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Single-Crystal Structure and Magnetic Behavior of a Molecule-Based Ferrimagnet $Mn[Mn_{0.2}Cr_{0.8}(CN)_6]·4H_2O$

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The compound with the stoichiometry $Mn^{III}[Mn^{III}_{0.2}Cr^{III}_{0.8}(CN)_6]·4H_2O$ (**1**), which was prepared by slow diffusion of an aqueous solution of $K_3[Cr(CN)_6]$ and a methanol solution of $[Mn(saltn)]ClO_4$ [saltn = *N*,*N*′-1,3-propylenebis(salicylideneiminato) dianion] through a U-shaped tube containing silica gel, has been characterized by elemental analysis, ICP analysis, XPS, single-crystal X-ray structure analysis, and magnetic measurements. The complex has a face-centered cubic lattice analogous to Prussian blue and indicates ferrimagnetic ordering below $T_c = 63$ K.

Introduction

There has been continuous interest in the molecule-based magnetic materials of cyano-bridged dimetallic assemblies because of their interesting magnetic, magneto-optical and optoelectronic properties.[1,2] It is known that Prussian blue (PB) analogues, derived from hexacyanometalate ions $[M(CN)_6]^{n-}$ and simple transition metal ions, exhibit magnetic ordering at critical temperatures as high as 376 K and form a family of magnetic materials.[2] On the basis of powder XRD results, PB analogues are generally thought to have a face-centered cubic structure, but detailed structural studies are still limited because of the difficulty in obtaining single crystals.[3] On the other hand, in order to clarify the magnetostructural correlation of cyano-bridged dimetallic systems, a wide variety of hybrid Prussian blue complexes derived from $[M(CN)_6]^{n-}$ (M = Fe, Cr, Mn, Co) and coordinatively unsaturated transition metal complexes have been studied structurally and magnetically.[4] These complexes assume oligonuclear, 1D, 2D, and 3D structures and exhibit ferro-, ferri-, and metamagnetic behavior. For instance, the reaction between $[Mn(salen)]ClO_4$ [salen = *N*,*N*′-ethylenebis(salicylideneiminato) dianion] and $[M(CN)_6]^{3-}$ (M = Fe, Cr) has already led to two dimetallic heptanuclear Mn_6M clusters.[5] Recently, we had expected to obtain another cyano-bridged Mn^{III}–Cr^{III} cluster by using $[Mn(saltn)]ClO_4$ [saltn = *N*,*N*′-1,3-propylenebis(salicylideneiminato) dianion] instead of $[Mn(salen)]ClO_4$ as a building block. Surprisingly, we found a novel PB analogue $Mn[Mn_{0.2}Cr_{0.8}(CN)_6]·4H_2O$ (**1**), which has a face-centered cubic lattice and shows ferrimagnetic ordering below 63 K. Here we report on its synthesis, crystal structure, and magnetic properties.

Results and Discussion

Synthesis and Characterization

Complex **1** was obtained as brown-yellow, quasi-ball-shaped single crystals by slow diffusion of a methanol solution of $[Mn(saltn)]ClO_4$ and an aqueous solution of $K_3[Cr(CN)_6]$ through a U-tube containing silica gel. It is insoluble in usual inorganic and organic solvents and stable in air. The elemental and inductively coupled plasma (ICP) analyses confirm the composition of **1** (see Experimental Section). The IR spectrum of **1** shows a sharp $\nu(C{\equiv}N)$ peak at 2161 cm^{-1}. The blue shift of the band $\nu(C{\equiv}N)$ relative to that of $K_3[Cr(CN)_6]$ (2130 cm^{-1})[6] suggests the formation of cyano bridges. A strong broad band around 3400 cm^{-1} indicates the presence of H_2O. The characteristic peaks from the ligand saltn are not found in the IR spectrum. The X-ray photoelectron spectroscopy (XPS) of **1** shows the peaks for $Cr(2p_{3/2})$ at 576.95 eV and for $Mn(2p_{3/2})$ at 641.9 eV, with a molar ratio Cr/Mn = 1:1.6. As shown in Table 1, the Mn $2p_{3/2}$ binding energy of **1** is close to those found for $K_3[Mn^{III}(CN)_6]$ and Mn_2O_3, and obviously different from those of $Mn^{II}_3[Cr(CN)_6]_2·16H_2O$, MnO, and MnO_2, which supports the oxidation state of +3 for Mn. The composition of $Mn[Mn_{0.2}Cr_{0.8}(CN)_6]·4H_2O$ for complex **1** is in agreement with the results of the crystal structural analysis and magnetic studies as discussed below.

