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A Distorted Trigonal Bipyramidal Manganese(II) Complex of the Schiff Base Ligand (L) Derived from 2,6-Pyridinedicarboxaldehyde and (1*R*,2*S*)-Norephedrine; the X-Ray Structure of $MnBr_2L$

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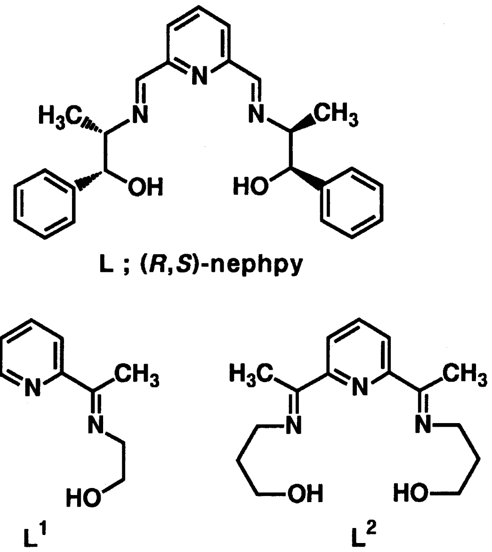
Synopsis. The title complex was synthesized and the structure was determined by the X-ray method. The oxygen atoms of the (1*R*,2*S*)-norephedrine moieties do not coordinate to manganese and the coordination polyhedron is a distorted trigonal bipyramid. The steric interactions between the bound bromide ions and the methyl and phenyl groups of the (1*R*,2*S*)-norephedrine moieties are suggested to influence the structure of the complex.

Several seven-coordinate manganese(II) complexes of a Schiff base ligand have been reported; the complexes have the N_3O_2 donor set of the ligand forming a pentagonal plane and two exogeneous donors as axial ligands.[1] In order to investigate the structural variation of manganese(II)-Schiff base complexes with the N_3O_2 donor set, we have determined the structure of a manganese(II) complex with the Schiff base ligand derived from 2,6-pyridinedicarboxaldehyde and (1*R*,2*S*)-norephedrine ((*R*,*S*)-nephpy) (Chart 1). In a seven-coordinate pentagonal bipyramidal structure, the complex would involve strong steric interactions between the axial ligands and the methyl and phenyl groups of the (1*R*,2*S*)-norephedrine moieties. Manganese complexes containing chiral Schiff base ligands are also of interest in connection with their catalytic properties for asymmetric oxidation of olefins.



L ; (*R*,*S*)-nephpy

L^1

L^2

Chart 1.

Experimental

Preparation of $[MnBr_2\{(R,S)\text{-nephpy}\}]\cdot 2H_2O$ and $[MnCl_2\{(R,S)\text{-nephpy}\}]$. These complexes were prepared under an argon atmosphere. A new Schiff base ligand, (*R*,*S*)-nephpy was prepared by addition of 2,6-pyridinedicarboxaldehyde (166 mg, 1.23 mmol) in methanol (15 cm^3) to a methanol solution (10 cm^3) of (1*R*,2*S*)-norephedrine (371 mg, 2.46 mmol). The solution was refluxed for 30 min to give a colorless solution. To this solution was added $MnBr_2\cdot 4H_2O$ (352 mg, 1.23 mmol) and the mixture was refluxed for about 30 min. The color of the solution changed to orange. The solution was filtered and the filtrate was concentrated to ca. 10 cm^3 under reduced pressure. Diethyl ether was slowly added to form a layer on the methanol solution, and the solution was left at room temperature for several hours to give yellow crystals, which were collected by filtration. Yield: 0.66 g. Found: C, 46.03; H, 4.80; N, 6.41%. Calcd for $C_{25}H_{27}N_3Br_2MnO_2\cdot 2H_2O$: C, 46.03; H, 4.79; N, 6.44%.

