of the four Mn–O bonds, having an average length of 1.912 (4, 4, 7) Å in Mn(acac)$_2$(NCS),[4] another member in this series, the Mn–O bonds in Mn(acac)$_2$(N$_3$) are somewhat shorter (0.025 Å) than those observed for "short" Mn–O bonds in other tetragonally distorted acetylacetonato complexes of Mn(III). Values of 1.943 (9, 13, 13), 1.935 (3, 3, 7), and 1.959 (5) Å have been determined for such bonds in β-Mn(acac)$_3$,[40] γ-Mn(acac)$_3$,[4] and Mn(acac)(*N*-phenylaminotroponiminato)$_2$,[3] respectively.

The Mn–N bond length of 2.245 (2) Å is ~0.25 Å longer than the "normal" Mn–N bonds observed in other compounds and 0.09 Å longer than the "long" Mn–N bond observed in Mn(acac)(*N*-phenylaminotroponiminato)$_2$.[3] While no O···N contact in the coordination polyhedron is less than 2.90 Å, the sum of the van der Waals radii for oxygen and nitrogen, all O···O contacts are less than the 2.80 Å van der Waals diameter of oxygen.

These observations are all consistent with a Mn(III) atom in the high-spin state with one 3d electron occupying each of the three nonbonding (d_{xy}, d_{xz}, and d_{yz}) metal orbitals and the fourth 3d electron occupying the antibonding d_{z^2} orbital (the *z* axis is collinear with the idealized fourfold axis of the coordination polyhedron). Preference of the metal for the acetylacetonate ligands with their "normal" distribution of negative charge and π-bonding capabilities over the bridging anionic X ligands which must share their net charge with two metals is probably responsible for the shortening of the four equatorial Mn–O bonds in Mn(acac)$_2$(N$_3$) and Mn(acac)$_2$(NCS) relative to the equatorial Mn–O bonds in other tetragonally elongated acetylacetonate complexes of manganese(III) and for the ~0.06-Å lengthening of the Mn–N bond over the value observed for a similar bond in the tetragonally elongated coordination polyhedron of Mn(TPP)(N$_3$)(CH$_3$OH)·CH$_3$OH where the azide ligand is coordinated to only

Table VI. Comparison of Metal–Ligand (M–L) Bond Lengths in Octahedral High-Spin Manganese (III) Complexes[a]

Compd	Ligand	Equatorial M–L, Å	Ligand	Axial M–L, Å	Ref
Homoligand Mn(LL)$_3$ Species					
γ-Mn(acac)$_3$	O	1.935 (3, 4, 7)	O	2.111 (4, 2, 2)	*e*
β-Mn(acac)$_3$[b]	O	2.000 (8, 12, 20)	O	1.943 (9, 13, 13)	*f*
Mn(trop)$_3$[c,d]	O	1.94 (1, 2, 2)	O	2.13 (1, 2, 2)	*g*
Mn(dtc)$_3$[d]	S	2.404 (8, 26, 31)	S	2.549 (7, 8, 8)	*h*
Homoligand Mn(L)$_6$ Species					
(K$_2$Na)[MnF$_6$]	F	1.86	F	2.06	*i*
K$_2$MnF$_5$·H$_2$O	F	1.832 (7, 11, 11)	F	2.072 (4)	*j*
Cs$_2$KMnF$_6$	F	1.92	F	2.07	*k*
(NH$_4$)$_2$MnF$_5$	F	1.840 (7, 2, 2)	F	2.091 (5)	*l*
Heteroligand Mn(LL)$_2$(L'L') Species					
Mn(acac)(pati)$_2$[d]	O(L')	1.959 (5)	O(L')	2.134 (5)	*m*
	N(L)	2.020 (5, 1, 1)	N(L)	2.153 (5)	
Heteroligand Mn(LL)$_2$(L')$_2$ Species					
Mn(acac)$_2$(N$_3$)	O(L)	1.910 (1, 0, 0)	N(L')	2.245 (2)	*n*
Heteroligand Mn(LL)$_2$(L')(L'') Species					
Mn(acac)$_2$(NCS)	O(L)	1.912 (4, 4, 7)	N(L')	2.189 (5)	*e*
			S(L'')	2.889 (2)	
Heteroligand Mn(L$_4$)(L')(L'') Species					
Mn(TPP)(N$_3$) (CH$_3$OH)·CH$_3$OH[d]	N(L)	2.031 (7, 10, 15)	O(L')	2.329 (8)	*e*
			N(L'')	2.176 (9)	
Heteroligand Mn(L$_2$L'$_2$)(L'')$_2$ Species					
Mn(salen)(AcO)[d]	O(L)	1.888 (4)	O(L'')	2.201 (5)	*o*
	N(L')	1.989 (5)			

