

Synthesis, Crystal Structure, and Magnetic Properties of a Novel Trinuclear Mixed-Valence Oxo-Bridged Manganese Complex Formed by Ligand-Substituted Reaction

$\text{Mn}_3\text{O}(\text{ClC}_6\text{H}_5\text{CO}_2)_2(\text{CH}_3\text{C}_6\text{H}_5\text{CO}_2)_4(3\text{-Methylpyridine}) \cdot 0.5\text{CH}_3\text{CN}$

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A trinuclear mixed-valence oxo-centred manganese complex has been synthesized by carboxylic acid-substituted reaction in CH_3CN solution $\text{Mn}_3\text{O}(\text{ClC}_6\text{H}_5\text{CO}_2)_2(\text{CH}_3\text{C}_6\text{H}_5\text{CO}_2)_4(3\text{-Methylpyridine}) \cdot 0.5\text{CH}_3\text{CN}$. It is a novel trinuclear Mn complex with mixed carboxylate bridge. The title complex crystallizes in the orthorhombic system, space group *Pbca*, with unit cell dimensions $a = 22.548(5)$ Å, $b = 23.070(5)$ Å, $c = 24.321(3)$ Å, $V = 12651(5)$ Å³, $Z = 4$, $R_1 = 0.0755$, and $wR_2 = 0.1627$. The crystal structure shows an oxo-centred Mn_3O unit with peripheral ligands provided by two different bridging carboxylic acids ligands (*m*-chlorobenzoic acid and *m*-methylbenzoic acid) and terminal 3-methylpyridine group. The variable temperature magnetic susceptibility (1.8–300 K) for the title complex has been measured and interpreted in terms of the Kambe vector-coupling method and Van Vleck equation, and the values of J , J' , and g are -8.42 cm⁻¹, -10.37 cm⁻¹, and 2.04 cm⁻¹, respectively. This indicates a weak antiferromagnetic exchange coupling among the manganese ions for the complex.

In recent years, there has been a continuous interest in the study on trinuclear oxo-centred manganese complexes with mixed valence [1–10]. Many interesting aspects of these complexes were studied, such as magnetochemistry [1–3], electron localization and delocalization [4], and the spin ground state variability [5, 6]. A great number of the trinuclear oxo-bridged mixed-valence manganese complexes with the different bridge ligands and terminal ligands have been reported, all of them being oxo-bridged by only one kind of carboxylic acid.

In the present work, a novel trinuclear mixed-valence manganese complex with mixed bridged ligands was prepared by ligands-substituted reaction: $\text{Mn}_3\text{O}(\text{ClC}_6\text{H}_5\text{CO}_2)_2(\text{CH}_3\text{C}_6\text{H}_5\text{CO}_2)_4(3\text{-Methylpyridine}) \cdot 0.5\text{CH}_3\text{CN}$. It is oxo-bridged by two kinds of carboxylic acids. The crystal structure and magnetic properties have been discussed in detail.

A summary of crystallographic data and refinement parameters is given in Table 1. Selected bond distances and angles are given in Tables 2 and 3. The title complex crystallizes in orthorhombic space group *Pbca*. The crystal structure is shown in Fig. 1. The Mn coordination geometry is a slightly distorted octahedron consisting of the central oxygen atom, four oxygen atoms from bridging carboxylate groups, and the nitrogen atom of a terminal 3-methylpyridine. The central O atom is slightly dis-

