

Synthesis and Magnetic Study of $\mu_{1,1}$ -Azido-Bridged Dinuclear Manganese(II) Complexes Based on Tripyridyl Ligands

Ming-Ming Yu,^[a] Zhong-Hai Ni,^[a] Chong-Chao Zhao,^[a] Ai-Li Cui,^[a] and Hui-Zhong Kou^{*[a]}

Keywords: Manganese / Dinuclear complexes / Crystal structures / Magnetic properties / Azido bridge

Three azido-bridged Mn^{II} complexes of formulas [Mn₂(N₃)₄-(ttp)₂] (**1**), [Mn₂(N₃)₄(ttp-N₃)₂] (**2**) and [Mn₂(N₃)₄(ttp-N₃)₂]₃[Mn^{III}(ttp-N₃)(N₃)₃]₂ (**3**), where ttp and ttp-N₃ represent 4'-*p*-tolyl-2,2':6',2''-terpyridine and 4'-*p*-azidomethylphenyl-2,2':6',2''-terpyridine, were synthesized and characterized by single-crystal X-ray diffraction analysis and magnetic studies. The Mn ions in complexes **1** and **2** are coordinated by three N atoms of the ttp or ttp-N₃ ligands, and they are connected by double end-on (EO) azide ligands; this forms a dinuclear Mn^{II} system with Mn–N–Mn bridging angles of 103.5 and 103.1°. The Br atoms of the –CH₂Br ligands were replaced by azido groups during the formation of complexes **2** and **3**. The structure of complex **3** comprises two structur-

ally similar Mn^{II} dimers with double end-on bridging azide groups and one mononuclear Mn^{III} structure. The bridging Mn–N–Mn angles in **3** are 104.2, 105.1, and 106.73°. Magnetic studies indicate the presence of intramolecular ferromagnetic superexchange. The strength of ferromagnetic coupling within the Mn₂ cores in **1–3** is dependent on the Mn–N–Mn bridging angles. The magnetic coupling constants for intermolecular exchange are 2.46(4), 2.25(2), and 1.92(4) cm^{−1} for **1**, **2**, and **3**, respectively, on the basis of Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2$.

(© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

During the last two decades chemists have been interested in the azido ligand for its versatile coordination modes and remarkable ability to transmit ferro- or antiferromagnetic interactions.^[1] The azido ligand is able to bridge metal ions in several forms, including the usual μ -1,1 (end-on, EO) or μ -1,3 (end-to-end, EE) mode^[2] and the unusual μ -1,1,3, μ -1,1,1, μ -1,1,1,1, μ -1,1,3,3 or μ -1,1,1,3,3,3 modes.^[3–6] EE bridging usually transmits antiferromagnetic interactions between the metallic centers, whereas EO bridging is known to transmit ferromagnetic interactions irrespective of what metal ions are involved.^[7] The theory of spin polarization developed by Kahn et al.^[8] has been used to interpret the magnetic interaction through the azido group in Cu^{II}, Ni^{II}, and Mn^{II} systems.^[9] Many studies concerning the ferromagnetic interactions in Cu^{II} and Ni^{II} end-on azido systems have been carried out extensively, and structure parameters, especially bridging angle, were found to be the main factors controlling the strength of the ferromagnetic interaction.^[10–13] For Mn^{II} systems with only end-on azido bridges, examples are limited.^[14,15] Recently, Aromí et al. found that there is a linear relationship be-

tween the exchange coupling constant (J) and the Mn–N–Mn bridging angle (θ) on the basis of results obtained for only four complexes.^[15a] We then prepared a series of end-on azido-bridged Mn^{II} complexes with the [Mn₂(phen)₄(N₃)₂]²⁺ core and improved the J – θ relationship.^[15b] Apparently, more effort should be exerted to make the assumption of the relation of J and θ more clear. Herein, we describe the syntheses, structures, and magnetic properties of three dinuclear Mn^{II} compounds with tridentate 4'-*p*-tolyl-2,2':6',2''-terpyridine (ttp) and 4'-*p*-bromomethylphenyl-2,2':6',2''-terpyridine (ttp-Br) ligands. Interestingly, the Br atoms in the ttp-Br ligands were replaced by azido groups to give the new 4'-*p*-azidomethylphenyl-2,2':6',2''-terpyridine (ttp-N₃) ligand, which then goes on to form complexes [Mn₂(N₃)₄(ttp-N₃)₂] (**2**) and [Mn₂(N₃)₄(ttp-N₃)₂]₃[Mn(ttp-N₃)(N₃)₃]₂ (**3**). The bridging Mn–N–Mn angle of complex **3** is the largest hitherto found in double EO azido-bridged dimeric Mn^{II} complexes.

