Syntheses and Characterization of Thiolate-Bridged Manganese(II) Complexes with NNS-Tridentate Thiolic Ligands

Masahiro MIKURIYA,* Fumiya ADACHI, Hirofumi IWASAWA, Makoto HANDA,†
Masayuki KOIKAWA,††,# and Hisashi ŌKAWA††
Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662
† Department of Chemistry, Faculty of Science, Shimane University, Matsue 690
††Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812

(Received May 30, 1994)

Manganese(II) complexes with 2-[(2-aminoethyl)amino]ethanethiol (HL_a), 2-[(3-aminopropyl)amino]ethanethiol (HL_b), 2-[(2-pyridylmethyl)amino]ethanethiol (HL_c), and 2-[[2-(2-pyridyl)ethyl]amino]ethanethiol (HL_d)–$[Mn(La)Cl]_n$ (**1**), $[Mn\{Mn(L_b)_2\}_2]Cl_2\cdot 2CH_3OH$ (**2**), $[Mn(L_c)Cl]_n$ (**3**), and $[Mn(L_d)Cl(CH_3OH)]_n$ (**4**) have been synthesized and characterized by elemental analyses, infrared and electronic spectroscopies, and magnetic susceptibilities (80—300 K). The crystal structures of all these complexes were determined by the single-crystal X-ray diffraction method. Complexes **1** and **3** have a thiolate-bridged polymeric chain structure in which each manganese atom is five-coodinated in a trigonal bipyramid. Complex **2** is a thiolate-bridged trinuclear manganese(II) complex displaying a linear arrangement of the three manganese atoms with the two Mn–Mn interactions being equidistant [3.420(1) Å]. Complex **4** is a thiolate-bridged polymeric infinite chain showing a distortion in the octahedral geometry around each manganese atom. The magnetic properties are discussed in relation to the crystal structures.

Thiolate complexes of the divalent metal ions of Mn to Zn have attracted much attention in the last two decades because of the recognition of their biological significance.[1—3] Of these metal thiolates, the chemistry of the manganese(II) thiolates is the least developed. So far, the manganese(II) thiolates are confined to those with several simple thiols such as thiophenol.[4—9] As part of a continuing project on metal thiolates,[10—16] we reported previously the syntheses and characterization of thiolate-bridged nickel(II) complexes by using tridentate thiolic ligands with a NNS-donor set, 2-[(2-aminoethyl)amino]ethanethiol (HL_a), 2-[(3-aminopropyl)amino]ethanethiol (HL_b), 2-[(2-pyridylmethyl)amino]ethanethiol (HL_c), and 2-[[2-(2-pyridyl)ethyl]-amino]ethanethiol (HL_d). These complexes are dinuclear and diamagnetic, and the coordination environments of the nickel(II) atoms are square-plane. In this study, we have extended our efforts to manganese chemistry and isolated novel polymeric and trinuclear manganese(II) complexes with these ligands. A similar study has been carried out previously by Handa et al.[17] Based on the magnetic data, they proposed dinuclear structures, $[Mn_2(L)_2Cl_2]$, and trinuclear structures, $[Mn\{Mn(L)_2\}_2]^{2+}$, for the manganese(II) complexes obtained from the reaction of equimolar amounts of manganese(II) salts and these thiolic ligands. However, they were not able to obtain crystals suitable for single-crystal X-ray diffraction studies. We have successfully performed structural analyses of this series of manganese thiolates. X-ray crystallography has confirmed the existence of the trinuclear species. Furthermore, this study has shown that although the other previous complexes were identified as dimeric, they are, in fact, repeat fragments of polymeric structures. All other data obtained point to the fact that the present complexes are indeed exactly the same as those reported by Handa et al. We herein report the syntheses, X-ray crystal structures, and magnetic properties of $[Mn(L_a)-Cl]_n$ (**1**), $[Mn\{Mn(L_b)_2\}_2]Cl_2\cdot 2CH_3OH$ (**2**), $[Mn(L_c)-Cl]_n$ (**3**), and $[Mn(L_d)Cl(CH_3OH)]_n$ (**4**). Preliminary results were reported elsewhere.[18]

Experimental

Syntheses of Complexes. The thiolic ligands—HL_a, HL_b, HL_c, and HL_d—were synthesized using a procedure described in the literature.[12] All reactions were performed under an atmosphere of argon using standard Schlenk techniques.

$[Mn(L_a)Cl]_n$ (1). To a solution of manganese(II) chloride tetrahydrate (111 mg, 0.83 mmol) in methanol (3 ml) was added a methanol solution (5 ml) of HL_a (100 mg, 0.83 mmol) and the mixture was allowed to stand overnight to give yellow prisms. These were collected by filtration (yield: 47 mg, 27%). Found: C, 22.83; H, 5.45; N, 13.37%. Calcd for $C_4H_{11}ClMnN_2S$: C, 22.92; H, 5.29; N, 13.37%. Diffuse reflectance spectrum λ_{max}/nm 223, 325sh, 374sh, and 446sh. μ_{eff} (290 K) per Mn/B.M. 4.94.

$[Mn\{Mn(L_b)_2\}_2]Cl_2\cdot 2CH_3OH$ (2). To a solution of manganese(II) chloride tetrahydrate (165 mg, 0.56 mmol) in methanol (3 ml) was added a methanol solution (5 ml) of HL_b (100 mg, 0.75 mmol). The mixture was allowed to stand for a few days to give greenish yellow prisms which were collected by filtration (yield: 64 mg, 41%). Found: C, 31.77; H, 7.26; N, 13.26%. Calcd for $C_{22}H_{60}Cl_2Mn_3N_8O_2S_4$: C, 31.73; H, 7.26; N, 13.46%. Diffuse reflectance spectrum λ_{max}/nm 238, 300sh, 428sh, and 486sh. μ_{eff} (291 K) per Mn/B.M. 5.00.

