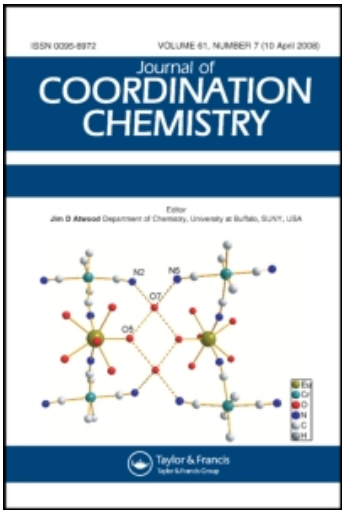

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A NEW OXO-CENTRED, MIXED-VALENCE HETEROTRINUCLEAR COMPLEX, $Mn(III)Ni(III)Mn(II)O(PhCOO)_6Py_3$ CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES

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A NEW OXO-CENTRED, MIXED-VALENCE HETEROTRINUCLEAR COMPLEX, $Mn(III)Ni(III)Mn(II)O(PhCOO)_6Py_3$ CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES

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A new mixed-valence heterotrinuclear complex, $Mn(III)Ni(III)Mn(II)O(PhCOO)_6Py_3$, was synthesized using NBu_4MnO_4 as an oxididant. In the reaction, Ni(II) was oxidized to Ni(III) while Mn(VII) was reduced to Mn(II) and Mn(III). Crystals are monoclinic, space group *C2/C*, with $a = 58.93(4)$, $b = 11.784(3)$, $c = 24.883(9)$ Å, $\beta = 100.64(4)°$, $V = 16983(13)$ Å^3 and $Dc = 1.35$ gcm^{-3} for $Z = 12$. The crystal structure was solved by direct methods to final $R = 0.083$, $R\omega = 0.095$. There are two kinds of trinuclear species in the unit cell. One is valence delocalized with Ni(2)—O(2) 1.86(2) Å and Mn—O(2) 1.92(1) Å (average value of Mn(II)—O and Mn(III)—O). The other is valence localized with Ni(III)—O(1) 1.84(1) Å, Mn(III)—O(1) 1.88(1) Å and Mn(II)—O(1) 1.97(1) Å. Variable temperature (1.5–300K) magnetic susceptibilities indicated an antiferromagnetic exchange interaction among the three metal ions.

Keywords: heterotrinuclear; mixed-valency; Nickel(III); X-ray structure; magnetic properties

INTRODUCTION

Trinuclear oxo-centred metal carboxylate assemblages of general composition $[M_3(O_2CR)_6L_3]^{n+}$ have been of intense interest for several decades.[1] These compounds serve as important models to study magnetic exchange interactions between metal ions with almost the same geometry[2–7] and as precursors of larger multinuclear assemblies whose novel magnetic properties are only now being

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realized.[8–12] These complexes have been limited to trinuclear[12] and mixed-metal trinuclear species.[13–15] Of them, the manganese compound has been most throughly studied on magnetic,[2] spectroscopy[16] and catalysis[17] grounds because there is strong coupling between localized d^5 electron configurations presumably through the central μ_3-O atoms between the manganese atoms.

We have recently synthesized and isolated two trinuclear, oxo-centred carboxylate complexes in which there are two manganese atoms and one other metal atom (cobalt,[18] nickel) with oxidation state II and III to the two manganese atoms and III for the other metal. The molecular structures and variable temperature susceptibilities of the nickel species has been determined.

EXPERIMENTAL

Measurements

Benzoic acid, $Ni(OAc)_2$, pyridine, absolute ethanol and CH_3CN were used as received. Elemental analyses for carbon, hydrogen and nitrogen were determined on a Perkin Elmer 240C analyzer. X-ray photoelectron spectra (XPS) were recorded on a VG MK II spectrometer using Mg K_α radiation and charge transfer correction with respect to the binding energy of C_{1S}. Variable temperature (1.5–300K) magnetic susceptibility measurements of the title complex were carried out on a CF-1 ESM magnetic balance at 1.2 T magnetic field.

Preparation

Preparation of NBu_4MnO_4 followed the procedure in reference 19.

$Mn_2Ni(PhCOO)_6(Py)_3$.

