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Article

Dinuclear Triple Helicates with Diazine Ligands: X-ray Structural, Electrochemical, and Magnetic Studies[†]

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A series of dinuclear complexes of Mn(III), Fe(III), and Co(III) with two diazine Schiff bases, H_2salhn and H_2mesalhn, is reported. The Schiff bases are prepared by condensation reactions of hydrazine with salicylaldehyde (H_2salhn) and with 2-hydroxyacetophenone (H_2mesalhn) in 1:2 mol ratio. X-ray crystallographic characterization reveals triple helical structures of [Co_2(salhn)$_3$], [Co_2(mesalhn)$_3$], and [Fe_2(mesalhn)$_3$]. In each complex, three dinucleating O,N,N,O donor ligands provide three diazine (═N–N═) bridges between the metal ions and facial O_3N_3 coordination spheres around them. The ligands are twisted about the N–N single bond and coordinate to the two metal ions in a helical fashion to generate the triple helical structure. The dicobalt(III) complex of mesalhn^{2-} is D_3-symmetric, while the diiron(III) analogue is very close to being of this symmetry. On the other hand, the dicobalt(III) complex of salhn^{2-} significantly deviates from the ideal D_3-symmetry due to the large range covered by the twist angles of the three ligands. In the crystal lattice of these complexes, intermolecular C–H•••O, C–H•••N, O–H•••O, C–H•••Cl, and π–π interactions involving the complex and the solvent molecules lead to one- and two-dimensional supramolecular structures. The complexes [Fe_2(mesalhn)$_3$] and [Co_2(mesalhn)$_3$] are redox active and display two successive metal-centered reductions on the cathodic side of Ag/AgCl reference electrode. Weak antiferromagnetic spin-coupling is operative between the two metal ions in [Mn_2(salhn)$_3$] ($J = -0.57(1)$ cm^{-1}) and in [Fe_2(mesalhn)$_3$] ($J = -2.82(4)$ cm^{-1}).

Introduction

The study of helical coordination complexes or helicates has become an area of intense research activity over the past decade.[1] The interest in such complexes is primarily due to their potential applications in enantioselective processes, designing optical devices and magnetic materials, probing DNA structures, and understanding helical self-organization processes operative in nature.[1,2] Design and synthesis of such helicates require ligands containing two or more metal chelating sites that are connected to each other by a spacer. If the coordination of metal ions to the chelating sites results in a twist along the spacer, a helical configuration of the ligand around the metal ions is produced. Metal ions that prefer tetrahedral coordination afford double helicates, and metal ions that prefer octahedral coordination afford triple helicates with such ligands possessing bidentate binding units.[3] Bis Schiff bases derived from hydrazine fall in this class of ligands, in which the two chelating sites are connected directly by a single bond. These easily prepared and inexpensive diazine ligands which provide the ═N−N═ fragment as the bridging unit between the two metal ions are extremely efficient in producing dinuclear metal-

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[†] Dedicated to Professor Animesh Chakravorty on the occasion of his 70th birthday.

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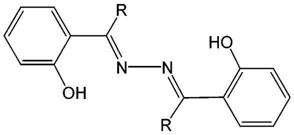
lohelicates due to the twisting along the N−N single bond. The neutral N_4-donor Schiff base *N*,*N*′-bis(picolinylidene)hydrazine was the very first ligand of this type used to synthesize dinuclear complexes of bivalent transition metal ions.[4] Triple helical structures were suggested for these cationic complexes. The X-ray structure of a dicobalt(II) complex with the Schiff base derived from 2-acetylpyridine and hydrazine was the first confirmation of the triple helicate motif in this type of complexes.[5] In recent times, a number of structurally characterized helical complexes have been reported with *N*,*N*′-bis(picolinylidene)hydrazine or its derivatives.[6] In contrast, there are very few reports on structurally characterized complexes with the very similar N_2O_2-donor Schiff base *N*,*N*′-bis(salicylidene)hydrazine (H_2salhn, two H's stand for the dissociable phenolic protons). The crystal structure of H_2salhn is known.[7] The compound is in the usual trans configuration with two intramolecular O−H···N hydrogen bonds. Two complexes, $[(CO)_2Rh(\mu\text{-salhn})Rh(CO)_2]$[8] and $[\{Co_3L(CH_3COO)(CH_3O)_3\}_2(\mu\text{-salhn})]$[9] ($H_3L$ is 2,6-bis-((salicylideneamino)methyl)-4-methylphenol), reported earlier contain salhn^{2-} as the bridging ligand. In both the complexes, the diazine fragment of salhn^{2-} is the only bridging unit between the two metal ions and it is in trans configuration as in the free Schiff base. Recently, we have reported a diruthenium(III) complex, $[Ru_2Cl_2(PPh_3)_2(\mu\text{-Cl})_2(\mu\text{-salhn})]$, where due to the additional two chloride bridges and the trans arrangement of the terminal chlorides the salhn^{2-} is in near cis configuration.[10] Before this diruthenium(III) complex, we reported a neutral diiron(III) complex of salhn^{2-}.[11] In $[Fe_2(\mu\text{-salhn})_3]$ (**1**), the three ligands provide the three diazine bridges between the metal ions and each of the three ligands is twisted along the N−N bond. This complex is the first example of a helical species prepared from H_2salhn. Recently the structures of **1** and an analogous complex with a substituted derivative of salhn^{2-} have been reported once again by another research group.[12]



H_2salhn (R = H)
H_2mesalhn (R = Me)

In this study, we have described a series of neutral dinuclear manganese(III), iron(III), and cobalt(III) complexes with the diazine Schiff bases H_2salhn and H_2mesalhn. The complexes, $[Mn_2(\mu\text{-salhn})_3]$ (**2**), $[Co_2(\mu\text{-salhn})_3]$ (**3**), $[Co_2(\mu\text{-mesalhn})_3]$ (**4**), and $[Fe_2(\mu\text{-mesalhn})_3]$ (**5**), have been characterized by analytical, spectroscopic, cryomagnetic, and electrochemical measurements. The X-ray structures are reported for the solvated crystals of **3**−**5**. As observed for **1**,[11] the two pseudooctahedral metal ions are bridged by three diazine (=N−N=) moieties from the three ligands and each ligand is twisted along the N−N single bond in these complexes. In the solid state, barring the molecules of **4** the molecules of the other two complexes (**3** and **5**) do not have the ideal D_3 symmetry.

Experimental Section

Materials. The Schiff bases H_2salhn and H_2mesalhn were prepared in ~95% yield by condensation reactions of 1 mol equiv of hydrazine and 2 mol equiv of salicylaldehyde or 2-hydroxyacetophenone in methanol.[11,13] All other chemicals and solvents used in this work were of analytical grade available commercially and were used without further purification.