[a] The first number in parentheses following each entry for an averaged bond length in the table is the rms value of the estimated standard deviation of a single value. The second and third numbers, when given, represent the mean and maximum deviation from the averaged value, respectively. [b] The six independent Mn–O bonds in this complex can be grouped into three pairs having averaged lengths of 1.944 (9, 13, 13), 1.988 (8, 4, 4), and 2.012 (8, 8, 8) Å in conformity with an orthorhombic distortion of the coordination polyhedron as well as into the four long–two short categories consistent with a tetragonal compression of the polyhedron. Results of a similar study for β-Mn(acac)$_3$ performed in this laboratory show similar results with the three pairs of Mn–O bonds averaging 1.943 (5, 7, 7), 1.985 (5, 2, 2), and 2.016 (5, 2, 2) Å, respectively. [c] The complex contains two crystallographically independent Mn(O$_2$C$_7$H$_5$)$_3$ molecules. Values in the table are for the molecule having a tetragonally elongated coordination polyhedron; the coordination polyhedron of the second molecule exhibits an orthorhombic distortion, having three pairs of Mn–O distances having averaged values of 1.94, 1.99, and 2.05 Å, respectively. [d] trop is the tropolonato anion, dtc is the *N,N*-diethyldithiocarbamato anion, pati is the *N*-phenylaminotroponiminato anion, salen is the *N,N'*-ethylenebis(salicylaldiminato) dianion, AcO is the acetate ion, and TPP is the α,β,γ,δ-tetraphenylporphinato dianion. [e] See ref 4. [f] J. P. Fackler, Jr., and A. Avdeef, *Inorg. Chem.*, **13**, 1864 (1974). [g] J. P. Fackler, Jr., A. Avdeef, and J. A. Costamagna, *ibid.*, **13**, 1854 (1974). [h] P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1883 (1972). [i] K. Knox, Abstracts, 6th International Congress of International Union of Crystallography, Rome, 1963; *Acta Crystallogr. (Suppl.), Sect. A*, **16**, 45 (1963). [j] A. J. Edwards, *J. Chem. Soc. A*, 2654 (1971). [k] V. S. Schneider and R. Hoppe, *Z. Anorg. Allg. Chem.*, **376**, 268 (1970). [l] D. R. Sears and J. L. Hoard, *J. Chem. Phys.*, **50**, 1066 (1969). [m] See ref 3. [n] This work. [o] See ref 35.

Table VII. Bond Lengths and Angles for the Acetylacetonate and Azide Ligands in Crystalline $Mn(O_2C_5H_7)_2(N_3)^a$

Type^b	Length, Å	Av^c	Type^b	Length, Å	Av^c
N_1-N_2	1.166 (2)		C_1-H_{11}	0.92 (4)	0.89 (5, 2, 3)
O_1-C_2	1.274 (2)	1.274 (2, 0, 0)	C_1-H_{12}	0.87 (5)	
O_2-C_4	1.274 (2)		C_1-H_{13}	0.87 (5)	
C_1-C_2	1.496 (3)	1.493 (3, 3, 3)	C_3-H_{31}	0.97 (3)	
C_4-C_5	1.490 (3)		C_5-H_{51}	0.79 (4)	0.88 (4, 8, 12)
C_2-C_3	1.378 (3)	1.382 (3, 4, 4)	C_5-H_{52}	1.00 (4)	
C_3-C_4	1.386 (3)		C_5-H_{53}	0.84 (3)	

