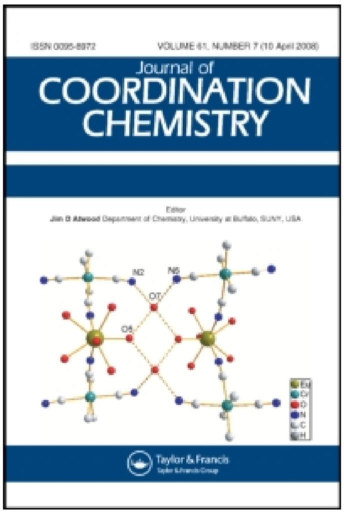

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AN ALKOXO-BRIDGED BINUCLEAR MANGANESE COMPLEX BIS(μ-PROPIONATO-O: O')-BIS(μ-3-SALICYLIDENE-AMINO-PROPANOLATO-O'',O''',N:O'') BISMANGANESE(III)

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AN ALKOXO-BRIDGED BINUCLEAR MANGANESE COMPLEX BIS(μ-PROPIONATO-O:O′)-BIS(μ-3-SALICYLIDENE-AMINO-PROPANOLATO-O″,O‴,N:O″) BISMANGANESE(III)

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The alkoxo-bridged binuclear complex of Mn^{III}, $[Mn_2(salpa)_2(C_2H_5{-}COO)_2]$ (H_2salpa = 3-salicylidene-amino-1-propanol), has been prepared and its crystal structure has been determined by X-ray diffraction. The structure of the title complex consists of discrete binuclear manganese units in which the Mn^{III} atoms are bridged by two alkoxo ligands *via* oxygen atoms and supported by two carboxylato bridging ligands in the *syn-syn* fashion. The complex lies about a crystallographic inversion center. Each Mn^{III} atom is located in an elongated octahedral environment with one imino N, one phenolic O and two alkoxo O atoms coordinated in the equatorial plane and two O atoms from carboxylato groups at the apical positions. The remarkably longer coordination bond distances in the axial direction are attributed to Jahn-Teller distortion at the d^4 manganese center. The distance between the manganese atoms is 2.8662(9) Å. The asymmetrical and symmetric stretching vibrations for carboxylato groups found at 1550 and 1440 cm^{-1}, respectively, with a separation of less than 200 cm^{-1} confirmed the bidentate mode of the carboxylato groups.

Keywords: Mn^{III}; Pivalate; Schiff base; Crystal structure

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INTRODUCTION

Binuclear metal complexes are of great interest not only in elucidating the magnetic coupling between metal ions but also in model compounds of the active sites of metalloenzymes [1,2]. Recently, three non-heme manganese-containing catalases have been isolated from *Lactobacillus plantarum* [3,4], *Thermus thermophilus* [5], and *Thermoleophilum album* [6], and have been structurally characterized. From extensive physicochemical studies, a binuclear oxo-bridged Mn-center is proposed [7]. The catalase Mn···Mn distance of ca. 3.6 Å, derived from EXAFS and X-ray crystal structure data on isolated enzymes [8], suggests that the oxo-bridges may be supported by one or two carboxylato bridges. Binuclear manganese complexes containing alkoxo and carboxylato bridges are proposed to be the model complexes for active sites of manganese catalases. Recently, several Mn^{III} complexes with 3-salicylideneamino-1-propanol and its homologues were prepared [9]. It was assumed that these complexes have di-μ-alkoxo bridged binuclear structures. This was later confirmed by crystal structure analysis [10]. A number of binuclear complexes of this type have been prepared and studied [11–13]. We are currently synthesizing manganese complexes which contain Schiff base ligands to mimic the environment of these manganese catalases. In this paper, we report a binuclear manganese complex containing alkoxo and carboxylato bridges.

EXPERIMENTAL

Physical Measurements

Analyses for C, H and N were carried out with a Perkin-Elmer Analyzer Model 240. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrophotometer with KBr discs. An X-ray crystal structure determination was carried out on a Siemens Smart CCD diffractometer. Magnetic moment measurements for the complex were performed on a Fudan University FDMT-A Faraday balance.