Physical Measurements. Microanalytical (C, H, N) data were obtained with a Thermo Finnigon Flash EA1112 series elemental analyzer. Infrared spectra were collected by using KBr pellets on a Jasco-5300 FT-IR spectrophotometer. A Shimadzu 3101-PC UV/vis/NIR spectrophotometer was used to record the electronic spectra. The proton NMR spectrum was recorded with the help of a Bruker 400 MHz spectrometer. The EPR spectra were recorded on a JEOL JES-FA200 spectrometer. Solution electrical conductivities were measured with a Digisun DI-909 conductivity meter. A CH-Instruments model 620A electrochemical analyzer was used for cyclic voltammetric experiments with dimethylformamide solutions of **2** and **3** and dichloromethane solutions of **4** and **5** containing tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The three-electrode measurements were carried out at 298 K under a dinitrogen atmosphere with a platinum disk working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode. Under identical conditions the $E_{1/2}$ $(=(E_{pa} + E_{pc})/2)$ and the ΔE_p $(=E_{pa} - E_{pc})$ values of the Fc^+/Fc (Fc, ferrocene) couple were 0.57 and 140 mV, respectively. The potentials reported in this work are uncorrected for junction contributions. The variable-temperature (18−300 K) magnetic susceptibility measurements with powdered samples were performed using the Faraday technique with a setup comprising a George Associates Lewis coil force magnetometer, a CAHN microbalance, and an Air Products cryostat. $Hg[Co(NCS)_4]$ was used as the standard. Diamagnetic corrections

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calculated from Pascal's constants[14] were used to obtain the molar paramagnetic susceptibilities.

Preparation of the Complexes. [$Mn_2(\mu$-salhn$)_3$] (2). To a suspension of H_2salhn (241 mg, 1 mmol) in methanol (20 mL) was added 112 mg (2 mmol) of KOH, and the mixture was stirred at room temperature until a clear yellow solution was obtained. To this clear solution was added 235 mg (0.67 mmol) of [Mn(acac)$_3$] and stirred at room temperature in air for 4 h. The brown solid separated was collected by filtration, washed with methanol, and dried in air. Yield: 110 mg (40%). Anal. Calcd for $Mn_2C_{42}H_{30}N_6O_6$: C, 61.17; H, 3.67; N, 10.19. Found: C, 61.15; H, 3.83; N, 9.96. Selected IR bands (cm^{-1}): 1601 (vs), 1576 (s), 1526 (s), 1468 (s), 1439 (s), 1373 (w), 1281 (m), 1192 (s), 1148 (s), 1015 (w), 976 (w), 926 (w), 903 (m), 756 (s), 685 (w), 579 (m), 457 (m), 419 (w). Electronic spectral data in $(CH_3)_2NCHO$ (λ, nm (ϵ, M^{-1} cm^{-1})): 420 (10 600)^{sh}, 370 (31 000)^{sh}, 356 (34 700), 295 (38 600).

[$Co_2(\mu$-salhn$)_3$] (3). To a 5:1 mixture of methanol and dichloromethane (30 mL) were added 241 mg (1 mmol) of H_2salhn and 112 mg (2 mmol) of KOH, and the mixture was stirred at room temperature until a clear yellow solution was obtained. To this solution was added 159 mg (0.67 mmol) of $CoCl_2{\cdot}6H_2O$, and the new solution was stirred at room temperature in air for 6 h. The complex precipitated as a brown solid was collected by filtration, washed with methanol, and dried in air. Yield: 175 mg (63%). Anal. Calcd for $Co_2C_{42}H_{30}N_6O_6$: C, 60.59; H, 3.63; N, 10.09. Found: C, 60.21; H, 3.42; N, 9.78. Selected IR bands (cm^{-1}): 1608 (vs), 1570 (s), 1539 (s), 1470 (s), 1445 (s), 1370 (w), 1279 (s), 1190 (s), 1150 (s), 1036 (m), 961 (m), 897 (m), 860 (m), 754 (s), 685 (m), 584 (s), 486 (m), 449 (s), 415 (w). Electronic spectral data in $(CH_3)_2NCHO$ (λ, nm (ϵ, M^{-1} cm^{-1})): 457, 420^{sh}, 331, 300.

[$Co_2(\mu$-mesalhn$)_3$] (4). H_2mesalhn (268 mg, 1 mmol) and KOH (112 mg, 2 mmol) were taken in 30 mL of methanol and stirred at room temperature. When a clear yellow solution was obtained, solid $CoCl_2{\cdot}6H_2O$ (159 mg, 0.67 mmol) was added and stirred again in air at room temperature for 4 h. The complex was precipitated as a dark brown solid. It was collected by filtration, washed with cold methanol, and dried in air. Yield: 220 mg (72%). Anal. Calcd for $Co_2C_{48}H_{42}N_6O_6$: C, 62.89; H, 4.62; N, 9.17. Found: C, 62.72; H, 4.45; N, 8.91. Selected IR bands (cm^{-1}): 1595 (s), 1560 (s), 1522 (s), 1437 (s), 1335 (s), 1240 (s), 1140 (m), 1020 (m), 937 (m), 862 (s), 754 (s), 621 (w), 577 (m), 521 (w), 446 (m), 415 (w). Electronic spectral data in CH_2Cl_2 (λ, nm (ϵ, M^{-1} cm^{-1})): 450 (14 900), 370 (15 500)^{sh}, 290 (54 000)^{sh}, 265 (83 400).

[$Fe_2(\mu$-mesalhn$)_3$] (5). H_2mesalhn (100 mg, 0.37 mmol) and $N(C_2H_5)_3$ (0.12 mL, 87 mg, 0.86 mmol) were taken in 10 mL of CH_3CN, and the solution was refluxed for 10 min. To the resulting clear yellow solution was added 50 mg (0.31 mmol) of $FeCl_3$, and the mixture was refluxed for another 15 min. It was then cooled to room temperature and stirred in air for 1 h. The complex separated as a brown crystalline material was collected by filtration, washed with cold methanol, and dried in air. Yield: 75 mg (67%). Anal. Calcd for $Fe_2C_{48}H_{42}N_6O_6$: C, 63.31; H, 4.65; N, 9.23. Found: C, 63.14; H, 4.55; N, 9.11. Selected IR bands (cm^{-1}): 1595 (s), 1564 (s), 1530 (s), 1437 (s), 1327 (s), 1240 (s), 1149 (w), 977 (w), 1034 (m), 916 (m), 860 (m), 756 (s), 611 (m), 527 (w), 497 (w), 422 (w). Electronic spectral data in CH_2Cl_2 (λ, nm (ϵ, M^{-1} cm^{-1})): 515 (5800)^{sh}, 440 (7700)^{sh}, 348 (27 500)^{sh}, 274 (41 300).