Type^b	Angle, deg	Av^c	Type^b	Angle, deg	Av^c
MnN_1N_2	131.3 (2)		$C_2C_3H_{31}$	117 (2)	118 (2, 1, 1)
MnO_1C_2	127.7 (1)	127.8 (1, 1, 1)	$C_4C_3H_{31}$	118 (2)	
MnO_2C_4	127.9 (1)		$C_2C_1H_{11}$	113 (3)	111 (3, 3, 8)
$N_1N_2N_1'$	177.5 (3)		$C_2C_1H_{12}$	119 (3)	
$O_1C_2C_1$	114.6 (2)	114.9 (2, 3, 3)	$C_2C_1H_{13}$	111 (3)	
$O_2C_4C_5$	115.2 (2)		$C_4C_5H_{51}$	109 (2)	
$O_1C_2C_3$	124.5 (2)	124.4 (2, 2, 2)	$C_4C_5H_{52}$	107 (2)	
$O_2C_4C_3$	124.2 (3)		$C_4C_5H_{53}$	107 (2)	
$C_1C_2C_3$	121.0 (2)	120.9 (2, 2, 2)	$H_{11}C_1H_{12}$	92 (4)	108 (4, 6, 16)
$C_5C_4C_3$	120.7 (2)		$H_{11}C_1H_{13}$	107 (4)	
$C_2C_3C_4$	124.4 (2)		$H_{12}C_1H_{13}$	113 (4)	
			$H_{51}C_5H_{52}$	107 (3)	
			$H_{51}C_5H_{53}$	116 (3)	
			$H_{52}C_5H_{53}$	110 (3)	

[a] Figures in parentheses are the estimated standard deviations of the individual measurements. [b] Atoms labeled in agreement with Tables II-IV and Figures 1-3. Atoms labeled with a prime are related to those in Tables II-IV by the inversion center at the origin of the unit cell. [c] The first number in parentheses after each averaged value is the rms value of the estimated standard deviation for an individual datum. The second and third numbers are the mean and maximum deviations from the average value, respectively.

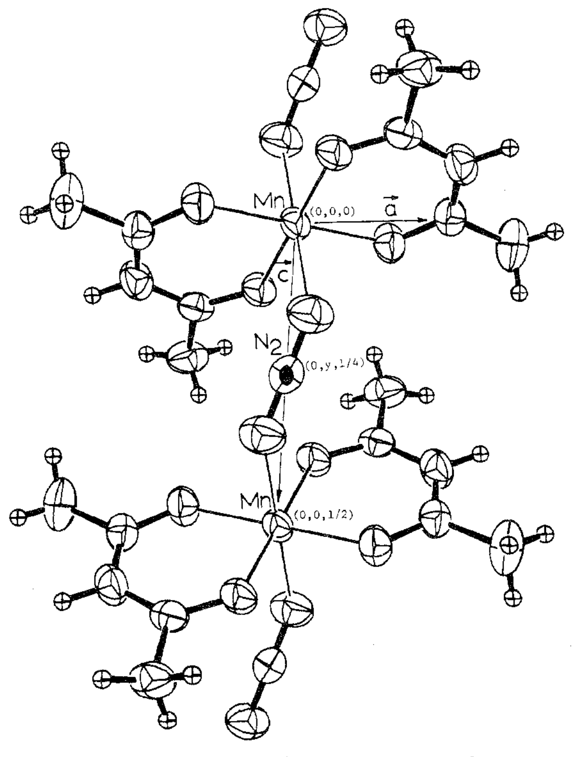


Figure 2. An ORTEP drawing showing a segment of one infinite chain of $Mn(acac)_2^+$ groups linked together by symmetrically bridging azide ligands. The crystallographic inversion centers at (0, 0, 0) and (0, 0, $^1/_2$) of space group $C_{2/c}$ are noted as is the crystallographic two-fold axis at (0, y, $^1/_4$).

one metal atom. This view is supported by the observation of two short Mn–O bonds of length 1.888 (4) Å for the oxygen atoms of the *N*,*N*'-ethylenebis(salicylaldiminato), salen, dianionic ligand in Mn(salen)(OAc),[35] a Mn(III) complex containing a bridging anionic acetate (OAc) ligand with Mn–O bond lengths of 2.201 (5) Å or ~0.09 Å longer than the "long" Mn–O bonds in γ-$Mn(acac)_3$.

