Synthesis, crystal structure and magnetic properties of cyanide bridged 2D coordination polymers [Mn(salen)]$_2$[Fe(CN)$_5$NO] and [Mn(salen)]$_2$[Ni(CN)$_4$]

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The synthesis, crystal structure and magnetic properties of cyanide bridged 2D coordination complexes [Mn(salen)]$_2$[Fe(CN)$_5$NO]$_1$ and [Mn(salen)]$_2$[Ni(CN)$_4$]$_2$ are reported. Complex 1 crystallizes in the orthorhombic space group Ccdd (a = 20.715 (4) Å, b = 20.718 (4) Å, c = 17.131 (3) Å, α = β = γ = 90°, Z = 8). Its structure displays an extended 2D neutral network formed by cyclic tetrameric [Mn-CN-Fe-CN-I]$_2$ units. Complex 2 also crystallizes in the orthorhombic space group Ccda (a = 20.390 (4) Å, b = 20.701 (4) Å, c = 16.779 (3) Å, α = β = γ = 90°, Z = 8) and shows an extended 2D neutral network formed by cyclic tetrameric [Mn-CN-Ni-CN-I]$_2$ units. The variable temperature magnetic susceptibility studies for both the complexes have been carried out in the temperature range 2-300 K which shows very weak antiferromagnetic interaction mediated by diamagnetic [Fe(CN)$_5$NO]$_2^-$ and Ni(CN)$_4^{2-}$ ions.

Molecular precursors related to hexacyanometalates, e.g., [M(CN)$_6$]$_{3-}$ (n = 2 or 3; M = Fe, Cr, Co, V, Mn) and [M(CN)$_4$]$^{2-}$ (M = Ni, Pt, Cd, Zn, Cu) find wide applicability in designing extended structures$^1$-10. These provide a rich variety of molecular species with considerably different structural consequences, magnetic and magneto-optical properties. Two of the bridging ligands which fall in this family are nitroprusside, [Fe(CN)$_5$NO]$^{2-}$ and nickel tetracyanide, [Ni(CN)$_4$]$^{2-}$. The reaction between [Mn(SB)]$^{2+}$ (SB = substituted salen; salen = N,N'-ethylene bis(salicylideneaminato) diamion) and [Fe(CN)$_5$]$^{3-}$ has already led to a variety of extended structures$^{11,12}$. But the report for bimetallic complexes of [Fe(CN)$_5$NO]$^{2-}$ with cis-[Ni(en)]$^{2+}$ (en = ethane-1,2-diamine) and with [Mn$^{III}$(SB)]$^{2+}$ has been made only recently$^{13}$. Since the nature of the Schiff base can affect the steric accessibility of Mn and its coordination number, we have furthermore synthesized and characterized the bimetallic complexes of [Fe(CN)$_5$NO]$^{2-}$ and [Ni(CN)$_4$]$^{2-}$ ions with [Mn$^{II}$(salen)]$^{2+}$ [salen = N,N'-bis(salicylidene)ethane-1,2-diamine], where a 2D network comprising the bimetallic Mn$_2$Fe and Mn$_2$Ni neutral layers are formed.

The antiferromagnetic coupling between the paramagnetic transition metal ions is often operative via diamagnetic building blocks such as [Co(CN)$_6$]$^{3-}$, [Mo(CN)$_6$]$^{4-}$, [W(CN)$_6$]$^{4-}$, [Ni(CN)$_4$]$^{2-}$ and [Fe(CN)$_5$NO]$^{2-}$ (refs$^{13-16}$). It was found that diamagnetic [Fe(CN)$_5$NO]$^{2-}$ ions can transmit weak antiferromagnetic interactions in [Ni(en)]$_2$[Fe(CN)$_5$NO]$_1$.$^7$ In addition to giving rise to different architectures, [Ni(CN)$_4$]$^{2-}$ can also transmit both ferromagnetic and antiferromagnetic interactions. The magnetic study also gains momentum from the recent report$^{18}$ of an optically controllable spin gate based on an exchange interaction between molecular components and on an MLCT between Fe$^{II}$ and NO in Ni[Fe(CN)$_5$NO]$_2$.5.3H$_2$O. The magnetic measurements for both 1 and 2 have been carried out in the temperature range 2-300 K, suggesting a very weak antiferromagnetic interaction mediated by the diamagnetic [Fe(CN)$_5$NO]$^{2-}$ and [Ni(CN)$_4$]$^{2-}$ ions.

