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FULL PAPER

An assembly compound $[K(18\text{-crown-}6)(MeOH)_2][Mn(5\text{-Clsalen})(H_2O)(MeOH)]_2[Fe(CN)_6]\cdot 4MeOH$ of isolated metal centers and conversion into a ferrimagnetic compound by desolvation [18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane, 5-Clsalen = *N*,*N*′-ethylenebis(5-chlorosalicylideneiminate)]

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The reaction of $[Mn(5\text{-Clsalen})(H_2O)]ClO_4$ with $[K(18\text{-crown-}6)(H_2O)_2]_3[Fe(CN)_6]$ in methanol gave a double salt, $[K(18\text{-crown})(MeOH)_2][Mn(5\text{-Clsalen})(H_2O)(MeOH)]_2[Fe(CN)_6]\cdot 4MeOH$ **1** [5-Clsalen = *N*,*N*′-ethylenebis-(5-chlorosalicylideneiminate), 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane]. Compound **1** crystallizes in the monoclinic space group *C*2/*c* with cell dimensions of $a = 29.065(5)$, $b = 14.261(8)$, $c = 18.443(6)$ Å, $\beta = 98.83(2)°$, $Z = 4$, $V = 7553(4)$ Å^3. The two $[Mn(5\text{-Clsalen})(H_2O)(MeOH)]^+$ cations and the $[Fe(CN)_6]^{3-}$ anion are hydrogen bonded, through the $Mn–OH_2\cdots NC–Fe$ and $Mn–MeOH\cdots NC–Fe$ linkages, to form a two-dimensional network structure; the $O\cdots N$ separation is 2.768(8) Å in the former linkage and 2.684(8) Å in the latter. The $[K(18\text{-crown-}6)(MeOH)_2]^+$ cations are situated between the two-dimensional layers. Compound **1** was partially desolvated in air to give $[K(18\text{-crown-}6)][Mn(5\text{-Clsalen})(H_2O)]_2[Fe(CN)_6]$ **1′** which exhibited a short range magnetic interaction due to the local formation of magnetically coupled sublattices. Compound **1′** was fully desolvated by heating to 180 °C to give $[K(18\text{-crown-}6)][Mn(5\text{-Clsalen})]_2[Fe(CN)_6]$ **2** which exhibited spontaneous magnetization due to the formation of a network extended by Mn–NC–Fe linkages throughout the lattice.

Introduction

The design of ordered network structures of paramagnetic centers is becoming an important current research subject for providing molecular-based magnetic materials exhibiting spontaneous magnetization. The use of paramagnetic metal complexes as the constituents has great advantages over organic radical constituents because electron spin(s) can be localized to each metal center and the ordered network structures (1-D, 2-D, and 3-D) of paramagnetic metal centers can be constructed by taking advantage of diverse stereochemistries of metal complexes.[1–5] Previously, one of the present authors (H. M.) reported 1-D and 2-D Mn(III)/Fe(III) assembly compounds derived from the reaction between $[Mn(SB)]^+$ and $[Fe(CN)_6]^{3-}$ (SB = quadridentate Schiff base).[6] The network structures of the assembly compounds vary depending upon the nature of the solvent used. For example, the reaction of $[Mn(5\text{-Clsalen})(H_2O)]ClO_4$ with $[NEt_4]_3[Fe(CN)_6]$ in methanol gave a solvated trinuclear species $[NEt_4][Mn(5\text{-Clsalen})(H_2O)]_2[Fe(CN)_6]$ having a bridging mode for $[(H_2O)Mn–Fe(CN)_6–Mn(H_2O)]^-$, whereas reaction in a DMF–MeCN–2-PrOH mixed solvent gave a two-dimensional layered compound $[NEt_4][Mn(5\text{-Clsalen})]_2[Fe(CN)_6]$ consisting of the octamer net unit $[–Mn–NC–Fe–CN–]_4$ [5-Clsalen = *N*,*N*′-ethylenebis(5-chlorosalicylideneiminate)].[6c] Further, it was found that the former compound could be transformed into the latter by desolvation.

From these bases, a stepwise synthetic strategy for ordered network structures *via* a solvated discrete core complex is proposed. In this work it is aimed to illustrate such a stepwise synthesis of an extended network from a discrete structural compound, with a hope to provide a new synthetic method for ferro- or ferri-magnetic materials. The reaction of $[Mn(5\text{-Clsalen})(H_2O)]ClO_4$ with $[K(18\text{-crown-}6)(H_2O)_2]_3[Fe(CN)_6]$ in methanol gave a double salt compound, $[K(18\text{-crown-}6)(MeOH)_2][Mn(5\text{-Clsalen})(H_2O)(MeOH)]_2[Fe(CN)_6]\cdot 4MeOH$ **1** (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane). X-Ray crystallography upon **1** has established that two $[Mn(5\text{-Clsalen})(H_2O)(MeOH)]^+$ cations and the $[Fe(CN)_6]^{3-}$ anion are hydrogen-bonded through $Mn–O(R)H\cdots NC–Fe$ (R = H, Me) linkages to form a two-dimensional network structure where the magnetic centers are essentially isolated from each other. In air, **1** was partially desolvated to form $[K(18\text{-crown-}6)][Mn(5\text{-Clsalen})(H_2O)]_2[Fe(CN)_6]$ **1′**. The fully desolvated compound $[K(18\text{-crown-}6)][Mn(5\text{-Clsalen})]_2[Fe(CN)_6]$ **2** was obtained when **1** and **1′** were heated to 180 °C. The magnetic properties of **1**, **1′** and **2** are studied to show the construction of an ordered network structure upon desolvation and the onset of magnetic ordering in the case of **2**.