Results and Discussion

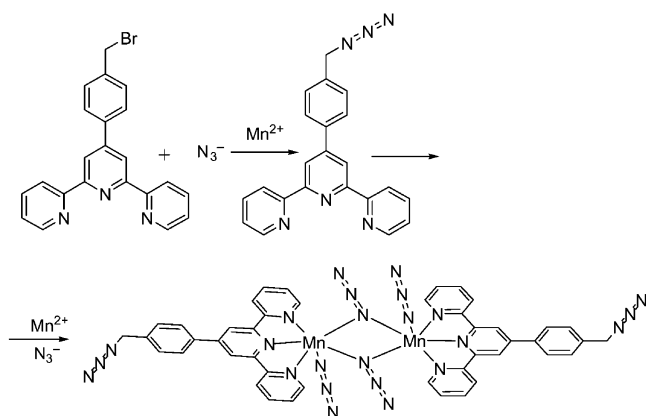
Synthesis and General Characterization

Tridentate ttp-type ligands are analogous to the commonly used 2,2':6',2''-terpyridine (terpy) ligand. Previously, Rojo et al. reported an end-on azide-bridged Mn^{II} dimer [Mn₂(terpy)₂($\mu_{1,1}$ -N₃)₂(N₃)₂]·2H₂O.^[14a] This complex has a bridging Mn–N–Mn angle of 104.6°, which is the

[a] Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China
Fax: +86-10-62771748
E-mail: kouhz@mail.tsinghua.edu.cn

Supporting information for this article is available on the WWW under <http://www.eurjic.org/> or from the author.

largest among the reported EO azido-bridged dimeric Mn^{II} complexes. In this work, we used ttp-type ligands in the hope of obtaining similar dimeric complexes. Complexes **1**–**3** were prepared and characterized. They have EO azido-bridged dimeric structures that are similar to $[\text{Mn}_2(\text{terpy})_2(\mu_{1,1}\text{-N}_3)_2(\text{N}_3)_2]\cdot 2\text{H}_2\text{O}$.^[14a] Interestingly, a 1D polymeric Mn^{II} complex, $[\text{Mn}(\text{tptz})(\mu_{1,1}\text{-N}_3)_2]_n$ ^[16] [tptz = 2,4,6-tris(2-pyridyl)-1,3,5-triazine], was synthesized with the tptz ligand that is similar to ttp. During the preparation of complexes **2** and **3**, ttp- N_3 formed in situ by substitution of the bromo group by an azido group (Scheme 1). In organic synthesis, sodium azide is often used as a reactant to substitute bromoalkyl groups.^[17] However, the substitution reaction of an azido group accompanied by crystallization of metallic complexes is rare. It is known that azide can stabilize divalent transition-metal ions when neutral pyridyl reagents are used as auxiliary ligands. We found that tripyridyl Mn^{II} can be slowly oxidized by oxygen dissolved in the solvent. The exposure to light accelerates the oxidation process. The formed neutral $[\text{Mn}(\text{ttp-}\text{N}_3)(\text{N}_3)_3]$ monomer cocrystallized with the Mn^{II} dimer in **3**.



Scheme 1. Possible formation mechanism of ttp- N_3 and complex **2**.

The IR spectra of three complexes show a strong peak at ca. 1600 cm^{-1} , which is assigned to the C=N stretching vibration in the pyridine rings of the ligands. The $\nu_{\text{asym}}(\text{N}_3^-)$ mode of complexes **1**–**3** appear at ca. 2000 – 2100 cm^{-1} . The splitting of the signals indicates the presence of both bridging and terminal azide ligands. The peaks at 2093 cm^{-1} for complex **2** and 2086 cm^{-1} for complex **3** should be assigned to the alkyl azido asymmetric stretching vibration.^[17] The peak at 2037 cm^{-1} for complex **3** may be due to the $\nu_{\text{asym}}(\text{N}_3^-)$ mode of the $[\text{Mn}^{\text{III}}(\text{ttp-}\text{N}_3)(\text{N}_3)_3]$ moiety by considering that the $[\text{Mn}^{\text{III}}(\text{terpy})(\text{N}_3)_3]$ analog exhibits a strong band at 2035 cm^{-1} .^[18] In addition, azido complexes are expected to show $\nu_{\text{sym}}(\text{N}_3^-)$ and deformation mode $\delta(\text{N}_3^-)$ at ca. 1300 – 1350 and ca. 620 cm^{-1} , respectively.^[18] For complexes **1**–**3**, only the symmetric azide stretching vibration was observed as a medium signal.