X-ray Crystallography. Single crystals of **3** were grown by slow evaporation of a dimethylformamide−acetonitrile (1:1) solution. On the other hand, single crystals of both **4** and **5** were obtained by slow evaporation of dichloromethane−acetonitrile (1:1) solutions of the complexes. The complex **3** crystallizes as **3**$\cdot 2(CH_3)_2NCHO{\cdot}H_2O$ in the $P\bar{1}$ space group, whereas **4** and **5** crystallize as **4**$\cdot 2H_2O$ and **5**$\cdot 2CH_2Cl_2$ in the space groups $R\bar{3}$ and $P\bar{1}$, respectively. Unit cell parameters and the intensity data for **3**$\cdot 2(CH_3)_2NCHO{\cdot}H_2O$ and **5**$\cdot 2CH_2Cl_2$ were obtained on a Bruker-Nonius SMART APEX CCD single-crystal diffractometer, equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube (λ = 0.710 73 Å) operated at 2.0 kW. The detector was placed at a distance of 6.0 cm from the crystal. Data were collected at 298 K with a scan width of 0.3° in ω and an exposure time of 30 s/frame. The SMART software was used for data acquisition, and the SAINT-Plus software was used for data extraction.[15] In each case, an absorption correction was performed with the help of SADABS program.[16] Unit cell parameters for **4**$\cdot 2H_2O$ were determined by the least-squares fit of 25 reflections having 2θ values in the range 18−21° on an Enraf-Nonius Mach-3 single-crystal diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The data were collected by the ω-scan method. The stability of the crystal was monitored by measuring the intensities of three check reflections after every 1.5 h during the data collection. No decay was observed during the 110 h exposure to X-ray. The ψ-scans[17] of 4 reflections having θ and χ values within 4−13 and 82−87°, respectively, were used for an empirical absorption correction. The programs of the WinGX package[18] were used for data reduction and absorption correction. In each case, the structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model but not refined. The SHELX-97 programs[19] were used for structure solution and refinement. The ORTEX6a[20] and Platon[21] packages were used for molecular graphics. Significant crystallographic data for **3**$\cdot 2(CH_3)_2NCHO{\cdot}H_2O$, **4**$\cdot 2H_2O$, and **5**$\cdot 2CH_2Cl_2$ are summarized in Table 1.

Results and Discussion

Synthesis and Properties. The complexes have been synthesized in moderate to good yields by reacting the metal ion starting material, the corresponding Schiff base, and the base (KOH or $N(C_2H_5)_3$) in ∼2:3:6 mole ratio. The elemental analysis data are satisfactory with the general molecular formula [M_2(salhn)$_3$] (M = Mn (**2**), Co (**3**)) and [M_2(mesalhn)$_3$] (M = Co (**4**), Fe(**5**)). The trivalent metal ion starting materials, [Mn(acac)$_3$] and $FeCl_3$, have been used for the synthesis of **2** and **5**, respectively. On the other hand, for the synthesis of **3** and **4** cobaltous chloride has been used as the starting material. As the reactions were performed under aerobic condition, the oxygen in air is the likely oxidizing agent during the synthesis of the two dicobalt(III)

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Table 1. Crystallographic Data for **3**·$2(CH_3)_2NCHO·H_2O$, **4**·$2H_2O$, and **5**·$2CH_2Cl_2$

param	**3**·$2(CH_3)_2NCHO·H_2O$	**4**·$2H_2O$	**5**·$2CH_2Cl_2$
formula	$Co_2C_{48}H_{46}N_8O_9$	$Co_2C_{48}H_{46}N_6O_8$	$Fe_2Cl_4C_{50}H_{46}N_6O_6$
fw	996.79	952.77	1080.43
cryst syst	triclinic	trigonal	triclinic
space group	$P\bar{1}$	$R\bar{3}$	$P\bar{1}$
a, Å	12.5167(8)	14.282(2)	11.931(3)
b, Å	14.8098(9)	14.282(2)	13.555(4)
c, Å	15.1124(9)	37.451(6)	15.319(4)
α, deg	62.845(1)	90	82.267(5)
β, deg	66.846(1)	90	88.161(4)
γ, deg	65.940(1)	120	76.548(4)
V, Å^3	2200.8(2)	6616(2)	2387.6(11)
Z	2	6	2
μ, mm^{-1}	0.822	0.814	0.889
reflcns collcd	18 608	10 507	25 088
unique reflcns	7991	3379	9506
reflcns $I \geq 2\sigma(I)$	4560	1351	4826
params	608	195	619
R1[a] $[I \geq 2\sigma(I)]$	0.0510	0.0840	0.0786
wR2[b] $[I \geq 2\sigma(I)]$	0.1029	0.1834	0.1454
GOF[c] on F^2	0.867	0.981	0.990

[a] $R1 = \Sigma(||F_o|| - ||F_c||)/\Sigma|F_o|$. [b] $wR2 = [\Sigma(w(|F_o|^2 - |F_c|^2)^2)/\Sigma(w|F_o|^2)]^{1/2}$. [c] $GOF = [\Sigma w(|F_o|^2 - |F_c|^2)^2]/(n - p)^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

complexes. Despite our several attempts we could not prepare $[Mn_2(mesalhn)_3]$. Both **4** and **5** are soluble in less polar solvents such as dichloromethane and chloroform. However, **2** and **3** are insoluble in nature. They are sparingly soluble in dimethylformamide and dimethyl sulfoxide only. In these solvents, the solubility of the former is slightly better than that of the latter. All the complexes are electrically nonconducting in solutions. As expected the dicobalt(III) complexes **3** and **4** are diamagnetic. On the other hand, the dimanganese(III) complex (**2**) and the diiron(III) complex (**5**) are paramagnetic.

Spectral Properties. In the infrared spectrum, none of the complexes displays the free Schiff base phenolic OH stretch. Thus, the ligands are dianionic in each complex. This observation together with the elemental analysis data and the electrically nonconducting nature of the complexes suggest the +3 oxidation state of the metal ions in these complexes. The intense band observed in the range 1608−1595 cm^{-1} is assigned to the C=N stretch. The C=N stretches for H_2salhn and H_2mesalhn appear at 1624 and 1622 cm^{-1}, respectively.[11,13c] Thus, there is a substantial low-energy shift of the C=N stretch due to metal coordination. The infrared spectra of the complexes of salhn^{2-} (**1**,[11] **2**, and **3**) are essentially identical except for small shifts of frequencies. The similarities in the IR spectra indicate that molecular structures of **2** and **3** are very similar to that of **1**.[11] There is a similar 1:1 correlation in the infrared spectra of the complexes of mesalhn^{2-} (**4** and **5**) suggesting similar molecular structures of both complexes. The X-ray structural studies (vide infra) confirm the above observations.

The electronic spectra of the complexes display multiple bands in the range 515−350 nm due to ligand-to-metal charge-transfer transitions.[11] The intense bands observed below 350 nm are likely to be due to intraligand transitions.

Although both the dicobalt(III) complexes **3** and **4** are diamagnetic, we could not record the proton NMR spectrum of **3** due to its very poor solubility. The proton NMR spectrum of **4** in $CDCl_3$ displays a singlet at δ 2.05 due to the methyl group protons. The appearance of a solitary signal for the methyl group protons suggests that not only all the three ligands but both halves of each mesalhn^{2-} in $[Co_2(mesalhn)_3]$ are magnetically equivalent at least on the NMR time scale. The aromatic protons appear as two multiplets centered at δ ~6.48 and ~7.16.

