Synthesis and Structures of Fe^{III} Complexes Bridged by Cyanorhenium Clusters

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The reaction of FeCl(L1) and FeCl(L2) [L1 = bis(3-salicylideneaminopropyl)amine, L2 = bis(3-salicylideneaminopropyl)-methylamine] with the Re_6 clusters $[Re_6Q_8(CN)_6]^{4-}$ (Q = Se, Te) led to the formation of the nanomolecular (≈2.5 nm) compounds $[(CN)_2Re_6Se_8\{(CN)Fe(L1)\}_4]\cdot 7H_2O$ (**1**) and $[(CN)_2Re_6Te_8\{(CN)Fe(L2)\}_4]\cdot 4CH_3CN\cdot 4H_2O$ (**2**). Both compounds were characterized by single-crystal X-ray diffraction analysis. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.2822(10)$, $b = 14.2524(10)$, $c = 15.8474(10)$ Å, $\alpha = 106.093(10)°$, $\beta = 101.992(10)°$, $\gamma = 92.438(10)°$, and Z = 1. Compound **2** crystallizes in the orthorhombic space group *Pbca* with $a = 19.3024(2)$, $b = 16.8134(3)$, $c = 35.9842(6)$ Å, and Z = 4. In these two compounds, only four pentadentate compartments are bonded to the Re_6 cluster for charge balancing. The magnetic-susceptibility data show that there is no evidence for interactions between Fe^{III} ions via the central Re_6 cluster in either compound. The observed effective magnetic moments suggest that there are low-spin Fe^{III} ions and high-spin Fe^{III} ions mixed in each compound.

Introduction

Over the past decade, molecule-based magnetic materials have been investigated extensively in the fields of physics and chemistry. A major target in these fields is to obtain discrete polynuclear compounds with high-spin ground states.[1−5] The well-known high-spin molecules were prepared by connecting a Prussian-blue-like hexacyanometallate and multidentate metal complexes via metal-CN-metal bonding;[6−17] the bridging cyanide ligand plays an important role in the spin interaction between metals.

Recently, water-soluble hexanuclear clusters $[Re_6Q_8(CN)_6]^{4-}$ (Q = S, Se, Te), which are an extended analogue of the Prussian-blue cluster $[Fe(CN)_6]^{4-}$, have been used to synthesize extended solid frameworks.[18−22] In these extended solid frameworks the metal ions are bridged by Re_6 clusters instead of Fe^{II} ions to form bigger cubic cavities which can include plenty of small solvent molecules as well as metal ions.[23−30] In a recent study we synthesized two- and three-dimensional frameworks containing $Mn(salen)^+$ units bridged by Re_6 clusters.[31,32] We found that changing the chalcogen Q in a $[Re_6Q_8(CN)_6]^{4-}$ cluster can control the dimensionality of infinite frameworks. We also synthesized discrete molecules, containing manganese porphyrin complexes instead of extended frameworks, which show a high catalytic activity in the epoxidation reaction of olefins by iodosylbenzene.[33] These results demonstrate that multinuclear metal clusters are good candidates as building blocks in the preparation of new heterogeneous catalysts and high-spin nanomolecules.

We now report new discrete nanomolecules containing high-spin Fe^{III} complexes linked to the Re_6 clusters $[(CN)_2Re_6Se_8\{(CN)Fe^{III}(L1)\}_4]\cdot 7H_2O$ and $[(CN)_2Re_6Te_8\{(CN)Fe^{III}(L2)\}_4]\cdot 4CH_3CN\cdot 4H_2O$ [L1 = bis(3-salicylideneaminopropyl)amine, L2 = bis(3-salicylideneaminopropyl)-methylamine]. These molecules can be described as expanded versions of $[Fe^{II}\{CNFe^{III}(L2)\}_6]Cl_2$.[16,17]

Results and Discussion

Synthesis and Characterization

Recently, a mixed-valence, mixed-spin, Prussian-blue-like heptanuclear complex was synthesized that contains a central low-spin $S = 0$ Fe^{II} ion linked to six high-spin $S = 5/2$ $Fe^{III}(L)$ species through cyanide bridges[16,17] [Equation (1)].

$$K_4[Fe(CN)_6] + Fe(L2)Cl \rightarrow [Fe^{II}\{CNFe^{III}(L2)\}_6]Cl_2 \qquad (1)$$

The pentadentate ligand L2 [bis(3-salycylideneaminopropyl)methylamine], shown below, was used in this reaction.

