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The Molecular Structure of a Schiff Base Complex, [*N*,*N'*-Ethylenebis(1-phenyl-2-imino-1-butanonato)](acetonitrile)manganese(III) Perchlorate

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Synopsis. The molecular structure of a novel Schiff base complex, [*N*,*N'*-ethylenebis(1-phenyl-2-imino-1-butanonato)](acetonitrile)manganese(III) perchlorate has been determined by X-ray diffraction method. The molecule has an elongated octahedral geometry around the metal atom.

A number of studies have been reported on the crystal structures of *N*,*N'*-bis(1-methyl-3-oxobutylidene)ethylenediamine type Schiff base complexes of transition metals such as Cu(II), Co(II), and V(II).[1] The chemical behavior of the Schiff base complexes of Mn(III) has also been paid attention because of important roles in some biochemical processes, e.g. in manganesesuperoxide dismutase[2,3] and pseudocatalase[4] which are known to contain Mn(III) ions. The structure of Mn(III) complex, [Mn(acen)Cl] containing a tetradentate *N*,*N'*-ethylenebis(4-imino-2-pentanonato) ligand (abbreviated to acen and formerly called *N*,*N'*-ethylenebis(acetylacetone iminato)), has been determined by X-ray analysis.[5] In this paper we describe the preparation and molecular structure of a novel Mn(III) Schiff base complex, [Mn(bzacen)(CH_3CN)(ClO_4)] containing a similar tetradentate *N*,*N'*-ethylenebis(1-phenyl-2-imino-1-butanonato) ligand (abbreviated to bzacen and formerly called *N*,*N'*-ethylenebis(benzoylacetone iminato)).

Experimental

The Schiff base, H_2bzacen and $Mn(C_2H_3O_2)_3\cdot 2H_2O$ were prepared as described previously.[6,7] A mixture of H_2bzacen and $Mn(C_2H_3O_2)_3\cdot 2H_2O$ was refluxed in 2-propanol for 3 h. The resulting precipitate was washed with 2-propanol and dissolved in methanol, to which aqueous solution of sodium perchlorate was added. Red thin-plate crystals were obtained by recrystallization from a mixed solution of benzene and acetonitrile.

Crystal Data. [$Mn(C_{22}H_{22}O_2N_2)(CH_3CN)(ClO_4)$], $M=541.44$, orthorhombic, space group *Pnma*, $a=9.077(1)$, $b=15.563(1)$, $c=17.205(2)$ Å, $U=2430.5$ Å^3, $Z=4$, $D_c=1.48$ g cm^{-3}, $D_m=1.49$ g cm^{-3}, μ(Mo $K\alpha$)$=7.3$ cm^{-1}.

A well-shaped crystal was mounted on an Enraf-Nonius CAD4 diffractometer. Accurate unit-cell parameters were determined by the least-squares fit of 2θ values of 25 strong reflections. Integrated intensities were collected by the θ-2θ scan technique with the scan rate of 5.5° min^{-1} and the scan width of $\Delta 2\theta=(1.2+0.7\tan\theta)°$. The scan was repeated with a slower rate for weak reflections. A total of 2552 independent reflections was obtained within $2°<2\theta<52°$. Intensity data were corrected for usual Lp effects but absorption and extinction corretions were ignored.

The structure was solved by the heavy atom method. The systematic absences suggested that the possible space group is either *Pnma* or *Pn*2_1*a*. When the space group is assumed as

Table 1. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-H Atoms with e.s.d.'s in Parentheses

