# The Synthesis and Characterization of Manganese(III) Complexes with the General Formula of $[Mn(X)(L)]^{n+}$ ($n$=0, 1) (X=$Cl^-$, $N_3^-$, Pyridine, *N*-Methylimidazole, L=*N*,*N*′-[(Methylimino)bis(trimethylene)]-bis[salicylideneaminate]: The X-Ray Crystal Structure of $[Mn(N\text{-MeIm})(L)][BPh_4]$

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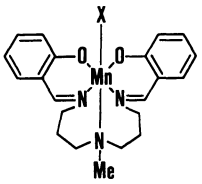
**Synopsis.** A series of manganese(III) complexes with the general formula of $[Mn(X)(L)]^{n+}$ ($n$=0, 1) have been prepared and characterized, where X=$Cl^-$, $N_3^-$, pyridine, *N*-methylimidazole, and L=quinquedentate Schiff base ligand *N*,*N*′-[(methylimino)bis(trimethylene)]bis[salicylideneaminate]. The X-ray analysis of $[Mn(N\text{-MeIm})(L)][BPh_4]$ confirmed that the coordination geometry of the manganese(III) ion is a tetragonal bipyramid in which two axial positions are occupied by a central amine nitrogen atom N(3) and an imidazole nitrogen atom N(4), with elongated bond distances of Mn–N(3)=2.388(6) Å and Mn–N(4)=2.251(6) Å.

Recently we have reported on imidazolate-bridged iron(III)–copper(II) and manganese(III)–copper(II) binuclear complexes.[1] As for the iron(III) and the manganese(III) component complexes of their binuclear complexes, complexes with a quinquedentate ligand *N*,*N*′-[methylimino)bis(trimethylene)]bis[salicylideneaminate], $[Fe(L)][BPh_4]$ and $[Mn(L)][BPh_4]$, were employed, because they can provide a coordination site by expanding coordination number. We have already reported on iron(III) complexes with the ligand and found that the iron(III) complexes with $[Fe(X)(L)]^{n+}$ ($n$=0, 1) constitute a family of spin-equilibrium complexes.[2,3] In this study, a series of manganese(III) complexes $[Mn(X)(L)]^{n+}$ ($n$=0, 1) (see the drawing) have been prepared and characterized.




## Experimental

**Syntheses. Ligand $[H_2L]$.** The quinquedentate ligand was prepared by mixing salicylaldehyde (40 mmol) and bis(3-aminopropyl)amine (20 mmol) in 100 $cm^3$ of methanol. This ligand solution was subsequently used for the preparation of the manganese(III) complexes.

**$[Mn(Cl^-)(L)]\cdot 1.5CH_3OH$.** To a solution of $[H_2L]$ (20 mmol) in 100 $cm^3$ of methanol was added a solution of manganese(III) acetate dihydrate (20 mmol) in 30 $cm^3$ of methanol. The mixture was then stirred at room temperature for 10 min. The resulting solution was gently warmed under stirring for 30 min. To the mixture was added LiCl (50 mmol). The dark green needle crystals thus precipitated were collected by suction filtration and dried.

**$[Mn(L)][BPh_4]\cdot 2CH_3OH$.** To a solution of $[H_2L]$ (10 mmol) in 50 $cm^3$ of methanol was added a solution of manganese(III) acetate dihydrate (10 mmol) in 30 $cm^3$ of methanol. The mixture was then stirred at room temperature for 30 min. To the mixture was added a solution of sodium tetraphenylborate (15 mmol) in 30 $cm^3$ of methanol. The resulting solution was gently warmed on a water bath for 20 min and then cooled to room temperature. After several hours, black needle crystals thus precipitated were collected by filtration and dried.

**$[Mn(N_3^-)(L)]\cdot 0.5H_2O$.** To a solution of $[Mn(Cl^-)(L)]$ $2CH_3OH$ (1 mmol) in 30 $cm^3$ of methanol was added sodium azide (1.5 mmol) in a minimum amount of water. The solution was then gently warmed on a water bath for 10 min and filtered. The filtrate was cooled to room temperature. After several hours, the black crystals thus precipitated were collected by filtration and dried.