Experimental

Physical measurements

Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Kyushu University. Infrared spectra were measured on KBr disks with a JASCO IR-810 and a Shimadzu FTIR-8600 spectrophotometers. Thermogravimetric analyses (TGA) were carried out on a Rigaku Denki TG-DTA apparatus, where the heating rate was 1.25 °C min^{-1} and the temperature range was 20–300 °C. Magnetic susceptibilities were preliminarily measured with a Faraday balance in the temperature range 80–300 K, where the calibrations were made with $[Ni(en)_3]S_2O_3$ (en = ethylenediamine). Magnetic

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susceptibilities were finally measured in the temperature range 1.8–280 K using a MPMS5 SQUID susceptometer (Quantum Design Inc.), where the applied magnetic fields were 10 and 5000 G. Field dependencies of magnetization up to 5.5 T, field-cooled magnetization, remnant magnetization, zero-field cooled magnetization, and hysteresis loop were measured on the same apparatus. Diamagnetic corrections were made using Pascal's constants.[7] Effective magnetic moments were calculated by the equation $\mu_{\mathrm{eff}} = 2.828(\chi_{\mathrm{M}}T)^{\frac{1}{2}}$, where χ_{M} is the magnetic susceptibility per formula unit.

X-Ray data collection, reduction and structure determination

Single crystals for the crystallographic analysis were prepared by the method described in the synthetic procedure. A crystal of dimensions 0.15 × 0.10 × 0.5 mm was encapsulated in a glass capillary together with a small amount of the mother liquor and used for data collection. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) and a 12 kW rotating anode generator. The data were collected at 23 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 55.0° at a scan speed of 16.0° min^{-1} (in ω). The weak reflections [$I < 10.0\sigma(I)$] were rescanned (maximum of 5 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. Of the 9228 reflections which were collected, 9022 were unique. The diameter of the incident beam collimator was 1.0 mm, the crystal to detector distance was 235 mm, and the computer-controlled detector aperture was set to 9.0 × 13.0 mm (horizontal vertical). The intensities of three representative reflections were measured after every 150 reflections. Over the course of the data collection, the standard reflections were monitored and the decay corrections were applied by a polynomial correction. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects.

The structure was solved by the direct method[8] and expanded using Fourier techniques.[9] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. Full-matrix least-squares refinements based on 5291 observed reflections [$I > 3.00\sigma(I)$] were employed, where the unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ were used. The weighting scheme was based on counting statistics. Plots of $\Sigma w(|F_o| - |F_c|)^2$ *vs.* $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. Neutral atomic scattering factors were taken from Cromer and Waber.[10] Anomalous dispersion effects were included in F_{calc}; the values $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[11] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[12] All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.[13] The fragility of the crystals and the existence of disorder made it difficult to improve the quality of the X-ray analysis and because of the existence of disorder, the atoms of the crown-ether moieties could not be exactly determined. Crystal data and details of the structure determinations are summarized in Table 1.

CCDC reference number 186/1193.

General procedures and materials

All chemicals and solvents used for syntheses were of reagent grade. The quadridentate Schiff base ligand H_2(5-Clsalen) was synthesized by reacting 5-chlorosalicylaldehyde and ethylenediamine in the molar ratio of 2:1 in methanol. [Mn(5-Clsalen)(H_2O)]ClO_4 was prepared according to the literature method[14] and characterized by C, H and N microanalyses and IR spectra. [K(18-crown-6)($H_2O)_2$]$_3$[Fe(CN)$_6$]·3H_2O was prepared by reacting K_3[Fe(CN)$_6$] and 18-crown-6 (1:3) in methanol as reported previously.[15] Since hexacyanoferrate(III) ions have a tendency to decompose upon heating and irradiation, the synthesis and crystallization of the Mn(III)Fe(III) complex **1** were carried out at room temperature in the dark. **CAUTION**: Perchlorate salts are potentially explosive and should be handled in small quantities.

Table 1 Crystallographic data for [K(18-crown-6)(MeOH)$_2$][Mn(5-Clsalen)(H_2O)(MeOH)]$_2$[Fe(CN)$_6$]·4MeOH **1**

Formula	$C_{58}H_{84}N_{10}O_{20}KMn_2Fe$
Formula weight	1587.99
Crystal system	Monoclinic
Space group	*C*2/*c* (no. 15)
T/°C	23 ± 1
λ/Å	0.71069
a/Å	29.065(5)
b/Å	14.261(8)
c/Å	18.443(6)
α/°	90
β/°	98.83(2)
γ/°	90
V/Å^3	7553(4)
Z	4
D_c/g cm^{-3}	1.396
μ(Mo-Kα)/cm^{-1}	7.86
No. of reflections	9228
R^a	0.062
$R_w{}^{b,c}$	0.067

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [c] $w = 1/[\sigma^2(F_o)]$.