Atom	x	y	z	B_{eq}[a]/Å^2
Mn	0.1787(3)	0.25	0.0350(2)	3.2
O	0.0903(9)	0.1641(5)	0.0969(5)	4.1
N	0.2759(9)	0.1659(6)	−0.0321(5)	3.2
C(1)	0.269(1)	0.0815(8)	−0.0248(6)	3.4
C(2)	0.185(1)	0.0414(7)	0.0340(6)	3.4
C(3)	0.102(1)	0.0816(7)	0.0888(6)	2.8
C(4)	0.021(1)	0.0324(7)	0.1502(6)	2.6
C(5)	0.013(1)	−0.0579(7)	0.1508(7)	3.7
C(6)	−0.058(1)	−0.0983(7)	0.2106(7)	4.4
C(7)	−0.123(1)	−0.0537(9)	0.2699(7)	5.2
C(8)	−0.119(1)	0.0330(9)	0.2696(7)	5.2
C(9)	−0.049(1)	0.0775(8)	0.2086(6)	3.6
C(10)	0.356(1)	0.0236(9)	−0.0786(7)	4.7
C(11)	0.367(2)	0.2040(9)	−0.0910(9)	6.3
Cl	−0.1898(6)	0.25	−0.0495(4)	5.3
O(1A)	−0.030(1)	0.25	−0.0533(8)	5.9
O(2A)	−0.241(2)	0.25	−0.1295(10)	10.1
O(3A)	−0.237(1)	0.1765(6)	−0.0092(7)	7.7
C(1S)	0.667(3)	0.25	0.1727(17)	10.3
C(2S)	0.520(3)	0.25	0.1415(14)	7.0
N(1S)	0.399(2)	0.25	0.1194(9)	5.5

a) As defined by Hamilton.[10]

Pnma considering the molecular symmetry of the present complex, the structure was reasonably solved. All the nonhydrogen atoms were refined anisotropically and the hydrogen atoms except for those of the methyl group were included in the structure factor calculation. The refinement of structure was carried out by the block-diagonal least-squares procedures using the *HBLS*-V program.[8] The final refinement converged the R and R_w factors to 0.084 and 0.106 for 999 observed reflections ($|F_o|>3\sigma(|F_o|)$), respectively. The weighting scheme used is $w=(\sigma^2+a|F_o|+b|F_o|^2)^{-1}$ where a and b used in the final refinement cycles are 0.2237 and 0.0003, respectively. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[9] The final atomic parameters are listed in Table 1.†

Results and Discussion

The molecular structure of the title complex is shown in Fig. 1 together with atomic numbering system. Bond distances and angles are listed in Table 2. During the course of the structure analysis, both ClO_4 anion and the CH_3CN solvent molecule were found to be coordinated to the Mn(III) atom. The molecule has crystallographic C_s symmetry, in which the Mn(III) atom is located onto a mirror plane together with atoms of two axial ligands, Cl, O(1A), O(2A), C(1S), C(2S), and N(1S).

The coordination geometry around the Mn(III) atom is elongated octahedral as expected for a high spin d^4 metal ion due to the Jahn-Teller effet. In the equatorial plane, the tetradentate bzacen ligand is coordinated to the metal atom with bond distances of Mn-O=1.889(9) and Mn-N=1.955(10) Å, which agree with the average values of the similar complex.[5] The bond distances between the Mn(III) atom and the axial ligands, Mn-O(1A)[2.44(2) Å] and Mn-N(1S)[2.47(2) Å] are about 0.5 Å longer than the corresponding distances between the metal and the bzacen ligand in the equatorial plane. The ClO_4 anion and CH_3CN molecule are semi-coordinated to the metal atom from

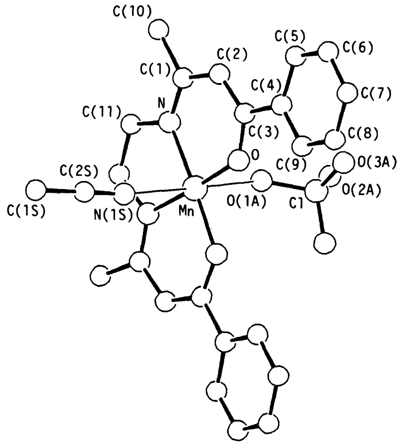

Fig. 1. The molecular structure of $[Mn(bzacen)(CH_3CN)(ClO_4)]$ together with atomic numbering system.