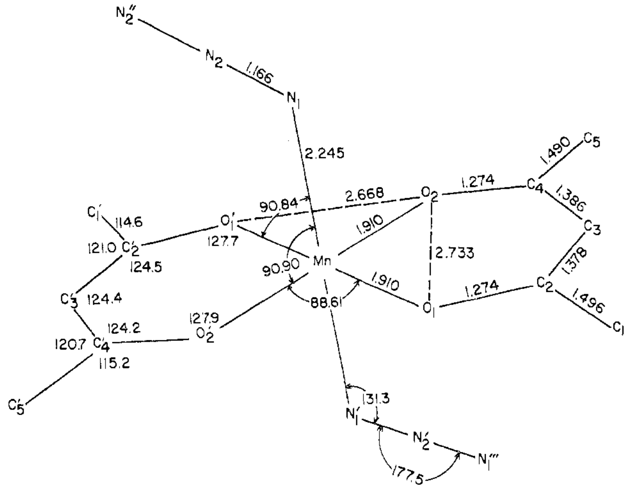
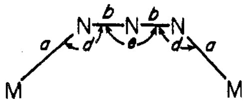


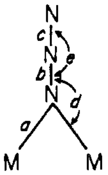
Figure 3. Diagram derived from the ORTEP drawing of Figure 1 showing selected bond lengths and bond angles in the solid-state structure of $Mn(acac)_2(N_3)$.

The entire seven-atom (excluding hydrogens) acetylacetonato ligand skeleton in $Mn(acac)_2(N_3)$, unlike those in other acetylacetonato complexes,[41,42] is quite planar with the maximum displacement of any atom from its least-squares mean plane (given by the equation $-0.0594X - 0.6314Y - 0.7732Z = 0.014$, where X, Y, and Z are orthogonal coordinates in Å along a, b, and c^*, respectively, of the crystallographic coordinate system) being 0.021 Å for O_1. With the manganese atom displaced by only 0.022 Å from the least-squares mean plane of the five-atom (O_1, O_2, C_2, C_3, C_4) acetylacetonato chelate ring, the angle of folding of the ligand along the $O_1 \cdots O_2$ polyhedral edge is only 1.06°. Intra- and intermolecular steric constraints are believed to be responsible for the major foldings of the six-membered acetylacetonato chelate ring ($-M-O_1-C_2-C_3-C_4-O_2-$) along $O_1 \cdots O_2$ edges of the coordination polyhedron observed in several other crystallographic studies as well as for the distortion of the ligand from planarity which often accompanies such a folding.[41,43-45]

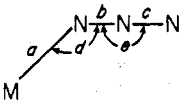
Table VIII. Comparison of Bond Lengths and Bond Angles for Coordinated Azide Ligands[a]