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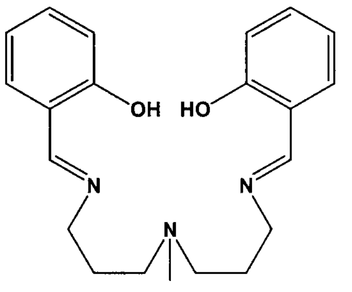

To obtain larger nanomolecules with similar pentadentate ligands, we used a face-capped octahedral Re_6 cluster ion instead of an Fe^{II} central ion. A similar reaction results in enlarged nanomolecules [Equation (2)].

$$Na_4[Re_6Q_8(CN)_6] + Fe(L1\text{ or }L2)Cl \rightarrow [(CN)_2Re_6Q_8\{(CN)Fe(L1\text{ or }L2)\}_4] \quad (2)$$

Nanomolecules $[(CN)_2Re_6Se_8\{(CN)Fe(L1)\}_4]\cdot 7H_2O$ (**1**) and $[(CN)_2Re_6Te_8\{(CN)Fe(L2)\}_4]\cdot 4CH_3CN\cdot 4H_2O$ (**2**) were prepared by a direct diffusion technique in which aqueous solutions of $Na_4[Re_6Se_8(CN)_6]$ and $Na_4[Re_6Te_8(CN)_6]$ were carefully layered with ethanol and acetonitrile solutions of FeCl(L1) and FeCl(L2), respectively. Single crystals of **1** and **2** were obtained within three days. We also tried to prepare $[(CN)_2Re_6Se_8\{(CN)Fe(L2)\}_4]$ and $[(CN)_2Re_6Te_8\{(CN)Fe(L1)\}_4]$, but we couldn't obtain suitable single crystals for a single crystal study. The IR spectra of **1** and **2** show all the peaks expected for the L1 and L2 ligand together with two peaks at 2117 and 2130 cm^{-1} originating from the vibrations of bridging and non-bridging cyanides.

Structure Description

$[(CN)_2Re_6Se_8\{(CN)Fe(L1)\}_4]\cdot 7H_2O$ (1, L1 = $C_{20}H_{23}N_3O_2$)

The asymmetric unit contains half an Re_6Se_8 cluster, two Fe(L1) units, and 3.5 water solvent molecules in a triclinic cell with $Z = 1$. A crystallographic center of inversion is located at the center of a Re_6Se_8 cluster. The structure of a complete molecule is shown in Figure 1. Four cyano groups of the Re_6Se_8 cluster are linked to the Fe(L1) unit with Fe−N(cyano) distances of 2.125(9) and 2.146(9) Å. The C(cyano)−N(cyano)−Fe angles are 154.6(9) and 154.1(9)°. The two oxygen atoms of the hydroxyl groups of the pentadentate ligand in $Fe(C_{20}H_{23}N_3O_2)$ unit are coordinated to the Fe^{III} ion, and are trans to the cyano group of the Re_6Se_8 cluster with O(hydroxy)−Fe−N(cyano) angles of 177.9(4)° and 177.6(4)°. Two salicylate groups are perpendicular to each other in linked Fe(L1) units. The distance between two Fe^{III} ions in the trans positions of the Re_6Se_8 cluster is around 14.1 Å. The largest distance between two atoms within compound **1** is over 2.5 nm, making it a nanosized molecule.