$[Mn(L_c)Cl]_n$ (3). To an *N,N*-dimethylformamide solution (5 ml) of manganese(II) chloride tetrahydrate (220 mg,

#Present address: Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840.

1.11 mmol) was added a solution of HL_c (200 mg, 1.19 mmol) in *N*,*N*-dimethylformamide (5 ml). The solution was allowed to stand for several days to form pale yellow prisms (yield: 119 mg, 42%). Found: C, 37.13; H, 4.30; N, 10.87%. Calcd for $C_8H_{11}ClMnN_2S$: C, 37.29; H, 4.30; N, 10.87%. Diffuse reflectance spectrum λ_{max}/nm 260, 318sh, and 447sh. μ_{eff} (290 K) per Mn/B.M. 5.01.

$[Mn(L_d)Cl(CH_3OH)]_n$ (4). To a methanol solution (5 ml) of manganese(II) chloride tetrahydrate (109 mg, 0.55 mmol) was added a solution of HL_d (100 mg, 0.55 mmol) in methanol (5 ml) and the mixture was allowed to stand for several days to form pale greenish yellow prisms (yield: 56 mg, 34%). Found: C, 39.54; H, 5.64; N, 9.16%. Calcd for $C_{10}H_{17}ClMnN_2OS$: C, 39.54; H, 5.49; N, 9.22%. Diffuse reflectance spectrum λ_{max}/nm 273, 368sh, and 449sh. μ_{eff} (290 K) per Mn/B.M. 5.30.

Measurements. Elemental analyses (C, H, and N) were carried out using a Perkin–Elmer 2400 Series II CHNS/O Analyzer. Infrared spectra were measured with a JASCO Infrared Spectrometer Model IR700 in the region 4000—400 cm^{-1} as a Nujol mull. The diffuse reflectance spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer Model UV-3100. The magnetic susceptibilities were measured by the Faraday method over the 80—300 K temperature range. The apparatus was calibrated using $[Ni(H_2NCH_2CH_2NH_2)_3]S_2O_3$.[19] The susceptibilities were corrected for the diamagnetism of the constituent atoms by using Pascal's constants.[20] The effective magnetic moments were calculated from the equation $\mu_{eff}=2.828\sqrt{\chi_A T}$, where χ_A is the atomic magnetic susceptibility.

X-Ray Crystal Structure Analysis. Diffraction data were collected on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation at 25±1°C. Crystal data and details concerning data collection are given in Table 1. The lattice constants were determined by a least-squares refinement based on 25 reflections with $20\leq 2\theta\leq 30°$. The intensity data were corrected for Lorentz-polarization effects, but not for absorption. The structures were solved by direct methods. Refinements were carried out by full-matrix least-squares methods. In the course of the refinement, it became apparent that the Mn, S, N1, and C2 atoms of **1** are disordered. These atoms were divided into two positions with an occupancy factor of 50%. Hydrogen atoms were not included in the calculation for **1**. For **2**, hydrogen atoms were inserted into their calculated positions. The hydrogen atoms of **3** and **4** were located from difference Fourier maps. All of the hydrogen atoms were fixed at their positions. The weighting scheme, $w=1/[\sigma^2(|F_o|)+(0.02|F_o|)^2+1.0]$, was employed. The final discrepancy factors, $R=\sum||F_o|-|F_c||/\sum|F_o|$ and $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, are listed in Table 1. All of the calculations were carried out on a Micro-VAXII computer using an Enraf–Nonius SDP program package.[21] The atomic coordinates and thermal parameters of the non-hydrogen atoms are listed in Table 2. The anisotropic thermal parameters of the non-hydrogen atoms, the atomic coordinates and temperature factors of the hydrogen atoms, and the F_o-F_c tables were deposited as Document No. 67073 at the Office of the Editor of the Bull. Chem. Soc. Jpn.

Results and Discussion

The infrared spectra of the thiolic ligands, HL_a, HL_b, HL_c, and HL_d, show a rather weak absorption near 2550 cm^{-1} which can be assigned to the SH stretching absorption band. The ν(SH) band of the thiolic ligands is absent in the IR spectra of the corresponding manganese thiolates. Crystals suitable for single-crystal X-ray structure determinations were grown from methanol for complexes **1**,**2**, and **4**, and from DMF for complex **3**.

Description of the Structures. $[Mn(L_a)Cl]_n$ (1). A conspicuous feature of the X-ray structure of **1** is polymerism which derives from the linkages of the manganese(II) ions by the sulfur atoms of the thiolate ligand L_a. The Mn(II) ions are related by a screw-axis giving rise to zig-zagging infinite chains (Fig. 1). These helical chains extend along the crystallographic *c*-axis. The Mn, S, N1, and C2 atoms exhibit positional disorder. This has been modeled and the occupancies refined to 50 : 50 for positions A and B. The Mn(A)–Mn(A)′ and Mn(B)–Mn(B)′ separations are 3.930(2) and 3.927(2) Å, respectively [primes refer to the equivalent position $(1-x, 1-y, z-1/2)$]. A view of the mononuclear fragment with the numbering scheme is given in Fig. 2. Selected bond distances and angles are listed in Table 3. The L_a ligand coordinates to the manganese atom with the thiolate sulfur atom, S, and the two amino nitrogen atoms, N1 and N2, in a facial fashion. The manganese atom is further coordinated by a chloride ion, Cl, and a thiolate sulfur atom of a neighboring mononuclear fragment, S′, forming a trigonal bipyramidal geometry whose equatorial plane is formed by the S, N2, and S′ atoms and whose apical positions are occupied by the N1 and Cl atoms. The Mn–S bond lengths

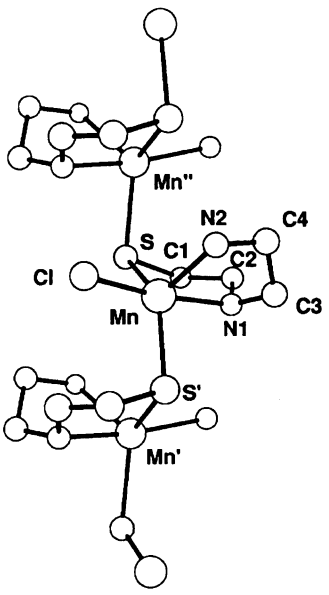

Fig. 1. Polymeric structure of $[Mn(L_a)Cl]_n$ (**1**).