The EPR-silent nature of the dimanganese(III) complex (**2**) is consistent with the d^4 configuration of the metal ions in this complex. In principle, the diiron(III) complex (**5**) can have spin states 5, 4, 3, 2, 1, and 0. Except for the lowest energy singlet state, the other states can give rise to EPR signals. As observed for **1**[11] the room temperature powder EPR spectrum of **5** displays a broad signal at $g \sim 2$. Cooling to low temperature (120 K) causes the sharpening of this signal.

Description of Molecular Structures. The molecular structures of **3**−**5** are shown in Figures 1−3. The bond parameters associated with the metal ions are listed in Tables 2−4. In all the complexes, each of the three ligands coordinates the two metal ions via the two phenolate-O and the two imine-N atoms. Thus, the metal ions are in facial O_3N_3 coordination spheres and connected by three diaza (=N−N=) bridges. The Co···Co distances in **3** and **4** are 3.4301(7) and 3.4814(22) Å, respectively. In comparison the Fe···Fe distance in **5** is significantly longer (3.8541(13) Å). The M−O(phenolate) and M−N(imine) bond lengths (Tables 2−4) in the dicobalt complexes (**3** and **4**) as well as in the diiron complex (**5**) are consistent with the +3 oxidation state of the metal ions.[9,11,12,22] In each complex, the ligands are twisted along the N−N single bonds to accommodate the two metal ions. As a result the triple helical structure is generated. Both the complexes of salhn^{2-} (**1** and **3**) crystallize in the space group $P\bar{1}$, and the asymmetric unit contains one full complex molecule in each case. The extent of twisting is very different for the three ligands in both **1** and **3** (Figure

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(22) (a) Ready, J. M.; Jacobson, E. N. *J. Am. Chem. Soc.* **1999**, *121*, 6086. (b) Reos, R. D.; Nardin, G.; Randacciu, L.; Tayzher, G.; Vrdoijak, V. *Inorg. Chim. Acta* **2003**, *349*, 249.

Table 2. Selected Bond Distances (Å) and Angles (°) for **3**$\cdot$2$(CH_3)_2NCHO\cdot H_2O$

Co(1)−O(1)	1.903(2)	Co(2)−O(2)	1.903(2)
Co(1)−O(3)	1.885(2)	Co(2)−O(4)	1.881(2)
Co(1)−O(5)	1.883(3)	Co(2)−O(6)	1.874(3)
Co(1)−N(1)	1.922(3)	Co(2)−N(2)	1.913(3)
Co(1)−N(3)	1.911(3)	Co(2)−N(4)	1.917(2)
Co(1)−N(5)	1.914(3)	Co(2)−N(6)	1.925(3)
O(1)−Co(1)−O(3)	87.84(10)	O(2)−Co(2)−O(4)	88.74(10)
O(1)−Co(1)−O(5)	89.07(11)	O(2)−Co(2)−O(6)	88.61(11)
O(1)−Co(1)−N(1)	92.15(10)	O(2)−Co(2)−N(2)	92.56(10)
O(1)−Co(1)−N(3)	88.97(11)	O(2)−Co(2)−N(4)	176.20(11)
O(1)−Co(1)−N(5)	176.31(11)	O(2)−Co(2)−N(6)	87.93(11)
O(3)−Co(1)−O(5)	86.77(11)	O(4)−Co(2)−O(6)	86.75(11)
O(3)−Co(1)−N(1)	174.73(12)	O(4)−Co(2)−N(2)	88.19(12)
O(3)−Co(1)−N(3)	93.49(11)	O(4)−Co(2)−N(4)	92.67(11)
O(3)−Co(1)−N(5)	89.04(11)	O(4)−Co(2)−N(6)	176.58(10)
O(5)−Co(1)−N(1)	87.97(11)	O(6)−Co(2)−N(2)	174.78(12)
O(5)−Co(1)−N(3)	178.00(11)	O(6)−Co(2)−N(4)	87.95(11)
O(5)−Co(1)−N(5)	92.72(11)	O(6)−Co(2)−N(6)	93.92(12)
N(1)−Co(1)−N(3)	91.78(12)	N(2)−Co(2)−N(4)	91.02(11)
N(1)−Co(1)−N(5)	91.14(11)	N(2)−Co(2)−N(6)	91.21(12)
N(3)−Co(1)−N(5)	89.27(12)	N(4)−Co(2)−N(6)	90.70(11)

Table 3. Selected Bond Distances (Å) and Angles (°) for **4**$\cdot$2H_2O[a]

Co(1)−O(1)	1.870(4)	Co(2)−O(2)	1.867(5)
Co(1)−N(1)	1.942(5)	Co(2)−N(2)	1.924(5)
O(1)−Co(1)−N(1)	92.7(2)	O(2)−Co(2)−N(2)	92.8(2)
O(1)−Co(1)−O(1A)	87.4(2)	O(2)−Co(2)−O(2A)	87.7(2)
O(1)−Co(1)−N(1A)	90.4(2)	O(2)−Co(2)−N(2A)	177.0(2)
O(1)−Co(1)−N(1B)	177.8(2)	O(2)−Co(2)−N(2B)	89.3(2)
N(1)−Co(1)−N(1B)	89.5(2)	N(2)−Co(2)−N(2B)	90.2(2)

[a] Symmetry transformations: A = $-x + y + 1, -x + 1, z$; B = $-y + 1, x - y, z$.