Preparation of [K(18-crown-6)(MeOH)$_2$][Mn(5-Clsalen)(H_2O)(MeOH)]$_2$[Fe(CN)$_6$]·4MeOH 1 and the partially-desolvated compound [K(18-crown-6)][Mn(5-Clsalen)(H_2O)]$_2$[Fe(CN)$_6$] 1′

To a solution of [Mn(5-Clsalen)(H_2O)]ClO_4 (254 mg, 0.5 mmol) in 30 cm^3 of methanol was added a solution of [K(18-crown-6)($H_2O)_2$]$_3$[Fe(CN)$_6$]·3H_2O (642 mg, 0.5 mmol) in 20 cm^3 of methanol. The resulting solution was filtered without stirring and the dark brown filtrate was allowed to stand for 2 days in the dark to give **1** as dark brown needles. The formula of **1** was determined by single crystal X-ray analysis. IR(KBr) for **1**: *ν*[C=N(imine)] 1600, 1632 (br) cm^{-1}; *ν*[C≡N(cyanide)] 2108 cm^{-1}.

The crystals readily effloresced in the air to give a partially desolvated compound [K(18-crown-6)][Mn(5-Clsalen)(H_2O)]$_2$[Fe(CN)$_6$] **1′**. Anal. Calc. for **1′**, $C_{50}H_{52}N_{10}O_{12}Cl_4KMn_2Fe$: C, 45.10; H, 3.94; N, 10.52. Found; C, 45.27; H, 3.80; N, 10.53%. IR(KBr) for **1′**: *ν*[C=N(imine)] 1600, 1626, 1638 (br) cm^{-1}; *ν*[C≡N(cyanide)] 2110 and 2133 cm^{-1}.

Preparation of the desolvated compound [K(18-crown-6)][Mn(5-Clsalen)]$_2$[Fe(CN)$_6$] 2

Thermogravimetric (TG) and differential thermal analyses (DTA) for **1** were carried out in the temperature range 20–300 °C with a heating rate of 1.25 °C min^{-1}. The weight loss corresponding to the crystal solvent molecules (8MeOH and 2H_2O) expected from the X-ray crystallography were observed, and all the crystal solvents were lost at *ca.* 150 °C. Thus, the desolvated sample **2** was prepared by heating **1** or **1′** to 180 °C. Anal. Calc. for **2**, $C_{50}H_{48}N_{10}O_{10}Cl_4KMn_2Fe$: C, 46.35; H, 3.73; N, 10.81. Found; C, 46.14; H, 3.79; N, 10.77%. IR (KBr): *ν*[C=N imine)] 1600, 1630, 1636 (br) cm^{-1}; *ν*[C≡N(cyanide)] 2110 cm^{-1}.

Results and discussion

Synthesis and characterization

In previous studies the reaction between [Mn(5-Clsalen)(H_2O)]ClO_4 and [NEt$_4$]$_3$[Fe(CN)$_6$] in methanol led to a discrete

Table 2 Relevant bond distances (Å) and angles (°) for **1** with the estimated standard deviations in parentheses[a]

Mn–N1	1.974(6)	Mn–N2	1.989(6)
Mn–O1	1.883(4)	Mn–O2	1.873(5)
Mn–O3	2.256(5)	Mn–O4	2.241(6)
Fe–C18	1.931(8)	Fe–C19	1.928(7)
Fe–C20	1.939(10)	C18–N3	1.142(9)
C19–N4	1.150(9)	C20–N5	1.15(1)
N1–Mn–O3	88.7(2)	N1–Mn–O4	89.8(2)
N2–Mn–O3	90.5(2)	N2–Mn–O4	88.1(2)
O3–Mn–O4	178.1(2)	O1–Mn–O3	92.1(2)
O1–Mn–O4	89.2(2)	O2–Mn–O3	89.2(2)
O2–Mn–O4	92.2(2)	C18–Fe–C19	90.5(3)
C18–Fe–C20	90.9(3)	C19–Fe–C20	91.4(3)
Fe–C18–N3	179.3(7)	Fe–C19–N4	178.6(8)
Fe–C20–N5	178.1(8)		
Hydrogen bond distances (Å)			
O3···N3	2.768(8)	O4*···N4	2.684(8)

[a] Symmetry operation (*): $x, \frac{1}{2} + y, \frac{1}{2} + z$.

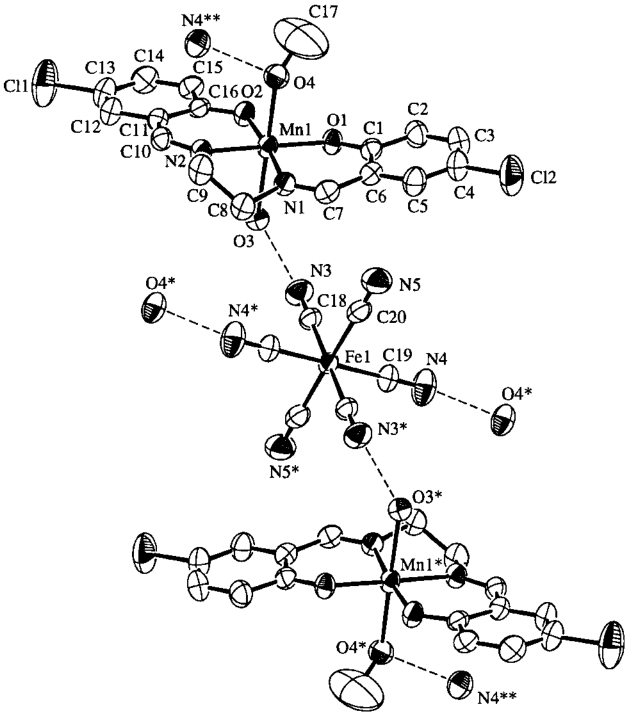

Fig. 1 ORTEP drawing of the $[Mn_2Fe]$ unit for **1** composed of hydrogen-bonded trinuclear species, $[Mn(5\text{-Clsalen})(H_2O)(MeOH)]_2[Fe(CN)_6]^-$ with the atom numbering scheme of the unique atoms.