type I



type II



type III

Complex	Type	a,[b] A	b,[b] A	c,[b] A	d,[b] deg	e,[b] deg	Ref
Bridging N_3^- Groups							
$Mn(acac)_2(N_3)$[c]	I	2.245 (2)	1.166 (2)		131.3 (2)	177.5 (3)	*h*
$[Cu(N_3)(P(C_6H_5)_3)_2]_2$	I	2.10 (1, 1, 2)	1.18 (1, 1, 2)		122 (1, 2, 4)	178 (1, 1, 1)	*i*
$[Pd_2(N_3)_6]^{2-}$[d]	II	2.00 (1, 1, 1)	1.24 (1)	1.14 (1)	128 (1, 1, 1)	175 (1)	*j*
	III	2.00 (1, 1, 1)	1.21 (1, 1, 1)	1.14 (1, 2, 2)	121 (1, 2, 2)	173 (1, 1, 1)	
$[(CO)_3Mn(N_3)_3Mn(CO)_3]^-$	II	2.08 (2, 2, 3)	1.22 (3, 2, 2)	1.15 (3, 3, 5)			*k*
$[Co(acac)_2(N_3)]_2$[c]	II	1.966 (4, 1, 4)	1.230 (7)	1.136 (8)	117.3 (4, 2, 2)	177.1 (9)	*l*
$[Ni_2(C_{14}H_{32}N_4)_2(N_3)_3]^+I^-$	I	2.13 (1, 2, 2)	1.17 (2)		142	179	*m*
Nonbridging N_3^- Groups							
$Mn(TPP)(N_3)(CH_3OH)\cdot CH_3OH$[c]	III	2.176 (9)	1.162 (10)	1.159 (10)	124.4 (8)	178 (2)	*n*
$Mn(TPP)(N_3)\cdot C_6H_6$[c]	III	2.045 (3)	1.168 (5)	1.168 (5)	127.0 (3)	178.3 (8)	*o*
$Cu(N_3)_2(NH_3)_2(NH_3)_2$	III	2.053 (8, 1, 1)	1.182 (10, 6, 6)	1.141 (13, 2, 2)	118.9 (5, 26, 26)	177.6 (7, 1, 1)	*p*
$[Co(NH_3)_5(N_3)](N_3)_2$[e]	III	1.943 (5)	1.208 (7)	1.145 (7)	125.2 (3)	179.3 (3)	*q*
$Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$	III	2.040 (13)	1.196 (18)	1.076 (18)	132 (1)	179 (1)	*r*
$Cu(Br)(N_3)(HN((CH_2)_2\text{-}N(C_2H_5)_2)_2)$	III	1.927 (6)	1.145 (8)	1.144 (9)	125.4 (5)	175.5 (10)	*s*
$[Fe(N_3)_5]^-$[f]	III	1.99 (3, 3, 5)	1.16 (3)		125.0		*t*
$Ni(NO)(P(C_6H_5)_3)_2(N_3)$	III	2.018 (8)	0.977 (9)	1.282 (11)	128.1 (9)	175.1 (11)	*u*
sym-$[Co(trenen)(N_3)]^{2+}$[c]	III	1.957 (6)	1.209 (7)	1.152 (7)	119.0 (5)	176.4 (9)	*v*
cis-$[Co(en)_2(N_3)_2]^+$[c,g]	III	1.97 (1)	1.13 (2, 2, 2)	1.19 (2, 5, 5)	120 (2, 1, 1)	179 (2, 0, 0)	*w*
$Zn(C_5H_5N)_2(N_3)_2$	III	1.94 (2, 1, 1)	1.16 (2, 1, 1)	1.13 (2, 0, 0)	129 (1, 0, 0)	175 (2, 2, 2)	*x*
$[Ru(en)_2(N_2)(N_3)]^+$[c]	III	2.121 (8)	1.17 (1, 9, 0)	1.14 (1, 6, 1)	116.7 (7)	180 (1)	*y*

[a] The first number in parentheses following each entry in the table for an averaged bond length or angle is the rms value of the estimated standard deviation of a single value. The second and third numbers when given represent the mean and maximum deviation from the averaged value, respectively. [b] The parameters being compared are shown in the accompanying drawings. [c] acac is the acetylacetonato anion, TPP is the [α,β,γ,δ-tetraphenylporphinato] dianion, trenen is 4-(2-aminoethyl)-1,4,7,10-tetraazadecane, and en is ethylenediamine. [d] The complex contained both terminal and bridging azido groups. [e] The crystal also contains noncomplexed azide anions having averaged N–N distances of 1.165 (7, 7, 7) A. [f] Only averaged N–N bond lengths were reported and no values for the $N_1N_2N_3$ angles were given. [g] Two-dimensional X-ray data only. [h] This work. [i] See ref 48. [j] W. P. Fehlhammer and L. F. Dahl, *J. Amer. Chem. Soc.*, 94, 3377 (1972). [k] R. Mason, *et al.*, *Chem. Commun.*, 496 (1971). [l] V. W. Day, unpublished results. [m] F. Wagner, *et al.*, *J. Amer. Chem. Soc.*, **96**, 2625 (1974). [n] See ref 4. [o] V. W. Day, unpublished results. [p] I. Agrell, *Acta Chem. Scand.*, 20, 1281 (1966). [q] G. J. Palenik, *Acta Crystallogr.*, 17, 360 (1964). [r] A. P. Gaughan, R. F. Ziolo, and Z. Dori, *Inorg. Chem.*, **10**, 2776 (1971). [s] R. F. Ziolo, *et al.*, *ibid.*, **11**, 3044 (1972). [t] J. Drummond and J. S. Wood, *Chem. Commun.*, 1373 (1969). [u] J. H. Enemark, *Inorg. Chem.*, **10**, 1952 (1971). [v] I. E. Maxwell, *ibid.*, **10**, 1782 (1971). [w] V. M. Padmanabham, R. Balasubramanian, and K. V. Muralidharan, *Acta Crystallogr., Sect. B,* **24**, 1638 (1968). [x] I. Agrell, *Acta Chem. Scand.*, **24**, 1247 (1970). [y] B. R. Davis and J. A. Ibers, *Inorg. Chem.*, 9, 2768 (1970).