Table 1. Crystal Data and Data Collection Details

Complexes	$[Mn(L_a)Cl]_n$ (1)	$[Mn\{Mn(L_b)_2\}_2]Cl_2\cdot 2CH_3OH$ (2)	$[Mn(L_c)Cl]_n$ (3)	$[Mn(L_d)Cl(CH_3OH)]_n$ (4)
Formula	$C_4H_{11}ClMnN_2S$	$C_{22}H_{60}Cl_2Mn_3N_8O_2S_4$	$C_8H_{11}ClMnN_2S$	$C_{10}H_{17}ClMnN_2OS$
F.W.	209.6	832.7	257.7	303.7
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$Pna2_1$	$C2/c$	$Pbca$	$P2_12_12_1$
a/Å	8.453(2)	23.523(6)	15.694(3)	12.975(3)
b/Å	14.158(4)	9.336(2)	16.944(2)	14.194(2)
c/Å	7.089(2)	18.273(5)	7.953(1)	7.312(2)
β/°		102.49(1)		
V/Å^3	848.4(4)	3918(2)	2114.9(6)	1346.6(5)
Z	4	4	8	4
D_c/g cm^{-3}	1.64	1.41	1.62	1.50
D_m/g cm^{-3}	1.63	1.43	1.63	1.49
$F(000)$	428	1748	1048	628
μ(Mo $K\alpha$)/cm^{-1}	19.8	12.9	16.0	12.7
Crystal dimensions/mm	0.31×0.41×0.56	0.21×0.36×0.41	0.18×0.26×0.32	0.11×0.12×0.38
2θ range/°	2.0—62.0	2.0—40.0	2.0—48.0	2.0—60.0
Total no. of observed reflections	1612	2144	1931	2319
No. of unique reflections with $I>3\sigma(I)$	1115	1428	1133	1050
Final no. of variables	77	186	118	145
Final redidiuals				
R	0.083	0.039	0.033	0.047
R_w	0.094	0.043	0.035	0.052

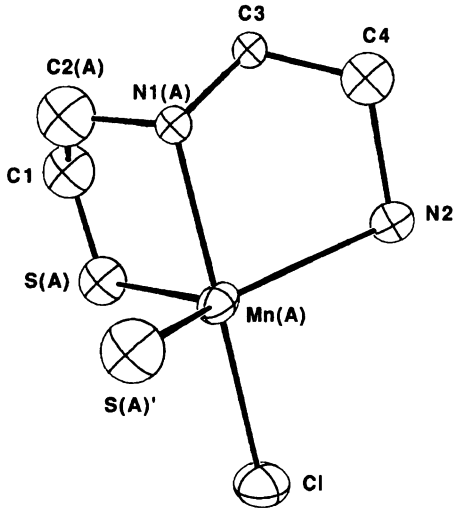

Fig. 2. Perspective view of mononuclear unit of $[Mn(L_a)Cl]_n$ (1). The disordered atoms for positions B are omitted for clarity.

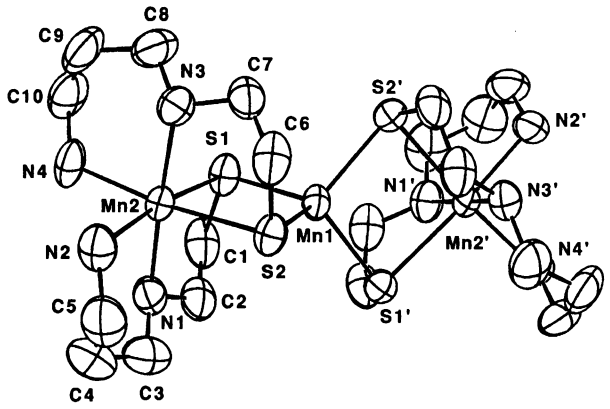

Fig. 3. Perspective view of trinuclear cation of $[Mn\{Mn(L_b)_2\}_2]Cl_2\cdot 2CH_3OH$ (2).

[Mn(A)–S(A) 2.521(6) Å, Mn(B)–S(B) 2.496(7) Å] are comparable to those of the Mn–S′ bond [Mn(A)–S(A)′ 2.536(5) Å, Mn(B)–S(B)′ 2.501(7) Å].