Some 4.05 g of $Ni(OAc)_2$ and 15 g of benzoic acid dissolved in 40 cm^3 of pyridine forming a blue solution, to which 2.28 g of NBu_4MnO_4 was slowly added with stirring. After reacting for 10 mins, pyridine was evaporated under reduced pressure, and a brown oily slurry was obtained, to which 200cm^3 of absolute alcohol was added with stirring; a precipitate deposited. The brown solid was filtered and washed three times with a little absolute alcohol, than redissolved in a minimum amount of acetonitrile and filtered. The filtrate was evaporated at room temperature for a few days, when black crystals were obtained Calc. for $C_{57}H_{45}N_3O_{13}Mn_2Ni$ (%): C, 59.6; H, 4.0; N, 3.7; Mn, 9.6; Ni, 5.1. Found: *Anal.* C, 59.2; H, 4.2; N, 4.6; Mn, 8.6; Ni, 4.6%.

X-ray Crystal Structure Determination

A cuboidal black crystal ($0.4 \times 0.3 \times 0.3$ mm) was used for X-ray diffraction. Data were collected on a Rigaku AFC5R diffractometer at 296K using graphite-monochromatic MoK_α (0.71069 Å) radiation and $\omega/2\theta$ scan mode. All reflection in the range of $2\theta < 46°$ were measured. Of 12137 independent reflections collected, 3325 observed reflections with $I > 3\sigma(I)$ were used in the structure calculation and all data were corrected for Lp factors and empirical absorption. The structure was solved by direct methods. Successive Fourier syntheses gave the coordinates of all the non-hydrogen atoms which were refined with anisotropic thermal parameters. All calculations were performed on a Micro VAX II computer using TEXSAN programs. Atomic coordinates for non-H atoms are given in Table I. Lists of H atom positions and anisotropic thermal parameters, together with observed and calculated structure factors are available on request, from the authors.

TABLE I Final fractional atomic coordinates and equivalent isotropic thermal parameters

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
Ni1	0.63860(6)	0.1495(3)	0.5525(1)	5.0(2)
Ni2	0.500	0.3327(4)	0.250	5.4(3)
Mn1	0.68848(5)	0.0220(3)	0.5493(1)	2.5(2)
Mn2	0.66866(5)	0.0491(3)	0.6645(1)	3.3(2)
Mn3	0.48148(5)	0.0950(3)	0.1903(1)	2.7(2)
O1	0.6647(2)	0.078(1)	0.5890(6)	3.8(7)
O2	0.500	0.175(2)	0.250	4(1)
O3	0.6347(2)	0.054(1)	0.4817(6)	4.1(8)
O4	0.6652(3)	−0.061(1)	0.4920(6)	4.9(9)
O5	0.6162(2)	0.040(1)	0.5798(6)	4.1(8)
O6	0.6354(3)	0.004(2)	0.6640(6)	6(1)
O7	0.6363(3)	0.267(1)	0.6116(7)	6(1)
O8	0.6610(3)	0.215(1)	0.6849(6)	5.4(9)
O9	0.6572(3)	0.268(1)	0.5161(6)	4.8(9)
O10	0.6850(3)	0.162(2)	0.4969(6)	4.9(9)
O11	0.7141(3)	0.107(2)	0.6008(7)	6(1)
O12	0.7025(3)	0.093(2)	0.6801(7)	5(1)
O13	0.6951(3)	−0.130(1)	0.5870(7)	6(1)
O14	0.6773(3)	−0.120(2)	0.6582(7)	6(1)
O15	0.4514(2)	0.183(1)	0.1874(6)	3.9(8)
O16	0.4656(3)	0.353(1)	0.2149(7)	5(1)
O17	0.4886(3)	0.205(2)	0.1276(6)	5(1)
O18	0.5099(3)	0.344(1)	0.1751(7)	4.6(9)
O19	0.5307(2)	−0.022(1)	0.2590(6)	4.4(8)
O20	0.5087(3)	0.001(1)	0.1771(6)	5(1)
N1	0.6089(3)	0.229(2)	0.5128(7)	3(1)
N2	0.7139(3)	−0.033(2)	0.5052(7)	5(1)
N3	0.6728(3)	0.013(2)	0.7487(8)	4(1)
N4	0.4629(3)	−0.002(2)	0.1267(7)	4(1)
N5	0.500	0.516(3)	0.250	7(2)
C1	0.6468(4)	−0.025(2)	0.4663(9)	3.0(5)