$[MnCl_2\{(R,S)\text{-nephpy}\}]$ was prepared in the same way except that $MnCl_2\cdot 4H_2O$ was used instead of $MnBr_2\cdot 4H_2O$ and the compound was recrystallized from acetonitrile. Found: C, 56.80; H, 5.32; N, 8.18%. Calcd for $C_{25}H_{27}N_3Cl_2MnO_2$: C, 56.94; H, 5.16; N, 7.97%.

These complexes were stable in the solid state and no indication of air oxidation was found. On the other hand, the complexes were somewhat less stable in solution. For example, the color of the acetonitrile solutions slowly changed from orange to brown in air over several weeks.

Crystal Structure Determination. Crystals of $[MnBr_2\{(R,S)\text{-nephpy}\}]$ suitable for structure determination were obtained by recrystallization from acetonitrile. An orange-yellow prismatic crystal having dimensions of $0.3\times0.3\times0.5$ mm^3 was sealed in a capillary tube and mounted on a Rigaku AFC-5R four-circle diffractometer equipped with graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.71073$ Å). Crystal data: $C_{25}H_{27}N_3Br_2MnO_2$, FW 616.3, orthorhombic, $P2_12_12_1$, $a=13.365(2)$, $b=16.058(2)$, $c=12.122(2)$ Å, $V=2601.6(5)$ Å^3, $Z=4$, $D_c=1.57$ g cm^{-3}, $\mu(\text{Mo }K\alpha)=35.56$ cm^{-1}. The unit cell dimensions and orientation matrix were determined from 25 reflections in the range $29<2\theta<30°$. Diffraction data were collected to $2\theta_{\max}=60°$ using the θ–2θ scan mode (scan range; $1.30+0.5\tan\theta/°$). No significant variation in intensities was observed for three standard reflections during data collection. Data were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied. All the calculations were carried out on a HITAC M-680H computer at the Computer Center of the Institute for Molecular Science. The manganese location was determined by the direct method using SHELXS-86[2] and the other non-hydrogen atoms were found by the usual Fourier methods using the Universal Crystallographic Computation Program System UNICS-III.[3] The 4334 reflections having $|F_o|>3\sigma(|F_o|)$ were used in the structure refinement, and block-diagonal least-squares refinement minimizing $\Sigma w(|F_o|-|F_c|)^2$ converged to R=0.070 and R_w=0.063. The atomic parameters of the non-hydrogen atoms are listed in Table 1.[4]

Infrared Spectra Measurements. Infrared spectra were recorded as potassium bromide pellets using a JASCO IR-810 spectrometer.

Results and Discussion

An ORTEP drawing of [MnBr$_2${(R,S)-nephpy}] is shown in Fig. 1. Two oxygen atoms of the (1R,2S)-norephedrine moieties do not coordinate to manganese and the manganese atom is five-coordinate. Since the complex is neutral with two bound bromide ions, the hydroxyl groups are not deprotonated. The IR spectrum of the complex showed two strong bands in the O–H stretching region at 3421 and 3523 cm^{-1}, and the bands were assigned to the alcoholic OH stretching vibrations. Selected bond lengths and angles are listed in Tables 2 and 3, respectively. The manganese atom has approximate trigonal-bipyramidal geometry where the three nitrogen atoms and the manganese atom are in the same plane. The Br(1)–Mn(1)–Br(2) angle is 117.7-

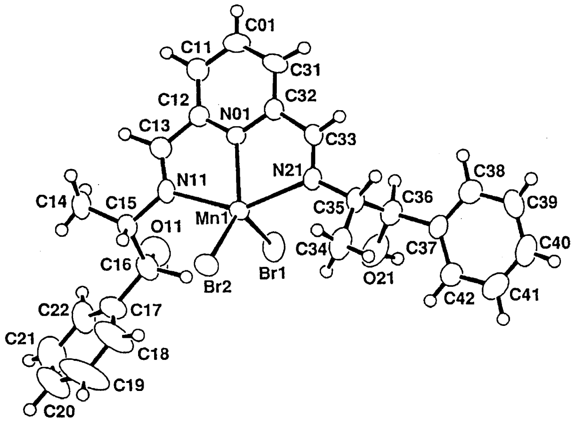


Fig. 1. An ORTEP drawing of [MnBr$_2${(R,S)-nephpy}].