$[Mn\{Mn(L_b)_2\}_2]Cl_2\cdot 2CH_3OH$ (2). The crystal structure of **2** consists of a trinuclear cation, $[Mn\{Mn(L_b)_2\}_2]^{2+}$, two chloride ions, and two methanol molecules. A perspective view of $[Mn\{Mn(L_b)_2\}_2]^{2+}$ is illustrated in Fig. 3. The three manganese atoms are linear (Mn2–Mn1–Mn2′=180°). The cation possesses C_2-symmetry with the crystallographic two-fold axis passing through Mn1 and the midpoint of S1 and S1′. The central manganese atom, Mn1, has a distorted tetrahedral geometry, while the terminal manganese atoms, Mn2 and Mn2′, have distorted octahedral coordination spheres. The Mn1–Mn2 distance of 3.420(1) Å is too long for any metal-metal bonding. The central Mn–S bond lengths [2.435(2), 2.443(2) Å] and S–Mn–S angles [100.87(6)—120.24(8)°] fall within the observed ranges for Mn–S bond distances [2.391(1)—2.503(1) Å], and S–Mn–S bond angles [88.59(6)—124.59(7)°], respectively, in a few tetrahedral Mn(II)-thiolates.[5—9] The thiolic ligand, L_b, forms a meridional bis-chelate with one thiolate sulfur atom and two amino nitrogen atoms coordinated to the terminal manganese atom. The terminal Mn–S distances [2.636(2)

Table 2. Fractional Positional Parameters and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^{2} [a]	Atom	x	y	z	B_{eq}/Å^{2} [a]
$[Mn(L_a)Cl]_n$ (**1**)					$[Mn(L_c)Cl]_n$ (**3**)				
Mn(A)	0.4654(4)	0.4438(2)	0.366	2.29(5)	Mn	0.20731(5)	0.02342(4)	0.7478(1)	2.61(1)
Mn(B)	0.4689(4)	0.4433(2)	0.2354(5)	2.34(5)	Cl	0.1040(1)	−0.07418(9)	0.8368(2)	4.62(3)
Cl	0.7060(3)	0.3563(2)	0.301(1)	3.86(5)	S	0.32176(8)	−0.02549(8)	0.9385(2)	2.89(2)
S(A)	0.5527(6)	0.5961(4)	0.2138(7)	2.07(8)	N1	0.3084(3)	0.1220(2)	0.7081(5)	2.69(8)
S(B)	0.5484(8)	0.5941(4)	0.391(1)	3.3(1)	N2	0.1440(3)	0.1355(2)	0.8199(5)	2.91(8)
N1(A)	0.235(2)	0.521(1)	0.389(2)	1.7(2)*	C1	0.4030(3)	0.0494(3)	0.8965(6)	3.1(1)
N1(B)	0.228(3)	0.534(2)	0.196(3)	3.9(4)*	C2	0.3634(3)	0.1281(3)	0.8594(6)	2.8(1)
N2	0.308(1)	0.3581(8)	0.181(2)	3.3(2)*	C3	0.2634(4)	0.1959(3)	0.6707(7)	3.3(1)
C1	0.376(1)	0.6679(8)	0.282(2)	3.5(2)*	C4	0.1797(3)	0.2026(3)	0.7642(6)	2.9(1)
C2(A)	0.223(2)	0.610(1)	0.285(3)	1.6(2)*	C5	0.1418(4)	0.2751(3)	0.7868(7)	4.0(1)
C2(B)	0.221(4)	0.611(2)	0.366(5)	5.7(8)*	C6	0.0633(4)	0.2785(3)	0.8670(8)	4.6(1)
C3	0.109(2)	0.454(1)	0.354(2)	4.5(3)*	C7	0.0263(4)	0.2101(3)	0.9249(7)	4.0(1)
C4	0.143(2)	0.403(1)	0.164(2)	4.1(3)*	C8	0.0680(3)	0.1400(3)	0.9005(7)	3.5(1)
$[Mn\{Mn(L_b)_2\}_2]Cl_2 \cdot 2CH_3OH$ (**2**)					$[Mn(L_d)Cl(CH_3OH)]_n$ (**4**)				
Mn1	0.500	0.4963(2)	0.750	3.62(3)	Mn	0.7669(1)	0.39889(8)	0.2558(2)	2.50(2)
Mn2	0.37364(4)	0.4970(1)	0.61581(5)	3.48(2)	Cl	0.9498(2)	0.4116(2)	0.3432(4)	3.96(5)
Cl	0.19956(8)	0.5230(2)	0.4379(1)	6.71(5)	S	0.7161(2)	0.5547(2)	0.4072(3)	3.11(4)
S1	0.47494(7)	0.3663(2)	0.63186(9)	4.77(4)	O	0.7285(6)	0.3282(4)	0.5368(8)	4.0(1)
S2	0.40967(7)	0.6273(2)	0.74726(9)	4.42(4)	N1	0.5922(6)	0.3982(6)	0.207(1)	3.4(2)
O	0.1221(5)	0.385(1)	0.5359(5)	17.1(4)	N2	0.7709(6)	0.2418(5)	0.1651(9)	2.9(1)
N1	0.3487(2)	0.2862(6)	0.6627(3)	5.4(1)	C1	0.5779(8)	0.5515(7)	0.362(1)	4.2(2)
N2	0.2817(2)	0.5810(6)	0.6115(3)	5.3(1)	C2	0.5384(8)	0.4522(8)	0.348(1)	4.1(2)
N3	0.4017(2)	0.7089(6)	0.5740(3)	4.7(1)	C3	0.5489(8)	0.3026(7)	0.185(1)	3.7(2)
N4	0.3438(2)	0.4254(7)	0.4950(3)	5.7(1)	C4	0.6017(8)	0.2522(8)	0.021(2)	3.7(2)
C1	0.4460(3)	0.1942(8)	0.6552(5)	6.3(2)	C5	0.6963(8)	0.1980(7)	0.072(1)	3.4(2)
C2	0.4014(3)	0.2067(8)	0.7017(4)	6.2(2)	C6	0.7069(9)	0.1035(7)	0.019(1)	4.8(2)
C3	0.3063(4)	0.296(1)	0.7103(5)	8.3(2)	C7	0.796(1)	0.0547(8)	0.064(2)	5.8(3)
C4	0.2498(3)	0.368(1)	0.6729(5)	8.7(3)	C8	0.8717(9)	0.0996(8)	0.160(1)	4.4(2)
C5	0.2524(3)	0.530(1)	0.6696(4)	7.3(2)	C9	0.8564(8)	0.1934(7)	0.206(2)	4.1(2)
C6	0.4191(3)	0.7981(7)	0.7040(4)	5.7(2)	C10	0.746(2)	0.2381(8)	0.603(2)	8.6(4)
C7	0.4425(3)	0.7865(7)	0.6338(4)	5.5(2)					
C8	0.4256(3)	0.699(1)	0.5055(4)	7.3(2)					
C9	0.3826(4)	0.638(1)	0.4390(4)	7.9(3)					
C10	0.3765(3)	0.477(1)	0.4390(4)	7.2(2)					
C11	0.0863(5)	0.427(2)	0.5832(7)	14.4(4)					

a) Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as 4/3-$[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$. b) Starred atoms were refined isotropically.