placed from the plane of the Mn_3 triangle. The bond lengths of Mn(1)—O(11), Mn(2)—O(11), Mn(3)—O(11) are 1.851(4) Å, 1.952(5) Å, and 1.898(4) Å, respectively. The different bond lengths among the central oxygen atom and manganese atoms indicate that the complex is in a valence-trapped situation. The Mn(2)—O(11) distance is the longest as expected for the lower oxidation state, so we can conclude that the Mn(2) is +2 manganese ion, and Mn(1) and Mn(3) are +3 manganese ions. The bond angles of Mn(1)—O(11)—Mn(2), Mn(1)—O(11)—Mn(3), Mn(3)—O(11)—Mn(2) are 123.2(2)°, 114.0(2)°, 122.8(2)°, respectively. The bond distances between the two Mn(III) ions (Mn(1), Mn(3)) and the four surrounding carboxylate oxygen atoms are slightly longer than that between the central Mn(2) ion and corresponding oxygen atoms. This is due to the fact that the Mn(III) (d^4) shows stronger Jahn—Teller effect than the Mn(II) (d^5). The overall structure is thus of the common “basic carboxylate” type seen for many other complexes [1–5, 7–10]. It is worth pointing out that the complex contains two different bridged carboxylate ligands. The carboxylate bridges in positions 7, 9 are *m*-chlorobenzoate, and the carboxylate bridges in positions 2, 3, 4, 5 are *m*-methylbenzoate. Except the central oxygen atom, the bond lengths of Mn ions and oxygen atoms provided by *m*-chlorobenzoate are little shorter than

Table 1. Crystal Data and Structure Refinement for the Title Complex

Complex	Mn ₃ O(ClC ₆ H ₅ CO ₂) ₂ (CH ₃ C ₆ H ₅ CO ₂) ₄ (3-Methylpyridine) · 0.5CH ₃ CN
Formula	C ₆₅ H _{58.5} N _{3.5} Cl ₂ O ₁₂ Mn ₃
Relative molecular mass M_r	1316.375
Colour	Black
Temperature	293(2) K
Wavelength	0.71073 Å
Radiation	MoK α
Crystal system	<i>Pbca</i>
Space group	Orthorhombic
Unit dimensions	$a = 22.548(5)$ Å $b = 23.070(5)$ Å $c = 24.321(5)$ Å
Volume	12651(5) Å ³
Z	4
Calculated density	1.382 Mg/m ³
Absorption coefficient	0.737 mm ⁻¹
$F(000)$	5424
Crystal size	0.20 mm × 0.20 mm × 0.20 mm
Θ range for data collection	1.52° to 26.95°
Reflections/collected/unique	50156/11021 [$R(\text{int}) = 0.1090$]
Completeness to $2\Theta = 26.95$	74.6 %
Absorption correction	Psi-scan
Max. and min. transmission	0.91 and 0.72
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	14021/59/828
Goodness-of-fit on F^2	1.308
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0755$, $wR_2 = 0.1627$
Extinction coefficient	0.0003(3)
Largest diff. peak and hole	0.982 $e \cdot \text{Å}^{-3}$ and $-0.434 e \cdot \text{Å}^{-3}$

Table 2. 10⁴ Numerical Values of Atomic Coordinates and 10³Å² of Equivalent Isotropic Displacement Parameters for the Title Complex

Atoms	x	y	z	$U(\text{eq})$
Mn(1)	956(1)	147(1)	7089(1)	49(1)
Mn(2)	285(1)	1104(1)	7915(1)	50(1)
Mn(3)	-358(1)	-121(1)	7440(1)	62(1)
O(11)	302(2)	387(2)	7489(2)	57(1)
N(11)	235(2)	1886(2)	8449(3)	62(2)
C(12)	20(3)	2395(3)	8228(4)	71(2)
C(13)	-84(3)	2874(3)	8567(4)	78(3)
C(14)	27(4)	2838(3)	9134(4)	90(3)
C(15)	251(3)	2330(3)	9370(4)	78(2)
C(16)	349(3)	1872(3)	9006(3)	65(2)
O(21)	1031(2)	989(2)	8335(2)	80(2)
O(22)	1494(2)	389(2)	7757(3)	79(2)
C(20)	1445(3)	686(3)	8203(3)	59(2)
C(21)	1905(3)	705(4)	8619(4)	81(3)
C(22)	2002(4)	1179(5)	8969(4)	117(4)
C(23)	2483(5)	1131(6)	9339(4)	171(7)
C(24)	2744(5)	582(8)	9285(9)	330(2)
C(25)	2554(12)	57(8)	9082(10)	550(5)
C(26)	2243(4)	203(6)	8616(6)	151(5)
O(31)	675(2)	1640(2)	7308(2)	68(1)
O(32)	1072(2)	987(2)	6712(2)	68(1)
C(30)	963(3)	1505(3)	6879(3)	54(2)
C(31)	1227(3)	1999(3)	6550(3)	58(2)
C(32)	1161(3)	2580(3)	6685(4)	87(3)
C(33)	1429(4)	3009(3)	6347(5)	148(6)
C(34)	1718(4)	2782(7)	5889(5)	190(10)
C(35)	1839(7)	2230(6)	5722(6)	450(3)
C(36)	1540(3)	1848(4)	6074(4)	85(3)