TABLE I (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
C2	0.6361(4)	−0.079(2)	0.4126(9)	3.7(5)
C3	0.6214(4)	−0.024(2)	0.374(1)	5.3(6)
C4	0.6141(5)	−0.072(3)	0.320(1)	7.2(8)
C5	0.6224(5)	−0.176(3)	0.312(1)	6.5(7)
C6	0.6364(5)	−0.236(3)	0.349(2)	9(1)
C7	0.6442(5)	−0.188(3)	0.399(1)	6.9(8)
C8	0.6743(5)	0.254(3)	0.496(1)	4.0(6)
C9	0.6821(4)	0.347(2)	0.465(1)	4.7(6)
C10	0.6971(5)	0.330(3)	0.430(1)	7.3(8)
C11	0.7060(6)	0.409(3)	0.400(1)	9(1)
C12	0.6965(6)	0.523(3)	0.403(1)	10(1)
C13	0.6803(6)	0.540(3)	0.435(2)	10(1)
C14	0.6728(5)	0.449(3)	0.468(1)	7.7(8)
C15	0.6475(4)	0.280(2)	0.662(1)	3.4(5)
C16	0.6412(5)	0.384(3)	0.688(1)	6.2(7)
C17	0.6529(5)	0.409(3)	0.741(1)	7.1(8)
C18	0.6474(6)	0.511(3)	0.766(1)	8.7(9)
C19	0.6315(6)	0.585(3)	0.740(2)	9(1)
C20	0.6187(6)	0.566(3)	0.691(2)	11(1)
C21	0.6264(5)	0.461(3)	0.662(1)	7.7(8)
C22	0.6179(4)	−0.003(2)	0.625(1)	3.6(5)
C23	0.5983(4)	−0.069(2)	0.640(1)	4.5(6)
C24	0.5781(6)	−0.075(3)	0.608(1)	8.4(9)
C25	0.5588(6)	−0.138(3)	0.620(2)	11(1)
C26	0.5614(5)	−0.194(3)	0.669(1)	6.2(7)
C27	0.5810(5)	−0.175(3)	0.702(1)	7.0(8)
C28	0.5989(5)	−0.118(3)	0.690(1)	6.6(7)
C29	0.7150(4)	0.128(2)	0.650(1)	3.7(5)
C30	0.7346(4)	0.211(2)	0.677(1)	4.8(6)
C31	0.7465(5)	0.269(3)	0.641(1)	6.5(7)
C32	0.7631(6)	0.350(3)	0.666(2)	9(1)
C33	0.7665(6)	0.366(3)	0.720(2)	10(1)
C34	0.7564(6)	0.313(3)	0.757(2)	10(1)
C35	0.7390(5)	0.231(3)	0.730(1)	8.1(8)
C36	0.6876(4)	0.174(2)	0.625(1)	4.0(6)
C37	0.6915(4)	−0.301(2)	0.640(1)	5.1(6)
C38	0.6948(5)	−0.372(3)	0.600(1)	8(1)
C39	0.6982(6)	−0.490(3)	0.610(2)	9(1)
C40	0.7000(6)	−0.525(4)	0.662(2)	10(1)
C41	0.6995(6)	−0.450(4)	0.703(2)	11(1)
C42	0.6938(5)	−0.338(3)	0.694(2)	9(1)
C43	0.4493(5)	0.288(3)	0.195(1)	4.6(6)
C44	0.4265(4)	0.340(2)	0.171(1)	4.5(6)
C45	0.4080(4)	0.278(2)	0.148(1)	4.3(6)
C46	0.3875(4)	0.325(2)	0.126(1)	5.0(6)
C47	0.3850(5)	0.438(3)	0.127(1)	6.6(7)
C48	0.4022(5)	0.506(3)	0.150(1)	7.1(8)
C49	0.4239(5)	0.454(3)	0.173(1)	6.4(7)
C50	0.5017(5)	0.291(3)	0.132(1)	4.6(6)
C51	0.5095(4)	0.334(2)	0.081(1)	4.6(6)
C52	0.4998(5)	0.290(3)	0.033(1)	7.0(8)
C53	0.5084(5)	0.328(3)	−0.015(1)	8.1(9)
C54	0.5251(6)	0.406(3)	−0.008(1)	9(1)
C55	0.5341(5)	0.455(3)	0.039(1)	8.1(8)