Preparation of $[Mn_2(salpa)_2(C_2H_5—COO)_2]$

3-aminopropanol (0.75 g, 10 mmol) was dissolved in absolute ethanol (20 mL) and salicylaldehyde (1.22 g, 10 mmol) was added to the solution.

The resulting solution was refluxed for 1.5 h. $Mn(ClO_4)_2 \cdot 6H_2O$ (3.60 g, 10 mmol) was added and the mixture become green. After 30 min triethylamine (1 mL, 10 mmol) was added to the solution, and the color changed to dark brown. After 2 h of stirring, triethylamine (1 mL, 10 mmol) and propionic acid (0.80 g, 10.5 mmol) were added to the solution, respectively, followed by stirring for 2 h. This solution was filtered and the filtrate was put aside in the dark. After five days, small crystals were obtained. Reaction of $[Mn_2(salpa)_2(MeCOO)_2]$ or $[Mn_2(salpa)_2Cl_2]$, which were previously prepared according to the references, with propionic acid in the presence of equimolar triethylamine also afford the product in high

TABLE I Crystal data and structure refinement

Compound	$[Mn_2(propionato)_2(salpa)_2]$
Color/shape	Brown/prismatic
Empirical formula	$C_{26}H_{32}Mn_2N_2O_8$
Formula weight	610.42
Temperature	293 K
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	9.098(3)
b (Å)	15.830(3)
c (Å)	9.304(2)
α (°)	90
β (°)	102.04(2)
γ (°)	90
V (Å^3)	1310.5(5)
Z	2
$D_{calct.}$ (g cm^{-3})	1.547
μ (Mo–Kα) (cm^{-1})	10.16
F(000)	632
Diffractometer	Siemens Smart CCD
Radiation	MoKα (λ = 0.71073 Å) Graphite monochromated
Scan type	ω-2θ
$2\theta_{max}$	50.06°
No. of reflections measured	Total: 4267; unique: 2263 ($R_{int} = 0.0216$)
Correction	Lp
Structure solution	Direct methods
Refinement	Full-matrix least-squares on F^2
No. observations ($I > 2\sigma(I)$)	1802
No. variables	172
Reflection/parameters ratio	10.6
Final R indices [$I >$ 2sigma(I)]	$R1 = 0.0327$, $wR2 = 0.0825$
R indices (all data)	$R1 = 0.0459$, $wR2 = 0.0908$
S	1.058
Max shift/error in final cycle	−0.003
Largest diff. peak and hole	0.264 and −0.433 eÅ^{-3}

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

Atom	*x/a*	*y/b*	*z/c*	*Ueq(Å²)*
Mn	3850(1)	−9370(1)	4880(1)	26(1)
O(1)	4886(2)	−9198(1)	7257(2)	34(1)
O(2)	6651(2)	−10214(1)	7431(2)	35(1)
O(3)	5922(2)	−9418(1)	4723(2)	26(1)
O(4)	1904(2)	−9357(1)	5217(2)	35(1)
N	3657(2)	−8153(1)	4275(2)	29(1)
C(1)	6014(3)	−9609(2)	7941(3)	31(1)
C(2)	6653(4)	−9335(2)	9504(3)	43(1)
C(3)	7846(4)	−9879(3)	10377(4)	71(1)
C(4)	6579(3)	−8973(2)	3696(3)	34(1)
C(5)	6216(3)	−8042(2)	3749(3)	42(1)
C(6)	4574(3)	−7841(2)	3253(3)	40(1)
C(7)	2693(3)	−7649(2)	4650(3)	33(1)
C(8)	1601(3)	−7867(2)	5505(3)	33(1)
C(9)	811(3)	−7217(2)	6043(3)	42(1)
C(10)	−283(3)	−7395(2)	6802(4)	49(1)
C(11)	−650(3)	−8228(2)	7000(3)	48(1)
C(12)	83(3)	−8879(2)	6480(3)	40(1)
C(13)	1237(3)	−8716(2)	5731(3)	31(1)

yield. Anal. Calcd. For $C_{26}H_{32}O_8N_2Mn_2$(%): C, 51.15; H, 5.28; N, 4.59. Found: C, 51.32; H, 5.25; N, 4.42.