Table 2. (Continued)

Atoms	x	y	z	$U(\text{eq})$
O(41)	-496(2)	-120(3)	8314(3)	98(2)
O(42)	-100(2)	711(2)	8624(2)	82(2)
C(40)	-382(3)	246(4)	8699(4)	75(3)
C(41)	-573(3)	124(5)	9292(5)	100(4)
C(42)	-848(4)	-422(5)	9388(5)	163(7)
C(43)	-959(9)	-534(8)	9927(6)	470(4)
C(44)	-984(7)	-111(6)	10325(6)	261(17)
C(45)	-691(4)	408(7)	10246(5)	198(9)
C(46)	-521(4)	535(6)	9707(5)	117(4)
O(51)	102(2)	-927(2)	7553(3)	90(2)
O(52)	976(2)	-690(2)	7474(2)	75(2)
C(50)	596(3)	-1013(3)	7659(3)	57(2)
C(51)	739(3)	-1527(3)	8008(3)	66(2)
C(52)	330(4)	-1927(3)	8184(4)	80(2)
C(53)	450(5)	-2409(4)	8497(4)	106(3)
C(54)	1001(5)	-2498(4)	8698(5)	116(4)
C(55)	1402(4)	-2096(4)	8540(4)	104(3)
C(56)	1290(3)	-1608(4)	8212(4)	89(3)
N(61)	1677(2)	-94(2)	6612(3)	65(2)
C(62)	1704(3)	-604(3)	6331(4)	79(3)
C(63)	2134(4)	-741(4)	5961(4)	93(3)
C(64)	2548(4)	-315(4)	5893(4)	95(3)
C(65)	2540(3)	201(3)	6177(4)	76(2)
C(66)	2105(3)	301(3)	6546(3)	71(2)
O(71)	-925(2)	585(2)	7361(3)	84(2)
O(72)	-463(2)	1385(2)	7612(2)	78(2)
C(70)	-890(3)	1112(3)	7497(3)	60(2)
C(71)	-1413(2)	1469(3)	7549(3)	59(2)
C(72)	-1912(3)	1221(3)	7357(4)	83(3)
C(73)	-2400(3)	1553(3)	7458(4)	95(3)

Table 2. (Continued)