TABLE I (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
C56	0.5259(5)	0.417(3)	0.087(1)	6.5(7)
C57	0.5261(4)	−0.040(2)	0.209(1)	3.9(5)
C58	0.5410(4)	−0.116(2)	0.182(1)	4.9(6)
C59	0.5586(6)	−0.172(3)	0.216(1)	9(1)
C60	0.5724(7)	−0.259(4)	0.189(2)	12(1)
C61	0.5697(7)	−0.252(4)	0.133(2)	11(1)
C62	0.5502(8)	−0.210(4)	0.106(2)	13(1)
C63	0.5358(6)	−0.133(3)	0.128(2)	9(1)
C64	0.6069(4)	0.339(2)	0.512(1)	4.2(6)
C65	0.5868(4)	0.396(2)	0.488(1)	5.4(6)
C66	0.5679(4)	0.334(2)	0.465(1)	5.0(6)
C67	0.5692(4)	0.222(2)	0.462(1)	4.3(6)
C68	0.5910(4)	0.175(2)	0.490(1)	3.7(5)
C69	0.7132(4)	−0.134(3)	0.484(1)	4.7(6)
C70	0.7296(5)	−0.170(2)	0.457(1)	5.8(7)
C71	0.7467(5)	−0.098(3)	0.449(1)	8.1(9)
C72	0.7488(5)	−0.000(3)	0.469(1)	7.6(8)
C73	0.7311(5)	0.039(3)	0.499(1)	6.4(7)
C74	0.6661(4)	−0.084(2)	0.765(1)	4.4(6)
C75	0.6691(5)	−0.113(3)	0.820(1)	6.9(8)
C76	0.6797(5)	−0.038(3)	0.857(1)	6.1(7)
C77	0.6868(4)	0.060(3)	0.843(1)	5.9(7)
C78	0.6833(4)	0.085(2)	0.786(1)	5.2(6)
C79	0.4425(5)	−0.048(3)	0.131(1)	6.0(7)
C80	0.4296(5)	−0.120(3)	0.090(1)	7.9(8)
C81	0.4401(6)	−0.142(3)	0.046(1)	9(1)
C82	0.4610(6)	−0.089(3)	0.041(1)	8.3(9)
C83	0.4725(5)	−0.015(3)	0.085(1)	6.5(7)
C84	0.490(1)	0.566(6)	0.200(2)	19(2)
C85	0.4893(8)	0.695(5)	0.197(2)	17(2)
C86	0.500	0.717(6)	0.250	15(2)

Crystal Data

$C_{57}H_{45}N_3O_{13}Mn_2Ni$, $M = 1148.6$, monoclinic, space group $C2/c$, with $a = 58.93(4)$, $b = 11.784(3)$, $c = 24.883(9)$ Å, $\beta = 100.64(4)°$, $V = 16983(13)$ Å^3, and $Dc = 1.35 gcm^{-3}$ for $Z = 12$, $\mu = 0.813 mm^{-1}$, $R = 0.083$ and $R\omega = 0.095$, $\omega = 1/\sigma^2(F)$.

RESULTS AND DISCUSSION

Crystal Structure

Acetate bridging $Mn(III)_2Ni(II)O$ species have been prepared by Cannon recently.[15] The title compound Mn(III)Ni(III)Mn(II) was synthesized with Bu_4NMnO_4 as oxididant. X-ray photoelectron spectra of the title complex

display two peaks at 856.1 and 642.6ev. The former belongs to $Ni2P_{3/2}$ and the latter belongs to $Mn2P_{3/2}$.