Table 4. Selected Bond Distances (Å) and Angles (°) for **5**$\cdot$2CH_2Cl_2

Fe(1)−O(1)	1.880(4)	Fe(2)−O(2)	1.896(4)
Fe(1)−O(3)	1.901(4)	Fe(2)−O(4)	1.887(4)
Fe(1)−O(5)	1.895(4)	Fe(2)−O(6)	1.896(4)
Fe(1)−N(1)	2.200(4)	Fe(2)−N(2)	2.178(4)
Fe(1)−N(3)	2.205(4)	Fe(2)−N(4)	2.196(4)
Fe(1)−N(5)	2.201(4)	Fe(2)−N(6)	2.204(4)
O(1)−Fe(1)−O(3)	98.88(16)	O(2)−Fe(2)−O(4)	97.51(17)
O(1)−Fe(1)−O(5)	94.72(16)	O(2)−Fe(2)−O(6)	98.70(16)
O(1)−Fe(1)−N(1)	83.53(15)	O(2)−Fe(2)−N(2)	84.38(16)
O(1)−Fe(1)−N(3)	94.66(16)	O(2)−Fe(2)−N(4)	170.10(16)
O(1)−Fe(1)−N(5)	170.11(15)	O(2)−Fe(2)−N(6)	91.51(16)
O(3)−Fe(1)−O(5)	98.46(16)	O(4)−Fe(2)−O(6)	97.23(18)
O(3)−Fe(1)−N(1)	168.52(16)	O(4)−Fe(2)−N(2)	91.60(17)
O(3)−Fe(1)−N(3)	83.79(16)	O(4)−Fe(2)−N(4)	83.91(17)
O(3)−Fe(1)−N(5)	91.00(16)	O(4)−Fe(2)−N(6)	170.79(17)
O(5)−Fe(1)−N(1)	92.50(16)	O(6)−Fe(2)−N(2)	170.16(16)
O(5)−Fe(1)−N(3)	169.90(15)	O(6)−Fe(2)−N(4)	90.81(16)
O(5)−Fe(1)−N(5)	83.67(16)	O(6)−Fe(2)−N(6)	83.21(17)
N(1)−Fe(1)−N(3)	84.83(15)	N(2)−Fe(2)−N(4)	85.78(15)
N(1)−Fe(1)−N(5)	86.79(15)	N(2)−Fe(2)−N(6)	87.39(16)
N(3)−Fe(1)−N(5)	86.45(15)	N(4)−Fe(2)−N(6)	86.88(15)

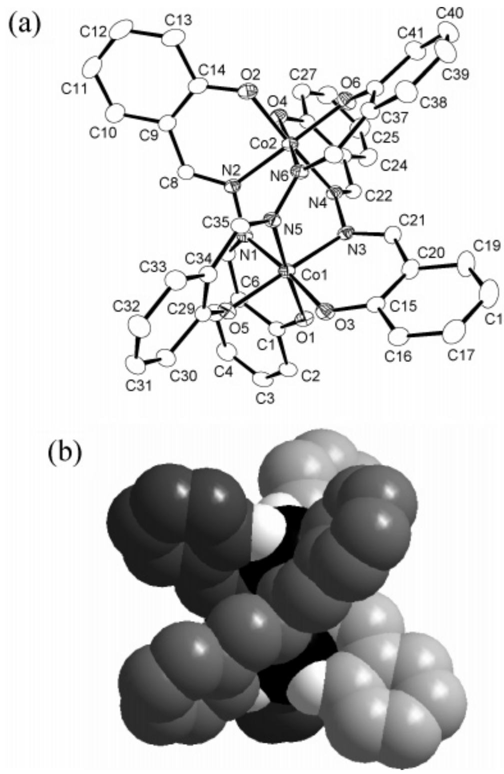

Figure 1. Molecular structure of $[Co_2(salhn)_3]$. Hydrogen atoms are omitted for clarity. (a) ORTEP diagram with the atom-labeling scheme. All atoms are represented by their 25% probability thermal ellipsoids. (b) Space-filling representation of the triple helical structure.

1). In **1**, the dihedral angles between the two salicylaldimine moieties of the three ligands are in the range 26.6−56.8°.[11] These dihedral angles are 31.78(12), 39.49(7), and 59.41(10)° in **3**. Thus, although the three bridging $salhn^{2-}$ in **1** and **3** are C_2-symmetric, they are not identical; hence, $[M_2(\mu\text{-salhn})_3]$ (M = Fe(III) and Co(III)) does not possess the ideal D_3 symmetry expected for a perfect triple helicate. In contrast, **4** crystallizes in the trigonal space group $R\bar{3}$ and the crystallographic 3-fold axis coincides with the molecular 3-fold axis that passes through the two metal ions. Consequently, both the metal centers have 1/3 occupancy and only one of the three ligands is present in the asymmetric unit. The dihedral angle between the two chelating fragments of $mesalhn^{2-}$ is 47.70(13)°. Thus, the extent of the helical twist along the N−N single bond is identical for all the three $mesalhn^{2-}$ in **4** and the molecules have the idealized D_3 symmetry (Figure 2). On the other hand, the diiron(III) complex of $mesalhn^{2-}$ (**5**) crystallizes in the space group $P\bar{1}$ and the asymmetric unit contains one complete molecule of the complex. As observed for **1** and **3** the extent of helical twist of the three ligands along the N−N single bond is different. However, here the dihedral angles (59.88(11), 64.02(10), and 66.49(12)°) between the two chelating fragments of the three $mesalhn^{2-}$ span significantly smaller range than those observed for **1** and **3**. Thus, the molecules of **5** are much closer to the ideal D_3 symmetry (Figure 3) compared to the molecules of **1** and **3**. Interestingly the dihedral angles indicate that the helical twist of $mesalhn^{2-}$ in **4** is significantly smaller than the average helical twist of $mesalhn^{2-}$ in **5**. As a consequence the Fe···Fe distance in **5** is longer by ~0.4 Å than the Co···Co distance in **4**.

Intermolecular Interactions. In the crystal lattice of **3**$\cdot$2$(CH_3)_2NCHO\cdot H_2O$, the $(CH_3)_2NCHO$ molecules exist as dimers via C−H···O and C−H···N interactions involving the O- and the N-atoms of the amide group and the C−H fragments of two methyl groups in a reciprocal fashion with respect to the hydrogen bond donors and acceptors (see Supporting Information, Figure S1).[23] The C···O and C···N

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[23] Desiraju, G. R.; Steiner, T. In *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, U.K., 1999.

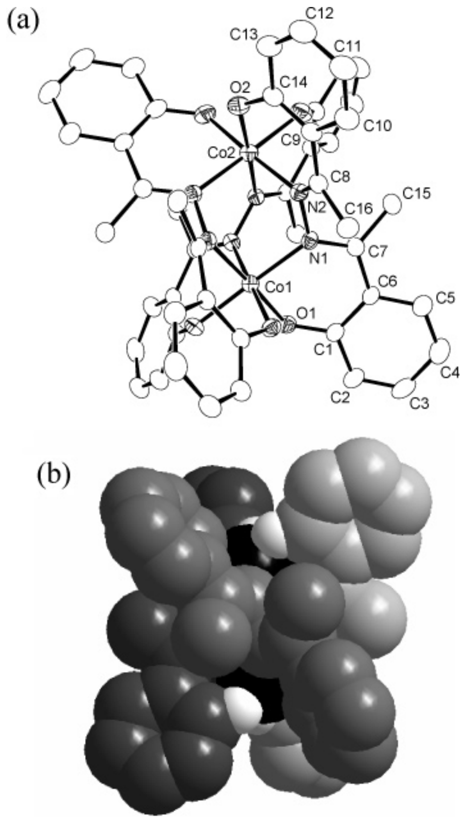


Figure 2. Molecular structure of $[Co_2(mesalhn)_3]$. Hydrogen atoms are omitted for clarity. (a) ORTEP diagram with the atom-labeling scheme. All atoms are represented by their 20% probability thermal ellipsoids. (b) Space-filling representation of the triple helical structure.