Atoms	x	y	z	$U(\text{eq})$
C(74)	-2391(3)	2081(4)	7714(4)	85(3)
C(75)	-1889(3)	2331(3)	7889(4)	74(2)
C(76)	-1406(3)	2005(3)	7804(3)	68(2)
N(81)	-1080(2)	-688(3)	7377(3)	78(2)
C(82)	-1571(3)	-509(4)	7633(4)	84(3)
C(83)	-2044(3)	-854(4)	7547(4)	98(3)
C(84)	-2022(3)	-1344(4)	7231(4)	92(3)
C(85)	-1540(3)	-1541(3)	6967(4)	77(2)
C(86)	-1079(3)	-1187(3)	7066(3)	72(2)
O(91)	-319(2)	-237(2)	6580(3)	79(2)
O(92)	568(2)	-174(2)	6355(2)	65(1)
C(90)	80(3)	-306(3)	6232(3)	59(2)
C(91)	-40(3)	-554(3)	5654(4)	66(2)
C(92)	-605(4)	-675(3)	5508(4)	98(3)
C(93)	-713(6)	-883(5)	4981(5)	123(4)
C(94)	-308(6)	-997(4)	4580(5)	118(4)
C(95)	257(5)	-881(4)	4733(4)	106(3)
C(96)	386(4)	-655(3)	5261(3)	72(2)
C(17)	405(5)	2275(5)	10023(5)	122(4)
C(27)	3088(6)	-304(9)	9184(13)	173(10)
C(37)	2109(4)	2255(4)	5144(4)	42(2)
C(47)	-759(11)	764(15)	10780(16)	61(6)
C(57)	2014(13)	-2281(12)	8733(14)	69(7)
C(67)	2979(4)	672(4)	6098(5)	88(3)
Cl(7)	-1881(1)	2998(1)	8213(2)	138(1)
C(87)	-1499(4)	-2095(4)	6623(5)	89(4)
C(97)	615(6)	-991(14)	4206(13)	44(4)
Cl(9)	827(7)	-964(16)	4230(14)	52(4)
O(1)	-1443(7)	3101(6)	9734(7)	136(5)
C(1)	-1360(6)	2631(5)	9672(7)	65(4)
C(2)	-1257(6)	2002(5)	9583(8)	85(5)

$U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

those of Mn ions and oxygen atoms provided by *m*-methylbenzoate. The reactive ability, coordination properties, and structure of the two carboxylic acids are very similar, which leads to the easy substitution. Fig. 2 shows the packing unit cell diagram of the title complex.

Variable temperature magnetic susceptibility data for the title complex were recorded for higher temperature to 1.8 K (Fig. 3). The value of $\chi_m T$ is $855 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 300 K and decreases with decreasing temperature, reaching $1.72 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 1.8 K. This behaviour obviously indicates a weak anti-ferromagnetic coupling interaction between the three manganese ions. The spin Hamiltonian was $H = -2[J_{12}(S_1 S_2) + J_{23}(S_2 S_3) + J_{31}(S_3 S_1)]$ used to fit the observed results, assuming the two Mn(III) ions to be equivalent, then here are two exchange parameters, $J = J_{12} = J_{32}$ and $J' = J_{13}$ for the Mn(III)—Mn(III) interaction. On the basis of this model, *Hendrickson et al.* have given a detailed mathematical expression [8] of the molar paramagnetic susceptibility for such trinuclear complex. The magnetic susceptibility data for the complex provided the best fit to the theoretical

Table 3. Numerical Values of Selected Bond Distances/ \AA and of Bond Angles/ $^\circ$ for the Title Complex