Materials and Methods

All the chemicals including manganese acetaete, methanol and acetoneitrile were of reagent grade. Sodium nitroprusside was purchased from Aldrich and used without further purification. Double distilled water was used throughout. The ligand salen$^{19}$ was synthesized according to the literature procedure and was checked by the elemental analysis and IR spec-
troscopy. [Mn(salen)OAc] was synthesized according to the reported method and was checked by the elemental analysis. K2[Ni(CN)4] was obtained as a by-product during the preparation of 1,4,8,11-tetrazacyclotetradecane (cyclam) ligand.

Physical measurements and X-ray crystallography

Microanalysis (CHN) was performed in a Perkin-Elmer 240C elemental analyzer. Magnetic susceptibility measurement was carried out with SQUID magnetometer down to 2 K. IR spectra were obtained on a Nicolet, MAGNA-IR 750 spectrometer with samples prepared as KBr pellets.

The X-ray diffraction measurements were carried out on a KUMA KM4CCD diffractometer for 1 and 2, all using a graphite monochromated Mo-Kα radiation. All data were corrected for Lorentz polarization effects. Absorption corrections based on least-squares fitting of |Fo - Fc| differences were also employed. The structure was solved by direct methods (SHELX 97) and refined by full-matrix least-squares based on F2 using SHELXL 97. Non-hydrogen atoms were refined with anisotropic thermal parameters, whereas the hydrogen atoms were included at calculated positions and refined isotropically. Information concerning crystallographic data collection and refinement of the structures for both 1 and 2 are given in Table 1.

Crystallographic data (excluding structural factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 212022 and 212023 for 1 and 2, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internet) + 44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk.

Synthesis of complexes

/Mn(salen)2[Fe(CN)2NO] (1) — To an aqueous solution (15 mL) of Na2[Fe(CN)2NO].2H2O (0.15 g, 0.5 mmol) was added very slowly a methanolic solution (30 mL) of [Mn(salen)OAc].H2O (0.4 g, 1 mmol) prepared as described in the literature. The dark brown solution was allowed to stand for 48 h in the dark. Brown-black crystals were formed by filtration and air-dried. Yield, 80%. IR (KBr) νC=N(imine) 1629, 1598 cm⁻¹; vC=N(cyanide) 2150 cm⁻¹; vN=O(nitrosyl) 1923 cm⁻¹. Anal. Calcd. for C37H28N10O5Mn2: C, 52.73; H, 3.32; N, 16.62%. Found. C, 52.54; H, 3.40; N, 16.35%. Suitable single crystals for X-ray diffraction were obtained on standing of the filtrate for another 24 h in the dark.

/Mn(salen)2[Ni(CN)4] (2) — To an aqueous solution (20 mL) of K2[Ni(CN)4] (0.12 g, 0.5 mmol) in a 100 cm³ beaker was added a methanolic solution (40 mL) of [Mn(salen)OAc].H2O (0.4 g, 1 mmol). The brown black microcrystalline product separated, was filtered and dried in air. IR (KBr) νC=N(imine) 1633, 1600 cm⁻¹; νC=N(cyanide) 2140 cm⁻¹. Anal. Calcd. for C36H36N8O5Mn2Ni: C, 52.5; H, 3.6; N, 13.6.