$[(CN)_2Re_6Te_8\{(CN)Fe(L2)\}_4]\cdot 4CH_3CN\cdot 4H_2O$ [2; L2 = $C_{20}H_{23}(NCH_3)N_2O_2$]

The asymmetric unit contains half an Re_6Te_8 cluster, two Fe(L2) units, and two acetonitrile and water solvent molecules in the space group *Pbca* with $Z = 4$. The complete

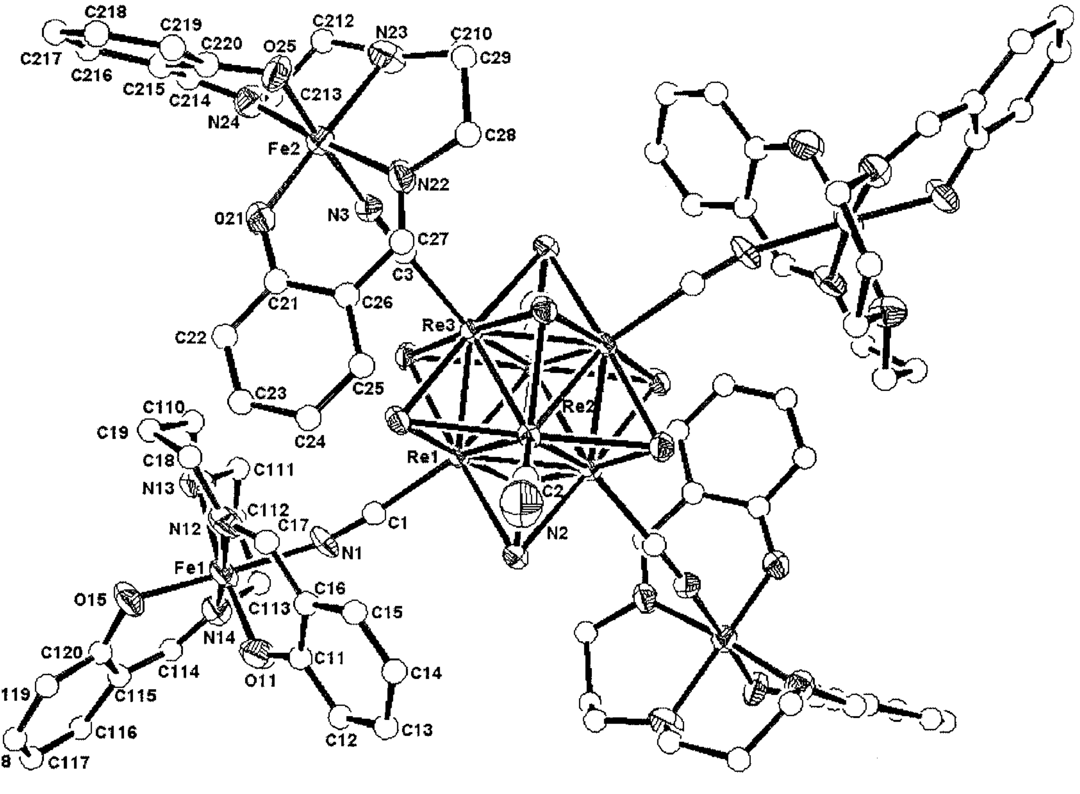

Figure 1. The structure of $[(CN)_2Re_6Se_8\{(CN)Fe(L1)\}_4]$; all hydrogen atoms have been omitted for clarity

structure is generated by the symmetry operation (−*x*, −*y* + 1, −*z* + 1). Figure 2 shows a whole molecule with Fe−N(cyano) distances of 2.070(10) and 2.070(9) Å. In contrast to compound **1**, The C(cyano)−N(cyano)−Fe angles in compound **2** are almost linear at 175.1(10)° and 177.8(11)°. The O(hydroxy)−Fe−N(cyano) angles are 177.9(4)° and 179.0(4)°. The distance between two Fe^{III} ions in the trans positions of the Re_6Te_8 cluster is around 14.4 Å. The largest distance between two atoms within the compound **2** is over 2.4 nm.