Mn(1)—O(1)	1.851(4)
Mn(1)—N(61)	2.073(6)
Mn(1)—O(22)	2.103(6)
Mn(1)—O(92)	2.102(5)
Mn(1)—O(52)	2.145(5)
Mn(1)—O(32)	2.160(5)
Mn(2)—O(72)	1.951(4)
Mn(2)—O(11)	1.952(5)
Mn(2)—O(21)	1.987(5)
Mn(2)—O(31)	2.116(5)
Mn(2)—O(42)	2.135(5)
Mn(2)—N(11)	2.227(6)
Mn(3)—O(11)	1.898(4)
Mn(3)—O(71)	2.079(5)
Mn(3)—N(81)	2.093(6)
Mn(3)—O(91)	2.111(6)
Mn(3)—O(51)	2.147(5)
Mn(3)—O(41)	2.147(8)
Mn(1)—Mn(3)	3.144(1)
O(11)—Mn(1)—N(61)	177.2(2)
O(11)—Mn(1)—O(22)	88.5(2)
N(61)—Mn(1)—O(22)	92.9(2)
O(11)—Mn(1)—O(92)	102.6(2)
O(92)—Mn(1)—N(61)	76.0(2)
O(22)—Mn(1)—O(92)	168.7(2)
O(11)—Mn(1)—O(52)	93.3(2)
N(61)—Mn(1)—O(52)	89.3(2)
O(22)—Mn(1)—O(52)	83.7(2)
O(92)—Mn(1)—O(32)	93.6(2)
O(11)—Mn(1)—O(32)	84.6(2)
O(22)—Mn(1)—O(32)	91.1(2)
O(92)—Mn(1)—O(32)	90.3(2)
O(52)—Mn(1)—O(32)	171.8(2)
O(11)—Mn(2)—O(31)	96.7(2)
O(11)—Mn(2)—O(21)	98.2(3)
O(72)—Mn(2)—O(11)	95.6(2)
O(11)—Mn(2)—N(11)	175.8(2)
O(21)—Mn(2)—N(11)	81.4(2)
O(72)—Mn(2)—N(11)	84.7(2)
N(11)—Mn(2)—O(31)	87.5(2)
N(11)—Mn(2)—O(42)	81.4(2)
O(21)—Mn(2)—O(72)	166.1(2)
O(72)—Mn(2)—O(31)	84.4(2)
O(21)—Mn(2)—O(31)	94.9(2)
O(72)—Mn(2)—O(42)	95.4(2)
O(11)—Mn(2)—O(42)	94.4(2)
O(21)—Mn(2)—O(42)	82.6(2)
O(31)—Mn(2)—O(42)	168.9(2)
O(11)—Mn(3)—O(71)	90.2(2)
O(11)—Mn(3)—O(91)	96.2(2)
O(71)—Mn(3)—O(91)	91.9(2)
O(11)—Mn(3)—O(51)	98.5(2)
O(71)—Mn(3)—O(51)	170.8(2)
O(91)—Mn(3)—O(51)	89.8(2)
O(11)—Mn(3)—O(41)	93.0(2)
O(71)—Mn(3)—O(41)	90.1(2)
O(51)—Mn(3)—O(41)	86.8(2)
O(91)—Mn(3)—O(41)	170.6(2)
O(11)—Mn(3)—N(81)	179.2(2)
O(71)—Mn(3)—N(81)	90.2(2)
O(91)—Mn(3)—N(81)	83.1(2)
O(51)—Mn(3)—N(81)	81.0(2)
O(41)—Mn(3)—N(81)	87.8(2)
Mn(1)—O(11)—Mn(2)	123.2(2)
Mn(1)—O(11)—Mn(3)	114.0(2)
Mn(2)—O(11)—Mn(3)	122.8(2)