| Complex | | | | |
|---|---|---|---|
| Formula | C37H28N10O5FeMn2 | C36H36N8O5Mn2Ni |
| Formula weight | 888.20 | 807.23 |
| Crystal system | Orthorhombic | Orthorhombic |
| Space group | Ccca (No. 68) | Ccca (No. 68) |
| a/Å | 20.715(4) | 20.390(4) |
| b/Å | 20.718(4) | 20.701(4) |
| c/Å | 17.131(3) | 16.779(3) |
| V/Å³ | 7352.2(2) | 7082(2) |
| Z | 8 | 8 |
| μ(360-Kα)/mm⁻¹ | 1.122 | 1.280 |
| Crystal dimension/mm | 0.12×0.16×0.18 | 0.14×0.14×0.18 |
| T/K | 100 | 100 |
| λMo-Kα/Å | 0.71073 | 0.71073 |
| Dmin-Max/° | 6.2-28.5 | 3.3-28.5 |
| Tot., Uniq. Data, R(int) | 13790, 3984, 0.080 | 13763, 2177, 0.068 |
| Observed data [I>2.0σ(I)] | 2892 | 1904 |
| R, wR2, S | 0.1581, 0.3125, 1.30 | 0.1464, 0.3154, 1.16 |
Found. C, 52.6; H, 3.7; N, 13.7%. Single crystal suitable for X-ray diffraction was obtained by slow diffusion of an acetonitrile solution of [Mn(salen)OAc].H₂O to an aqueous solution of K₂Ni(CN)₄.

Results and Discussion

The title compounds 1 and 2 are very stable at an ambient temperature. These are insoluble in most of the common organic solvents and in water. All efforts to get good quality single crystals failed resulting in poor refinement of the structures. However, other evidences agree well with the structures of both the complexes. The formulations of the complexes were made on the basis of the elemental analysis. The IR spectra of both exhibit bands due to the C=N of the Schiff base ligand at 1629 and 1598 cm⁻¹ for 1 and at 1633 and 1600 cm⁻¹ for 2. Intense C≡N stretching bands are observed at 2150 and 2140 cm⁻¹ for 1 and 2 respectively. The absorption band due to NO for 1 is observed at 1923 cm⁻¹. These observations are consistent with other polymeric structures reported for nitroprusside³³.

The structure of complex 1 displays an extended two-dimensional neutral network formed by cyclic tetrameric [-Mn-NC-Fe-CN⁻]₄ units with Fe atoms at the corners and Mn atoms at the edge of a distorted square grid in the ab-plane (Fig. 1). The [Mn(salen)]⁺ cations are coordinated to two [Fe(CN)₃NO]²⁻ anions through the nitrogen atoms of two cyano groups in the axial positions, while [Fe(CN)₃NO]²⁻ anions are linked to four [Mn(salen)]⁺ cations through the four equatorial bridging CN⁻ ligands. The [Fe(CN)₃NO]²⁻ anion contains two pairs of symmetrically equivalent equatorial bridging CN ligands at Fe-C distances of 1.927(10) and 1.936(10). The NO group is perfectly located among the six possible coordinating positions and is oriented parallel to the e-axis. The Fe-N distance (1.663(17) Å) is much shorter than the other Fe-C distances which are between 1.927-1.936 Å. These values are in good agreement with other polymeric structures reported so far for nitroprusside³³.

The manganese site displays a distorted octahedral geometry owing to the strong Jahn-Teller effect as expected for a high spin d⁶ manganese(III) ion. The N₂O₂ donor atoms of the salen ligand coordinate to the equatorial positions of the Mn site. The Mn-O distances of the [Mn(salen)]⁺ cations are 1.875(9) and 1.885(9) Å while the Mn-N distances are 1.983(11) and 1.993(11) Å which are quite at par with reported values³³. Two equivalent N atoms from CN-bridging ligands of the nitroprusside coordinate axially to the Mn(III) center with distances 2.276(9) and 2.277(9) Å. The selected bond length and bond angles are shown in Table 2.

The structure of [Mn(5-Brsalen)][Fe(CN)₃NO] reported recently³³ comprises of an extended 2D neutral network through cyclic tetrameric [-Mn-NC-Fe-CN⁻]₄ units. The structure reported by us is comparable to it in that the Mn-Fe layers are neutral leading to a shorter interlayer distance.