trinuclear Mn_2Fe compound $[NEt_4][Mn(5\text{-Clsalen})(H_2O)]_2[Fe(CN)_6]$ whereas the reaction in a DMF–MeCN–2-PrOH mixed solvent led to a 2-D network compound $[NEt_4][Mn(5\text{-Clsalen})]_2[Fe(CN)_6]$.[6c] In this study the use of $[K(18\text{-crown-6})(H_2O)_2]_3[Fe(CN)_6]$ instead of $[NEt_4]_3[Fe(CN)_6]$ in the reaction in methanol led to a double salt $[K(18\text{-crown-6})(MeOH)_2][Mn(5\text{-Clsalen})(H_2O)(MeOH)]_2[Fe(CN)_6]\cdot 4MeOH$ **1**. The formula of this compound was determined based on X-ray crystallography as discussed below. The IR spectrum of **1** shows only one $\nu(C{\equiv}N)$ mode at 2108 cm^{-1} in spite of the existence of two types of cyanide groups in the crystal (see structural discussion). The occurrence of hydrogen bonding in the crystal is inferred from the complicated vibrations in the region 2800–3300 cm^{-1}. Compound **1** was highly efflorescent and the sample upon standing overnight in air was transformed into $[K(18\text{-crown-6})][Mn(5\text{-Clsalen})(H_2O)]_2[Fe(CN)_6]$ based on elemental analyses. The $\nu(C{\equiv}N)$ vibration for **1′** splits into two (2110 and 2133 cm^{-1}). This fact suggests that the crystal structure of **1** in the bulk is changed by air-drying. In order to measure the desolvation process, thermogravimetric analysis was conducted upon **1**. The results indicated continuous weight loss corresponding to eight methanol molecules and two water molecules in the temperature range from room temperature to 150 °C, providing finally the desolvated compound $[K(18\text{-crown-6})][Mn(5\text{-Clsalen})]_2[Fe(CN)_6]$ **2**. IR bands typical of hydrogen bonding are absent in the spectrum of **2**. Only one CN stretching mode is found at 2110 cm^{-1} for **2** in spite of the existence of two CN stretching modes in **1′**, and this fact suggests that full desolvation leads to further structural change in the bulk material.

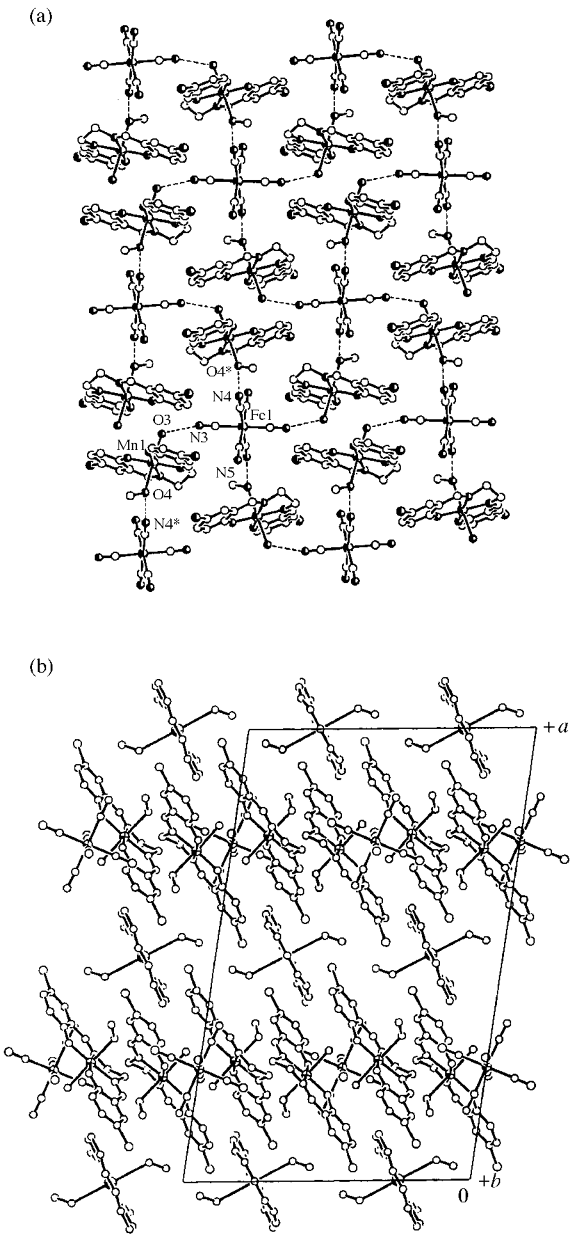

Fig. 2 (a) Hydrogen-bonded two-dimensional network structure for **1**, in which a net unit is consisted of a hydrogen bonded cyclic $[\cdots(MeOH)Mn(H_2O)\cdots NC\text{–}Fe\text{–}CN\cdots]_4$. (b) Perpendicular view against the projection of 2-D network, $[K(18\text{-crown-6})(MeOH)_2]^+$ cations are located in the interlayers arranged in a one-dimensional column.