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Table 1. Manganese $2p_{3/2}$ binding energies [eV] of some manganese compounds.

Complex **1**	$Mn_3[Cr(CN)_6]_2\cdot 16H_2O$[3e]	$K_3[Mn(CN)_6]_3$	MnO	Mn_2O_3	MnO_2	Ref.
641.9	641.35	641.65				This work
		641.6				[2g]
			641.0	641.9	642.5	[7]
			640.9	641.8	642.5	[8]
			641.0	641.7	642.2	[9]

It can be inferred that the six-membered ring MnN_2C_3 in $[Mn(saltn)]^+$ has a lower stability with respect to the five-membered ring MnN_2C_2 in $[Mn(salen)]^+$ because of the less favorable entropy change required for the formation of six-membered rings.[10] Therefore, the $[Mn(saltn)]^+$ can dissociate more easily into Mn^{3+}, which reacts with $[Cr(CN)_6]^{3-}$ to produce the more stable complex **1**. The formation reactions for complex **1** can be shown as follows:

$[Mn(saltn)]^+ \rightarrow Mn^{3+} + saltn^{2-}$

$1.2Mn^{3+} + [Cr(CN)_6]^{3-} + 4H_2O \rightarrow Mn[Mn_{0.2}Cr_{0.8}(CN)_6]\cdot 4H_2O + 0.2Cr^{3+}$

It should be pointed out that complex **1** can only be obtained in low yields by the above slow diffusion method and cannot be synthesized as a bulk powder by directly mixing the same ingredients in solution (i.e. without the method with the U-tube); direct mixing immediately results in a black precipitate. The IR spectrum of the black product shows a $\nu(C\equiv N)$ peak at 2126 cm^{-1} and a series of characteristic peaks for saltn, which suggests the formation of the $[Cr(CN)_6]^{3-}/[Mn(saltn)]^+$ adduct. Although the reason of the formation of the two different products is not clear at present, according to the reaction conditions, we infer that the synthesis of complex **1** would be dominated by thermodynamic factors, while that of the black product would be controlled by kinetic factors.

Crystal Structure

X-ray crystallography shows that **1** belongs to the cubic space group $Fm\bar{3}m$, $a = b = c = 10.7632(7)$ Å, $V = 1246.9(1)$ Å^3. These data are comparable to those for $NaMn[Cr(CN)_6]$,[3a] $Mn_3[Mn(CN)_6]_2\cdot xH_2O$,[3b] $Mn_3[Cr(CN)_6]_2\cdot xH_2O$,[3e] and $K_{0.2}Mn_{1.4}[Cr(CN)_6]\cdot 6H_2O$.[3g] The crystal structure of **1** is shown in Figure 1. Each unit cell contains four $Mn[Mn_{0.2}Cr_{0.8}(CN)_6]\cdot 4H_2O$ units. The Mn1 atom occupies the position (0, 1/2, 1/2) and Cr1(Mn2) atom is in the position (1/2, 1/2, 1/2). Because of the Cr/Mn molar ratio of 2:3 on the basis of ICP analysis, the Cr atoms are partially replaced by Mn atoms and the occupancy of Cr1/Mn2 is 0.8:0.2, which is similar to that of $NMe_4Mn[(Mn, Cr)(CN)_6]\cdot 3H_2O$[3c] reported by Babel et al. In complex **1**, both the Mn and Cr atoms are six-coordinate and have an octahedral geometry, and are linked through cyano-bridges to form a face-centered cubic framework. The Cr atom is bonded to the carbon atoms of the CN^- ligands as in $K_3[Cr(CN)_6]$. The Mn1 atom is coordinated to the nitrogen atoms of the CN^- groups and the Mn2 atom to the carbon atoms, which would result in Mn1 and Mn2 with high-spin and low-spin ground states, respectively. The Mn1–N–C–Cr1(Mn2) linkage is linear, and the bond lengths are 2.155(9) Å [Mn1–N], 1.120(10) Å [C–N], and 2.106(14) Å [Cr1(Mn2)–C]. The Mn1···Cr1(Mn2) distance is 5.3816 Å. Because of the Jahn–Teller effect, the high-spin (HS) Mn^{III} ions should usually occupy the distorted octahedral sites. For example, the structure of the Mn^{III} (HS)-Fe^{II} Prussian blue analogues in a low-temperature state is not face-centered cubic but tetragonal because of the Jahn–Teller effect.[11] In complex **1**, it is likely that Jahn–Teller distortion occurs, but the macroscopic X-ray diffraction technique only presents a statistical distribution of distorted Mn^{III} polyhedron. Water molecules occupy the vacancies in the unit cell, and O2 is structurally disordered. It must be pointed out that the structure of complex **1** could not be solved properly according to the $Mn_3[Cr(CN)_6]_2\cdot xH_2O$ model.[3b,3e] This fact further supports the oxidation state of +3 for Mn. Generally, the structure and composition of a generic PB-like compound $A_p[B(CN)_6]_q\cdot x$H2O depend on the oxidation states of the cations A and B: for A(III) and B(III), a A/B molar ratio of 1:1 is found, while for A(II) and B(III), a ratio of 3:2 is found. For the former, the coordination spheres of A and B are $\{A(NC)_6\}$ and $\{B(CN)_6\}$, while for the latter, one third of the $[B(III)(CN)_6]$ vacancies are filled by water molecules, therefore, the coordination sphere of B is the same but the mean coordination sphere of A becomes $\{A(NC)_4(H_2O)_2\}$.[1a] Complex **1** is a unique example in which the valence of both the cations A and B is +3, but the A/B molar ratio is 3:2 instead of 1:1. The reason for the special stoichiometry that **1** presents is unclear at present.