In the Re_6 cluster-centered compounds **1** and **2** the Re_6 clusters are linked to only four Fe^{III} complexes, whereas in the Fe^{II}-centered compound there are six Fe^{III} complexes attached in $[Fe^{II}\{CNFe^{III}(L2)\}_6]Cl_2$. The Re_6 cluster-centered compounds do not need any cations or anions to balance the charge while the Fe^{II}-centered compound contains two chloro anions. It is known that the Fe−N distance of low-spin complexes is shorter(ca. 1.9 Å) than that of high-spin complexes (ca. 2.2 Å). The Fe−N distances observed in the title compounds are between those reported in high-spin Fe^{III} complexes and low-spin Fe^{III} complexes.[40,41] In the Re_6 cluster-centered molecule, the distance between Fe^{III} ions through the central Re_6 cluster is about 14 Å, which is much longer than in the Fe^{II}-containing molecule (ca. 10 Å). The size of the Re_6 cluster-centered molecule is more than 2.5 nm, as compared to that of the Fe^{II}-centered molecule (2 nm).

Magnetic Properties

The temperature-dependent magnetic data of both compounds **1** and **2** are shown in Figure 3. The magnetic susceptibility data of both **1** and **2** can be clearly described using the Curie−Weiss law $\chi = \chi_o + C/(T - \theta)$. At room temperature, the effective magnetic moments of compounds **1** and **2** are 9.97 and 9.91 μ_B, respectively. These values are close to the value for a molecule with two uncoupled high-spin and two uncoupled low-spin Fe^{III} ions. There is no evidence of magnetic exchange coupling between Fe^{III} ions via the central Re_6 cluster in either compound, while the magnetic properties of the Fe^{II} ion-centered compound revealed a ferromagnetic interaction between the high-spin Fe^{III} ions of six ligands around Fe^{II}. The reason for the absence of magnetic coupling between Fe^{III} ligands in the title compounds is because the central diamagnetic Re_6 cluster core is too large to mediate magnetic interactions.

In summary, we have synthesized new Re_6 cluster-centered nanosize molecules with four Fe^{III} complexes connected to $[Re_6Q_8]^{2+}$ (Q = Se, Te) clusters. This demonstrates that an Re_6-type multinuclear metal cluster can be an effective basis to make new molecules by bridging multidentate