and 2.662(2) Å] fall within the range of those of the six-coordinate Mn(II)-thiolate found in the mixed-valence Mn(II)–Mn(III) complex, $[(PPh_4)_2][Mn_3(pdt)_5]$ (where pdt^{2-} represents 1,3-propanedithiolate) (2.554—2.677 Å).[22] However, to date, there has been no structural report on octahedral Mn(II)-thiolate. The Mn–N bond lengths [2.267(5)—2.286(5) Å] compare well with those that are usually observed for manganese(II) complexes [2.100(4)—2.380(4) Å].[23] To our knowledge, this is the first example of a structurally-characterized linear trinuclear manganese(II) complex displaying [*Oh-Td-Oh*] geometry. The chloride ions are in the vicinity of the amino nitrogen atoms of the ligand as indicated by the distances Cl···N2 3.382(5) Å and Cl···N4 3.450(6) Å which suggest the occurrence of hydrogen bonding. The chloride ions are further hydrogen-bonded to the methanol molecules as implied by the Cl···O (CH_3OH) distance of 3.100(11) Å.

$[Mn(L_c)Cl]_n$ (3). The crystal structure consists of infinite polymeric chains similar to those of **1** (Fig. 4). In each chain, the manganese ions related by screw-axis symmetry are linked by the thiolate sulfur atom of the ligand L_c. The Mn–Mn separation is 4.271(1) Å. As can be seen in Fig. 5, the geometry about the manganese ion may be regarded as a distorted trigonal bipyramid with S, N2, and S′ atoms being in the equatorial plane while the N1 and Cl atoms occupy the apical positions. The Mn–S and Mn–S′ bond lengths are 2.492(1) and 2.503(1) Å, respectively. These values are intermediate between those of tetrahedral[5—9] and octahedral[22] Mn(II) thiolates. Structurally-determined trigonal-bipyramidal Mn(II) thiolates are not available for comparison.

$[Mn(L_d)Cl(CH_3OH)]_n$ (4). The crystal struc-

Table 3. Selected Interatomic Distances (Å) and Bond Angles (°) with Their Estimated Standard Deviations in Parentheses

$[Mn(L_a)Cl]_n$ (**1**)[a]			
Mn(A)–Mn(A)′	3.930(2)	Mn(B)–Mn(B)′	3.927(2)
Mn(A)–Cl	2.425(4)	Mn(B)–Cl	2.398(4)
Mn(A)–S(A)	2.521(6)	Mn(B)–S(B)	2.496(7)
Mn(A)–S(A)′	2.536(5)	Mn(B)–S(B)′	2.501(7)
Mn(A)–N1(A)	2.24(2)	Mn(B)–N1(B)	2.43(2)
Mn(A)–N2	2.22(1)	Mn(B)–N2	1.86(1)
Mn(A)′ –Mn(A)–Mn(A)″	128.8(1)	Mn(B)′ –Mn(B)–Mn(B)″	129.0(1)
S(A)–Mn(A)–S(A)′	128.6(1)	S(B)–Mn(B)–S(B)′	128.9(3)
Cl–Mn(A)–S(A)	96.4(2)	Cl–Mn(B)–S(B)	97.4(2)
Cl–Mn(A)–S(A)′	96.9(2)	Cl–Mn(B)–S(B)′	97.5(2)
Cl–Mn(A)–N1(A)	173.1(5)	Cl–Mn(B)–N1(B)	175.3(6)
Cl–Mn(A)–N2	96.5(3)	Cl–Mn(B)–N2	108.6(4)
S(A)–Mn(A)–N1(A)	82.3(5)	S(B)–Mn(B)–N1(B)	79.9(6)
S(A)–Mn(A)–N2	113.0(3)	S(B)–Mn(B)–N2	147.5(4)
S(A)′ –Mn(A)–N1(A)	89.2(4)	S(B)′ –Mn(B)–N1(B)	87.2(6)
S(A)′ –Mn(A)–N2	114.5(3)	S(B)′ –Mn(B)–N2	67.6(4)
N1(A)–Mn(A)–N2	78.0(5)	N1(B)–Mn(B)–N2	72.8(6)
Mn(A)–S(A)–Mn(A)′	102.0(2)	Mn(B)–S(B)–Mn(B)′	103.6(2)
$[Mn\{ Mn(L_b)_2\}_2]Cl_2 \cdot 2CH_3OH$ (**2**) [b]			
Mn1–Mn2	3.420(1)	Mn2–S1	2.636(2)
Mn1–S1	2.435(2)	Mn2–S2	2.662(2)
Mn1–S1′	2.435(2)	Mn2–N1	2.273(6)
Mn1–S2	2.443(2)	Mn2–N2	2.286(5)
Mn1–S2′	2.443(2)	Mn2–N3	2.270(6)
		Mn2–N4	2.267(5)
Mn2–Mn1–Mn2′	180	S2–Mn2–N1	96.5(1)
S1–Mn1–S1′	120.24(8)	S2–Mn2–N2	89.3(1)
S1–Mn1–S2	100.87(6)	S2–Mn2–N3	81.2(1)
S1′ –Mn1–S2	108.08(6)	S2–Mn2–N4	169.8(2)
S1–Mn1–S2′	108.08(6)	N1–Mn2–N2	89.5(2)
S1′ –Mn1–S2′	100.87(6)	N1–Mn2–N3	177.4(2)
S2–Mn1–S2′	119.92(8)	N1–Mn2–N4	93.5(2)
S1–Mn2–S2	90.42(6)	N2–Mn2–N3	91.8(2)
S1–Mn2–N1	81.9(1)	N2–Mn2–N4	88.7(2)
S1–Mn2–N2	171.2(2)	N3–Mn2–N4	88.9(2)
S1–Mn2–N3	96.8(1)	Mn1–S1–Mn2	84.71(6)
S1–Mn2–N4	93.1(2)	Mn1–S2–Mn2	84.00(6)