Crystal structure of 1

An ORTEP drawing of the $[Mn(5\text{-Clsalen})(H_2O)(MeOH)]_2[Fe(CN)_6]^-$ entity along with the numbering scheme of the unique atoms and the hydrogen bonding modes is shown in Fig. 1. Selected bond distances and angles are reported in Table 2.

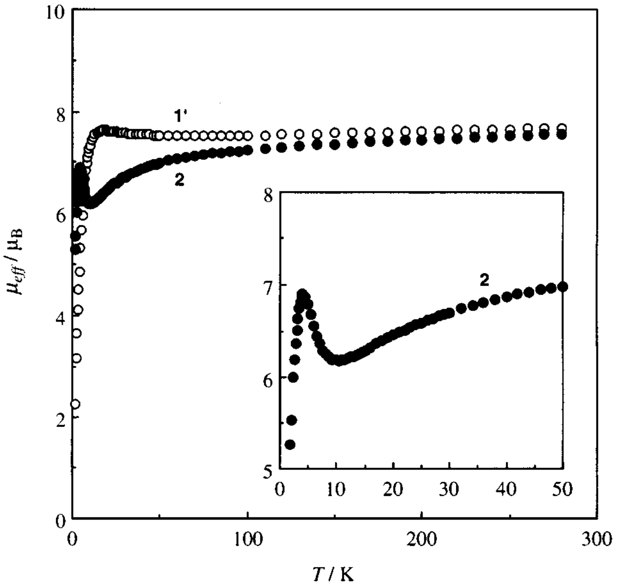

Fig. 3 Plot of μ_{eff} per Mn_2Fe for **1′** (○) and **2** (●) *vs.* *T*.

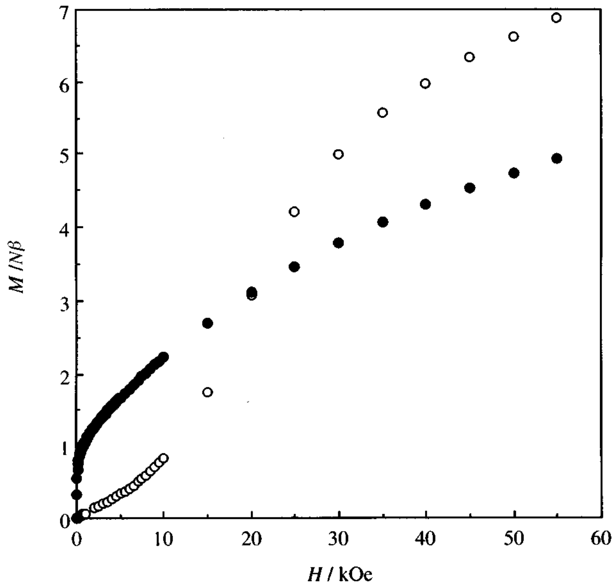

Fig. 4 Magnetization (at 1.8 K) as a function of the external magnetic field up to 55 kOe for **1′** (○) and **2** (●).

X-Ray crystallography indicates a hydrogen-bonded two-dimensional network constructed by the $[Mn(5\text{-Clsalen})(H_2O)(MeOH)]^+$ cation and the $[Fe(CN)_6]^{3-}$ anion (Fig. 2). The $[Mn(5\text{-Clsalen})(H_2O)(MeOH)]^+$ cation has an axially elongated octahedral geometry about the metal ion. The equatorial sites are occupied by the N_2O_2 donor atoms of the quadridentate dianionic 5-Clsalen ligand with average bond distances of ⟨Mn–N⟩ 1.983 Å and ⟨Mn–O⟩ 1.878 Å. The two apical sites are occupied by the water oxygen O(3) and the methanol oxygen O(4). The axial bond distances [Mn–O(3) 2.256(5) and Mn–O(4) 2.241(6) Å] are much longer than the in-plane related Mn–O and Mn–N bond distances. The $[Fe(CN)_6]^{3-}$ anion is hydrogen-bonded through *trans* cyano nitrogens N(3) and N(3*), to the aqua proton of two $[Mn(5\text{-Clsalen})(H_2O)(MeOH)]^+$ cations with an atomic separation O(3)···N(3) [O(3*)···N(3*)] of 2.768(8) Å. Similarly, hydrogen bonds exist between the cyano nitrogens N(4) and N(4*) of the $[Fe(CN)_6]^{3-}$ anion and the methanol proton of two $[Mn(5\text{-Clsalen})(H_2O)(MeOH)]^+$ cations with an atomic separation O(4)···N(4) [O(4*)···N(4*)] of 2.684(8) Å. The four cyano groups associated with the hydrogen bonding reside on a plane. Fig. 2(a) shows the two-dimensional network consisting of hydrogen-bonded octanuclear $[\cdots(MeOH)Mn(H_2O)\cdots NC\text{–}Fe\text{–}CN\cdots]_4$ units. The $[K(18\text{-crown-6})(MeOH)_2]^+$ cation is located between the two-dimensional layers without any noticeable interaction with the 2-D layers [Fig. 2(b)]. Because of the complicated disorder, the atomic coordinates for 18-crown-6 of $[K(18\text{-crown-6})(MeOH)_2]^+$ could not be precisely determined.