Crystal Structure Determination

A brown prismatic crystal of the complex having approximate dimensions of 0.20 × 0.20 × 0.30 cm was mounted on a glass fiber. All measurements were made on a Siemens Smart CCD area-detector diffractometer with graphite monochromated Mo−Kα radiation. The data were collected using the ω-2θ scan technique. Of the 2263 reflections which were collected, 1802 were unique ($R_{\mathrm{int}} = 0.0216$). The linear absorption coefficient, μ, for Mo−Kα radiation is 10.16 cm^{-1}. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 with statistical weighting, anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located using riding mode and refined isotropically. Programs employed were Siemens SMART [14] and SAINT [15] control and integration software, and Siemens SHELXL-PLUS [16] structure solution and refinement software. A summary of data collection and structure refinement is given in Table I; the final atomic positional parameters, selected bond lengths and bond angles are given in Tables II and III, respectively.

TABLE III Selected inter-atomic distances (Å) and bond angles (°)

Mn-O4	1.861(2)
Mn-O3	1.922(2)
Mn-O3*	1.957(2)
Mn-N	2.004(2)
Mn-O2*	2.204(2)
Mn-O1	2.233(2)
Mn-Mn*	2.8662(9)
N-C7	1.286(3)
N-C6	1.475(3)
O1-C1	1.268(3)
O2-C1	1.262(3)
O3-C4	1.417(3)
O4-C13	1.322(3)
C1-C2	1.512(4)
C2-C3	1.487(4)
C4-C5	1.513(4)
C5-C6	1.503(4)
C7-C8	1.438(4)
C8-C9	1.404(4)
C8-C13	1.410(4)
C9-C10	1.365(4)
C10-C11	1.381(4)
C11-C12	1.370(4)
C12-C13	1.400(4)
O4-Mn-O3	174.49(8)
O4-Mn-N	90.35(8)
O3-Mn-N	92.71(8)
O4-Mn-O1	92.94(8)
N-Mn-O1	98.95(8)
C1-O1-Mn	124.4(2)
C4-O3-Mn	126.2(2)
C13-O4-Mn	126.4(2)
C7-N-Mn	123.0(2)
C6-N-Mn	118.3(2)

Symmetry code, *: $-x+1,\ -y-2,\ -z+1$.

RESULTS AND DISCUSSION

Synthesis

Generally, manganese(II) complexes can easily be oxidized to manganese(III) complexes by molecular oxygen in the air when the reaction is carried out aerobically. Organic bases, *e.g.*, triethylamine may enhance the rate of such reactions. Preparation of Mn_2O_2 type complexes may be achieved either by the reaction of a Schiff base with the manganese(II) salt in a basic solution or by axial ligand substitution reactions. Normally, manganese(III) ions having a d_4 electronic configuration are susceptible to Jahn-Teller distortion. This effect causes the coordination bond distances in the axial direction to be longer than those in the equatorial plane indicating a weaker metal-ligand interaction. These axial ligands are susceptible to substitution reactions. We have succeeded in preparing a series of binuclear complexes through axial substitution reactions using $[Mn_2(salpa)_2Cl_2]$ or $[Mn_2(salpa)_2(H_2O)_2] \cdot 2ClO_4$ which contain the Mn_2O_2 core. The possible mechanism is shown in Figure 1. The title complex may be prepared by several methods. Carboxylato ligand substitution may also be used for the preparation of the complex.

