

Research Article

Syntheses and Crystal Structures of Two Transition Metal Complexes (M = Mn and Co) Containing Malonate and Reduced Imino Nitroxide Radicals

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Two novel transition metal complexes with malonate and reduced imino nitroxide radicals, $[\text{Co}(\text{mal})(\text{Him2-py})_2](\text{ClO}_4)$ **1** and $[\text{Mn}(\text{mal})(\text{Him2-py})_2](\text{H}_2\text{O})$ **2** (Him2-py = 1-hydroxy-2-(2'-pyridyl)-4,4,5,5-tetramethylimidazoline) have been synthesized and their crystal structures were determined by X-ray diffraction method. During the reaction, one-electron reduction of the N–O radical moiety in IM2py has been reviewed. The structural analyses reveal that two title complexes are isostructural and crystallize in monoclinic space group *C*2. For the complex **1**, $a = 17.004(9)$, $b = 10.753(5)$, $c = 9.207(5)$ Å with $\beta = 113.856(8)^\circ$. For the complex **2**, $a = 16.721(5)$, $b = 10.897(5)$, $c = 9.253(3)$ Å with $\beta = 120.807(6)^\circ$. In two complexes, the coordination number around the metal ion is six, and the coordination sphere is a distorted octahedron. Two nitrogen atoms from Him2-py and two oxygen atoms from malonate are in the basal plane, and two nitrogen atoms from pyridyl rings of Him2-py at the axial position.

1. Introduction

The design and synthesis of transition metal complexes with organic free radicals is one of the major challenges in the field of molecular magnetic materials [1]. Nitronyl nitroxide (NN) radicals are normally used as spin carriers to the development of molecular-based magnetic materials. However nitroxides can undergo redox reactions with transition metal ions under certain conditions [2, 3]. In fact, nitronyl free radicals are in an oxidation state intermediate between those of the hydroxylamino anion and the nitrosonium cation. Up to now, relatively little work has been devoted to the study of the redox properties of metal-nitroxyl systems and only a few complexes containing metal ions bound to the reduced monoradical have been reported [4–9]. It is known that nitronyl nitroxide radicals can undergo redox reaction with transition metal ions, yielding complexes in which the IMHR reduced form of IM acts as a diamagnetic ligand [7]. In order to extend our knowledge of extremely rich chemistry of such systems, it is necessary to further explore the reactions between metal ion and nitronyl nitroxide radicals. In this paper, we will report that syntheses and

structural characterization about two novel transition metal compounds with malonate and reduced imino nitroxide radicals, $[\text{Co}(\text{mal})(\text{Him2-py})_2](\text{ClO}_4)$ **1** and $[\text{Mn}(\text{mal})(\text{Him2-py})_2](\text{H}_2\text{O})$ **2** (Him2-py = 1-hydroxy-2-(2'-pyridyl)-4,4,5,5-tetramethylimidazoline).

2. Experimental

2.1. Syntheses. 2-(2'-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl (im2-py) was prepared according to the methods reported [10].

$[\text{Co}(\text{mal})(\text{Him2-py})_2](\text{ClO}_4)$ **1**: an aqueous solution (10 mL) of $\text{Na}_2(\text{mal})$ (0.148 g, 1 mmol) was added to a mixture of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.365 g, 1 mmol) and im2-py (0.436 g, 2 mmol) in 25 mL of methanol (pH = 6 ~ 8). The mixture was stirred for 2 h and filtered. The filtrate was kept at room temperature for 1 month to grow well-formed orange crystals of $[\text{Co}(\text{mal})(\text{Him2-py})_2](\text{ClO}_4)$. Yield: 45%. Anal. Calcd. (%) for: C, 47.38; H, 4.96; N, 12.34. Found (%): C, 46.52; H, 4.92; N, 12.06. IR (KBr): $\nu_{(\text{py})}$ 1448 cm^{-1} , 1386 cm^{-1} , $\nu_{(\text{NO})}$ 1357 cm^{-1} , $\nu_{\text{ascco-}}$ 1650 cm^{-1} , $\nu_{\text{ascco-}}$ 1455 cm^{-1} .

TABLE 1: Summary of the crystallographic data and collections for two complexes.

