APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organomet. Chem. 2004; **18**: 176–180
Materials, Nanoscience and Catalysis AOC
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.604

Alloyed transition-metal complexes of tricyanomethide (tcm), $[Mn_{1-x}Co_x(tcm)_2]$

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Received 14 August 2003; Accepted 28 November 2003

Alloying in the coordination polymer $[Mn_{1-x}Co_x(tcm)_2]$, (tcm = $[C(CN)_3]^-$) has been attempted and the physical properties have been investigated. All compounds are isostructural, but the lattice parameters and the distance between manganese and the adjacent nitrogen atom decrease with increasing cobalt content x. Magnetic susceptibility measurements show a Curie–Weiss behavior, with decreasing Weiss temperature with increasing cobalt content. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: alloyed complex; coordination polymer; synthesis; X-ray crystal structure; magnetic susceptibility

INTRODUCTION

In recent years, metal-based magnets have attracted considerable attention in view of their coordination and physical properties. Many examples of one-, two- and three-dimensional (1D, 2D and 3D) magnetically interacting networks have been reported.[1–5] In 1986, Miller *et al.*[6] published the first organic material to become ferromagnetically ordered, demonstrating that a magnet could be made using organic materials. Judicious choice of appropriate molecular building blocks provides the means to create a rich variety of new materials with interesting structural and magnetic properties.[7,8] Typically, these compounds consist of paramagnetic transition-metal ions linked together with organic ligands of various sizes, shapes, and bonding motifs to afford polymeric arrays. The ligand can have a range of coordination modes, but the two most common types are bidentate, with two coordinating nitrogen atoms, and tridentate, with three coordinating nitrogen atoms.

Three-coordination of dicyanoamide ($[N(CN)_2]$, dca) to divalent paramagnetic metal centers affords binary rutile-like structures of $[M(dca)_2]$ (M = Cr, Mn, Fe, Co, Ni and Cu). Weak ferromagnetism has been found for M = Cr, Mn and Fe below 47 K,[9] 16 K[10,11] and 19 K[12] respectively, whereas the M = Cu analogue is only paramagnetic down to 2 K.[10] For M = Co and Ni, ferromagnetic ordering occurs below 9 K and 21 K respectively.[13,14] Many analogous two-ligand systems have been reported. For example, $[Mn(dca)_2(pyz)]$ (pyz = pyrazine) shows 3D antiferromagnetic order below 2.53 K.[5]

The tricyanomethide ($[C(CN)_3]$, tcm) anion is another versatile ligand for the construction of coordination polymers. Doubly interpenetrating rutile-like networks are formed in the isomorphous series $[M(tcm)_2]$ (M = Cr, Mn, Fe, Ni, Co, Cu, Zn, Cd and Hg).[15,16] In contrast to the ferromagnetic ordering in $[M(dca)_2]$, $[M(tcm)_2]$ shows antiferromagnetic behavior $[Mn(tcm)_2]$ undergoes an antiferromagnetic transition at 5 K.[17–20] Similar self-penetrating networks are present in $[M(dca)(tcm)]$, M = Co, Ni, and Cu,[21] where dca and tcm are arranged alternately. The network is closely related to, but not identical to, the rutile networks. The cobalt and nickel compounds show ferromagnetic ordering below 3.5 K and 8.0 K respectively.[21] The nitrogen atom of the tcm ligands can participate in hydrogen-bonding interactions as well as in coordination bonds. Examples include the complicated chiral 3D network with hexagonal symmetry in $[Cd(tcm)(B(OMe)_4)x\mathrm{MeOH}]$,[22] and the 3D network in $[Hg(tcm)_2]$[23] and $[(CH_3)Tl(tcm)]$.[23] In the 3D rutile-like networks in $[M(tcm)_2(H_2O)_2(Me_4pyz)]$ (M = Co, Ni, Me_4pyz = tetramethylpyrazine), a tcm ligand coordinates to two metals and is hydrogen bonded to one water molecule.[24] In order to explore the possibility of ferromagnetic interaction in a mixed-metal system $[M_{1-x}M'_{-x}(tcm)_2]$, we report here on the structural and magnetic properties of $[Co(tcm)_2]$ and the alloy system $[Mn_{1-x}Co_x(tcm)_2]$ (Fig. 1).

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Contract/grant sponsor: Ministry of Education, Science, Sports and Culture, Japan.