Table 2. Bond Distances and Angles for Non-H Atoms with e.s.d.'s in Parentheses

(a) Bond distance/Å			
Mn-O	1.889(9)	Mn-N	1.955(10)
Mn-O(1A)	2.43(2)	Mn-N(1S)	2.47(2)
N-C(1)	1.32(2)	N-C(11)	1.44(2)
C(1)-C(2)	1.41(2)	C(1)-C(10)	1.51(2)
C(2)-C(3)	1.36(2)	C(3)-O	1.30(2)
C(3)-C(4)	1.50(2)	C(4)-C(5)	1.41(2)
C(4)-C(9)	1.38(2)	C(5)-C(6)	1.37(2)
C(6)-C(7)	1.37(2)	C(7)-C(8)	1.35(2)
C(8)-C(9)	1.41(2)	C(11)-C(11′)	1.43(4)
C(1S)-C(2S)	1.44(4)	C(2S)-N(1S)	1.16(3)
Cl-O(1A)	1.46(2)	Cl-O(2A)	1.45(2)
Cl-O(3A)	1.40(1)		
(b) Bond angle/°			
O-Mn-N	92.9(4)	O-Mn-N′	177.0(4)
O-Mn-O′	90.1(4)	N-Mn-N′	84.1(4)
O-Mn-O(1A)	91.3(5)	N-Mn-O(1A)	89.0(5)
O-Mn-N(1S)	90.7(5)	N-Mn-N(1S)	89.0(5)
O(1A)-Mn-N(1S)	177.3(6)	Mn-O-C(3)	127.3(8)
Mn-N-C(1)	126.2(9)	Mn-N-C(11)	113.5(9)
C(1)-N-C(11)	120(1)	N-C(1)-C(2)	122(1)
N-C(1)-C(10)	121(1)	C(2)-C(1)-C(10)	117(1)
C(1)-C(2)-C(3)	127(1)	C(2)-C(3)-C(4)	122(1)
O-C(3)-C(2)	125(1)	O-C(3)-C(4)	113(1)
N-C(11)-C(11′)	114(1)	C(1S)-C(2S)-N(1S)	177(3)
O(1A)-Cl-O(2A)	106(1)	O(1A)-Cl-O(3A)	109(1)
O(2A)-Cl-O(3A)	112(1)	O(3A)-Cl-O(3A′)	109(1)

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† The tables for anisotropic temperature factors of non-hydrogen atoms, for atomic coordinates of hydrogen atoms, and for observed and calculated structure factors are deposited as Document No. 8882 at the Office of the Editor of Bull. Chem. Soc. Jpn.

both apical sites. This six-coordinate octahedral geometry in the present complex is in contrast with the five-coordinate square-pyramidal structure in [Mn(acen)Cl].[5] The coordination ability of the solvent molecule may affect the resulted structure of the present complex.

Bond distances and angles in the chelate ligand agree within experimental errors, with the values reported hitherto in the similar complexes.[1,5] As observed in the tetradentate acen ligand in Schiff base complexes, the delocalization of double bonds within the N–C(1)–C(2)–C(3)–O chelate ring is also observed in this bzacen ligand. The bridging CH_2–CH_2 bond distance in this ligand, C(11)–C(11′)=1.43(4) Å is somewhat shorter than the expected value. Similar shortened CH_2–CH_2 distances observed in the acen ligand were reported in the Mn(III)[5] and V(IV)[11] complexes [1.40(1) and 1.42(3) Å, respectively].

All the atoms except for two phenyl groups in the bzacen ligand are coplanar with the Mn(III) atom, the maximum atomic deviation from the least-squares plane being 0.03 Å. The plane of the phenyl group is also almost included in the co-plane of the chelate atoms of the bzacen ligand. The dihedral angle between these two planes is only 6.8°.

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