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A mononuclear manganese(III) complex of an asymmetric macrocyclic ligand with a ring contraction $[MnHL^2(ClO_4)](ClO_4) \cdot 2.5H_2O$

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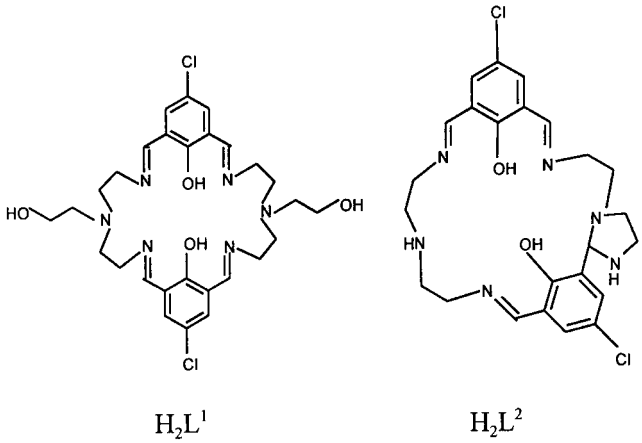
Abstract

The template reaction of sodium 2,6-diformyl-4-chlorophenolate and *N*,*N*-bis(2-aminoethyl)-*N*-hydroxyethylamine followed by *in situ* transmetallation of $Mn(ClO_4)_2$ results in a mononuclear manganese(III) complex of one 21-membered asymmetric 2:2 Schiff base macrocycle, in which a hydroxyethyl group of the amine has been eliminated and ring contraction at one chamber of the macrocycle has occurred to form an imidazolidine ring. An X-ray study indicates that the geometry about the manganese(III) ion is distorted octahedral. The electrochemical behavior of this complex in MeCN has been studied by cyclic voltammetry.

Introduction

In our previous research, the preparation of Schiff base macrocycles and their polynuclear metal complexes was accomplished by a sodium template technique [1–3]. On the basis of this method, diethylenetriamine and tris(2-aminoethyl)amine derivatives have been reacted with sodium 2,6-diformyl-4-substituted phenolates to produce new macrocyclic ligands, in which some anticipated pendant-arm macrocyclic complexes have been obtained. However, a few unexpected complexes, such as the mononuclear iron(III) complex accompanied by a ring-contraction and group elimination have been generated [4–6]. Herein we describe the synthesis, crystal structure and electrochemical properties of a mononuclear manganese(III) complex of a macrocyclic ligand (H_2L^2) in which ring-contraction has occurred through elimination of expected pendant arms.



H_2L^1 H_2L^2

Experimental

Materials

The sodium salt of 2,6-diformyl-4-chlorophenolate (sdcp) was prepared as described previously [1]. All other solvents and chemicals were of analytical grade and were used without further purification. *Caution*: Although no problem were encountered in this work, transition metal perchlorates are potentially explosive and should be handled in small quantities.

N,N-bis(2-aminoethyl)-N-hydroxyethylamine chloride (dhap · 3HCl · 2H₂O)

A solution of salicyladehyde (23.20 g, 0.19 mol) with diethylenetriamine (9.78 g, 0.095 mol) in EtOH (400 cm^3) was stirred at room temperature for 0.5 h, then $2\text{-}ClCH_2CH_2OH$ (7.62 g, 0.095 mol) and dry Na_2CO_3 (10.07 g, 0.095 mol) were added. The resulting mixture was stirred under reflux for 30 h. After filtering and concentrating to remove the solvent, the remaining oil was treated with 5 mol dm^{-3} HCl in EtOH (500 cm^3). The suspension was kept refluxing for 5 h, and then filtered. The product was collected and recrystallised from H_2O–MeOH. Yield: 82%. (Found: C, 24.5; H, 8.3; N, 14.5, $C_6H_{24}Cl_3N_3O_3$ calcd.: C, 24.6; H, 8.2; N, 14.4%.)