ture is made up of infinite polymeric chains formed by thiolate bridges of mononuclear $[Mn(L_d)Cl(CH_3OH)]$ units. A perspective view of the mononuclear unit is shown in Fig. 6. The thiolate ligand, L_d, forms a meridional chelate with the thiolic sulfur, amino nitrogen, and pyridyl nitrogen atoms coordinated to the manganese atom [Mn–S 2.559(3), Mn–N1 2.295(7), Mn–N2 2.326(7) Å]. The Mn–S distance lies within the range of those of the six-coordinate Mn(II) thiolate moiety in $[(PPh_4)_2][Mn_3(pdt)_5]$.[22] The Mn–N bond lengths compare well with the values usually observed for manganese(II) complexes [2.100(4)—2.380(4) Å].[23] The manganese atom is further coordinated by the methanol oxygen atom and chloride ion at distances of 2.340(6) and 2.463(3) Å, respectively. In addition, a thiolate sulfur atom of a neighboring mononuclear unit approaches the manganese atom [Mn–S′ 2.642(3), Mn–Mn′ 4.669(2) Å, Mn–S′–Mn′ 127.7(1)° {primes refer to the equivalent position $(3/2-x,\ 1-y,\ z-1/2)$}] forming a distorted octahedron. Thus the mononuclear units are linked in a helical chain parallel to the *c* axis throughout the crystal structure (Fig. 7). This Mn–S′ interaction is not weak because the Mn–S′ distance is comparable to those in the six-coordinate Mn(II) thiolate and the manganese atom is displaced by 0.17 Å from the mean plane formed by the S, N1, N2, and Cl atoms toward the approaching thiolate sulfur atom, S′. Overall, the structure of the complex may be best described as a polymeric helical chain.

Electronic Spectra and Magnetic Susceptibilities. The diffuse reflectance spectra of the complexes show very weak peaks or shoulders in the visible region. These absorptions may be attributed to the spin forbidden d–d transitions in the high-spin manganese(II) ion.

Table 3. (Continued)

$[Mn(L_c)Cl]_n$ (**3**) [c]			
Mn–Mn′	4.271(1)	Mn–Cl	2.422(2)
Mn–S	2.492(1)	Mn–N1	2.325(4)
Mn–S′	2.503(1)	Mn–N2	2.219(4)
Mn′ –Mn–Mn′ ′	137.23(2)	S–Mn–N1	80.2(1)
S–Mn–S′	137.23(5)	S–Mn–N2	116.8(1)
Cl–Mn–S	94.47(5)	S′–Mn–N1	88.9(1)
Cl–Mn–S′	100.06(5)	S′–Mn–N2	99.2(1)
Cl–Mn–N1	170.8(1)	N1–Mn–N2	74.1(1)
Cl–Mn–N2	102.1(1)	Mn–S–Mn′	117.52(6)
$[Mn(L_d)Cl(CH_3OH)]_n$ (**4**)[d]			
Mn–Mn′	4.669(2)	Mn–O	2.340(6)
Mn–S	2.559(3)	Mn–N1	2.295(7)
Mn–S′	2.642(3)	Mn–N2	2.326(7)
Mn–Cl	2.463(3)		
Mn′ –Mn–Mn′ ′	103.08(3)	S–Mn–N2	163.1(2)
S–Mn–S′	102.90(8)	S′–Mn–O	166.3(1)
Cl–Mn–S	94.2(1)	S′–Mn–N1	86.1(2)
Cl–Mn–S′	98.7(1)	S′–Mn–N2	87.8(1)
Cl–Mn–O	90.5(3)	O–Mn–N1	85.7(2)
Cl–Mn–N1	172.8(2)	O–Mn–N2	81.0(3)
Cl–Mn–N2	97.1(3)	N1–Mn–N2	88.4(2)
S–Mn–O	86.3(2)	Mn–S–Mn′	127.7(1)
S–Mn–N1	79.5(2)		

a) Primes and double primes refer to the equivalent positions $(1-x, 1-y, z-1/2)$ and $(1-x, 1-y, z+1/2)$, respectively. b) Primes refer to the equivalent positions $(1-x, y, 3/2-z)$. c) Primes and double primes refer to the equivalent positions $(1/2-x, -y, z-1/2)$ and $(1/2-x, -y, z+1/2)$, respectively. d) Primes and double primes refer to the equivalent positions $(3/2-x, 1-y, z-1/2)$ and $(3/2-x, 1-y, 1-z)$, respectively.