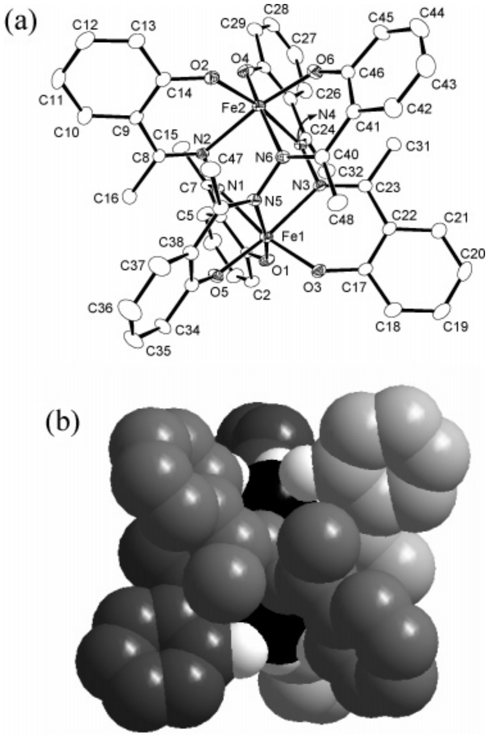


Figure 3. Molecular structure of $[Fe_2(mesalhn)_3]$. Hydrogen atoms are omitted for clarity. (a) ORTEP diagram with the atom-labeling scheme. All atoms are represented by their 20% probability thermal ellipsoids. (b) Space-filling representation of the triple helical structure.

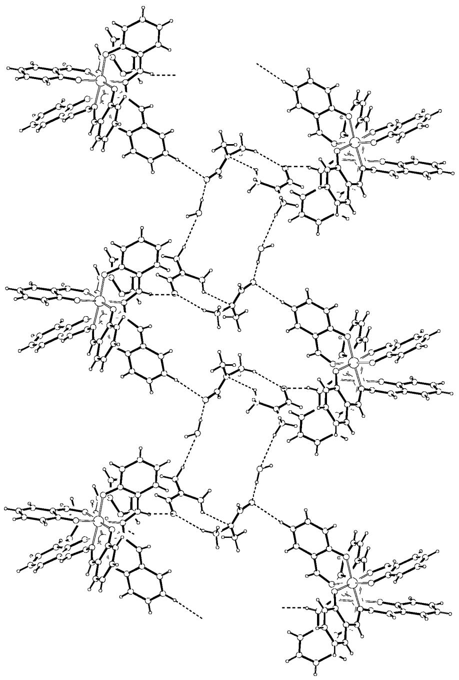
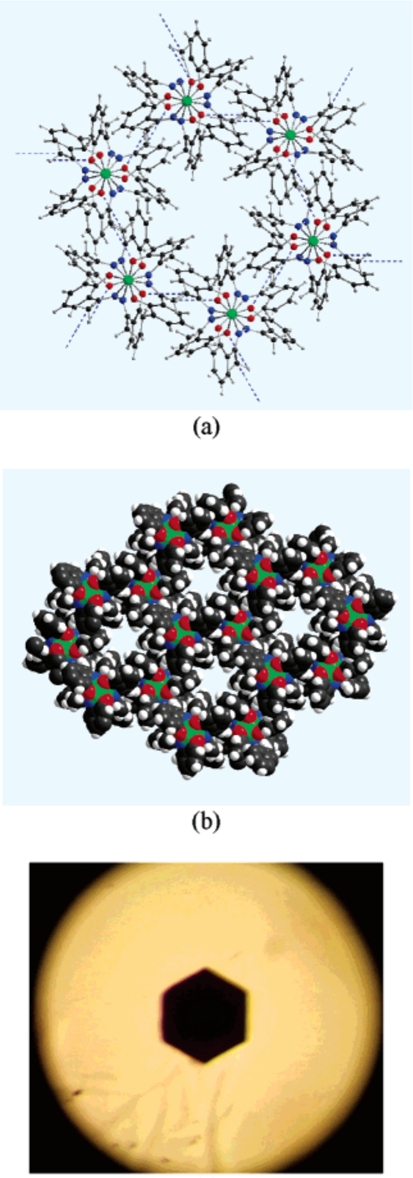


Figure 4. One-dimensional arrangement of $[Co_2(salhn)_3]\cdot 2(CH_3)_2NCHO\cdot H_2O$.

distances are 3.408(14) and 3.344(13) Å, respectively. The C−H···O and C−H···N angles are 164 and 152°, respectively. The water molecule is also involved in two hydrogen-bonding interactions (O−H···O and C−H···O) as donor as well as acceptor with two $(CH_3)_2NCHO$ molecules (Figure S1). The O···O and C···O distances are 2.679(10) and 3.573(11) Å, respectively. The O−H···O and C−H···O angles are 160 and 171°, respectively. The interactions involving the water molecule are roughly orthogonal to the interactions between the two $(CH_3)_2NCHO$ molecules. Consequently, two dimers of $(CH_3)_2NCHO$ are bridged by two water molecules and a rectangular structure is formed (Figure S1). These rectangular motifs are bridged by the dinuclear helicates due to two more C−H···O interactions involving the O-atoms of the $(CH_3)_2NCHO$ molecules and the C−H fragments from azomethine (−CH=N−) group (C···O, 3.177(16) Å; C−H···O, 162°) and benzene ring (C···O, 3.438(11) Å; C−H···O, 157°). Self-organization via all these noncovalent intermolecular interactions led to a one-dimensional supramolecular structure of the **3**$\cdot 2(CH_3)_2NCHO\cdot H_2O$ units in the crystal lattice (Figure 4).

Unlike **3**$\cdot 2(CH_3)_2NCHO\cdot H_2O$, the crystal packing of **4**$\cdot 2H_2O$ is apparently not directed by the trapped solvent molecules. Both the water molecules are disordered with 1/3 site occupancy on the special positions. One of the O-atoms is on the same 3-fold axis that passes through the two Co centers and is very close to its symmetry equivalent. The O···O distance in this water dimer is 2.51 Å. The nearest (3.32 Å) H-atom to this O-atom is from a benzene ring (C2−H) of the ligand. On the other hand, the other O-atom is located on the 3-fold axis that passes through the center of the hexagon formed by the complex molecules. In this case also the nearest (3.44 Å) H-atom belongs to the same benzene ring (C4−H). The packing of the D_3-symmetric molecules of **4** is shown in Figure 5. The molecules are arranged



(a)

(b)

(c)

Figure 5. Projection of (a) hexagonal packing and (b) space-filling representation of the two-dimensional layered structure of [Co_2(mesalhn)$_3$] onto the *ab*-plane. (c) Hexagonal morphology of the single crystal of [Co_2(mesalhn)$_3$]·$2H_2O$.

hexagonally along the *c*-axis, which is also parallel to the Co···Co molecular axis. Each molecule is connected to its three neighbors via C−H···O interactions involving the hydrogen atom of a methyl group and one phenolate-O in a reciprocal fashion (Figure 5a). The C···O distance and the C−H···O angle are 3.467(9) Å and 161°, respectively. As a result, a two-dimensional layered structure parallel to the *ab*-plane is formed (Figure 5b). Interestingly, the morphology of the single crystals of **4**·$2H_2O$ is also perfectly hexagonal (Figure 5c).