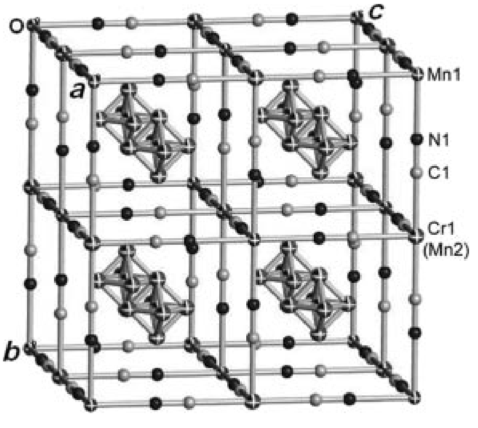

Figure 1. Unit cell diagram of complex **1**.

Magnetic Properties

The magnetic susceptibilities of complex **1** were measured with an applied field of H = 100 Oe in the temperature range 2–300 K. The plot of $\chi_M T$ vs. T is given in Figure 2. At room temperature, the value of $\chi_M T$ per $Mn_{1.2}Cr_{0.8}$ unit is 5.02 cm^3 K mol^{-1} (6.34 μ_B), which is slightly higher than the spin-only value of 4.7 cm^3 K mol^{-1} (6.13 μ_B) expected for an uncoupled spin system ($1 \cdot S_{Mn}$ = 2, $0.2 \cdot S_{Mn}$ = 1, $0.8 \cdot S_{Cr}$ = 3/2) with g = 2.0. On lowering the temperature, the $\chi_M T$ value gradually decreases and reaches a minimum of 4.43 cm^3 K mol^{-1} (5.95 μ_B) at 140 K (inset in Figure 2). Upon further cooling, $\chi_M T$ increases to a maximum of 3005 cm^3 K mol^{-1} (155 μ_B) at 52 K and then decreases below this temperature. The dependence of $1/\chi_M$ on T obeys the Curie–Weiss law [$\chi = C/(T - \theta)$] in the temperature range 300–140 K with a Weiss constant of θ = –44 K. The negative Weiss constant and the shallow minimum in the $\chi_M T$ vs. T curve both indicate the presence of an antiferromagnetic coupling between adjacent Mn^{III} (S = 2) and Cr^{III} (S = 3/2) [or Mn^{III} (S = 1)] ions through the cyanide bridges. The abrupt increase in the $\chi_M T$ value at about 65 K suggests the onset of the three-dimensional magnetic ordering. The decrease in the $\chi_M T$ value below 52 K may be due to the zero-field splitting effect and/or the field saturation of the magnetization. This is characteristic of ferrimagnetic behavior. The temperature dependence of the zero-field alternating current (ac) magnetic susceptibility taken at 10 Hz (Figure 3) shows that the real part (χ') and the imaginary part (χ'') of the ac magnetic susceptibility both have a maximum at 63 K and 64 K, respectively, which indicates that T$_c$ of **1** is 63 K.