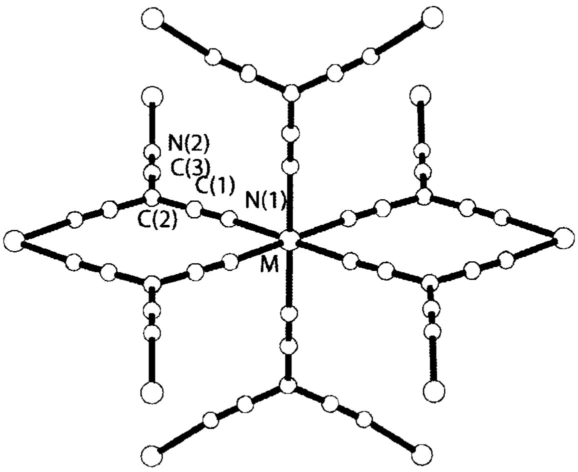

Figure 1. Crystal structure of $[Mn_{1-x}Co_x(tcm)_2]$.

Table 1. EDS results for $[Mn_{1-x}Co_x(tcm)_2]$

Sample	Nominal Mn : Co	x (from EDS)
1	0 : 1	1.0
2	1 : 1	0.96
3	10 : 1	0.92
4	20 : 1	0.88
5	50 : 1	0.84
6	100 : 1	0.66
7	500 : 1	0.55

EXPERIMENTAL

Synthesis

K(tcm) was prepared according to the published procedure[25] and $MnCl_2 \cdot 6H_2O$ and $CoCl_2$ were used as purchased. Slow evaporation was used for crystallization. K(tcm) and the metal salts were each dissolved in a minimum amount of water, and the mixed solution was allowed to evaporate. After 5–6 weeks, light-colored crystals were obtained. The crystals were collected and washed with water. These complexes were insoluble in water or in ordinary organic solvents. For the alloy system $[Mn_{1-x}Co_x(tcm)_2]$, a mixture of $MnCl_2 \cdot 6H_2O$ and $CoCl_2$ was used (1 : 500). The Co : Mn ratio of the crystals obtained was analyzed by energy dispersive spectroscopy (EDS) (Table 1).

X-ray diffraction

The single-crystal X-ray measurements were carried out on an AFC-7R four-circle diffractometer at room temperature. The structure was solved by the Patterson method, and all atoms were refined anisotropically. The crystallographic data are listed in Table 2. The computer programs used were a part of teXsan.[26]

Magnetic measurements

The magnetic susceptibilities of $[Co_{0.55}Mn_{0.45}(tcm)_2]$ (1.50 mg) and $[Co(tcm)_2]$ (1.02 mg) were measured by a Quantum Design SQUID magnetometer under a magnetic field of 1 T

Table 2. Crystallographic data for $[Mn_{1-x}Co_x(tcm)_2]$

	$x = 0$[a]	$x = 0.55$	$x = 0.96$	$x = 1$
Empirical formula	C_8N_6Mn	$C_8N_6Mn_{0.045}Co_{0.55}$	$C_8N_6Mn_{0.04}Co_{0.96}$	C_8N_6Co
Formula Weight (g mol^{-1})	235.06	237.33	238.91	239.07
Temperature (K)	293	293	293	293
Wavelength (Å)	0.7107	0.7107	0.7107	0.7107
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group, Z	*Pmna*, 2	*Pmna*, 2	*Pmna*, 2	*Pmna*, 2
Unit cell dimensions				
a (Å)	7.742(5)	7.538(2)	7.475(2)	7.477(2)
b (Å)	5.411(6)	5.298(2)	5.251(1)	5.243(2)
c (Å)	10.561(3)	10.500(2)	10.446(2)	10.430(5)
V (Å^3)	442.5(5)	419.3(1)	410.0(1)	408.9(2)
Density (g cm^3)	–	2.328	2.328	1.942
Crystal size (mm^3)	–	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.2	0.2 × 0.2 × 0.2
Crystal color/shape	–	colorless/plate	colorless/plate	colorless/plate
2θ range (deg)	8–60	8–60	8–60	8–60
Independent reflections	–	756	721	743
Parameters/data ($I \geq 2\sigma_1$)	–	41/418	41/521	41/333
R_1, wR_2 ($I \geq 2\sigma_1$) (%)	0.065; 0.083	0.043; 0.048	0.083; 0.100	0.112; 0.138

[a] Ref. 17.

between 2 and 300 K. The diamagnetic parts were subtracted according to Pascal's law.[27]

RESULTS AND DISCUSSION

Crystal structure

In the alloy systems, the cobalt content of the crystals obtained, as estimated by EDS (Table 1), is much larger than the nominal composition. For example, a nominal composition Co : Mn = 1 : 1 has given $x = 0.96$. Thus, a large excess of Mn (500 : 1) is used to obtain approximately 1 : 1 crystals. All crystals are isostructural (Table 1 and Fig. 2), and the metal atom has nearly octahedral coordination. The distances are listed in Table 3.