Magnetic properties of the partially-desolvated compound 1′

Since **1** was efflorescent in air, magnetic measurements were carried out for the partially desolvated compound **1′**. X-Ray crystallography for **1** indicated that the paramagnetic centers were essentially isolated from each other although these exists hydrogen bonding between the $[Mn(5\text{-Clsalen})(H_2O)(MeOH)]^+$ cation and the $[Fe(CN)_6]^{3-}$ anion. Thus, no marked magnetic interaction is expected for **1**. The partially desolvated compound **1′**, on the other hand, showed a significant temperature dependence for its magnetic moment. The plot of the effective magnetic moment μ_{eff} *vs.* temperature per Mn_2Fe unit is shown in Fig. 3. The value of μ_{eff} at room temperature, 7.67 μ_B, is slightly larger than the spin-only value of 7.14 μ_B for the magnetically dilute three-spin system $(S_{Mn}, S_{Fe}, S_{Mn}) = (2, 1/2, 2)$, where the spin-only value is calculated by assuming *g* values of $g_{Mn} = 2.00$ and $g_{Fe} = 2.00$. As the temperature is lowered, the magnetic moment gradually decreased to reach a rounded minimum of 7.52 μ_B around 70–75 K, gradually increased to a maximum of 7.63 μ_B at 19 K and sharply decreased down to 2.28 μ_B at 1.8 K. Such magnetic behavior suggests that the Mn–NC–Fe linkages are locally formed by partial desolvation, providing magnetically condensed sublattices. The plot of $1/\chi_M$ *vs.* *T* in the temperature range 80–300 K obeys the Curie–Weiss law with a negative Weiss constant θ of 5.8 K, indicating an antiferromagnetic interaction in the Mn(III)–NC–Fe(III) unit. The slight increase of μ_{eff} with lowering temperature from 70 to 19 K implies a short range magnetic interaction among the antiferromagnetically coupled sublattices (ferrimagnetic spin coupling). The sharp decrease of μ_{eff} below 19 K probably arises from the zero-field splitting of the manganese(III) ion[16] and/or an intermolecular antiferromagnetic interaction.

Magnetization was measured as a function of the external magnetic field at 1.8 K and is shown in Fig. 4. The magnetization first increased slowly with increasing applied field, then more sharply in the range 10–25 kOe and again gradually above 30 kOe ($1\ \text{Oe} = 10^3\ \text{A m}^{-1}$). The behavior up to 20 kOe resembles that observed for $K[Mn(5\text{-Clsalen})(H_2O)]_2[Fe(CN)_6]\cdot 4H_2O$[6b] and $[NEt_4][Mn(5\text{-Clsalen})(H_2O)]_2[Fe(CN)_6]$[6c] which contain a discrete trinuclear linked core [Mn-NC–Fe–CN–Mn]. This fact strongly suggests that a similar trinuclear core is formed locally in the partially desolvated compound **1′**. The magnetization of **1′** at 55 kOe is *ca.* 7 *Nβ*, *N* being Avogadrós number and β the electronic Bohr magnetron, which corresponds to the expected value for an antiferromagnetically coupled trinuclear $Mn^{III}{}_2Fe^{III}$ unit, however, the curve shows a further increasing tendency of magnetization at higher applied field. The tendency of the magnetization to exceed 7*Nβ* at high magnetic field suggests the presence of magnetically isolated Mn(III) ($S = 2$) and Fe(III) ($S = 1/2$) centers in **1′**.

Magnetic properties of desolvated compound 2

The magnetic behavior of the fully desolvated compound **2** is quite different from that of **1′**. A plot of the effective magnetic moment μ_{eff} *vs.* temperature per Mn_2Fe unit is shown in Fig. 3. The value of μ_{eff} at room temperature, 7.56 μ_B, is slightly larger than the spin-only value of 7.14 μ_B for the magnetically dilute three-spin system $(S_{Mn}, S_{Fe}, S_{Mn}) = (2, 1/2, 2)$. As the temperature was lowered, the magnetic moment gradually decreased to the minimum of 6.18 μ_B at 10.5 K, abruptly increased to a maximum of 6.91 μ_B at 4 K and sharply decreased to 5.27 μ_B at 1.8 K. The plot of $1/\chi_M$ *vs.* *T* above 10 K obeys the Curie–Weiss

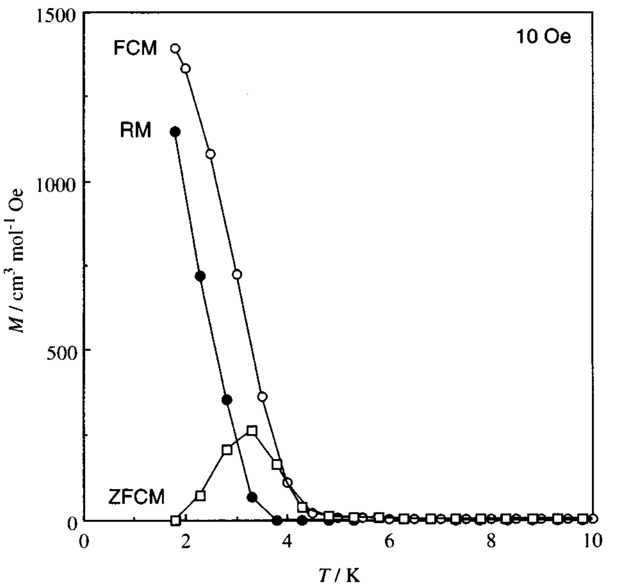

Fig. 5 FCM (field-cooled magnetization; ○), RM (remnant magnetization; ●), and ZFCM (zero-field cooled magnetization; □) *vs.* T for **2** at 10 Oe. The solid lines are a guide for the eye.