	Complex 1		Complex 2	
Empirical formula	C ₂₇ H ₃₄ ClCoN ₆ O ₁₀		C ₂₇ H ₃₆ MnN ₆ O ₇	
Formula weight	696.98		611.56	
Crystal system, space group	<i>Monoclinic, C2</i>		<i>Monoclinic, C2</i>	
Unit cell dimensions	<i>a</i> = 17.004(9) Å <i>b</i> = 10.753(5) Å <i>c</i> = 9.207(5) Å	$\beta = 13.856(8)^\circ$	<i>a</i> = 16.721(5) Å <i>b</i> = 10.897(5) Å <i>c</i> = 9.253(3) Å	$\beta = 120.807(6)^\circ$
Volume	1539.6(14) Å ³		1448.1(9) Å ³	
Z, Calculated density	2, 1.504 Mg/m ³		2, 1.403 Mg/m ³	
Absorption coefficient	0.710 mm ⁻¹		0.511 mm ⁻¹	
F(000)	724		642	
Crystal size	0.18 × 0.16 × 0.14 mm ³		0.24 × 0.22 × 0.18 mm ³	
θ range for data collection	2.30 to 25.10°		2.35 to 25.01°	
Limiting indices	-20 ≤ <i>h</i> ≤ 20, -12 ≤ <i>k</i> ≤ 11, -9 ≤ <i>l</i> ≤ 10		-19 ≤ <i>h</i> ≤ 14, -12 ≤ <i>k</i> ≤ 12, -11 ≤ <i>l</i> ≤ 11	
Reflections collected/unique	3755/2253 (<i>R</i> (int) = 0.0318)		3730/2519 (<i>R</i> (int) = 0.0154)	
Completeness to $\theta = 25.10$	95.4%		100.0%	
Absorption correction	Semi-empirical from equivalents		Semi-empirical from equivalents	
Max. and min. transmission	1.000000 and 0.711602		1.000000 and 0.754606	
Refinement method	Full-matrix least-squares on <i>F</i> ²		Full-matrix least-squares on <i>F</i> ²	
Data/restraints/parameters	2253/47/228		2519/2/190	
Goodness-of-fit on <i>F</i> ²	1.037		1.107	
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> 1 = 0.0502, <i>wR</i> 2 = 0.1257		<i>R</i> 1 = 0.0401, <i>wR</i> 2 = 0.1069	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0583, <i>wR</i> 2 = 0.1311		<i>R</i> 1 = 0.0418, <i>wR</i> 2 = 0.1091	
Absolute structure parameter	0.00(3)		0.0(2)	
Largest diff. peak and hole	1.136 and -0.285 e.Å ⁻³		0.745 and -0.294 e.Å ⁻³	

[Mn (*mal*)(Him2-py)₂] (H₂O) **2** was obtained using the same procedure as that of the complex **1**. The filtrate was kept at room temperature for 20 days to grow well-formed orange crystals of [Mn (*mal*)(Him2-py)₂] (H₂O). The yield was about 55%. Anal. Calcd. (%) for: C, 53.12; H, 6.01; N, 14.02. Found (%): C, 52.72; H, 5.93; N, 13.74. IR (KBr): $\nu_{(Py)}$ 1450 cm⁻¹, 1396 cm⁻¹, $\nu_{(NO)}$ 1365 cm⁻¹, ν_{asCOO-} 1645 cm⁻¹, ν_{sCOO-} 1471 cm⁻¹.

2.2. Crystal Structure Determination and Refinement. All measurements were made on a Bruker Smart 1000 diffractometer equipped with graphite-monochromated *MoK α* radiation ($\lambda = 0.71073$ Å). The data were collected at room temperature. A summary of the crystallographic data is given in Table 1. These structures were solved by direct methods using the SHELXS97 program [11]. Full-matrix least-squares refinements on *F*² were carried out using SHELXL97 [12]. A summary of the crystallographic data and collections are listed in Table 1. These significant bond parameters for two complexes are given in Tables 2 and 3, respectively. Views

of the molecular structures for compounds **1** and **2** are shown, respectively, in Figures 1 and 2. The sketch of the intermolecular hydrogen bonds of two complexes are shown in Figure 3 and 4, respectively.

3. Results and Discussion

The data of Δ (= $\nu_{as} - \nu_s$) of IR reveal that each malonate dianion binds metal ions in bidentate mode, leading to a mononuclear structure. The bands of the N–O stretching vibration appear at ca. 1357 cm⁻¹ and 1365 cm⁻¹ for complex **1** and **2**, respectively, which suggest that one Him2py are chelated metal ion by pyridyl and imino nitrogen atoms with the five-membered ring.