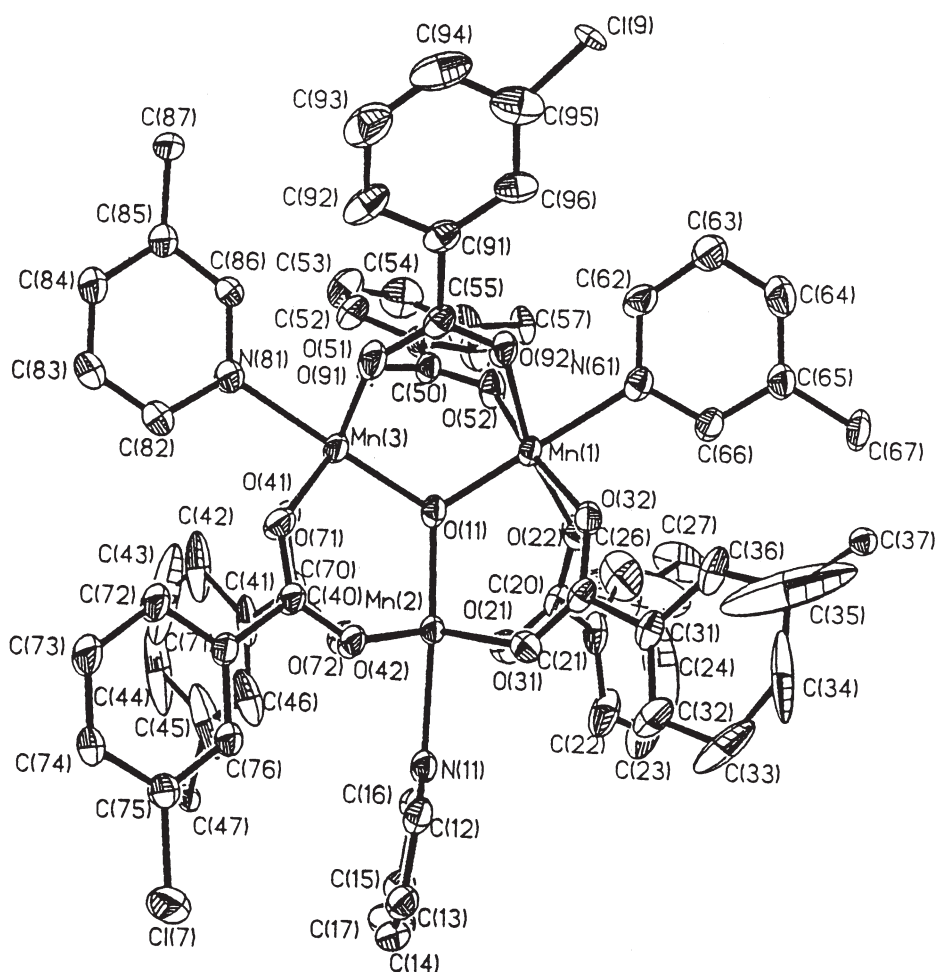


Fig. 1. Crystal structure of the title complex (hydrogen atoms are omitted for clarity).

equation (cf. Fig. 3). The fitting parameters are obtained: $J = -8.42 \text{ cm}^{-1}$, $J' = -10.37 \text{ cm}^{-1}$, $g = 2.07$, and $J/J' = 0.812$.

EXPERIMENTAL

Appropriate care was taken in the use of organic permanganates and perchlorate. All manipulations were performed under aerobic conditions. All the reagent grade solvents were used without further purification. A yield was calculated from the stoichiometric reaction. NBu_4MnO_4 was synthesized according to Ref. [11].

Contents of C, H, and N were found by Erba 1106 elemental analyzer. Infrared spectra ($400\text{--}4000 \text{ cm}^{-1}$) were recorded from KBr pellets in a Nicolet 7199B spectrophotometer. Magnetic susceptibility measurements were carried out on a Quantum Design Maglab System 2000 Squid magnetometer in the temperature range $1.8\text{--}300 \text{ K}$ in an applied field of 10 T . Magnetization measurements were carried out with the Quantum Design magnetometer. Pascal's constants were used to estimate the diamagnetic cor-

rections. The fit was carried out by using the Nonlinear Regression Analysis Program, Version 3.0.

Diffraction data for a crystal with dimensions $0.20 \text{ mm} \times 0.20 \text{ mm} \times 0.20 \text{ mm}$ were obtained from the measurement of graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a CCD face probe four-circle diffractometer, and were collected by the $\omega - 2\theta$ scan technique. The structures were solved by direct methods. All nonhydrogen atoms were refined anisotropically by full-matrix least-squares methods. The hydrogen atoms were added geometrically and not refined. All calculations were performed using SHELXS-97 and SHELXL-97.