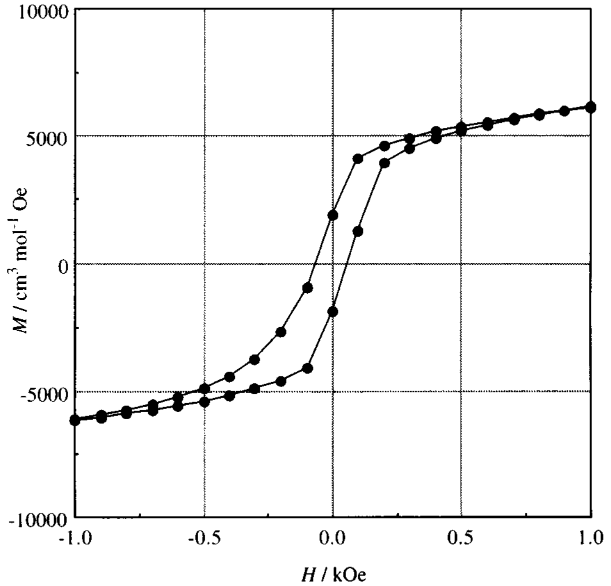

Fig. 6 Hysteresis loop ($M/N\beta$ *vs.* T) for **2** at 1.8 K. The remnant magnetization is 2000 cm^3 mol^{-1} Oe, and the coercive field is 100 Oe. The solid line is a guide for the eye.

law with a negative Weiss constant θ of −8.4 K, indicating the operation of an antiferromagnetic interaction between adjacent metal ions. The abrupt increase of μ_{eff} below 10 K suggests the onset of ferrimagnetic ordering.

In order to confirm the onset of magnetic ordering at low temperature, FCM (field-cooled magnetization), RM (remnant magnetization), and ZFCM (zero-field cooled magnetization) were measured in the temperature range 1.8–10 K and the results are shown in Fig. 5. In the FCM measured under the applied magnetic field of 10 Oe, the magnetization showed a rapid increase below 4 K (T_c) up to 1400 cm^3 mol^{-1} Oe at 1.8 K. When the applied field was switched off at 1.8 K, a RM (1200 cm^3 mol^{-1} Oe) was observed which vanished at *ca.* 4 K upon warming. The ZFCM, obtained by cooling under zero field and warming under 10 Oe, showed a maximum at 3.4 K, as expected for a polycrystalline ferrimagnet.

Magnetization as a function of the external magnetic field was measured at 1.8 K and the result is shown in Fig. 4. The magnetization curve showed a sudden increase to *ca.* 1 $N\beta$ at 500 Oe (not observed for **1′**) and then increases linearly to 5 $N\beta$ under the highest applied field of 55 kOe. The sharp increase in magnetization is an indication of the onset of magnetic ordering over the lattice. The magnetization value of 5 $N\beta$ under the highest applied field of 55 kOe is lower than the expected saturation value for the $Mn^{III}{}_2Fe^{III}$ unit (7 $N\beta$). Such a slow saturation of magnetization can be attributed to a large zero-field splitting of Mn(III) as discussed for **1′**.[6b,16]

A hysteresis loop was observed for **2** at 1.8 K (Fig. 6); the coercive field is *ca.* 100 Oe and the remnant magnetization is 2000 cm^3 mol^{-1} Oe. This lends support to the formation of a two-dimensional network extended by Mn–NC–Fe linkages over the lattice.

It should be mentioned that the magnetic behavior of compound **2** resembles that of [NEt$_4$][Mn(5-Clsalen)]$_2$[Fe(CN)$_6$][6c] and [NEt$_4$][Mn(salen)]$_2$[Fe(CN)$_6$],[17] which have a similar two-dimensional network structure consisting of an octamer net unit [–Mn–NC–Fe–CN–]$_4$ and exhibit an onset of ferrimagnetic ordering ($T_N = ca.$ 7 K). This suggests that a similar two-dimensional network structure is constructed in compound **2** upon desolvation.

Conclusion

The reaction of [Mn(5-Clsalen)(H$_2$O)]ClO$_4$ with [K(18-crown-6)(H$_2$O)$_2$]$_3$[Fe(CN)$_6$] in methanol gave a double salt, [K(18-crown-6)(MeOH)$_2$][Mn(5-Clsalen)(H$_2$O)(MeOH)]$_2$[Fe(CN)$_6$]·4MeOH **1**. The two [Mn(5-Clsalen)(H$_2$O)(MeOH)]$^+$ cations and the [Fe(CN)$_6$]$^{3-}$ anion in this compound are hydrogen bonded, through Mn–OH$_2$···NC–Fe and Mn–MeOH···NC–Fe linkages, to form a two-dimensional network structure; the O···N separation is 2.768(8) Å in the former linkage and 2.684(8) Å in the latter. The [K(18-crown-6)(MeOH)$_2$]$^+$ cations are situated between the two-dimensional layers. Compound **1** was partially desolvated in air to give [K(18-crown-6)][Mn(5-Clsalen)(H$_2$O)]$_2$[Fe(CN)$_6$] **1′** which showed a short range antiferromagnetic interaction due to the local formation of magnetically coupled sublattices. Compound **1′** was fully desolvated by heating to 180 °C to form [K(18-crown-6)][Mn(5-Clsalen)]$_2$[Fe(CN)$_6$] **2** which exhibited a spontaneous magnetization due to the formation of a network extended by Mn–NC–Fe linkages over the lattice.