Table 1. Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors ($B_{eq}=4/3\{\sum_i\sum_j B_{ij}\,\boldsymbol{a}_i\cdot\boldsymbol{a}_j\}$)

Atom	x	y	z	B_{eq}/Å^2
Mn(1)	−8524(1)	−319(1)	−3286(1)	2.6
Br(1)	−8546(1)	−289(1)	−5348(1)	4.2
Br(2)	−8941(1)	987(1)	−2296(1)	3.6
O(11)	−6051(5)	536(4)	−5247(5)	5.2
O(21)	−10885(4)	−818(5)	−5195(5)	5.8
N(01)	−7903(4)	−1499(4)	−2798(5)	2.6
N(11)	−6790(5)	−172(4)	−3151(5)	3.0
N(21)	−9882(4)	−1273(4)	−3102(5)	2.7
C(01)	−7111(7)	−3040(5)	−2368(11)	6.0
C(11)	−6468(7)	−2360(5)	−2519(10)	4.9
C(12)	−6907(6)	−1599(5)	−2731(7)	3.1
C(13)	−6338(6)	−832(5)	−2886(7)	3.3
C(14)	−5129(7)	606(5)	−3048(8)	4.0
C(15)	−6257(6)	634(5)	−3258(6)	3.0
C(16)	−6524(6)	1005(5)	−4395(7)	3.9
C(17)	−6187(7)	1905(5)	−4443(7)	4.4
C(18)	−6804(10)	2500(7)	−3939(11)	8.0
C(19)	−6568(13)	3333(7)	−3942(14)	11.0
C(20)	−5686(10)	3575(6)	−4472(11)	8.0
C(21)	−5069(9)	3008(8)	−4972(11)	7.9
C(22)	−5344(7)	2155(6)	−4990(8)	5.2
C(31)	−8130(7)	−2940(5)	−2464(9)	4.3
C(32)	−8508(6)	−2168(4)	−2670(7)	3.1
C(33)	−9595(6)	−1982(5)	−2783(7)	3.1
C(34)	−11300(6)	−307(6)	−2918(8)	5.1
C(35)	−10980(6)	−1198(5)	−3238(7)	3.0
C(36)	−11249(6)	−1416(5)	−4438(8)	3.8
C(37)	−12371(6)	−1492(5)	−4566(7)	3.3
C(38)	−12847(7)	−2234(5)	−4290(8)	4.4
C(39)	−13880(7)	−2306(5)	−4380(9)	5.0
C(40)	−14437(7)	−1663(6)	−4780(8)	4.6
C(41)	−13987(7)	−924(6)	−5084(7)	4.6
C(42)	−12949(6)	−839(5)	−4981(8)	4.0

Table 2. Bond Lengths (l/Å)

Mn(1)-Br(1)	2.500(1)		
Mn(1)-Br(2)	2.480(1)		
Mn(1)-N(01)	2.151(6)		
Mn(1)-N(11)	2.335(6)		
Mn(1)-N(21)	2.386(6)		
O(11)–C(16)	1.425(11)	O(21)–C(36)	1.415(11)
N(01)–C(12)	1.344(10)	N(01)–C(32)	1.354(10)
N(11)–C(13)	1.261(10)	N(21)–C(33)	1.262(10)
N(11)–C(15)	1.483(10)	N(21)–C(35)	1.481(10)
C(01)–C(11)	1.402(12)	C(01)–C(31)	1.377(13)
C(11)–C(12)	1.378(11)	C(31)–C(32)	1.361(11)
C(12)–C(13)	1.461(11)	C(32)–C(33)	1.489(11)
C(14)–C(15)	1.531(12)	C(34)–C(35)	1.543(12)
C(15)–C(16)	1.543(12)	C(35)–C(36)	1.539(12)
C(16)–C(17)	1.514(12)	C(36)–C(37)	1.513(11)
C(17)–C(18)	1.403(15)	C(37)–C(38)	1.392(12)
C(17)–C(22)	1.367(14)	C(37)–C(42)	1.397(12)
C(18)–C(19)	1.373(17)	C(38)–C(39)	1.389(13)
C(19)–C(20)	1.397(22)	C(39)–C(40)	1.362(13)
C(20)–C(21)	1.370(18)	C(40)–C(41)	1.381(14)
C(21)–C(22)	1.419(16)	C(41)–C(42)	1.399(13)