Complexes **1**, **2**, and **3** are slightly soluble in MeCN, but they are not soluble in alcohol solvents. The electronic spectra of compounds **2** and **3** in MeCN are similar and a

shoulder band at 400 – 450 nm is apparent; this shoulder is responsible for the color of the compounds. The spectrum of **1** in MeCN shows no apparent absorption in the visible region, which is consistent with the light color of the complex. Relative to the spectra of the ttp and ttp-Br ligands, the UV absorptions related to the $n\text{--}\pi^*$ or $\pi\text{--}\pi^*$ transitions within the ligands show an obvious redshift, which is due to better planarity of the tripyridyl group accompanied by chelation to Mn^{II} ions (see the Supporting Information).

Crystal Structure of Complexes **1**, **2**, and **3**

Crystal data are summarized in Table 1. Selected bond lengths and angles of complexes **1**, **2**, and **3** are included in Table 2. ORTEP representations of the crystallographic molecular structure of complexes **1**, **2**, and **3** are shown in Figures 1, 2, and 3.

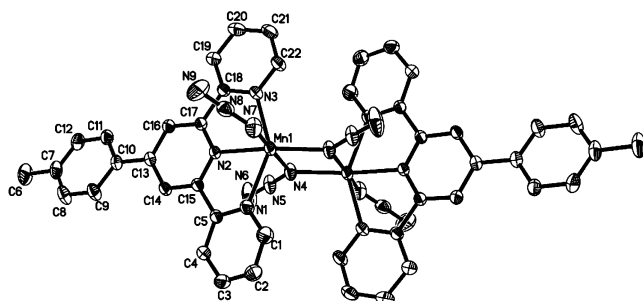
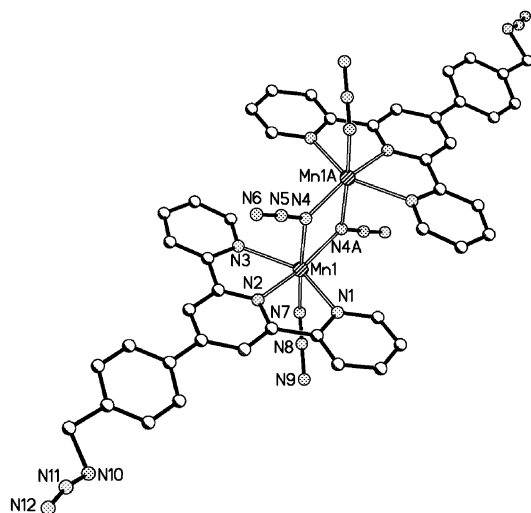
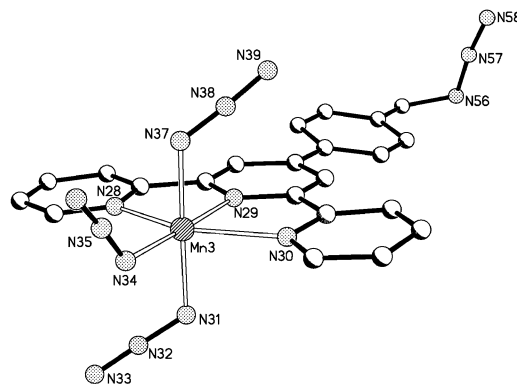
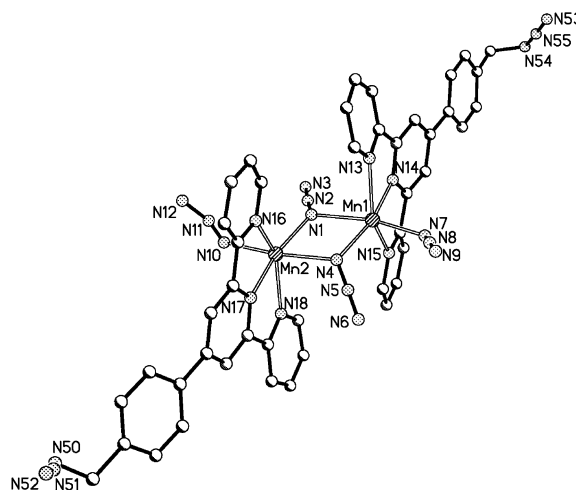
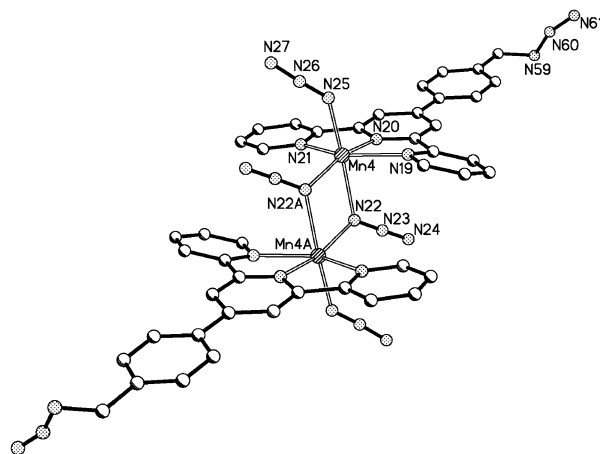
Table 1. Crystallographic data for complexes **1**, **2**, and **3**.