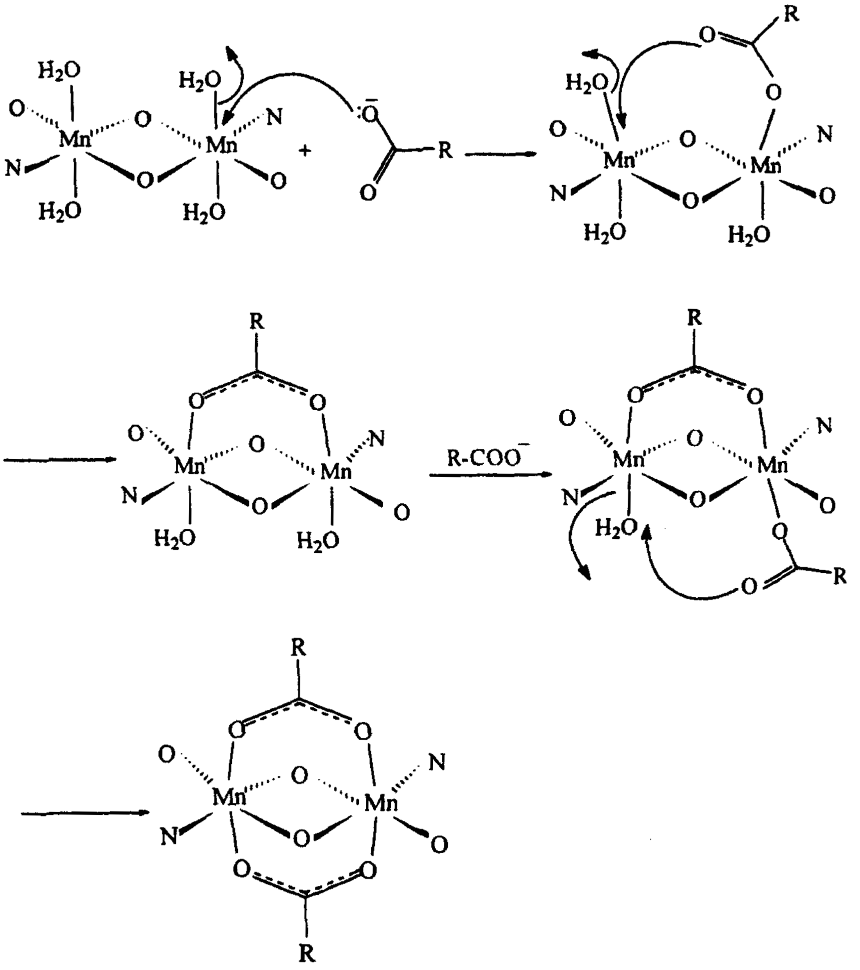

FIGURE 1 Proposed mechanism for the axial substitution reactions.

Crystal Structure

The X-ray crystal structure analysis confirmed the expected dimeric form as shown in Figure 2. Two bidentate propionato groups form bridges between the two Mn atoms. Each Mn^{III} atom is in a distorted octahedral environment. Two alkoxo O atoms, an imine N atom and a phenolic O atom form an equatorial plane. The carboxylato O atoms occupy the axial positions. The equatorial Mn–N (imine) bond distance of 2.004(2) Å is comparable to that reported for other Mn^{III} complexes containing equatorial Mn^{III}–N (imine) bonds [12, 13]. However, it is slightly shorter than the Mn1 – N (amine) distance (2.116 Å) found in $[Mn_3(L')_2(mcba)_2(OCH_3)_2]$ (Hmcba = *m*-chlorobenzoic acid, H_2L' = N,N-bis(2-hydroxybenzyl)-N′,N′-dimethylethylenediamine) [17]. This is probably due to the larger steric effect of tertiary amines. The axial bond distances of 2.233(2) Å for Mn–O1 and 2.204(2) Å for Mn–O2 are significantly longer than those in the equatorial plane from Jahn–Teller distortion as observed in mononuclear Mn^{III} complexes [18]. The Mn–Mn distance of 2.8662(9) Å is comparable to that of $[Mn_2(salpa)_2(CH_3COO)_2]$ (2.869 Å) [10] and $[Mn_2(salpa)_2(C_6H_5COO)_2]$ (2.855 Å) [19] but remarkably shorter than that found in $[Mn_2(salpa)_2(H_2O)_2Cl_2]$ (3.001 Å) [20] and $[Mn_2(salpa)_2Cl_2(MeOH)_2]$ (3.011 Å) [12]. The four-membered Mn_2O_2 ring is exactly planar owing to the presence of an inversion center. Bond distances and angles for each Schiff base ligand (salpa^{2-}) are normal. Each salpa^{2-} coordinates to Mn^{III} atom as a tridentate ligand forming two six-membered chelate rings with the alkoxo O atom bridging to the other Mn^{III} atom. The carboxylato groups are involved in the bridges in a *syn–syn* conformation