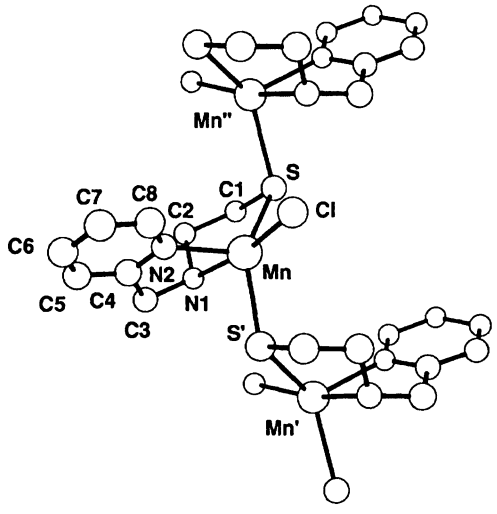

Fig. 4. Polymeric structure of $[Mn(L_c)Cl]_n$ (**3**).

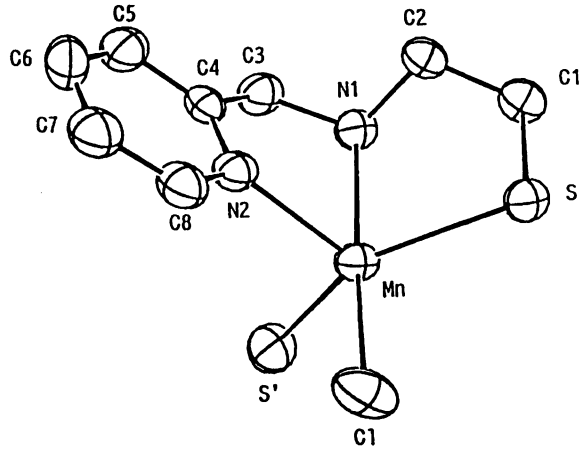

Fig. 5. Perspective view of mononuclear unit of $[Mn(L_c)Cl]_n$ (**3**).

The effective magnetic moments of these complexes fall in the range 4.94—5.30 B.M./Mn at room temperature, showing values lower than the spin-only magnetic moment (5.92 B.M./Mn) for a high-spin d^5 system. The magnetic susceptibilities were measured over the range 80—300 K. The magnetic behavior of **2** is similar to that of the trinuclear species described by Handa et al.[17] The magnetic data were analyzed by an isotropical Heisenberg model, $\mathscr{H}=-2J(\boldsymbol{S}_1\cdot\boldsymbol{S}_2+\boldsymbol{S}_2\cdot\boldsymbol{S}_3)-2J_{13}\boldsymbol{S}_1\cdot\boldsymbol{S}_3$ assuming (1) the terminal and central manganese(II) ions are all high-spin ($S_1=S_2=S_3=5/2$) and (2) the exchange interaction between the nearest neighboring manganese(II) ions are identical ($J=J_{12}=J_{23}$) and the interaction between the terminal manganese(II) ions is negligible ($J_{13}=0$). The resulting best fit with $g=2.05$

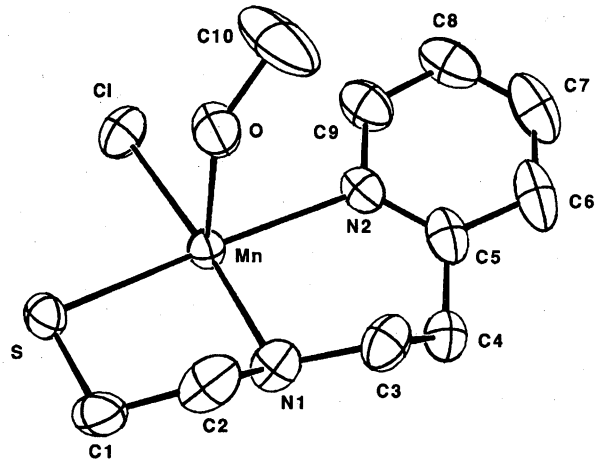

Fig. 6. Perspective view of mononuclear unit of $[Mn(L_d)Cl(CH_3OH)]_n$ (**4**).

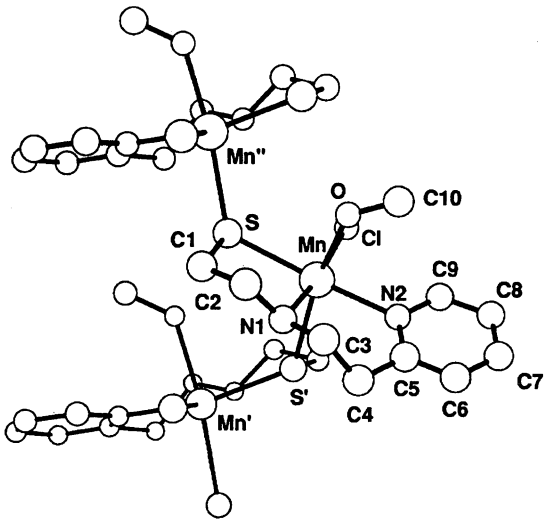

Fig. 7. Polymeric structure of $[Mn(L_d)Cl(CH_3OH)]_n$ (**4**).

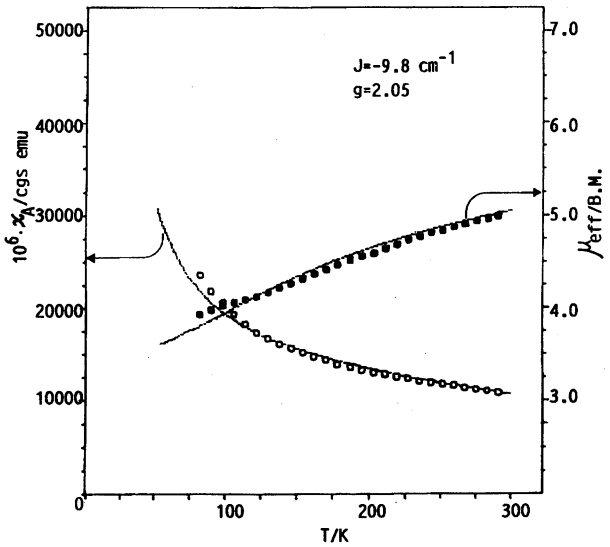

Fig. 8. Temperature dependence of the magnetic susceptibility (O) and effective magnetic moment (●) of $[Mn\{Mn(L_b)_2\}_2]Cl_2 \cdot 2CH_3OH$ (**2**).