The crystal structures of both complexes have several features in common. The single-crystal X-ray structures of complexes **1** (Figure 1) and **2** (Figure 2) confirm the bidentate chelation of ligand. The complexes **1** and **2** consist of mononuclear molecule [Co(*mal*)(Him2-py)₂] (ClO₄) and [Mn (*mal*)(Him2-py)₂] (H₂O). The metal ion is located

TABLE 2: Selected bond distances (Å) and bond angles (°) for the complex 1.

Co(1)–O(2)	1.879(4)	C(1)–C(2)	1.360(9)
Co(1)–N(1)	1.945(4)	O(2)–Co(1)–O(2)#1	95.0(3)
Co(1)–N(2)	1.947(5)	O(2)–Co(1)–N(1)#1	93.8(2)
O(1)–N(3)	1.400(6)	O(2)–Co(1)–N(1)	86.8(2)
N(1)–C(5)	1.336(7)	N(1)#–Co(1)–N(1)	179.1(4)
N(1)–C(1)	1.354(8)	O(2)–Co(1)–N(2)#1	175.0(2)
N(2)–C(6)	1.296(7)	N(1)–Co(1)–N(2)#1	97.2(2)
N(2)–C(10)	1.490(8)	O(2)–Co(1)–N(2)	87.67(16)
N(3)–C(6)	1.336(7)	N(1)–Co(1)–N(2)	82.1(2)
N(3)–C(7)	1.469(8)	N(2)#1–Co(1)–N(2)	90.0(3)

Symmetry transformations used to generate equivalent atoms: no. 1 $-x, y, -z$.

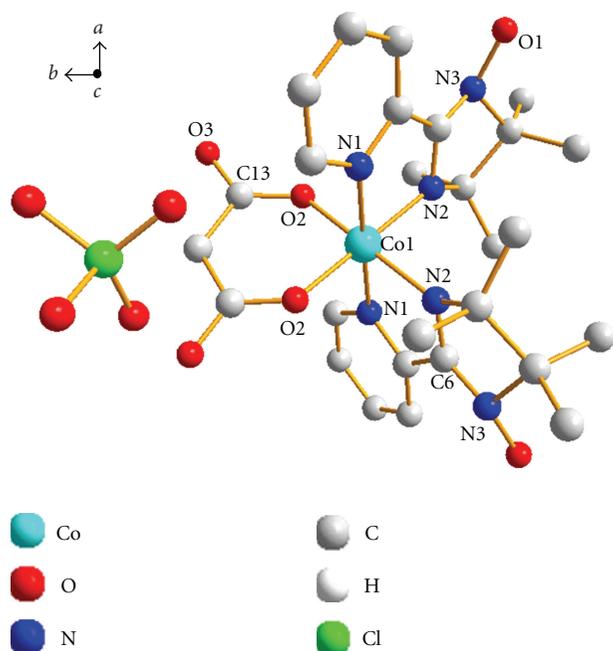


FIGURE 1: Diamond views of complex 1. Hydrogen atoms are omitted for clarity.

in a distorted octahedral environment, formed by the four nitrogen atoms (N(1), N(2), N(1)#, N(2)#) of the two bidentate imino nitroxide radicals and two oxygen atoms (O(2), O(2)#) of the same malonate group. The axial positions are occupied by nitrogen atoms (N(1), N(1)#) from pyridyl rings. The pyridyl rings of the im2-py ligands are nonplanar, and that is a consequence of steric crowding from the im2-py ligands of the same molecule.

For complex 1, the distances of Co(1)–O(2) is 1.879(4) Å and the N–O bond distances are 1.400(6) Å, which show that the complex is consisted of Co(III) and reduced species IMHR [7]. For 2, the length of Mn(1)–O(2) is 2.022(3) Å and that of N–O is 1.406(4) Å, clearly indicative of the reduced form of the radical [13–16]. In complex 1, the C2–N1 and C2–N2 bond lengths of the IMH2py are 1.296(7)

TABLE 3: Selected bond distances (Å) and bond angles (°) for the complex 2.