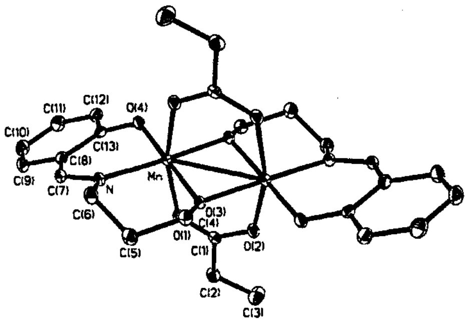

FIGURE 2 Crystal structure of $[Mn_2(propionato)_2(salpa)_2]$ with thermal ellipsoids (50% probability level). Hydrogen atoms (excluding those of water molecules) were omitted for clarity.

either above or below the Mn_2O_2 plane. The carboxylato bite distance for O1 $\cdots$ O2 (2.246 Å) is remarkably shorter than the manganese–manganese distance making the Mn–O(COO) bonds deviate by several degrees from the axis perpendicular to the equatorial plane with the O1–Mn–O2^i bond angle being 164.06(7)° (symmetry codes: i, $1-x$, $-2-y$, $1-z$). The crystal packing is achieved through van der Waals contact.

IR Spectrum

A strong absorption band at $1550\,cm^{-1}$ is assigned to the asymmetric vibration of the bidentate carboxylato groups. The symmetric C—O vibration is observed at $1440\,cm^{-1}$. When a carboxylato ligand acts as a monodentate ligand, the asymmetrical and the symmetric C—O stretching bands of the carboxylato ion shift to higher and to lower frequencies, respectively [21]. The $\Delta\nu$, which is the separation between the asymmetric vibration frequency (ν_{as}) and the symmetric vibration frequency (ν_s) of the carboxylato group, is larger than $200\,cm^{-1}$. When the carboxylato ligand acts as a bidentate ligand to chelate or bridge to one or two metal ion(s), both the asymmetric and the symmetric C—O stretching bands shift in the same direction to lower frequencies with a change of the metal–O bonding. The $\Delta\nu$ is smaller than $200\,cm^{-1}$. For the complex, the $\Delta\nu$ value is smaller than $200\,cm^{-1}$. This suggests that the complex is bridged by carboxylato ligands. The ν(O–H) bands corresponding to the two hydroxy groups in the Schiff bases, are not observed. This means that the Schiff base has been deprotonated and acts as a dianionic ligand. The band from the imine group at $1612\,cm^{-1}$ is shifted by $15\,cm^{-1}$ to lower frequency compared with the free Schiff base ligand.

Magnetic Measurement

The magnetic moment for the complex is 4.09 B.M. at room temperature (300 K) which is lower than the moment found for most high-spin mononuclear Mn^{III} complexes but is similar to related alkoxo bridged binuclear Mn^{III} complexes due to the antiferromagnetic spin-exchange interaction between a pair of Mn^{III} atoms [9].

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Supplementary Data

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 134996. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-(0)1223-336033 or e-mail: deposit@chemcrys.cam.ac.uk).

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