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[MnHL²(ClO₄)](ClO₄)

EtOH (5 cm^3) was added to a mixture of dhap·3HCl·2H_2O (0.29 g, 1 mmol) with NaOH (0.12 g, 3 mmol) in H_2O (1 cm^3). After the precipitated NaCl was removed, the solution was added to a suspension of sdcp (0.21 g, 1 mmol) in EtOH (30 cm^3). The mixed solution was then stirred for 2 h on an ice-water bath, and $Mn_2(ClO_4)_2 \cdot 6H_2O$ (0.36 g, 1 mmol) was added. The solution was then heated under reflux for further 5 h. Yellow precipitates were collected, washed with EtOH and dried over P_2O_5, yield 63%. (Found: C, 38.5; H, 3.2; N, 10.9, $C_{24}H_{27}Cl_4N_6O_{10}Mn$ calcd.: C, 38.1; H, 3.6; N, 11.1%.) I.r. (KBr, cm^{-1}): 3312w (NH), 1660s (C═N), 1642s (C═N), 1100vs (ClO_4^-), 978w (ClO_4^-). FAB: $[MnL^2]^+$ 556.

Physical measurements

C, H and N analyses were performed with a Perkin-Elmer 1400C microanalyser. I.r. spectra (4000–400 cm^{-1}), as KBr pellets, were recorded on a Nicolet FT-IR 170X spectrophotometer. Positive f.a.b. mass spectra were measured utilizing a VG-2AB-HS mass spectrometer with NOBA as the matrix solvent. A BAS-100B electrochemical analyzer (BAS Co., USA) was used for the electrochemical measurements which were carried out under an N_2 atmosphere in MeCN solution (*ca.* 1×10^{-3} mol dm^{-1}) containing *n*-Bu_4NClO_4 (TBAP, 0.1 mol dm^{-1}) as the supporting electrolyte. A three-electrode system was employed with a glassy carbon as the working, a platinum wire as an auxiliary and a saturated calomel electrode (s.c.e.) as the reference electrode.

Crystal structure determination

Orange red plate crystals, suitable for X-ray determination, were grown from a solution of the complex in 1:3 MeCN–MeOH. Crystal data for $[MnHL^2(ClO_4)](ClO_4) \cdot 2.5H_2O$[a]: Empirical formula $C_{24}H_{27}Cl_4MnN_6O_{12.50}$, dimensions $0.30 \times 0.20 \times 0.20$ mm, triclinic, space group $P\bar{1}$, $a = 10.948(2)$ Å, $b = 12.415(2)$ Å, $c = 14.079(3)$ Å, $\alpha = 74.765(1)°$, $\beta = 70.33(2)°$, $\gamma = 73.49(2)°$, $V = 1697.8(6)$ $Å^3$, $Z = 2$. Data were measured on a Siemens P4 four-circle diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 296 K using ω–2θ scan method. A total of 5834 reflections were collected, of which 4923 were independent and 2311 ($R_{int} = 0.0666$) observed and 509 parameters led to convergence, with a final value of $R1 = 0.0765$ and $wR2 = 0.1556$ with $I > 2\sigma(I)$.

Data collection, crystal structure solution and refinement method have been reported previously [6]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2. Hydrogen atoms were placed in their calculated positions with C—H = 0.93 Å, assigned to fixed isotropic thermal parameters at 1.2 times of the atom they attached and allowed to ride on their respective parent atoms. Oxygen atoms of the perchlorate anions were considered disordered. The s.o.f. were refined freely using free variables; Cl—O distances were restrained using SADI. Water molecules O(2w) and O(3w), O(3w)′ were also refined disorderedly. The s.o.f. of O(2w) is fixed at 0.5; O(3w) and O(3w)′ were refined using free variables. Because of the lower intensity of observed reflections, the hydrogen atoms of the water molecules cannot be found from DIFMAP.

[a] CCDC number: 131493. Empirical formula of this compound does not include the hydrogen atoms of the crystalline water molecules

Results and discussion

Spectroscopic characterisation of the complex

The expected pendant macrocycle L^1 formed by the sodium template condensation between sdcp and dhap was not observed when the product was spectroscopically analyzed. In the i.r. spectrum of the complex, the absence of a band with the characteristic stretching frequency of the carbonyl group and the primary amine suggests that condensation has been completed. However, two strong C═N absorption bands appear at 1660 and 1642 cm^{-1}, indicating that one imine group is associated with an OH moiety in the macrocycle. A band at 3312 cm^{-1} suggests the formation of a secondary amine, hinting at the loss of the hydroxyethyl group from the amine, dhap, in the course of the condensation. The positive f.a.b. spectrum of the complex shows a peak at 556 corresponding to $[MnL^2]^+$, demonstrating that group elimination and ring contraction have happened and that a mononuclear manganese(III) complex has been generated, which is consistent with the i.r. spectra and microanalytical data.