Mn(1)–O(2)	2.022(3)	N(3)–C(7)	1.468(5)
Mn(1)–N(2)	2.075(4)	C(1)–C(2)	1.379(7)
Mn(1)–N(1)	2.116(3)	O(2)#1–Mn(1)–O(2)	88.88(19)
O(1)–N(3)	1.406(4)	O(2)#1–Mn(1)–N(2)	167.69(15)
O(2)–C(13)	1.251(6)	O(2)–Mn(1)–N(2)	89.92(11)
O(3)–C(13)	1.238(6)	N(2)–Mn(1)–N(2)#1	93.8(2)
N(1)–C(1)	1.312(5)	N(2)–Mn(1)–N(1)#1	100.87(15)
N(1)–C(5)	1.360(5)	O(2)#1–Mn(1)–N(1)	90.13(15)
N(2)–C(6)	1.287(5)	O(2)–Mn(1)–N(1)	91.38(16)
N(2)–C(10)	1.485(5)	N(2)–Mn(1)–N(1)	77.65(15)
N(3)–C(6)	1.367(5)	N(1)#1–Mn(1)–N(1)	177.9(3)

Symmetry transformations used to generate equivalent atoms: no. 1 $-x, y, -z$.

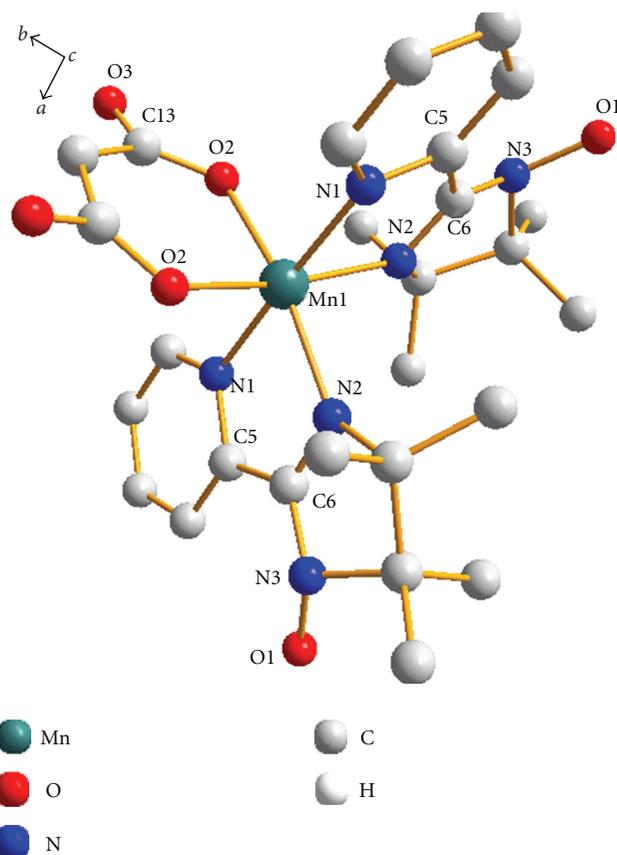


FIGURE 2: Diamond views of complex 2. Hydrogen atoms are omitted for clarity.

and 1.336(7) Å, respectively, as well as the C2–N1 and C2–N2 bond lengths of the IMH2py are 1.287(5) and 1.367(5) Å in complex 2, which are rather close to those of the reduced imino nitroxide complex [6–9]. These structural changes result from the one-electron reduction of the N–O radical moiety in IM2py. N(1)–M–N(1)# angles do not significantly deviate from orthogonal, ranging from

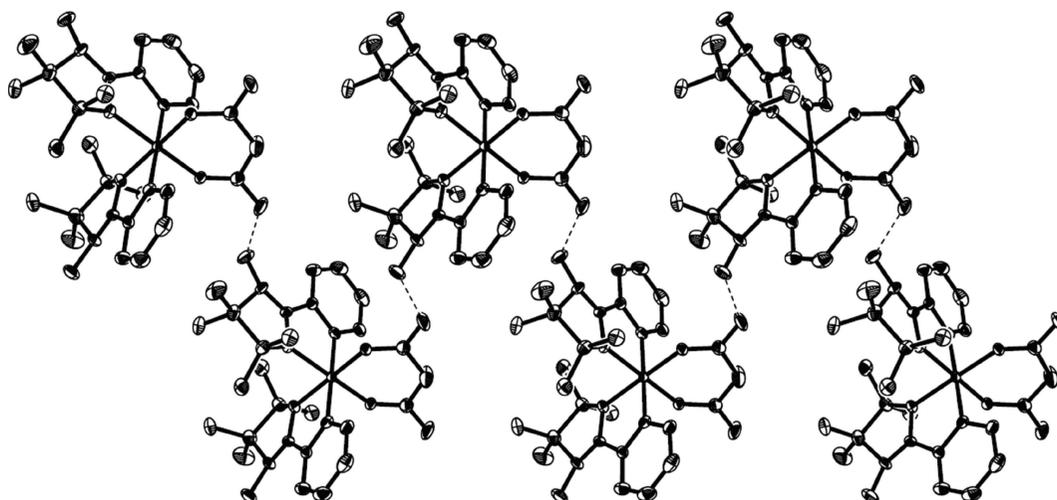


FIGURE 3: View of the unit of the complex 1 showing 1-D zigzag chain formed by O–O interaction along *a* axis.