**$[Mn(X)(L)][BPh_4]$ (X=Py, *N*-MeIm).** To a solution of $[Mn(L)][BPh_4]$ in 30 $cm^3$ of methanol was added pyridine or *N*-methylimidazole (ca. 1.5 times by mole ratio). The solution was then warmed on a water bath for 10 min and then filtered. The filtrate was cooled to room temperature. After several hours, the black crystals thus precipitated were collected and dried.

**Physical Measurements.** The elemental analyses were performed by Mr. Shinichi Miyazaki at the Technical Service Center of Kumamoto University. The melting points were measured on a Yanagimoto micro melting point apparatus and were uncorrected. The electrical conductivity measurements were carried out on a Denki Kagaku Keiki AOC-10 digital conductometer on ca. $10^{-3}$ mol $dm^{-3}$ acetonitrile solutions. The infrared spectra were recorded on KBr discs with a JASCO A-702 spectrophotometer. The magnetic susceptibilities were obtained by the Faraday method at room temperature using a Cahn 2000 electric balance. The susceptibilities were corrected for the diamagnetism of component atoms by the use of Pascal's constants. The molar effective magnetic moment was calculated by means of this equation $\mu_{eff}=2.828\sqrt{\chi_A T}$.

**X-Ray Diffraction Study of $[Mn(N\text{-MeIm})(L)][BPh_4]$.** The diffraction data were obtained on a Rigaku AFC-5 four-circle diffractometer at the Faculty of Science, Kyushu University, using graphite-monochromatized Mo $K\alpha$ radiation at 20±1 °C. Data concerning the conditions for crystallographic data collection and structure refinement is as follows: Formula=$MnO_2N_5C_{49}BH_{51}$, F.W.=807.7, triclinic, space group=$P\bar{1}$, $a$=11.680(5) Å, $b$=16.617(4) Å, $c$=11.649(4) Å, $\alpha$=104.30(4)°, $\beta$=99.81(2)°, $\gamma$=93.26(2)°, $V$=2147.2 $Å^3$, $D_{calcd}$=1.249 g $cm^{-3}$ ($Z$=2), $D_{measd}$=1.22 g $cm^{-3}$ (by the floatation method in an aqueous KI solution), crystal dimension 0.4×0.3×0.3 mm,

Table 1. Fractional Atomic Coordinates ($\times 10^4$) of [Mn(N-MeIm)(L)][$BPh_4$], with their Estimated Standard Deviations in Parentheses