The molecular structure is shown in Figure 1, and selected bond distances and angles are given in Table II. Each metal atom has slightly distorted octahedral coordination geometry with four oxygen atoms from bridging benzoate groups, a μ_3-oxygen atom and a nitrogen atom of a terminal pyridine. The pyridine rings are essentially perpendicular to the trinuclear complex, probably as a result of increased steric interactions between the pyridine rings and the benzoate phenyl group. There are two kinds of Mn_2NiO species in the unit cell. One is valence localized in which the distances of three metal atoms to μ-O are 1.84(1), 1.88(1) and 1.97(1) Å, respectively. Considering the oxidation state of the metal atoms in the title compound and M—O the bond distances Mn(III)—O 1.863, Mn(II)—O 2.034 Å in $[Mn(III)_2Mn(II)O(3\text{—}Cl\text{—}Py)_3(OAc)_6]$,[20] and Mn(III)—O 1.817 Å, Mn(II)—O 2.154 Å in $[Mn_3O(PhCOO)_6(Pyr)_2(H_2O)]$[2] and by analogy $Mn(III)Co(III)Mn(II)O(PhCOO)_6Py_3$,[18] we could classify the three M—O bonds as followings: 1.84(1) Å is of Ni(III)—O(1), 1.88(1) Å is Mn(III)—O(1) and 1.97(1) Å is Mn(II)—O(1). The other species is valence delocalized in which Ni(2)—O(2) is 1.86(2) Å, and Mn—O(2) (1.92(1) Å) is a statistical average of Mn(III)—O (1.88(1) Å) and Mn(II)—O (1.97(1) Å).

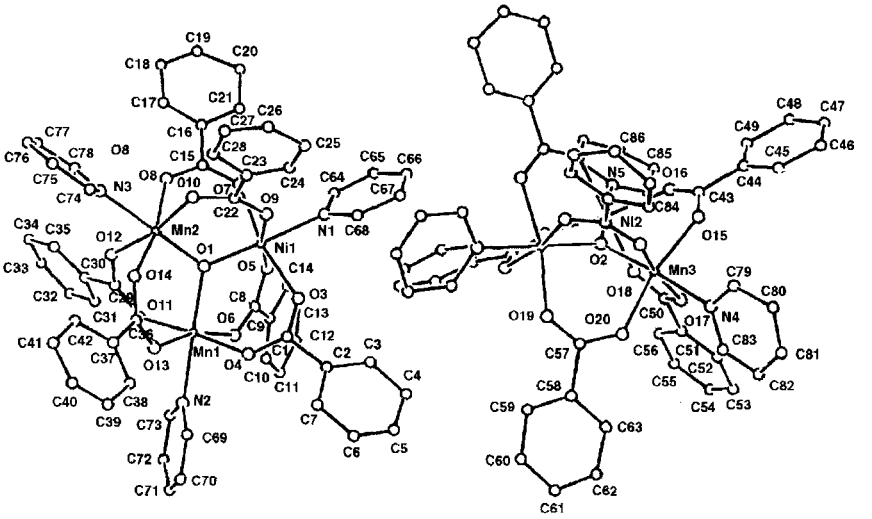

FIGURE 1 The molecular structures of (a): $[Mn(III)Mn(II)Ni(III)O(PhCOO)_6Py_3]$ and (b), that of $[Ni(III)Mn(II, III)_2O(PhCOO)_6Py_3]$.

TABLE II Selected bond lengths (Å) and bond angles(°)