The virtual planarity of the seven-membered ligand skeleton, the small folding angle of the six-membered chelate ring, and the absence of any intermolecular contacts which are smaller than the corresponding sum of van der Waals radii indicate a favorable packing of undistorted $Mn(acac)_2^+$ species bridged symmetrically by azide ligands in the three-dimensional lattice.

Bond lengths and angles within the acetylacetonate and azide ligands are shown in Figure 3 and are given with their estimated standard deviations in Table VII. Chemically equivalent bond lengths and angles not involving hydrogen atoms within the acetylacetonato ligand differ by less than two standard deviations. The averaged values of bond angles not involving hydrogen atoms and the averaged values of 1.274 (2, 0, 0), 1.382 (3, 4, 4), and 1.493 (3, 3, 3) Å for the C–O, C–C(chelate ring), and C–C(methyl) bond lengths, respectively, are in good agreement with values obtained for corresponding bonds in other accurate structural studies of compounds containing nonbridging bidentate acetylacetonato ligands.[46,47]

Table VIII gives a comparison of the bonding parameters involving the coordinated azide ligand in $Mn(acac)_2(N_3)$ with those determined for coordinated azide ligands in several other compounds. The $Mn-N_1-N_2$ bond angle of 131.3 (2)° falls within the range of 117–142° for similar entries in Table VIII and is most comparable to the 132° angle observed in $Cu_2(N_3)_2((CH_2P(C_6H_5)_2)_2)_3$.[48] While the N_1-N_2 bond length of 1.166 (2) Å does not differ significantly from any of the values for corresponding bonds in Table VIII, it is most similar to the values observed in the azido(α,β,γ,δ-tetraphenylporphinato)manganese(III) complexes.

Acknowledgment. We wish to thank Professor J. P. Fackler, Jr., for kindly furnishing preprints of his work and Professor J. L. Hoard of Cornell University for providing the results of piezoelectric tests for $Mn(acac)_2(N_3)$. Support from the UNL-Research Council and a generous grant of computer time from the UNL-Computing Center are gratefully acknowledged. Summer support from Conoco and the 3M Company is acknowledged by B. R. S.

Registry No. $Mn(acac)_2(N_3)$, 52242-29-2; $Mn(acac)_2(NCS)$, 52242-31-6; $Mn(acac)_2Cl$, 14690-80-3; $Mn(acac)_2Br$, 51371-60-9; $Mn(acac)_2(NCS)(py)$, 53078-67-4; pyridine, 110-86-1; $Mn(acac)_3$, 14284-89-0.

Supplementary Material Available. A listing of structure factor amplitudes for $Mn(acac)_2(N_3)$ 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 AIC403509.

References and Notes

(1) Presented before the 8th Midwest Regional American Chemical Society Meeting, Columbia, Mo., 1972, and the American Crystallographic Association summer meeting, Storrs, Conn., 1973.

(2) B. Morosin and J. R. Brathovde, *Acta Crystallogr.*, **17**, 705 (1964).

(3) M. Bartlett and G. J. Palenik, *Chem. Commun.*, 416 (1970).

(4) V. W. Day, B. R. Stults, E. L. Tasset, R. O. Day, and R. S. Marianelli, *J. Amer. Chem. Soc.*, **96**, 2650 (1974).