The conversion of **1** into **2** through the partially desolvated intermediate **1′** is schematically shown in Scheme 1. In complex **1** (Scheme 1, top) the two axial sites of [Mn(5-Clsalen)]$^+$ are blocked by water and methanol ligation. The Mn–OH$_2$···NC–Fe and Mn–MeOH···NC–Fe hydrogen bonds between the adjacent [Mn(5-Clsalen)(H$_2$O)(MeOH)]$^+$ and [Fe(CN)$_6$]$^{3-}$ ions provides a 2-D network structure, but the metal centers are magnetically isolated from each other in the hydrogen-bonded network. The methanol cap of [Mn(5-Clsalen)(H$_2$O)(MeOH)]$^+$ is released in air and the resulting vacant site is occupied by a cyano nitrogen of the adjacent [Fe(CN)$_6$]$^{3-}$, providing another hydrogen-bonded 2-D network of trinuclear [Mn^{III}–NC–Fe^{III}–CN–Mn^{III}] units (bottom right). The water cap can be released by heating **1′** at 150 °C and this site is occupied by a cyano nitrogen of [Fe(CN)$_6$]$^{3-}$ in the adjacent trinuclear unit, providing a cyanide-bridged 2-D network (bottom left). The conversion of isolated oligomeric centers into an ordered syructure by desolvation was recently reported by one of us (H. M.).[18] This work illustrates the first conversion of isolated monometallic centers into an ordered network through an oligomeric intermediate.

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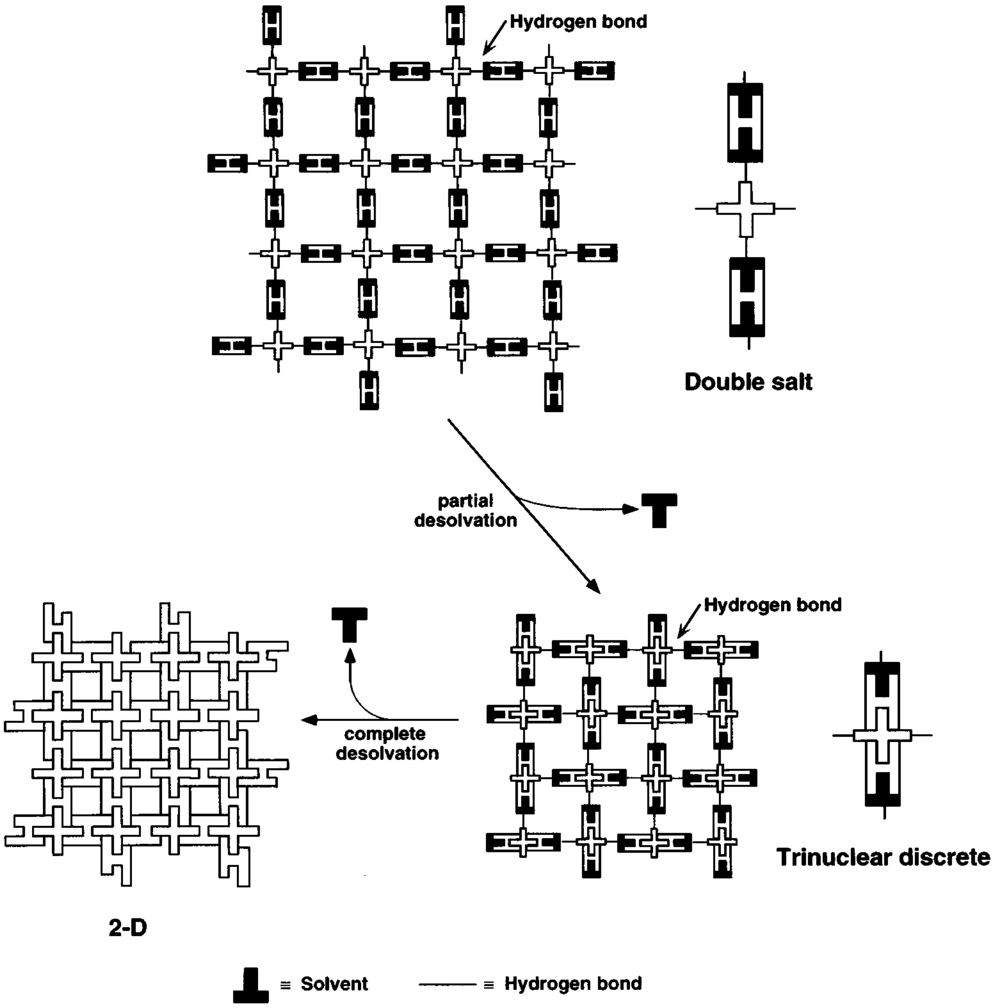

Scheme 1

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