Complex

$\text{Mn}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$ (2.00 g; 8.15 mmol) and *m*-chlorobenzoic acid (9.64 g; 61.4 mmol) were dissolved in mixed solvents of absolute ethanol and 3-methylpyridine, then 1.15 mmol of solid NBu_4MnO_4 was added in small portions. During stirring, the brown-green precipitate was formed. The precipitate was filtered off, washed with cold ethanol and ether,

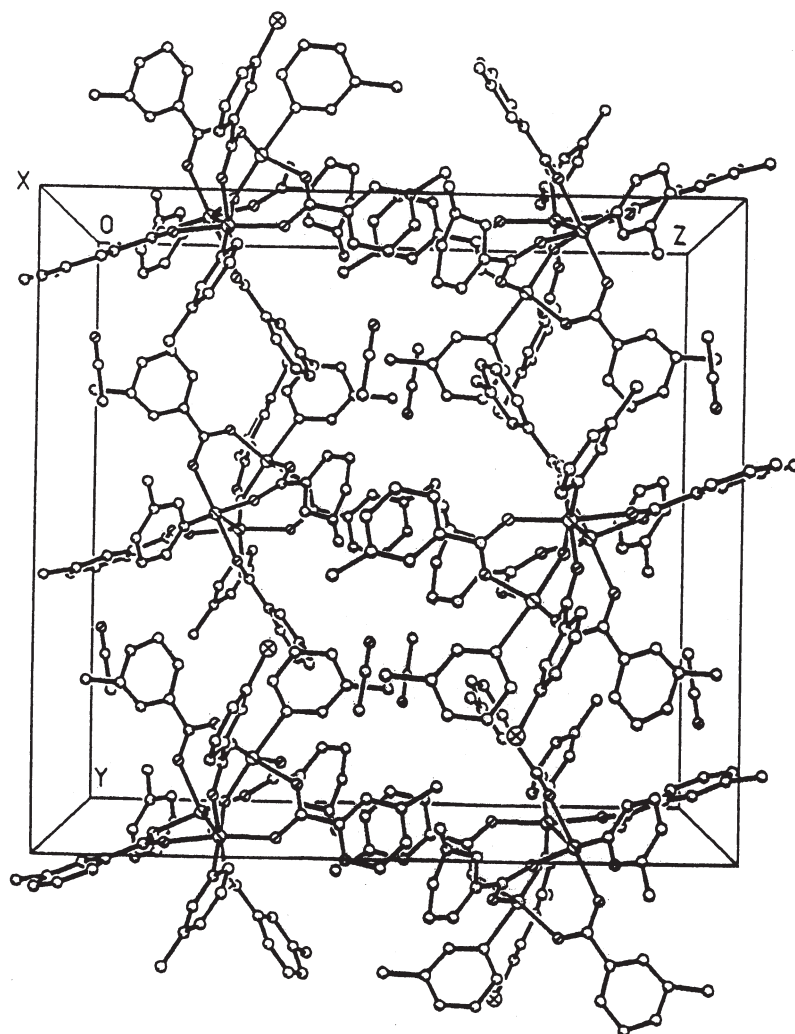


Fig. 2. Packing unit cell diagram of the title complex.

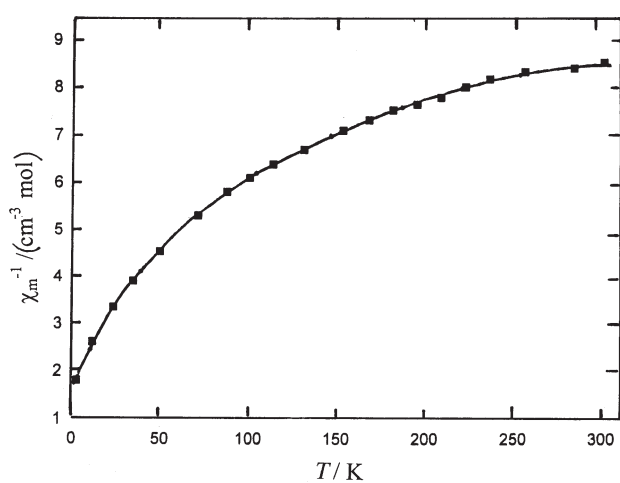


Fig. 3. Temperature dependence of magnetic susceptibility for the title complex. The solid line results from a fit of the data to the appropriate theoretical equation.