| Atom | X | Y | Z | $B_{eqv}$ | Atom | X | Y | Z | $B_{eqv}$ |
|---|---|---|---|---|---|---|---|---|---|
| Mn | 943(1) | 2497(1) | 2863(1) | 3.9 | C22 | 2840(7) | 3904(5) | 2563(7) | 6.8 |
| O1 | 1361(3) | 1490(2) | 1965(3) | 4.1 | C23 | 3228(8) | 4185(6) | 1694(10) | 9.2 |
| O2 | 574(4) | 3553(3) | 3662(4) | 4.6 | C24 | 2160(7) | 2970(5) | 847(7) | 6.4 |
| N1 | 2207(4) | 2465(3) | 4261(4) | 4.0 | C25 | 2983(8) | 3607(7) | −596(9) | 9.0 |
| N2 | −500(4) | 2419(3) | 1601(4) | 3.7 | B | 3998(6) | 7621(4) | 2099(6) | 3.4 |
| N3 | −295(4) | 1793(3) | 3821(4) | 3.8 | C26 | 2750(5) | 8022(4) | 2105(5) | 3.2 |
| N4 | 2168(4) | 3164(3) | 2024(4) | 4.4 | C27 | 1704(5) | 7489(4) | 1838(5) | 3.9 |
| N5 | 2804(6) | 3572(5) | 572(6) | 7.7 | C28 | 622(5) | 7778(4) | 1790(6) | 4.7 |
| C1 | 2452(5) | 1295(4) | 1984(5) | 3.8 | C29 | 523(6) | 8632(5) | 2018(7) | 5.5 |
| C2 | 2707(6) | 749(4) | 948(6) | 4.9 | C30 | 1527(6) | 9171(4) | 2267(6) | 5.3 |
| C3 | 3812(7) | 500(5) | 958(7) | 6.1 | C31 | 2617(5) | 8870(4) | 2308(5) | 4.1 |
| C4 | 4690(6) | 764(5) | 1972(7) | 5.8 | C32 | 5118(5) | 8336(4) | 2647(6) | 4.0 |
| C5 | 4447(6) | 1303(4) | 2978(6) | 5.0 | C33 | 5203(6) | 8870(4) | 3808(6) | 5.1 |
| C6 | 3345(5) | 1583(4) | 3009(5) | 3.8 | C34 | 6157(7) | 9453(5) | 4368(7) | 6.5 |
| C7 | 3129(5) | 2103(4) | 4135(5) | 4.3 | C35 | 7054(7) | 9537(5) | 3776(9) | 7.8 |
| C8 | 2021(6) | 2866(5) | 5494(5) | 5.1 | C36 | 7016(7) | 9041(5) | 2634(9) | 7.7 |
| C9 | 1098(6) | 2339(5) | 5846(6) | 6.1 | C37 | 6053(6) | 8450(4) | 2072(7) | 5.6 |
| C10 | −153(8) | 2280(6) | 5094(7) | 8.2 | C38 | 4129(5) | 7003(3) | 3018(5) | 3.2 |
| C11 | −3(8) | 955(6) | 3805(9) | 8.7 | C39 | 4946(5) | 6422(4) | 2981(5) | 3.9 |
| C12 | −1517(7) | 1796(6) | 3280(8) | 7.6 | C40 | 5149(6) | 5953(4) | 3827(6) | 4.8 |
| C13 | −1865(6) | 1315(4) | 1906(6) | 5.2 | C41 | 4513(7) | 6056(4) | 4747(6) | 5.3 |
| C14 | −1155(6) | 1584(4) | 1049(6) | 4.5 | C42 | 3712(6) | 6624(4) | 4820(6) | 5.2 |
| C15 | −888(6) | 3056(4) | 1309(5) | 4.2 | C43 | 3515(5) | 7089(4) | 3970(5) | 4.1 |
| C16 | −393(6) | 3910(4) | 1885(6) | 4.5 | C44 | 3963(5) | 7112(4) | 686(5) | 3.4 |
| C17 | −629(6) | 4530(4) | 1281(7) | 5.7 | C45 | 4097(6) | 7563(4) | −173(6) | 4.7 |
| C18 | −185(7) | 5345(5) | 1801(8) | 7.0 | C46 | 4050(7) | 7166(5) | −1381(6) | 5.8 |
| C19 | 469(8) | 5564(4) | 2955(8) | 7.0 | C47 | 3840(7) | 6319(5) | −1804(6) | 6.3 |
| C20 | 702(7) | 4971(4) | 3611(7) | 6.0 | C48 | 3659(7) | 5849(4) | −1008(6) | 5.8 |
| C21 | 296(6) | 4124(4) | 3059(6) | 4.4 | C49 | 3728(6) | 6252(4) | 214(6) | 4.5 |

Table 2. Elemental Analytical Data, Melting Points, Molar Electrical Conductances Measured in Acetonitrile, and Effective Magnetic Moments at 293 K

| Complex | C(%) | H(%) | N(%) |
|---|---|---|---|
| [Mn($Cl^-$)(L)·1.5$CH_3OH$ | 55.25(55.16) | 5.96(6.38) | 8.97( 8.58) |
| [Mn($N_3^-$)(L)·0.5$H_2O$ | 55.16(55.14) | 5.71(5.73) | 18.11(18.37) |
| [Mn(L)][$BPh_4$]·2$CH_3OH$ | 71.71(71.48) | 6.71(6.76) | 5.40( 5.32) |
| [Mn(Py)(L)][$BPh_4$]·0.5$CH_3OH$ | 74.00(73.90) | 6.44(6.39) | 6.58( 6.83) |
| [Mn(N-MeIm)(L)][$BPh_4$] | 72.76(72.86) | 6.43(6.36) | 8.24( 8.67) |

| Complex | Mp $\theta_m$/°C | $\Lambda_M$/S $mol^{-1}$ $cm^2$ | $\mu_{eff}$/B.M. |
|---|---|---|---|
| [Mn($Cl^-$)(L)]·1.5$CH_3OH$ | 210 | 35 | 4.9 |
| [Mn($N_3^-$)(L)]·0.5$H_2O$ | 205 | 10 | 4.6 |
| [Mn(L)][$BPh_4$]·2$CH_3OH$ | 185 | 92 | 4.9 |
| [Mn(Py)](L)][$BPh_4$]·0.5$CH_3OH$ | 166 | 92 | 4.7 |
| [Mn(N-MeIm)(L)][$BPh_4$] | 163 | 96 | 4.7 |

Calcd values are in parentheses.