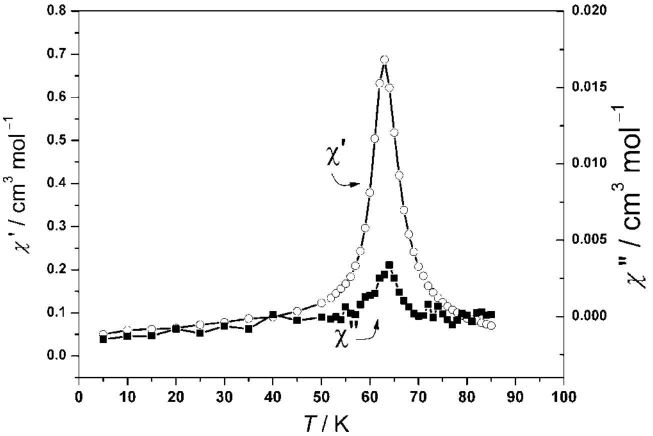

Figure 3. Real (χ') and imaginary (χ'') ac magnetic susceptibilities as a function of temperature at 10 Hz for complex **1**.

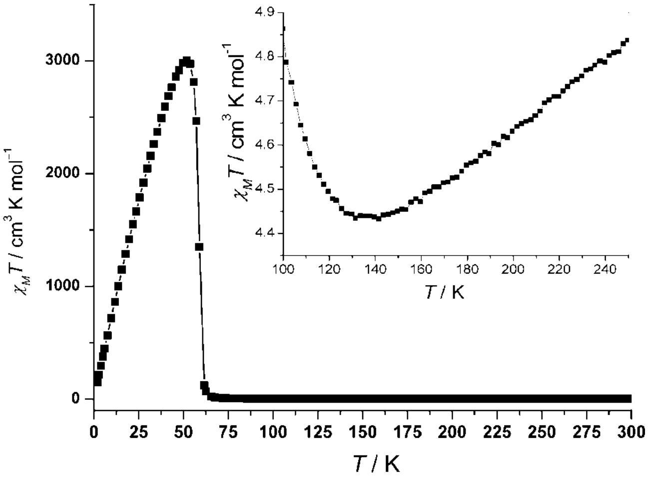

Figure 2. Temperature dependence of $\chi_M T$ for complex **1** measured at 100 Oe. Inset displays the minimum of $\chi_M T$ at 142 K, the signature of ferrimagnetism.

The field dependence of the magnetization with an applied field of 0–70 kOe, measured at 1.8, 55 and 80 K, respectively, is shown in Figure 4. At 80 K, the magnetization increases linearly and shows typical paramagnetic behavior. At 55 K, the magnetization first increases sharply and then slowly, thus displaying a property of a magnet. At 1.8 K, the magnetization increases sharply in the low-field region and reaches saturation above ca. 1.0 kOe. The saturation magnetization M_s = 3.1 Nβ is much higher than the expected value of 1.2 Nβ for the antiferromagnetic $Mn_{1.2}Cr_{0.8}$ system. The inconsistency in M_s values was also observed in some other PB analogues.[2a,2f,3a] The higher M_s value of **1** is perhaps due to the disorder of the paramagnetic ions.[2f] The magnetic hysteresis loop at 1.8 K (Figure 5) reveals no significant hysteretic behavior typical of a soft magnet, which is consistent with the symmetrical cubic three-dimensional structure.[2a–2c,3a] The antiferromagnetic interaction between the Mn^{III} (S = 2) and Cr^{III} (S = 3/2) [or Mn^{III} (S = 1)] ions can be rationalized in terms of the overlap of the magnetic orbitals of these ions.[1a]

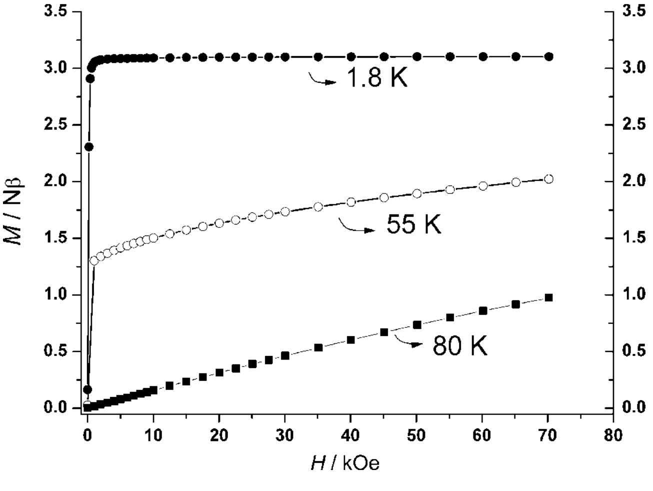

Figure 4. Field dependence of the magnetization at 1.8, 55, and 80 K for complex **1**.