Crystal structure of the manganese(III) complex

The *ORTEP* drawing of the complex cation with its numbering scheme is shown in Figure 1, and selected bond lengths and angles are listed in Table 1. The structure contains a mononuclear cation, $[MnHL^2(ClO_4)]^+$, with one perchlorate anion as the counter ion, together with 2.5 molecules of water. The resulting compartment ligand is a 21-membered asymmetric 2:2 Schiff base macrocycle with a five-member imidazolidine outer ring in one chamber of the macrocycle as though it resulted from ring closure of sdcp with diethylenetriamine. The formation of imidazolidine in one chamber and the binding of a manganese(III) ion in the other hemisphere of the ring have seriously twisted the macrocyclic skeleton, forcing two benzene planes to be staggered with a dihedral angle of 86.2°. The metal atom has a configuration of a distorted

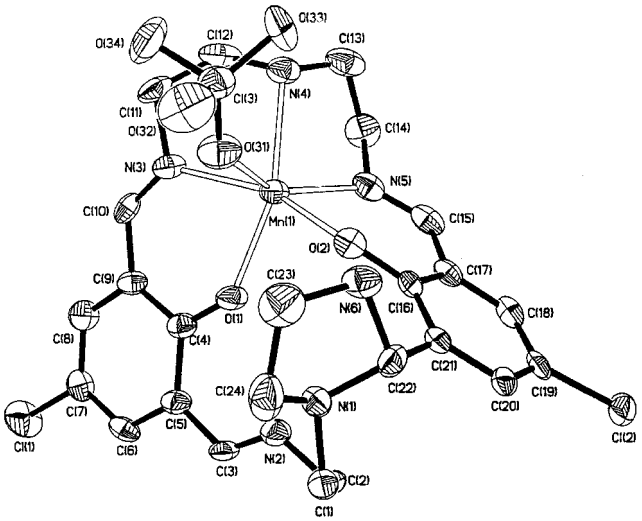


Fig. 1. Molecular structure of the complex cation, $[MnHL^2(ClO_4)]^+$.

Table 1. Selected bond lengths (Å) and angles (°) for $[MnHL^2(ClO_4)]^+$ with e.s.ds in parentheses

Bond distances (Å)			
Mn(1)—O(2)	2.080(6)	Mn(1)—O(1)	2.217(6)
Mn(1)—N(5)	2.199(9)	Mn(1)—N(3)	2.227(8)
Mn(1)—O(31)	2.330(6)	Mn(1)—N(4)	2.339(8)
Bond angles (°)			
O(2)—Mn(1)—O(1)	84.0(2)	O(2)—Mn(1)—N(5)	81.6(3)
O(1)—Mn(1)—N(5)	105.6(3)	O(2)—Mn(1)—N(3)	156.9(3)
O(1)—Mn(1)—N(3)	79.9(2)	N(5)—Mn(1)—N(3)	118.7(3)
O(2)—Mn(1)—O(31)	81.0(2)	O(1)—Mn(1)—O(31)	102.6(2)
N(5)—Mn(1)—O(31)	144.9(3)	N(3)—Mn(1)—O(31)	86.5(3)
O(2)—Mn(1)—N(4)	123.9(2)	O(1)—Mn(1)—N(4)	151.2(2)
N(5)—Mn(1)—N(4)	74.8(3)	N(3)—Mn(1)—N(4)	75.2(3)
O(31)—Mn(1)—N(4)	90.3(3)		

octahedron, in which the equatorial plane is composed of two phenoxy oxygen atoms, one imine nitrogen atom and a secondary amine nitrogen atom, while two apical positions are occupied by the other imine nitrogen atom and a perchlorate anion. All the metal–donor bond distances are within the normal range [7, 8].