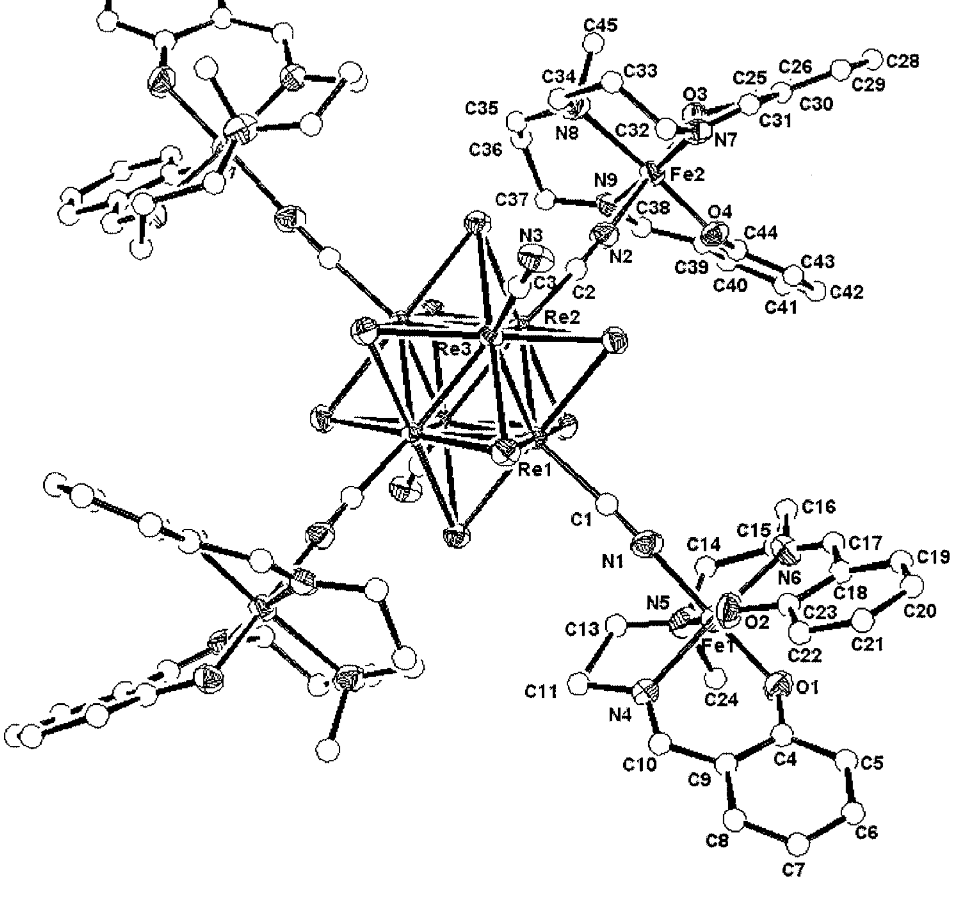

Figure 2. The structure of $[(CN)_2Re_6Te_8\{(CN)Fe(L2)\}_4]$; all hydrogen atoms have been omitted for clarity

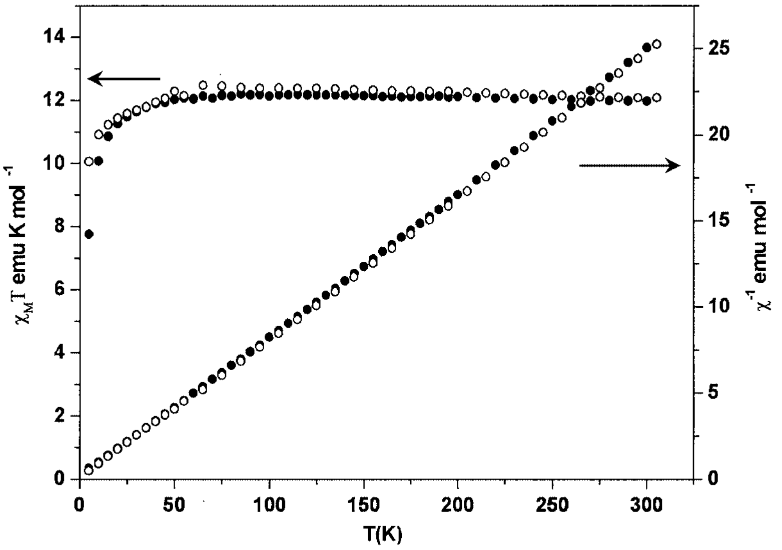

Figure 3. The magnetic susceptibility data and reciprocal susceptibility data of compound **1** (filled circle) and compound **2** (open circle) as a function of temperature

ligands. These results also suggest that if we choose proper magnetic elements for the similar M_6-type (M = transition metals such as Mo, Nb, W) multinuclear metal clusters, magnetic coupling between the M_6-type cluster and the ligand metal complex could be achieved.

Experimental Section

General Remarks: All experimental manipulations were performed in air. The compounds FeCl(L1), FeCl(L2), and $Na_4[Re_6Q_8(CN)_6]$ (Q = Se, Te) were prepared as described previously.[11,18] Other reagents were purchased from Aldrich and used as received. IR spectra were measured on a BIO RAD FTS 135 spectrometer as KBr pellets. Elemental analysis for carbon, nitrogen, and hydrogen was carried by using an EA1108 (Carlo Erba Instrument, Italy). Magnetic susceptibility data were obtained with an MPMS5 Quantum Design SQUID magnetometer. The magnetic measurements on single crystals were carried out under increasing temperatures (5−300 K) with a 5000 G applied field.

FeCl(L1): A typical preparation produced black crystals (yield: 75%). $C_{20}H_{23}ClFeN_3O_2$ (428.7): calcd. C 56.03, H 5.40, N 9.80; found C 55.92, H 5.60, N 9.94.

FeCl(L2): A typical preparation produced black crystals (yield: 78%). $C_{21}H_{25}ClFeN_3O_2$ (442.7): calcd. C 57.99, H 5.82, N 9.56; found C 56.97, H 5.69, N 9.49.