(5) (a) D. M. Collins, W. R. Scheidt, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 6689 (1972); (b) A. B. Hoffman, D. M. Collins, V. W. Day, E. B. Fleischer, T. S. Srivastava, and J. L. Hoard, *ibid.*, **94**, 3620 (1972).

(6) J. L. Hoard, *Science*, **174**, 1295 (1971), and references cited therein.

(7) B. R. Stults, V. W. Day, E. L. Tasset, and R. S. Marianelli, *Inorg. Nucl. Chem. Lett.*, **9**, 1259 (1973).

(8) W. J. Geary, *Coord. Chem. Rev.*, **7**, 84 (1971), and references cited therein.

(9) G. Schwarzenbach and H. Flaschka, "Complexometric Titrations," Methuen, London, Great Britain, 1969, p 230.

(10) R. B. Fischer and D. G. Peters, "Quantitative Chemical Analysis," W. B. Saunders Co., Philadelphia, Pa., 1969, p 253.

(11) A. Earnshaw, "Introduction to Magnetochemistry," Academic Press, New York, N. Y., 1968.

(12) R. G. Charles, *Inorg. Syn.*, 7, 183 (1963).

(13) (a) G. H. Cartledge, *J. Amer. Chem. Soc.*, **73**, 4416 (1951); (b) G. H. Cartledge, *ibid.*, **74**, 6015 (1952).

(14) The number in parentheses following each *m/e* value is the relative abundance of the corresponding ion with mass 154 taken as the base peak for all complexes.

(15) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1969, pp 89, 101.

(16) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1968, p 166.

(17) D. T. Cromer and J. L. Mann, *Acta Crystallogr., Sect. A*, **24**, 324 (1968).

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

(19) See paragraph at end of paper regarding supplementary material.

(20) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley-Interscience, New York, N. Y., 1970.

(21) M. Mikami, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta, Part A*, **23**, 1037 (1967).

(22) S. Pinchas, B. L. Silver, and I. Laulicht, *J. Chem. Phys.*, **46**, 1506 (1967).

(23) K. Nakamoto, C. Udovich, and J. Takemoto, *J. Amer. Chem. Soc.*, **92**, 3973 (1970).

(24) P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4812 (1960).

(25) K. Bowman and Z. Dori, *Inorg. Chem.*, **9**, 395 (1970).

(26) R. Ziolo, J. Thick, and Z. Dori, *Inorg. Chem.*, **11**, 626 (1972).

(27) W. Beck, W. P. Fehlhammer, P. Pollmann, and R. S. Tobias, *Inorg. Chim. Acta*, **2**, 467 (1968).

(28) R. F. Ziolo and Z. Dori, *J. Amer. Chem. Soc.*, **90**, 6560 (1968).

(29) D. R. Herrington and L. J. Boucher, *Inorg. Nucl. Chem. Lett.*, **7**, 1091 (1971).

(30) R. J. H. Clark and C. S. Williams, *Spectrochim. Acta*, **22**, 1081 (1966).

(31) A. R. Davis, C. J. Murphy, and R. A. Plane, *Inorg. Chem.*, **9**, 423 (1970).

(32) S. C. Jain and R. Rivest, *Inorg. Chim. Acta*, **4**, 291 (1970).

(33) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

(34) C. G. McDonald and J. S. Shannon, *Aust. J. Chem.*, **19**, 1545 (1966).

(35) J. E. Davis, B. M. Gatehouse, and K. S. Murray, *J. Chem. Soc., Dalton Trans.*, 2523 (1973).

(36) A. Earnshaw, E. A. King, and L. K. Larkworthy, *J. Chem. Soc. A*, 1048 (1968).

(37) R. L. Martin, "New Pathways in Inorganic Chemistry," University Press, Cambridge, 1968, p 175.

(38) A. P. Gineberg, *Inorg. Chim. Acta*, **5**, 45 (1971).

(39) The first number in parentheses following an averaged value is the rms value of the estimated standard deviation of a single value. The second and third numbers, when given, represent the mean and maximum deviation from the averaged value, respectively.