The lattice parameter decreases with increasing x (Fig. 3). At the same time, the M–N distance shortens; the equatorial M–N(1) shrinks from 2.236(4) Å for manganese to 2.09(3) Å for cobalt and the axial M–N(2) decreases from 2.256(6) Å for manganese to 2.17(3) Å for cobalt. This is consistent with the smaller ionic radius of Co^{2+} compared with Mn^{2+}. However, the distortion from the octahedral coordination is very small (~1%).

Table 3. Selected bond distances of $[Mn_{1-x}Co_x(tcm)_2]$

	Bond length (Å)			
Bond	$x = 0$[a]	$x = 0.45$	$x = 0.96$	$x = 1$
M–N(1)	2.236(4)	2.15(4)	2.115(8)	2.09(3)
M–N(2)	2.256(6)	2.202(6)	2.15(3)	2.17(3)
N(1)–C(3)	1.161(9)	1.141(6)	1.14(3)	1.12(3)
N(2)–C(2)	1.442(3)	1.143(9)	1.13(4)	1.06(4)
C(2)–C(1)	1.399(9)	1.406(9)	1.42(2)	1.44(3)

[a] Ref. 17.

Magnetic properties

The temperature dependence of the magnetic susceptibility for $[Co(tcm)_2]$ is shown in Fig. 4. The susceptibility obeys the Curie–Weiss law at a Weiss temperature of −1 K and a Curie constant of 0.698 emu K mol^{-1}. The χT plot decreases with

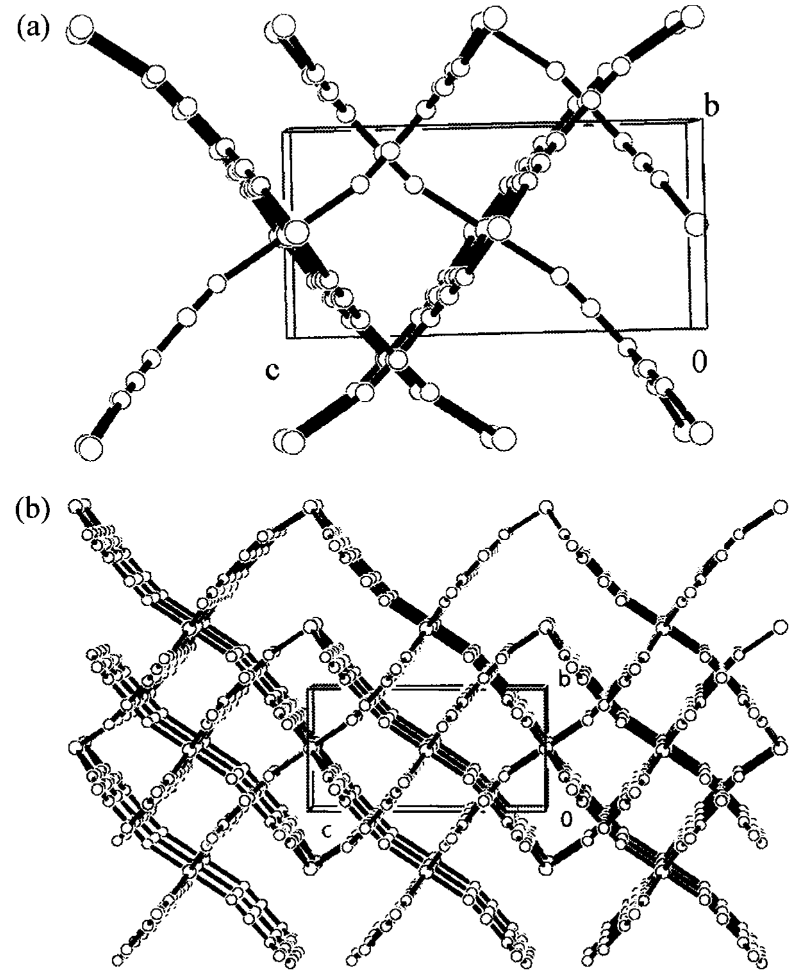

Figure 2. Crystal structure of $[Mn_{1-x}Co_x(tcm)_2]$ viewed along the *a* axis: (a) two chain units; (b) network of the interwoven chain units.