Table 3. Selected Bond Angles (ϕ/°)

Br(1)–Mn(1)–Br(2)	117.7(1)
Br(1)–Mn(1)–N(01)	107.2(2)
Br(1)–Mn(1)–N(11)	94.6(2)
Br(1)–Mn(1)–N(21)	95.5(2)
Br(2)–Mn(1)–N(01)	134.3(2)
Br(2)–Mn(1)–N(11)	96.0(2)
Br(2)–Mn(1)–N(21)	109.1(2)
N(01)–Mn(1)–N(11)	71.8(2)
N(01)–Mn(1)–N(21)	72.7(2)
N(11)–Mn(1)–N(21)	144.4(2)

(1)°. Brooker et al.[5)] reported the structure of a pentagonal-bipyramidal manganese(II) complex, *trans*(Cl, Cl)-[$MnCl_2L^1$] (Cl–Mn–Cl: 178.8(1)°) where the Schiff base ligand (L^1) was derived from 2,6-diacetylpyridine and 2-amino-1-ethanol, and the structure of an octahedral complex, *cis*(NCS,NCS)-[$Mn(NCS)_2L^2$] (SCN–Mn–NCS: 92.8(1)°) where L^2 was derived from 2,6-diacetylpyridine and 3-amino-1-propanol. Both L^1 and L^2 have the N_3O_2 donor set just as our ligand does, but have no bulky substituents on the amino alcohol moieties. The [$Mn(NCS)_2L^2$] complex takes a polymeric structure, and the oxygen atom of an alcohol combines with the neighboring unit. Neither a polymeric structure nor the coordination of an alcohol chain from another unit was observed in the present [$MnBr_2${(*R*,*S*)-nephpy}] complex. The distance between the manganese and the oxygen of the neighboring (*R*,*S*)-nephpy ligand is longer than 3.7 Å. The bond distance of Mn(1)–N(01) (2.151(6) Å) is shorter than that reported for [$MnCl_2L^1$] (2.289(2) Å). The short Mn(1)–N(01) distance in [$MnBr_2${(*R*,*S*)-nephpy}] may result from the geometrical constraint of the ligand. The pyridine-diimine part is very rigid and the angle of N(11)–Mn(1)–N(21) (144.4(2)°) in [$MnBr_2${(*R*,*S*)-nephpy}] is larger than that in [$MnCl_2L^1$] (137.2(1)°), and thus the N(01) atom in the former is forced close to the manganese.

The length of the alkyl chains of the amino alcohol moieties seems to affect the geometry of a complex; the alkyl chain forming a five-membered chelate ring stabilizes the pentagonal-bipyramidal structure more than a longer chain does. It should be noted that the two oxygen atoms of the (1*R*,2*S*)-norephedrine moieties, which are expected to be incorporated into the five-membered chelate rings, are not coordinated to the manganese in [$MnBr_2${(*R*,*S*)-nephpy}]. The presence of the bulky substituents, the phenyl and the methyl groups, may be responsible for this. If the complex took a pentagonal-bipyramidal structure, there would be severe steric repulsions between the axial bromide ions and the phenyl and/or methyl groups. We prepared [$MnCl_2${(*R*,*S*)-nephpy}] in the hope that the manganese atom would become seven-coordinate, since smaller chloride ions cause less steric repulsion. The IR spectrum of the dichloro complex is, however, very similar to that of the dibromo complex, suggesting that the former also has a distorted trigonal-bipyramidal structure. It seems that the steric repulsion in the dichloro complex is still too large to form a seven-coordinate structure.

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