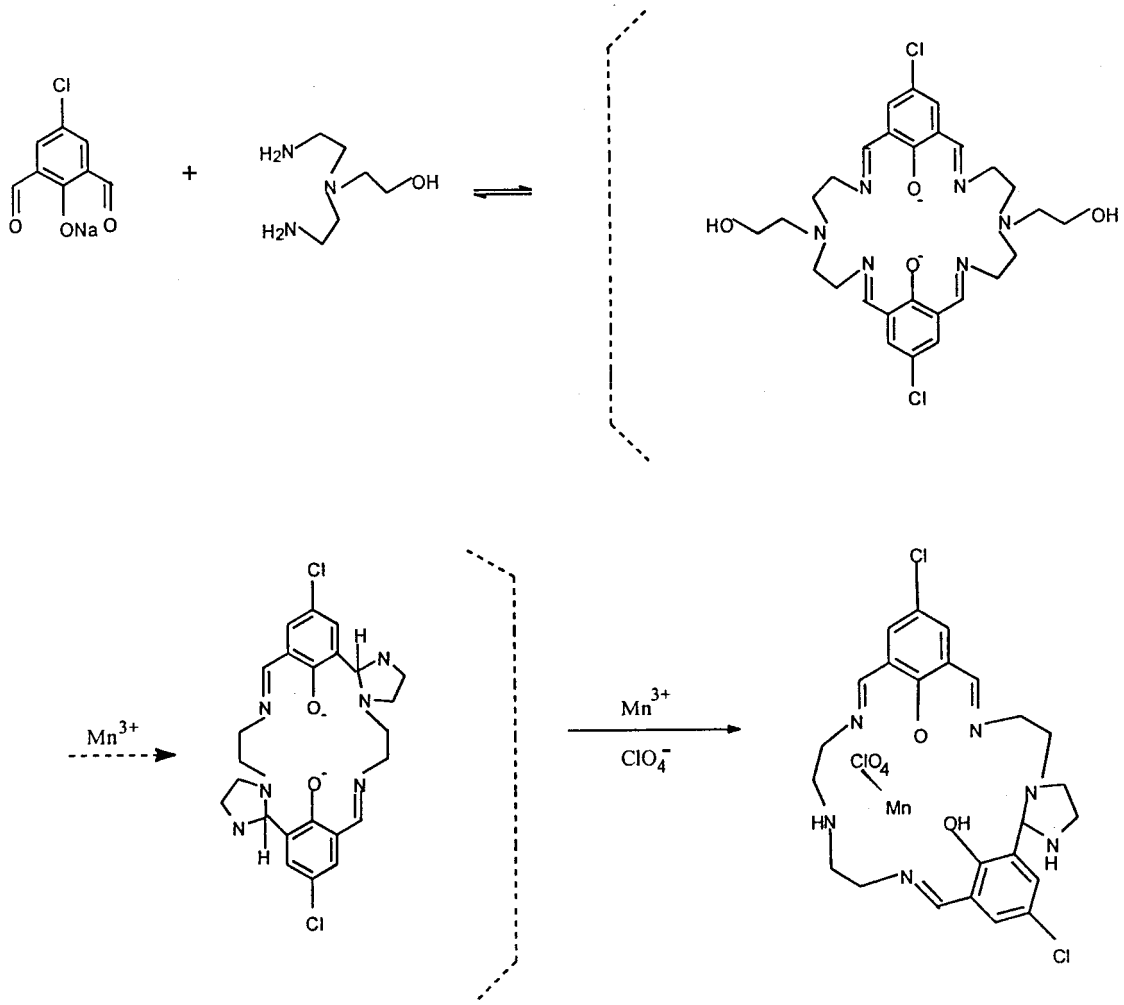
A similar ring contraction has been observed for the 2:2 Schiff base macrocycle prepared by condensation of 2,6-diformyl-4-chlorophenol and 1,5-diamino-3-azapentane [9, 10] in the presence of lanthanide(III) ions. While alkaline earth metals (Ca^{2+}, Sr^{2+}, Ba^{2+}) are involved with the condensation of 2,6-diacetylpyridine with diethylenetriamine, ring-contraction also occurred [11, 12]. This macrocycle contains an 18-member inner ring, two imine bands and two five-member imidazoline outer rings. Further experiments confirmed that the ring-contraction and the ring-expansion were reversible by this ligand [12]. Recently, we have reported a mononuclear iron(III) complex prepared by a similar method, using the 2-hydroxybenzyl group as its pendant arm [6]. The X-ray structure of the iron complex shows that two pendant arms are also eliminated and the resulting contracted macrocycle is the same as that in the present manganese complex. However, the expected dinuclear cadmium(II,II) and manganese(II,II) complexes with two pendant arms in the macrocyclic skeleton have also been obtained [6, 13, 14]. The possible group elimination process is proposed in Scheme 1. It is presumed that the nucleophilic addition of the third amine to the adjacent imine in the presence of the high oxidation state of metals (which is probably due to the oxidation by air in the presence of phenolate) and the departure of the 2-hydroxyethyl group from the tertiary nitrogen at the same time would happen, forming two imidazolidine rings. When reacting with the metal ion a ring-expansion would occur in one chamber and the other remaining as it is. It is suggested that the resulting small ring cavity can match the size of a manganese(III) or iron(III) ion. But the detailed mechanism is still not clear.