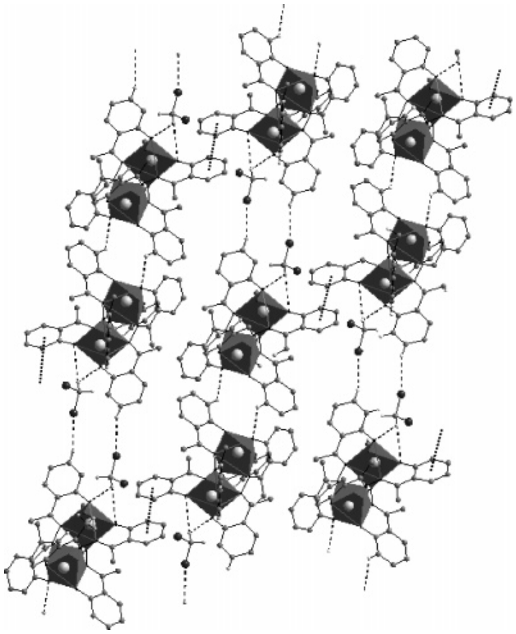


Figure 6. Two-dimensional network of [Fe_2(mesalhn)$_3$]·$2CH_2Cl_2$. For clarity one of the CH_2Cl_2 molecules that does not participate in the self-organization process is not shown.

The molecules of **5** form discrete dimers due to a pair of reciprocal C−H···O interactions involving a metal-coordinated phenolate-O and a benzene ring C−H group (Figure S2). The C···O distance and the C−H···O angle are 3.416(6) Å and 134°, respectively. One of the two CH_2Cl_2 molecules present in the asymmetric unit acts as donor in a bifurcated hydrogen bonding interaction involving two metal-coordinated phenolate-O atoms and as an acceptor in a C−H···Cl interaction involving a benzene ring C−H group.[23,24] The C···O distances and the C−H···O angles are 3.543(7) and 3.305(8) Å and 140 and 133°, respectively. The C···Cl distance and C−H···Cl angle are 3.655(7) Å and 157°, respectively. These weak interactions connect the C−H···O bridged dimers of **5** leading to a one-dimensional ordering of the **5**·CH_2Cl_2 units (Figure S3 and Figure 6). One of the benzene rings of each complex molecule in this chainlike structure is involved in $\pi-\pi$ interaction with the benzene ring of a molecule that belongs to the adjacent chain. The interplanar distance and the centroid-to-centroid distances are 3.410 and 3.646(4) Å, respectively. As the successive molecules in a particular chain are inverse symmetry related, these $\pi-\pi$ interactions alternate from one side to another side of each chain and a two-dimensional organization of the **5**·CH_2Cl_2 units is formed (Figure 6). The second CH_2Cl_2 molecule present in the asymmetric unit is connected to the complex molecule by a C−H···Cl interaction (C···Cl, 3.425(9) Å; C−H···Cl, 122°) involving a benzene ring C−H group. It does not participate in any other noncovalent interaction.

Electrochemical Properties. Electron-transfer characteristics of all the complexes have been investigated with the help of cyclic voltammetry. Due to solubility reasons the cyclic voltammograms of the dimanganese(III) and dicobalt(III) complexes (**2** and **3**) of salhn^{2-} were recorded using dimethylformamide solutions. None of the two complexes display any response within ±1.5 V (vs Ag/AgCl). In **2**, it is very likely that the +3 oxidation state of each metal ion is well-stabilized by the three salicylaldiminate ligands and hence reduction to +2 state is very difficult. Considering

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(24) Thallapally, P. K.; Nangia, A. *Cryst. Eng. Commun.* **2001**, *3*, 114.

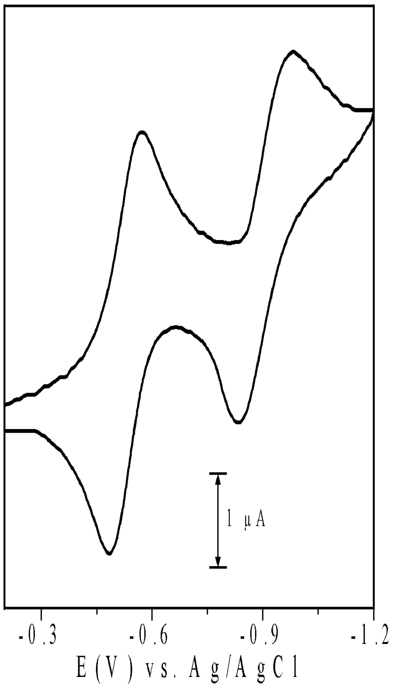

Figure 7. Cyclic voltammogram (scan rate 50 mV s^{-1}) of $[Fe_2(mesalhn)_3]$ in CH_2Cl_2 solution (0.1 M TBAP) at a platinum electrode at 298 K.

that **4** is redox active (vide infra), the absence of any response for **3** is unexpected. Possibly very low concentration of **3** due to its poor solubility is responsible for not observing any redox response in the cyclic voltammogram. However, it may be noted that the analogous diiron(III) complex (**1**) in dichloromethane displays two quasi-reversible metal-centered reduction responses at −0.52 and −0.80 V (vs SCE). As observed for **1**, the complexes of mesalhn^{2-} (**4** and **5**) in dichloromethane display two reductions on the cathodic side of the Ag/AgCl reference electrode. For the dicobalt(III) complex (**4**) both the responses are irreversible. The values of the cathodic peak potentials (E_{pc}) are −0.99 and −1.40 V. On the other hand, the responses observed for the diiron(III) complex (**5**) are reversible (Figure 7). The $E_{1/2}$ values are −0.54 and −0.98 V. The corresponding ΔE_p values are 70 and 80 mV, respectively. The one electron stoichiometry of these responses has been confirmed by comparing the current heights with known one-electron redox processes under identical conditions.[10,11] The first response is assigned to the M^{III}_2 to $M^{III}M^{II}$ reduction, and the second response is assigned to the $M^{III}M^{II}$ to M^{II}_2 reduction process. The potentials of **4** are shifted by ~0.4 V to the cathodic side compared to the potentials of **5**. This shift is most likely due to the larger ligand field stablilization in the low-spin dicobalt(III) complex (**4**) than that in the high-spin diiron(III) complex (**5**).