Description of the structure of complex 2

Molecular view of the hetero-bimetallic assembly of 2 projected in the ab-plane is shown in Fig. 2. The bond distances and angles are reported in Table 3. As shown in the figure, the two dimensional network layered structure consists of cyclic tetrameric [-Mn-NC-Ni-CN⁻]₄ units with the Ni atoms located at the corner and Mn atoms at the edges of the nearly square grid in the ab plane. The [Mn(salen)]⁺ ions are linked to two [Ni(CN)₃]⁻² anions through the N atoms of two cyano groups in the axial positions. The [Ni(CN)₃]⁻² anions with the metal located on a symmetry plane are coordinated to four [Mn(salen)]⁺ cations through the four equatorial CN⁻ ligands. This is also supported by the IR stretching frequencies for C≡N which shows only a sharp signal at 2140 cm⁻¹. This is much higher than that for the free [Ni(CN)₃]⁻². The Ni-C distances in the bridge are not perfectly equivalent (Ni-C, 1.876(16) and 1.89(2) Å). The cyanide groups show different

Fig. 1—Molecular structure of [Mn(salen)][Fe(CN)₃NO] 1 projected in the ab-plane
Table 2 — Selected bond distances (Å) and bond angles (°) for complex 1

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<th>Bond lengths</th>
<th>Bond angles</th>
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<td>Fe1-N40</td>
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<td>O1-Mn1-N10</td>
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<tr>
<td>Mn1-N1</td>
<td>C20-Fe1-C20</td>
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<tr>
<td>Mn1-N10</td>
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</tbody>
</table>

Bond lengths

- Fe1-N40 = 1.663(17) Å
- Fe1-C10 = 1.936(10) Å
- Mn1-O1 = 1.875(9) Å
- Mn1-N1 = 1.983(11) Å
- Mn1-N10 = 2.276(9) Å

Bond angles

- N30-Fe1-C20 = 85.2(3)°
- O1-Mn1-N10 = 89.8(3)°
- O1-Mn1-O1_b = 95.4(4)°
- C20-Fe1-C20 = 170.4(4)°

Symmetry transformations used to generate equivalent atoms: b = x,-1/2-y,1/2-z; c = -x,y,1/2-z; e = 1/2-x,-y,z.

Table 3 — Selected bond distances (Å) and angles (°) for complex 2

<table>
<thead>
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<tr>
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<td>Mn1-N10</td>
</tr>
<tr>
<td>C10-Ni1-C20</td>
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</table>

Bond lengths

- Ni1-C10 = 1.89(2) Å
- Mn1-O1 = 1.892(12) Å
- Mn1-N1 = 1.982(17) Å
- Mn1-N10 = 2.255(15) Å
- C10-Ni1-C20 = 89.8(8)°

Bond angles

- C20-Ni1-C20 = 179.3(7)°
- N20-Mn2-N20_c = 171.9(6)°
- O2-Mn2-N2 = 92.3(6)°
- C10-N10-Mn1 = 167.4(13)°
- O2-Mn2-O2_c = 93.5(5)°
- O2_c-Mn2-N2 = 173.0(6)°
- C20-N20-Mn2 = 156.9(14)°

Symmetry transformations used to generate equivalent atoms: c = -x,y,1/2-z; e = 1/2-x,-y,z.

Fig. 2 — Molecular structure of [Mn(salen)]_4[Ni(CN)_4]_4, 2, projected in the ab-plane.

Geometries being more linearly coordinated in the basal plane of manganese, but significantly bent at the apical positions of the distorted octahedral manganese environment [Mn-N=C bond angles are 167.4 (13)° and 156.9 (14)° respectively]. In the equatorial plane of [Mn(salen)]^2+ moiety, the Mn-O distances are 1.892 (12) and 1.90 (12) Å and those of Mn-N are 1.982 (17) and 1.963 (16) Å. The two N atoms of bridging cyanide group occupy the apical positions. The intrachain Ni-Ni (10.413(2) Å) and Mn-Mn (10.483(2) Å) distances are very large. The shortest through space Mn–Mn distances are 7.500(4) Å for 2.