(40) J. P. Fackler, Jr., and A. Avdeef, *Inorg. Chem.*, **13**, 1864 (1974).

(41) S. Koda, *et al.*, *J. Chem. Soc. D.*, 1321 (1971).

(42) The crystal structure of Mn(acac)$_2$(NCS), see ref 4, shows the seven-atom (excluding hydrogen atoms) acetylacetonate ligand to be nonplanar, having deviations from planarity as large as 0.09 Å.

(43) R. B. Von Dreele, J. J. Stezowski, and R. C. Fay, *J. Amer. Chem. Soc.*, **93**, 2887 (1971).

(44) J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, **2**, 243 (1963).

(45) M. R. Caira, J. M. Haigh, and T. R. Nassimbeni, *Inorg. Nucl. Chem. Lett.*, **8**, 109 (1972).

(46) E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, **88**, 2951 (1966).

(47) P. K. Hon and C. E. Pfluger, *J. Coord. Chem.*, **3**, 67 (1973).

(48) R. F. Ziolo, A. P. Gaughan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *Inorg. Chem.*, **10**, 1289 (1971).

Contribution from the Department of Chemistry,
University of Michigan, Ann Arbor, Michigan 48104

Crystal and Molecular Structure of Cyanobis(1,10-phenanthroline)copper(II) Nitrate Monohydrate

OREN P. ANDERSON*

Received June 26, 1974 AIC40414F

The crystal and molecular structure of cyanobis(1,10-phenanthroline)copper(II) nitrate monohydrate, $[Cu(N_2C_{12}H_8)_2CN](NO_3)\cdot H_2O$, has been determined from three-dimensional single-crystal X-ray diffraction data, collected by counter techniques. The dark-blue crystals are triclinic, space group $P\bar{1}$ (No. 2), with two formula units in a unit cell of dimensions $a = 10.816$ (2) Å, $b = 12.098$ (2) Å, $c = 10.118$ (2) Å, $\alpha = 105.62$ (2)°, $\beta = 110.10$ (2)°, $\gamma = 66.68$ (2)°. The structure was refined by full-matrix least-squares methods to a weighted R of 0.076 for 2392 independent reflections with $I > 3\sigma(I)$. The coordination geometry of the monomeric complex ion is based on a distorted trigonal bipyramid with the cyanide ligand bonding to copper(II) in an equatorial position. Bond lengths are as follows: Cu–N(equatorial), 2.123 (6) and 2.102 (6) Å; Cu–N(axial), 2.001 (10) and 2.014 (10) Å; Cu–C, 1.935 (10) Å; C–N(cyanide), 1.16 (1) Å. The water molecule of hydration is found to be hydrogen bonded simultaneously to the nitrogen atom of the coordinated cyanide ion and to one of the nitrate oxygen atoms.

Introduction

The most interesting aspects of the coordination chemistry of copper(II) can be succinctly summarized: (1) the variety of coordination geometries available about Cu(II), (2) the influence of the 3d^9 electronic distribution on the coordination geometry, and (3) the relative stability *vs.* the 1+ oxidation state as a function of coordinating ligand and coordination geometry. With regard to the last point, it has long been known that several ligands, among them the iodide and cyanide ions, do not generally form stable complexes with the cupric ion. In aqueous solution at ordinary temperatures, cyanide reduces copper(II) to cuprous cyanide, with simultaneous formation of cyanogen.[1] At low temperatures in nonaqueous solvents, the existence of complex ions such as the tetracyanocuprate(II) anion has been claimed, although the ion has not been isolated.[2]

Recently, it has been shown that by choosing ligands which strongly prefer to coordinate the cupric rather than the cuprous ion, it is possible to stabilize the copper(II) ion sufficiently to allow direct bonding between cyanide and the cupric ion in aqueous solution at ordinary temperatures. Such was the case for the stable complexes $[Cu(tet\text{-}a)CN]ClO_4\cdot H_2O$ (tet-a = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) and $[Cu_2A_2(CN)](ClO_4)_3$ (A = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene),[3] the

---

* Address correspondence to the Department of Chemistry, Colorado State University, Fort Collins, Colo. 80523.