For a weakly coupled (vide infra) dinuclear complex the difference in the metal-centered redox potentials can be calculated with the help of an electrostatic model.[25] The $\Delta E_{1/2}$ values calculated for the diiron(III) complexes **1** and **5** by using the electrostatic equation $\Delta E_{1/2} = q^2/4\pi\epsilon_0 Dr$ (r is the distance between the metal centers obtained in the X-ray structures) and assuming a continuous dielectric with a dielectric constant equal to that of the solvent dichloromethane used for cyclic voltammetry are 0.40 and 0.41 V, respectively. The experimental $\Delta E_{1/2}$ values are 0.28[11] and 0.44 V for **1** and **5**, respectively. The $\Delta E_{1/2}$ value (0.45 V) calculated for **4** is very close to the difference (0.41 V) in the two cathodic peak potentials (E_{pc}) observed in its cyclic voltammogram. Thus, for $[Fe_2(salhn)_3]$ (**1**) the magnitude of the dielectric constant in the intermetallic space is higher than that of the solvent. On the other hand, for the complexes of mesalhn^{2-} (**4** and **5**) the dielectric medium in the region between the two metal centers is similar to that provided by the solvent around the complex molecules.

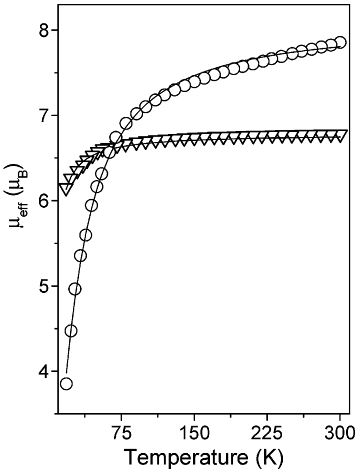

Figure 8. Temperature dependence of the effective magnetic moments of $[Mn_2(salhn)_3]$ (▽) and $[Fe_2(mesalhn)_3]$ (○). The continuous lines were generated from the best least-squares fit parameters given in the text.

Magnetic Properties. The magnetic susceptibilities of the dimanganese(III) and the diiron(III) complexes (**2** and **5**) were measured in the temperature range 18−300 K at a constant magnetic field of 5 kG with powdered samples of the complexes. For each complex the effective magnetic moment (μ_{eff}) decreases gradually with the decrease of temperature indicating antiferromagnetic interaction between the two metal ions (Figure 8). At 300 K the μ_{eff} value (6.78 μ_B) of **2** is very close to the spin-only moment (6.93 μ_B) of a dimer containing two metal ions with $S = 2$ spin states. The moment of **2** decreases to 6.15 μ_B at 18 K. In contrast, the change in the μ_{eff} value on cooling is more dramatic in the case of **5**. The μ_{eff} value (7.85 μ_B) at 300 K is slightly smaller than the spin-only moment (8.37 μ_B) expected for a diiron(III) complex where both the metal ions are high spin ($S = 5/2$). At 18 K the μ_{eff} value decreases to 3.85 μ_B. The data were fitted using the expressions for χ_M vs T derived from the isotropic spin-exchange Hamiltonian $H = -2JS_1 \cdot S_2$, where $S_1 = S_2 = 2$ (for **2**) and $S_1 = S_2 = 5/2$ (for **5**).[26] The best least-squares fits[27] were obtained with $J = -0.57(1)$ cm^{-1} and $g = 1.958(3)$ (for **2**) and $J = -2.82(4)$ cm^{-1} and $g = 1.944(9)$ (for **5**). Very weak to strong intramolecular antiferromagnetic coupling has been observed for dicopper-

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[25] Serr, B. R.; Andersen, K. A.; Elliott, C. M.; Anderson, O. P. *Inorg. Chem.* **1988**, *27*, 4499.

[26] O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.

[27] Chandramouli, G. V. R.; Balagopalakrishna, C.; Rajasekharan, M. V.; Manoharan, P. T. *Comput. Chem.* **1996**, *20*, 353.

(II) complexes containing one or two ═N−N═ bridges.[6a−c,e] The extent of twisting of the dinucleating ligand along the N−N single bond largely determines the magnitude of the antiferromagnetic spin-exchange between the metal centers in these complexes. It has been found that if the twist angle is ~70°, effective orthogonality between the magnetic orbitals of the Cu(II) centers and that between the nitrogen p-orbitals involved in the spin-exchange process is attained.[6b−d] Except for these dicopper(II) complexes, magnetic properties of very few dinuclear complexes of other 3d metal ions containing the diazine bridge are reported. These are the diiron(III) complex[11] of salhn^{2-} (**1**) and some dimetal(II) (M = Ni,[4d,e,6d] Co,[4e] and Mn[6d]) complexes with *N*,*N*′-bis(picolinylidene)hydrazine or its derivatives. All these complexes contain three ═N−N═ bridges between the metal ions and exhibit no spin-exchange or very weak intramolecular spin-exchange. In the dimanganese(II) and dinickel(II) complexes, the average dihedral angles between the two chelate rings formed by each dinucleating ligand are ~68 and ~70°, respectively.[6d] These twist angles are very similar to the twist angle found as the orthogonal limit for the dicopper(II) complexes which contain similar neutral ligands. Among the present series of weakly antiferromagnetic triple helicates (**1**, **2**, and **5**) with the dianionic ligands salhn^{2-} and mesalhn^{2-}, the X−ray structure of **2** could not be determined due to the lack of single crystals. Although in **1** the twist angles (26.6−56.8°) are significantly lower than the orthogonal limit (70°) reported before, for **5** these (59.88−66.49°) are close to the orthogonal limit.

Conclusion

Dinuclear triple helicates of trivalent metal ions (Mn(III), Fe(III), and Co(III)) with the Schiff bases derived from 1 mol equiv of hydrazine and 2 mol equiv of salicylaldehyde (H_2salhn) or 2-hydroxy acetophenone (H_2mesalhn) are described. All the complexes have the general formula [M_2(Rsalhn)$_3$] (R = H and Me). In these complexes, two pseudooctahedral metal ions enforce the twisting of the two chelating sites of each ligand along the N−N single bond to generate the triple helical structure. The dicobalt(III) complex of mesalhn^{2-} has the ideal and the corresponding diiron(III) analogue has a very close to D_3-symmetric triple helical structure. On the other hand, although triple helical but as observed previously for the diiron(III) complexes of salhn^{2-}, the extent of twisting of the three ligands differ considerably in the dicobalt(III) complex of salhn^{2-}. In the crystal lattice, self-organization via noncovalent intermolecular interactions involving the complex and the solvent molecules provide one- and two-dimensional supramolecular structures. The diiron(III) and the dicobalt(III) complexes are redox active and display two metal-centered reductions. The magnetic properties of both the dimanganese(III) and the diiron(III) complexes indicate the presence of weak antiferromagnetic spin-exchange.

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Supporting Information Available: X-ray crystallographic files in CIF format for **3**·2$(CH_3)_2NCHO\cdot H_2O$, **4**·2H_2O, and **5**·2CH_2Cl_2, the rectangular structure of the $\{2(CH_3)_2NCHO\cdot H_2O\}_2$ unit (Figure S1), the C−H···O bridged dimer of **5** (Figure S2), and one-dimensional ordering of **5**·CH_2Cl_2 units (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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