$\mu$(Mo $K\alpha$)10.2 $cm^{-1}$, scan mode $\theta$-2$\theta$, scan speed 6° $min^{-1}$, scan width (1.1+0.5 tan$\theta$)°, 2$\theta$ range 2.5—48°, octant collected $h$, $\pm k$, $\pm l$, no. of unique reflections data used 3960, $R$=6.48%, $R_w$=6.60%.

The intensity data were corrected for the Lorentz-polarization effect but not for the absorption. The structure was solved by the heavy atom method and refined by the block-diagonal least-squares method, in which weight $w$=1 was adopted for all the reflections. The hydrogen atoms were included in the structure factor calculations, but not refined. The calculations were carried out by the use of UNICS III computer program system[4] on a FACOM M 780 computer at the Computer Center of Kyushu University. The final positional parameters are given in Table 1.

## Results and Discussion

The elemental analytical data, melting points, molar electrical conductivities, and effective magnetic moments at room temperature are given in Table 2. Either complex, [Mn($Cl^-$)(L)] or [Mn(L)][$BPh_4$]2$CH_3$-OH, can be used as the starting compound for the synthesis of other complexes by using a way similar to that used for iron(III) complexes.[2,3] The chloro ion of [Mn($Cl^-$)(L)] is easily substituted by $N_3^-$ ion to

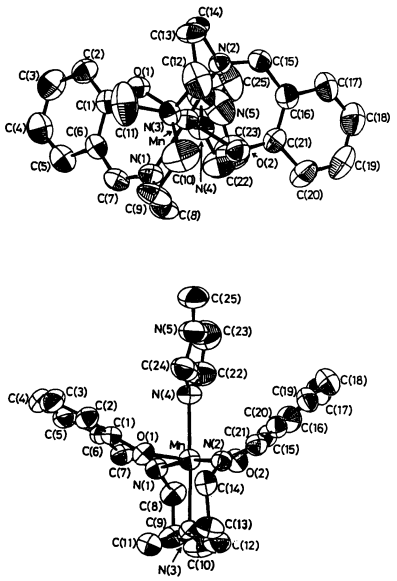



Fig. 1. Perspective drawing of the cation [Mn(*N*-MeIm)(L)]$^+$ with the atom numbering scheme.

produce the azide complex. The molar electrical conductances of the complexes [Mn($Cl^-$)(L)] and [Mn($N_3^-$)(L)] are not zero. This indicates that the unidentate ligands, such as $Cl^-$ and $N_3^-$, are partially dissociated in the acetonitrile solutions. The electrical conductances of [Mn(L)][$BPh_4$], [Mn(*N*-MeIm)(L)]-[$BPh_4$], and [Mn(Py)(L)][$BPh_4$] are consistent with that of the 1:1 electrolyte. The effective magnetic moments of all the complexes indicate that the manganese(III) ions are in high-spin state ($S$=2).

**Structural Description of [Mn(*N*-MeIm)(L)][$BPh_4$].**[5] A perspective drawing of the [Mn(*N*-MeIm)(L)]$^+$ cation with the atom numbering scheme is shown in Fig. 1. The bond distances and angles are given in tables which are deposited as supplementary data.[5] The manganese(III) ion assumes a tetragonal bipyramidal coordination geometry, where the equatorial plane comprises $N_2O_2$ donors of two salicylideneamine moieties and where the two axial positions are occupied by the central amine nitrogen of L and a nitrogen of *N*-methylimidazole. The two salicylideneaminate moieties construct a shallow cave, in which the *N*-MeIm ligand is positioned. The geometry is similar to that of the analogous iron(III) complex [Fe(4-Mepy)(L)]$^+$.[2] A drastic difference between the iron(III) and manganese(III) complexes is found in the metal-axial ligand bond distances. The bond distances between the manganese(III) ion and the axial ligands are elongated, as in Mn–N(3)=2.388(6) Å and Mn–N(4)=2.251(6) Å, while the corresponding distances of the iron(III) analogue are 2.035(6) Å and 2.010(6) Å.[2]

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**References**

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5) The bond distances and angles, H-atom coordinates, and anisotropic thermal parameters are deposited as supplementary data as Document No. 8830 at the office of the Editor of the Bull. Chem. Soc. Jpn.