Ni(1)—O(1)	1.84(1)	Ni(1)—O(3)	2.07(2)
Ni(1)—O(7)	2.05(2)	Ni(1)—O(9)	2.08(2)
Ni(1)—O(5)	2.05(1)	Ni(1)—N(1)	2.06(2)
Ni(2)—O(2)	1.86(2)	Ni(2)—O(18)	2.06(2)
Ni(2)—O(16)	2.07(2)	Ni(2)—N(5)	2.15(3)
Mn(1)—O(1)	1.97(1)	Mn(1)—O(13)	2.03(2)
Mn(1)—O(10)	2.08(2)	Mn(1)—O(4)	2.04(1)
Mn(1)—O(11)	2.05(2)	Mn(1)—N(2)	2.11(2)
Mn(2)—O(1)	1.88(1)	Mn(2)—O(6)	2.03(1)
Mn(2)—O(12)	2.03(2)	Mn(2)—O(14)	2.07(2)
Mn(2)—O(8)	2.08(2)	Mn(2)—N(3)	2.11(2)
Mn(3)—O(2)	1.92(1)	Mn(3)—O(20)	2.03(1)
Mn(3)—O(15)	2.04(1)	Mn(3)—O(19)	2.08(1)
Mn(3)—N(4)	2.09(2)	Mn(3)—O(17)	2.13(2)
O(1)—Ni(1)—O(7)	96.7(6)	O(1)—Ni(1)—O(3)	96.9(6)
O(1)—Ni(1)—O(9)	93.6(6)	O(1)—Ni(1)—O(5)	94.5(6)
O(1)—Ni(1)—N(1)	178.8(7)	O(2)—Ni(2)—O(18)	93.8(5)
O(2)—Ni(2)—(16)	96.6(5)	O(2)—N(2)—N(5)	180.00
O(1)—Mn(1)—O(13)	99.1(6)	O(1)—Mn(1)—O(10)	93.1(6)
O(1)—Mn(1)—O(4)	93.5(6)	O(1)—Mn(1)—O(11)	91.9(6)
O(1)—Mn(1)—N(2)	177.3(7)	O(1)—Mn(2)—O(6)	95.8(6)
O(1)—Mn(2)—O(12)	94.6(7)	O(1)—Mn(2)—O(14)	94.9(7)
O(1)—Mn(2)—O(8)	94.7(6)	O(1)—Mn(2)—N(3)	178.7(8)
O(2)—Mn(3)—O(20)	92.3(6)	O(2)—Mn(3)—O(15)	98.3(6)
O(2)—Mn(3)—O(19)	93.8(6)	O(2)—Mn(3)—N(4)	175.8(7)
O(2)—Mn(3)—O(17)	96.2(6)	Ni(1)—O(1)—Mn(2)	20.9(8)
Ni(1)—O(1)—Mn(1)	120.8(7)	Mn(1)—O(1)—Mn(2)	118.2(7)
Ni(2)—O(2)—Mn(3)	119.4(5)	Mn(3)—O(2)—Mn(3)	

There are eight asymmetry units in the unit cell, and each contains 1.5 trinuclear complex units, $[Mn_2NiO(PhCOO)_6Py_3]$, in which one trinuclear unit has bond delocalized structure and the other half trinuclear unit has bond localized structure.

Magnetic Properties

Variable temperature (1.5K–300K) magnetic susceptibility data have been recorded for a microcrystalline sample of the title complex. As seen in Figure 2, the effective magnetic moment (μ_{eff}) per molecule decreases slowly down to 70K ($5.8\mu_B$) below which it decreases quite rapidly ($6.12\mu_B$ at 35K to $2.2\mu_B$ at 1.5K). This indicates that there is weaker antiferromagnetic exchange at $T > 70K$ and stronger antiferromagnetic exchange at $T < 35K$ among the three metal atoms.

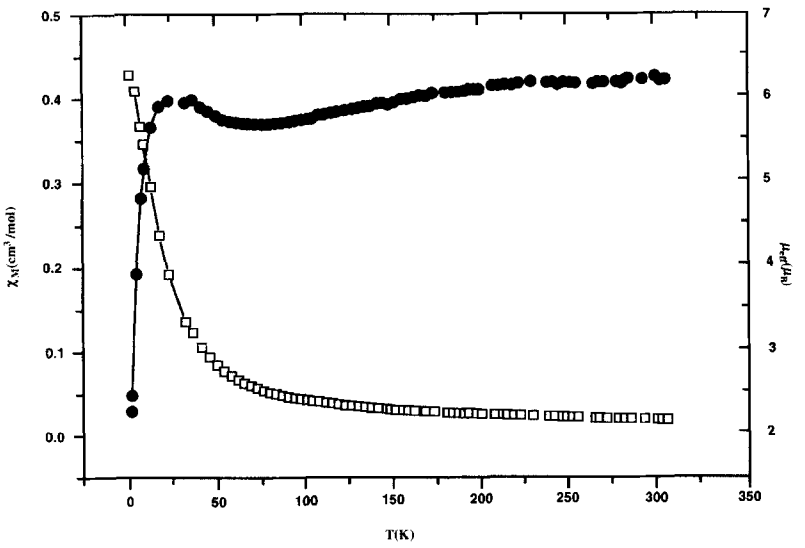

FIGURE 2 Temperature dependence of the magnetic susceptibility χ_M (□□□) and the effective magnetic moment μ_{eff} (•••) for the title complex.

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