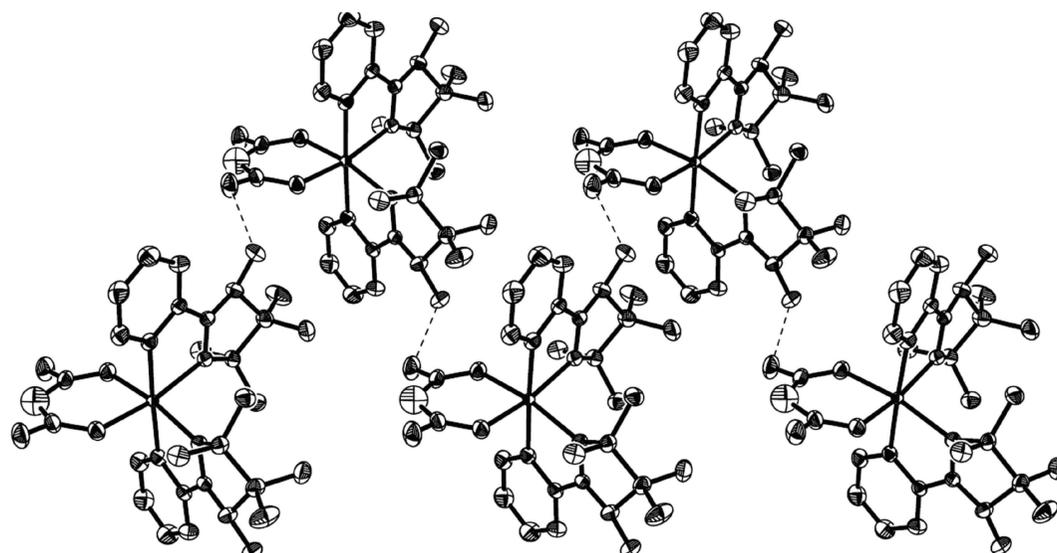


FIGURE 4: View of the unit of the complex 2, showing 1-D zigzag chain formed by O–O interaction along *a* axis.

179.1(4)° to 177.9(3)°. Details of two complexes can be found in supplementary material available online at doi: 10.1155/2011/257521. The dihedral angles between pyridyl ring (N1C5C4C1) and imino nitroxide group (N2C6N3O1) are 12.8° (for complex 1) and 12.9° (for complex 2), respectively. For complex 1, noncoordinated ClO_4^- anions insert in the crystal spacing as well as noncoordinated H_2O molecules insert there for complex 2.

Sketch of the intermolecular hydrogen bonds of the complex 1 and 2 are shown in Figure 2, 3, respectively. In the crystal packing of two complexes, hydrogen bonds of O–O type have been observed between the hydrogen atom from the coordinated malonate and the oxygen atom from adjacent Him2-py, thus one-dimensional structures are formed. Among the 1-D chains, the oxygen atoms from the

NO groups of Him-2py and the *mal* form hydrogen bonds, and the distances of $\text{O}(+x, +y, +z) \cdots \text{O}(1/2 - x, 1/2 + y, -z)$ are 2.612 Å (for complex 1) and 2.627 Å (for complex 2), respectively.

As we know, there were several reports on metal complexes with a reduced nitroxide radical. However, no example in which $\text{M}(\text{mal})_2$ converts the IMR radical into IMHR has been reported. The mechanistic details of the reduction of nitroxide radical are not completely clear, but it is likely that the formation of Him2-py is favored by acidic impurities and standing for a long time. The reduced radical can exist in two tautomeric forms [7], the amidino oxide and iminohydroxylamine. Since the nitrogen atom from the imino group here is involved in the coordinating metal ion, the reduced radical form should be the latter [6].

As mentioned in the experimental part of this paper, the cobalt reactant is cobalt(II) perchlorate hexahydrate. However, the reaction product is cobalt(III) complex **1** due to the oxidation of Co(II) to Co(III) in air. The result is corresponding to those lectures [17–19].

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