It should be mentioned that the magnetic properties of complex **1** are similar to those of the Mn^{II}/Cr^{III} complexes, such as $[Mn(en)]_3[Cr(CN)_6]_2 \cdot 4H_2O$ (T_c = 69 K),[4d,4m] $Mn_3[Cr(CN)_6]_2 \cdot 12H_2O$ (T_c = 63 K),[4m] $NaMn[Cr(CN)_6]$ (T_c = 60 K),[3a] and $K_{0.2}Mn_{1.4}[Cr(CN)_6] \cdot 6H_2O$ (T_c = 66 K).[3g] Especially, it is somewhat surprising that the Mn^{III}-based

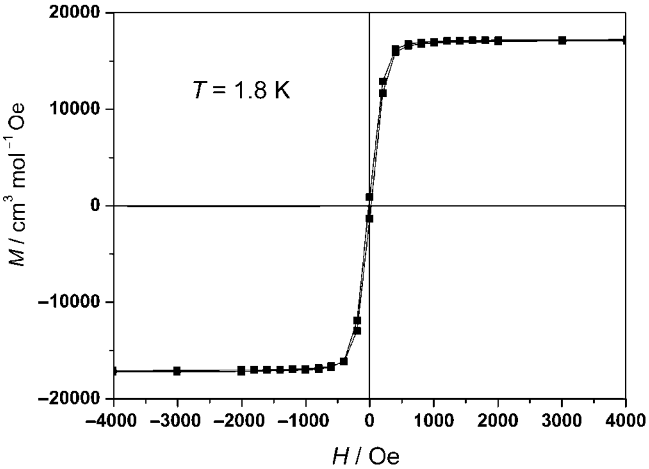

Figure 5. Magnetic hysteresis loop at 1.8 K for complex **1**.

system of **1** has such a low coercive field as found for Mn^{II}-based systems since both high- and low-spin (LS) Mn^{III} are much more anisotropic than high-spin (HS) Mn^{II}. This may be related to the extremely complex magnetic properties of the Mn^{III} (LS) species because of strong spin-orbit coupling. In addition, it is interesting to note that $[Mn(en)]_3[Cr(CN)_6]_2\cdot 4H_2O$ has a higher magnetic phase-transition temperature (T_c) than the ligand-free Mn^{II}/Cr^{III} and Mn^{III}/Cr^{III} systems. Lu et al.[3g] recently demonstrated that the T_c value of $K_{0.2}Mn_{1.4}[Cr(CN)_6]\cdot 6H_2O$ can be substantially modulated through a dehydration/rehydration treatment and increases to 99 K after dehydration in which a weight loss of 23.4% is reached. This indicates that the T_c value is sensitive to subtle changes in structure and composition. By considering the fact that the Mn^{II}/Mn^{III} Prussian blue analogues, such as $Mn^{II}_3[Mn^{III}(CN)_6]_2\cdot xH_2O$ (T_c = 35.5 K) [3b] and $CsMn^{II}[Mn^{III}(CN)_6]\cdot 1/2H_2O$ (T_c = 31 K),[12] have lower magnetic phase-transition temperatures than the Mn^{II}/Cr^{III} analogues, it would be expected that the partial substitution of low-spin Mn^{III} for Cr^{III} in complex **1** would reduce its T_c value. On the other hand, unlike complex $Mn_3[Cr(CN)_6]_2\cdot 12H_2O$,[4m] complex **1** does not have $[Cr(CN)_6]^{3-}$ vacancies in the crystal structure, which would increase the T_c value. The above two factors counteract each other, which results in a value of T_c = 63 K in complex **1**. From the magnetic point of view, complex **1** is essentially a ternary metal Prussian blue system [high-spin Mn^{III}/low-spin Mn^{III}/Cr^{III}]. Hashimoto et al.[13] have systematically investigated the magnetic behavior of a series of ternary-metal Prussian blue analogues $(Ni^{II}_xMn^{II}_{1-x})_{1.5}[Cr^{III}(CN)_6]\cdot zH_2O$, which incorporate both ferromagnetic Ni^{II}–Cr^{III} (J_{NiCr}) and antiferromagnetic Mn^{II}–Cr^{III} (J_{MnCr}) exchange interactions. The magnetic properties such as the saturation magnetization, the Weiss constant, and the coercive field could be tuned by changing the molar ratios *x*. However, the T_c values of these complexes almost remained the same (≈ 70 K). In complex **1**, both Mn^{III}(HS)–Cr^{III} and Mn^{III}(HS)–Mn^{III}(LS) exchange interactions are antiferromagnetic. Therefore, unlike the situation in the $(Ni^{II}_x Mn^{II}_{1-x})_{1.5}[Cr^{III}(CN)_6]\cdot zH_2O$ system, the magnetic properties of **1** could not change from antiferromagnetic to ferromagnetic by changing the molar ratios of the metal ions.