and dried in vacuum. Layering the solution of CH_2Cl_2 by using hexane gave small microcrystals of the products after several days. Yield 45 % based on Mn. For $\text{C}_{43}\text{H}_{35.5}\text{N}_{2.5}\text{Cl}_6\text{O}_{10}\text{Mn}_3$ $w_i(\text{calc.})/\%$: C 50.12, H 3.18, N 2.57; $w_i(\text{found})/\%$: C 50.12, H 5.27, N 2.69. FTIR (KBr): $\nu_{\text{as}}(\text{COO})$ 1564 cm^{-1} , $\nu_{\text{s}}(\text{COO})$ 1387 cm^{-1} .

The above trinuclear complex (2.73 g; 2.0 mmol) was dissolved into mixed solvents of acetonitrile and 3-methylpyridine (40 cm^3), excess of *m*-methylbenzoic acid was added and stirred overnight. After filtration, the black filtrate was placed for about one month and the black blank crystal was formed. Yield 22 % based on Mn. For $\text{C}_{65}\text{H}_{58.5}\text{N}_{3.5}\text{Cl}_2\text{O}_{12}\text{Mn}_3$ $w_i(\text{calc.})/\%$: C, 59.25, H 4.44, N 3.72; $w_i(\text{found})/\%$: C 59.39, H 4.27, N 3.77. FTIR (KBr): $\nu_{\text{as}}(\text{COO})$ 1595 cm^{-1} , $\nu_{\text{s}}(\text{COO})$ 1394 cm^{-1} , 1390 cm^{-1} .

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REFERENCES

1. Baikie, A. R. E., Hursthouse, M. B., New, D. B., and Thornton, P., *J. Chem. Soc., Chem. Commun.* 1978, 62.
2. Zhang, S. W., Wei, Y. G., Liu, Q., and Shao, M. C., *Polyhedron* 15, 1014 (1996).
3. An, J., Chen, Z. D., Bian, J., Jin, X. L., Wang, S. X., and Xu, G. X., *Inorg. Chim. Acta* 287, 82 (1999).
4. Wu, R. W., Poyraz, M., Sowrey, F. E., Anson, C. E., Wocadle, S., Powell, A. K., Jayasooriya, U. A., Cannon, R. D., Nakamoto, T., Katada, M., and Sano, H., *Inorg. Chem.* 37, 1913 (1998).
5. Ribas, J., Albsela, B., Stoeckli-Evans, H., and Christou, G., *Inorg. Chem.* 36, 2352 (1997).
6. McCusker, J. K., Jiang, H. G., Wang, S. Y., Christou, G., and Hendrickson, D. N., *Inorg. Chem.* 31, 1874 (1992).
7. Baikie, A. R. E., Hursthouse, M. B., New, L., Thornton, P., and White, R. C., *J. Chem. Soc., Chem. Commun.* 1984, 684.
8. Vincent, J. B., Chang, H. R., Folting, K., Huffman, H. C., Christou, G., and Hendrickson, D. N., *J. Am. Chem. Soc.* 109, 5703 (1987).
9. Gerbelen, N. V., Timtso, G. A., Manole, O. S., Struchkov, Yu. T., Batsanov, A. S., and Grebenzo, S. V., *Koord. Khim.* 20, 357 (1994).
10. Xu, H., Li, J. Y., Liu, Q., Xu, Z., You, X. Z., and Yu, K. B., *Chin. J. Struct. Chem.* 13, 272 (1994).
11. Sala, T. and Sargent, M. V., *J. Chem. Soc., Chem. Commun.* 1987, 253.