Electrochemical study

The cyclic voltammogram of the macrocyclic manganese(III) complex examined in MeCN (1.0×10^{-3} mol dm^{-3} at 25 °C) with n-Bu_4NClO_4 (0.1 mol dm^{-3}) as the supporting electrolyte at different scan rates and the i_p *versus* $v^{1/2}$ curve are shown in Figure 2 and Figure 3, respectively. Figure 2 exhibits only one pair of redox peaks corresponding to the redox couple of manganese(II)/manganese(III), the average formal potential [$E^\circ = (E_{pa} + E_{pc})/2$] is *ca.* +502 mV. At scan rates less than 20 mV s^{-1}, the peak-to-peak separation is 60 mV, exhibiting a reversible electrode process when considering the fact that peak current is proportional to the square root of scan rate. With increasing scan rates, the peak-to-peak separation increases and the electrode reaction becomes a quasi-reversible process.

On the basis of the equation $i_d = 4nFDrc$, the diffusion coefficient of the complex was determined using a Pt microdisk electrode ($\phi = 10$ μm), where i_d is the limiting current, r is the electrode radius corrected using a MeCN solution containing the same concentration of ferrocence and n-Bu_4NClO_4, and other parameters have their usual meaning. The diffusion coefficient of the complex obtained is 4.09×10^{-6} cm^2 s^{-1}.

As mentioned above, at a higher scan rate the electrode process at a glassy carbon electrode is quasi-reversible and is controlled by the diffusion rates of this complex in solution and the electron transfer between the complex and the electrode. Supposing that the diffusion coefficients of reduction and oxidation states of the complex are equal, according to Nicholson's [15] equation ($0.3 < \alpha < 0.7$), the electron transfer rate constant, k_s, of 3.4×10^{-3}, 5.9×10^{-3}, 7.7×10^{-3}, 9.4×10^{-3}, and 1.08×10^{-2} cm s^{-1} can be obtained at scan rates of 20, 60, 100, 150 and 200 mV s^{-1}, respectively, with an average value of 7.4×10^{-3} cm s^{-1}.



Scheme 1. The proposed process for the formation of the complex.

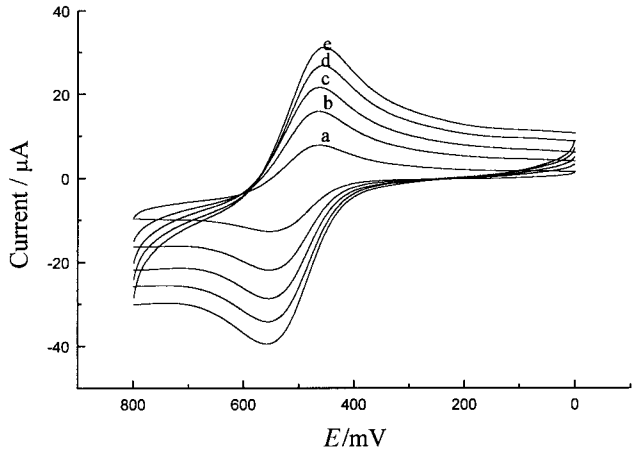


Fig. 2. Cyclic voltammograms of the complex in CH_3CN (1×10^{-3} mol dm^{-3}) containing 0.1 mol dm^{-3} n-Bu_4NClO_4 on a glass carbon electrode at the scan rate of 20 mV s^{-1} (a), 60 mV s^{-1} (b), 100 mV s^{-1} (c), 150 mV s^{-1} (d) and 200 mV s^{-1} (e).

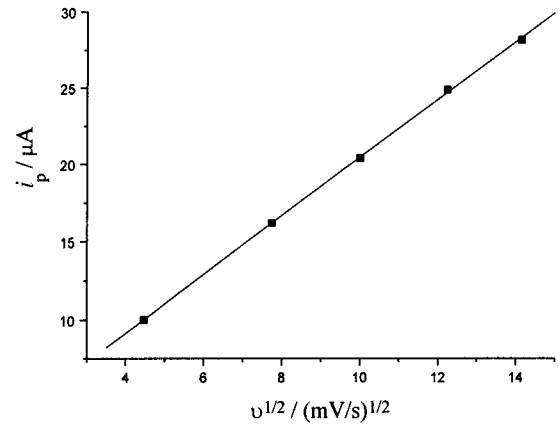


Fig. 3. The curve of i_p *verus* $v^{1/2}$.

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