Conclusions

A novel Prussian blue type ferrimagnet $Mn[Mn_{0.2}Cr_{0.8}(CN)_6]\cdot 4H_2O$ has been structurally and magnetically characterized. The complex has a cubic lattice and shows ferrimagnetic ordering below 63 K. This temperature is relatively high in all cyano-bridged complexes characterized by single-crystal structure analysis.[3,4] To the best of our knowledge, complex **1** is the first A(III)-B(III) type PB analogue characterized by single-crystal structure analysis and provides a unique example for the study of structure and magnetic properties of the PB analogues.

Experimental Section

Measurements: Elemental analyses for C, H and N were performed with a Perkin–Elmer 240C analyzer. Mn and Cr analyses were carried out with a Jarrell–Ash 1100+2000 inductively coupled plasma quantometer. IR spectra were recorded on a Nicolet FT-170SX spectrometer with KBr pellets in the 4000–400 cm^{-1} region. X-ray photoelectron spectra (XPS) were obtained by using an ESCALAB MK-II spectrometer. The magnetic measurements were performed on microcrystalline powder obtained from crushed single crystals by using a Quantum Design MPMS-XL SQUID magnetometer. Diamagnetic corrections were made by using Pascal's constants. Effective magnetic moments were calculated with the equation $\mu_{eff} = 2.828(\chi_M \times T)^{1/2}$, where χ_M is the magnetic susceptibility per formula unit.

Preparations: All chemicals and solvents were reagent grade and were used without further purification. $[Mn(saltn)]ClO_4$ was synthesized by mixing $Mn(OAc)_3\cdot 2H_2O$, $saltnH_2$, and $NaClO_4$ in a molar ratio of 1:1:1.5 in methanol according to a method reported previously.[14] $K_3[Cr(CN)_6]$ was prepared by the literature method.[15]

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled in small quantities with care.

$Mn[Mn_{0.2}Cr_{0.8}(CN)_6]\cdot 4H_2O$ (1): Complex **1** was obtained as brown-yellow, quasi-ball-shaped single crystals by slow diffusion of a methanol solution (15 cm^3) of $[Mn(saltn)]ClO_4$ (0.15 mmol) and an aqueous solution (15 cm^3) of $K_3[Cr(CN)_6]$ (0.15 mmol) through a U-tube containing silica gel at room temperature. The resulting crystals were collected, washed with H_2O and EtOH, and dried in air. This complex is insoluble in usual inorganic and organic solvents and stable in air. Yield: 4.8 mg. $C_6H_8Cr_{0.8}Mn_{1.2}N_6O_4$ (335.71): calcd. C 21.46, H 2.4, Cr 12.39, Mn 19.64, N 25.04; found C 21.21, H 2.61, Cr 12.3, Mn 20.0, N 24.95. IR: $\tilde{\nu}_{max}$ = 3400 (vs), 2161 (s), 1613 (s), 990 (m), 478 (s) cm^{-1}.

X-ray Crystallography: Diffraction data were collected at 293(2) K on a Bruker SMART APEX CCD area detector diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) with the ϕ and ω scan mode. Empirical absorption correction was made with SADABS. The structures were solved by direct methods and refined by full-matrix least-squares techniques based on F^2 with the SHELXTL-97 program package. Crystal data for **1**: $C_6H_8Cr_{0.8}Mn_{1.2}N_6O_4$, M = 335.71, cubic, space group $Fm\bar{3}m$, a =

10.7632(7) Å, $\alpha = 90°$, $V = 1246.9(1)$ Å^3, $Z = 4$, $D_c = 1.788$ g/cm^3, $F(000) = 167$, $\mu = 1.928$ mm^{-1}, $S = 0.91$. 1887 reflections measured, 106 unique. Final $R_1 = 0.029$ and $wR_2 = 0.074$ for 62 observed reflections [$I > 2\sigma(I)$]. CCDC-284959 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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