$[(CN)_2Re_6Se_8\{(CN)Fe(L1)\}_4]\cdot 7H_2O$ (1): Dark purple rod-type crystals were obtained by the direct diffusion technique. A water solution of $Na_4[Re_6Se_8(CN)_6]$ was carefully layered with an ethanol solution of FeCl(L1). IR (KBr): ν(CN) 2117 cm^{-1}.

Table 1. Crystallographic data for compound **1** and **2**

	1	**2**
Empirical formula	$C_{86}H_{88}Fe_4N_{18}O_{15}Re_6Se_8$	$C_{98}H_{124}Fe_4N_{22}O_{12}Re_6Te_8$
Molecular weight	3586.02	4163.59
Temperature	293(2) K	150(2) K
Wavelength	0.71074 Å	0.71073 Å
Crystal system, space group	Triclinic, $P\bar{1}$	Orthorhombic, *Pbca*
a (Å)	12.2822(10)	19.3024(2)
b (Å)	14.2524(10)	16.8134(3)
c (Å)	15.8474(10)	35.9842(6)
α (°)	106.093(10)	90
β (°)	101.992(10)	90
γ (°)	92.438(10)	90
Volume (Å^3)	2592.4(3)	11678.3(3)
Z, calculated density (mg/m^3)	1, 2.297	4, 2.368
Reflections collected/unique	10881/10162 [*R*(int) = 0.0347]	48836/10285 [*R*(int) = 0.0913]
Data/restraints/parameters	10162/0/612	10285/0/677
Goodness-of-fit on F^2	1.036	1.065
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0521$, $wR2 = 0.1446$	$R1 = 0.0507$, $wR2 = 0.1186$
R indices (all data)	$R1 = 0.0793$, $wR2 = 0.1600$	$R1 = 0.0737$, $wR2 = 0.1301$
Largest diff. peak	3.935	1.707

$C_{86}H_{88}Fe_4N_{18}O_{15}Re_6Se_8$ (3586.0): calcd. C 29.34, H 2.65, N 7.11; found C 29.70, H 2.67, N 7.25.

[(CN)$_2$Re$_6$Te$_8${(CN)Fe(L2)}$_4$]·4CH$_3$CN·4H$_2$O (2): Dark purple plate crystals were also obtained by the direct diffusion technique. A water solution of $Na_4[Re_6Te_8(CN)_6]$ was carefully layered with an acetonitrile solution of FeCl(L2). IR (KBr): ν(CN) 2117 cm^{-1}. $C_{98}H_{124}Fe_4N_{22}O_{12}Re_6Te_8$ (4163.6): calcd. C 27.44, H 2.51, N 6.36; found C 27.55, H 2.57, N 6.43.

X-ray Crystallographic Study: The X-ray diffraction data for compound **1** were collected on an Enraf−Nonius CAD-4 Mach3 diffractometer equipped with a monochromator in the Mo-K_α (λ = 0.71073 Å) incident beam. The crystal was mounted on a glass fiber. A description of the data collection techniques for this diffractometer has been given before.[34] The final cell parameters for **1** were obtained from least-squares fit to 25 reflections in the range $9.44 \le \theta \le 10.62°$. Intensities were corrected for Lorentz and polarization effects but not for absorption. The crystal structure was determined by direct methods and Fourier techniques. All the calculations were performed on an IBM Pentium computer using SHELXS-97 and SHELXL-97, and atomic scattering factors for all non-hydrogen atoms were supplied by SHELXS-97.[35] All hydrogen atoms were located in the calculated positions. The molecular structure was drawn with the Ortep-3 for Windows program.[36]
The diffraction data for compound **2** were collected on a Nonius Kappa-CCD diffractometer using Mo-K_α (λ = 0.71073 Å) radiation.[37] The crystals were mounted on glass fibers in epoxy resin. The CCD data were integrated and scaled using the DENZO-SMN software package,[38] and the structures were solved and refined by using SHEXTL V5.0.[39] All non-hydrogen atoms were located in the calculated positions. The crystallographic data for compounds **1** and **2** are listed in Table 1.
CCDC-206671 (**1**) and -206672 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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