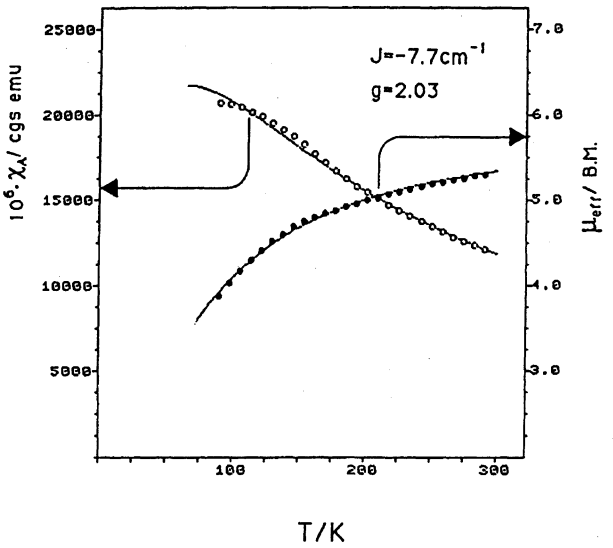

Fig. 9. Temperature dependence of the magnetic susceptibility (O) and effective magnetic moment (●) of $[Mn(L_d)Cl(CH_3OH)]_n$ (**4**).

and $J=-9.8$ cm^{-1} is shown as the solid line in Fig. 8. An antiferromagnetic exchange interaction may occur through the bridging thiolate groups. The magnetic behaviors of **1**, **3**, and **4** (Fig. 9) are similar to those of the previously reported ones ("dinuclear" complexes) providing that these complexes are exactly the same, i.e. polymeric. The magnetic data were explained using the dimer equation ($S_1=S_2=5/2$) based on the Heisenberg model, $\mathcal{H}=-2JS_1 \cdot S_2$, in the same way as those for Handa's compounds. The best fitting parameters are $J=-9.5$ cm^{-1}, $g=1.95$ for **1**; $J=-8.1$ cm^{-1}, $g=1.93$ for **3**; $J=-7.7$ cm^{-1}, $g=2.03$ for **4**. These results show that the limited magnetic data cannot provide definitive evidence for the molecular structures of manganese thiolates.

References

1) I. G. Dance, *Polyhedron*, **5**, 1037 (1986).
2) P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev.*, **76**, 121 (1987).
3) V. B. Krebs and G. Henkel, *Angew. Chem.*, **103**, 785 (1991).
4) P. P. Power and S. C. Shoner, *Angew. Chem., Int. Ed. Engl.*, **30**, 330 (1991).
5) D. Swenson, N. C. Baenziger, and D. Coucouvanis, *J. Am. Chem. Soc.*, **100**, 1932 (1978).
6) T. Costa, J. R. Dorfman, K. S. Hagen, and R. H. Holm, *Inorg. Chem.*, **22**, 4091 (1983).
7) A. D. Watson, C. P. Rao, J. R. Dorfman, and R. H. Holm, *Inorg. Chem.*, **24**, 2820 (1985).
8) K. Greiwe, B. Krebs, and G. Henkel, *Inorg. Chem.*, **28**, 3713 (1989).
9) N. Ueyama, A. Kajiwara, N. Yasuoka, and A. Nakamura, *Chem. Lett.*, **1991**, 1401.
10) M. Mikuriya, S. Kida, and I. Murase, *Bull. Chem. Soc. Jpn.*, **60**, 1180 (1987).

11) M. Handa, M. Mikuriya, H. Ōkawa, and S. Kida, *Chem. Lett.*, **1988**, 1555.
12) M. Handa, M. Mikuriya, Z. J. Zhong, H. Ōkawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **61**, 3883 (1988).
13) M. Handa, M. Mikuriya, and H. Ōkawa, *Chem. Lett.*, **1989**, 1663.
14) M. Mikuriya, S. Shigematsu, M. Handa, and T. Kohzuma, *Transition Met. Chem.*, **16**, 532 (1991).
15) M. Mikuriya, M. Handa, S. Shigematsu, S. Funaki, F. Adachi, and H. Ōkawa, *Bull. Chem. Soc. Jpn.*, **65**, 512 (1992).
16) M. Mikuriya, M. Handa, S. Shigematsu, S. Funaki, T. Fujii, H. Ōkawa, K. Toriumi, T. Koshiba, and H. Terauchi, *Bull. Chem. Soc. Jpn.*, **66**, 1104 (1993).
17) M. Handa, H. Ōkawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **61**, 3353 (1988).
18) M. Mikuriya, F. Adachi, H. Iwasawa, M. Handa, M. Koikawa, and H. Ōkawa, *Inorg. Chim. Acta*, **179**, 3 (1991).
19) N. F. Curtis, *J. Chem. Soc.*, **1961**, 3147.
20) P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York (1956), pp. 78 and 91.
21) B. A. Frenz, "The SDP-User's Guider," Enraf-Nonius, Delft, The Netherlands (1985).
22) J. L. Seela, K. Folting, R. -J. Wang, J. C. Huffman, G. Christou, H. -R. Chang, and D. N. Hendrickson, *Inorg. Chem.*, **24**, 4454 (1985).
23) B. Mabad, P. Cassoux, J. -P. Tuchagues, and D. N. Hendrickson, *Inorg. Chem.*, **25**, 1420 (1986).