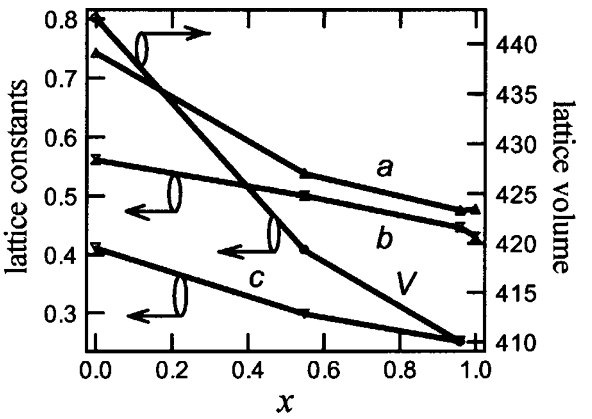

Figure 3. Decrease of lattice parameters from manganese to cobalt. For clarify we have used only the fraction values (Δ*a*: value of *a* minus numerical value of *a*) of *a*, *b* and *c*.

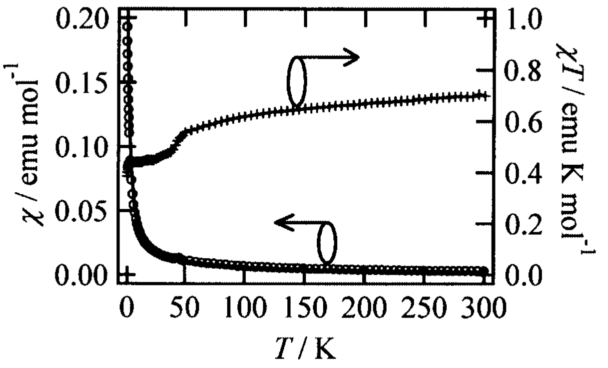

Figure 4. Temperature dependence of the magnetic susceptibility of [Co(tcm)$_2$] χ (open circles) and χT (+ sign).

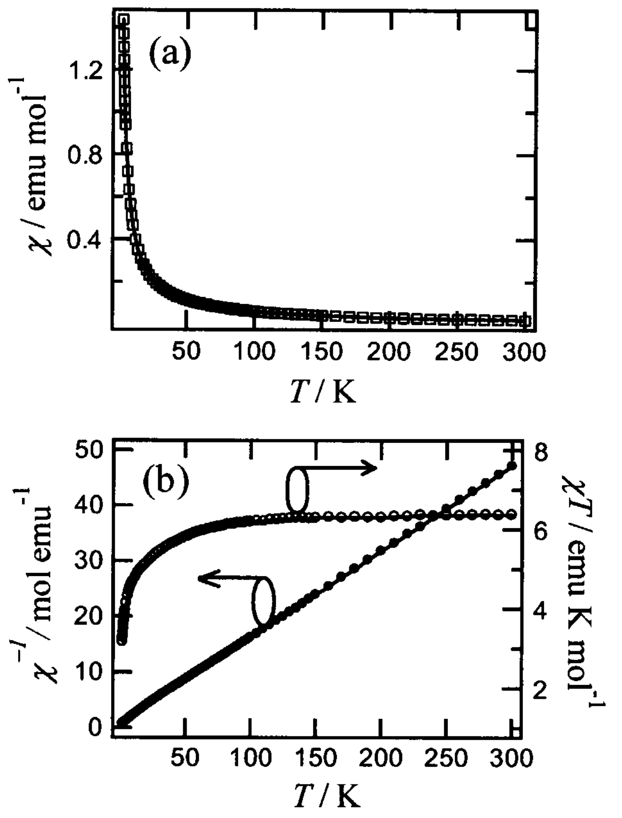

Figure 5. Temperature dependence of (a) the magnetic susceptibility χ of [Mn$_{0.45}$Co$_{0.55}$(tcm)$_2$] and (b) χT (filled circles) and χ^{-1} (open circles).

decreasing temperature, indicating that the metal atoms have antiferromagnetic interaction.

The temperature dependence of the magnetic susceptibility of [Mn$_{0.45}$Co$_{0.55}$(tcm)$_2$] is shown in Fig. 5. The susceptibility obeys the Curie–Weiss law with a Weiss temperature of −2.5 K and a Curie constant of 6.235 emu K mol^{-1}. The χT plot exhibits a rapid decrease at low temperatures, indicating the existence of antiferromagnetic interaction.

The Weiss temperature decreases continuously from −9 K for manganese to −1 K for cobalt, in the alloy system. The large Weiss temperature for the manganese compound is associated with the $S = 5/2$ spin, where all d-orbitals contribute to the magnetic interactions.

CONCLUSION

The alloy system [Mn$_{1-x}$Co$_x$(tcm)$_2$] ($x = 0, 0.04, 0.45$) has been prepared and structurally and magnetically characterized. The lattice constants and M–N distances shorten continuously from mangenes to cobalt and the magnetic interaction also gradually decreases from mangenese to cobalt. No ferromagnetic transition has been observed in the alloyed complexes.

Acknowledgements

M. S. acknowledges the financial support of the Ministry of Education, Science, Sports and Culture, Japan.

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