Magnetic properties

In order to observe the magnetic properties of the samples, the magnetization studies were performed for both the compounds down to 2 K. Fig. 3 shows the variation of $\chi_M T$ and $\chi_M^{-1}$ with temperature for 1. In the temperature range 50-300 K the product $\chi_M T$ remains almost constant with the value 5.11-5.17 emu-mol⁻¹-K. The value of $\chi_M T$ is less than that of the expected value for two non-interacting Mn^3+ ions (6.0 emu-mol⁻¹-K considering $g = 2$ and $S = 2$) which might be due to the presence of small but magnetically significant amounts of diamagnetic impurities in our compounds. With the decrease in temperature below 50 K the value of $\chi_M T$ decreases systematically.
The variation of $\chi_T^M$ with $T$ exhibits almost linear temperature dependence throughout the whole temperature range and obeys Curie-Weiss law giving $C = 5.16$ and a very small value of Weiss constant $\theta = -0.75K$. The slight decrease of $\chi_T^M$ below 50 K and the negative Weiss constant $\theta$ suggest a very weak antiferromagnetic interaction between Mn(III) ions, if it exists mediated by the diamagnetic $[\text{Fe(CN)}_5\text{NO}]^{2-}$ ions.

Figure 4 shows the temperature variation of $\chi_T^M$ and $\chi_M$ for 2. The value of $\chi_T^M$ is observed around 5.31-5.81 emu-mol$^{-1}$K in the temperature range 30-300 K which is still less than that of the expected value for two isolated Mn$^{2+}$ ions. However, this value for $[\text{Mn(salen)}]_2[\text{Ni(CN)}_4]$ is quite larger than that of $[\text{Mn(salen)}]_2[\text{Fe(CN)}_5\text{NO}]$. The magnetic susceptibility above 30 K obeys Curie-Weiss law. A plot of $\chi_M^T$ vs. $T$ produce $C = 6.02$ and $\theta = -12.8 K$. The rather large negative Weiss constant suggests the stronger antiferromagnetic interaction than that of nitropside based complex.

From the crystal structure data, the shortest through space Mn–Mn distances are 7.467(3) Å and 7.500(4) Å for 1 and 2 respectively. These Mn–Mn distances are too large to contribute to the magnetic interaction of sizable strength through dipolar magnetic interactions. In such a case the superexchange pathway through the diamagnetic $[\text{Fe(CN)}_5\text{NO}]^{2-}/[\text{Ni(CN)}_4]^{2-}$ takes the leading role to contribute to the magnetic interaction. The Mn–Mn distances through the diamagnetic $[\text{Fe(CN)}_5\text{NO}]^{2-}/[\text{Ni(CN)}_4]^{2-}$ anions are 10.561(2) Å and 10.483(2) Å for 1 and 2 respectively which are quite large and, therefore, the observed interaction is very weak. The rather strong exchange interaction for 2 may be attributed to the comparably shorter Mn-Mn distance than that of 1. A quantitative theoretical treatment of the magnetic data for both the complexes are not possible due to the complex nature of the interaction. The observed antiferromagnetic interaction mediated by the diamagnetic Ni(CN)$_2^-$ and [Fe(CN)$_5$NO]$^{2-}$ ions, however, is consistent with similar systems reported earlier.$^{20,32}$ The very weak magnetic interaction observed for 1 reminds us of the antiferromagnetic interaction mediated by the diamagnetic Ag$^{+}$ ion$^{26}$. The conclusion which can be drawn from this study is that these compounds do not fit very well with the purpose of investigating the interaction of paramagnetic ions through diamagnetic cyanide building blocks. This is due to their 2D structure. It would be better to use similar trimeric units of the type Mn-Ni-Mn or Mn-FeNO-Mn.

Acknowledgement

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References