	1	2	3
Chemical formula	$\text{C}_{44}\text{H}_{34}\text{N}_{18}\text{Mn}_2$	$\text{C}_{44}\text{H}_{32}\text{N}_{24}\text{Mn}_2$	$\text{C}_{176}\text{H}_{128}\text{N}_{102}\text{Mn}_8$
<i>F</i> _w	924.77	1006.82	4111.32
<i>T</i> / K	293	293	293
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
<i>a</i> / Å	8.608(2)	14.725(3)	14.757(3)
<i>b</i> / Å	10.371(2)	13.230(3)	14.883(3)
<i>c</i> / Å	23.806(5)	11.751(2)	22.828(5)
α / °	90	90	78.40(3)
β / °	92.74(3)	97.01(3)	78.78(3)
γ / °	90	90	69.47(3)
<i>V</i> / Å ³	2122.8(7)	2272.2(8)	4557.1(16)
<i>Z</i>	2	2	1
ρ_{calcd} / g cm ^{−3}	1.447	1.472	1.498
<i>F</i> (000)	948	1028	2098
GOF (<i>S</i>)	1.054	1.050	1.044
Data/restraints/paras	4824/0/290	9769/0/281	15905/15/1288
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.0322	0.0559	0.0507
<i>wR</i> ₂ (all data)	0.0930	0.1093	0.1472

Complexes **1** and **2** exhibit centrosymmetric dimers $[\text{Mn}(\text{N}_3)_2(\text{ttp})_2]$ or $[\text{Mn}(\text{N}_3)_2(\text{ttp-}\text{N}_3)_2]$, respectively. The Mn^{II} ions in complexes **1** and **2** are linked by double end-on bridging azide groups. The other two azide moieties act as terminal ligands. In complex **1**, each Mn ion exhibits a slightly distorted octahedral coordination sphere and the three nitrogen atoms of the terpy ligand [Mn1–N1: 2.269(1) Å, Mn1–N2: 2.224(1) Å, Mn1–N3: 2.279(2) Å] and the nitrogen atom of one bridging azide group [Mn1–N4A: 2.127(1) Å (*A*: 2 − *x*, − *y*, 1 − *z*)] form the equatorial plane. The nitrogen atom of one terminal azido group [Mn1–N7: 2.153(2) Å] and the nitrogen atom of the second bridging group [Mn1–N4: 2.363(2) Å] are situated in the axial positions. The existence of an inversion center causes the Mn–N4–Mn1A–N4A bridging unit to form a plane. In this dimeric unit, the Mn cations are separated from each other by 3.528(4) Å. The bridging Mn–N4–Mn1A angle is 103.5°. The bridging and terminal azido ligands are quasilinear and the N4–N5–N6 and N7–N8–N9 angles measure 177.03 and 178.22°, respectively.

Table 2. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$] for complexes **1**, **2**, and **3**.

1			
Mn1–N1	2.2689(14)	Mn1–N2	2.2238(14)
Mn1–N3	2.2786(15)	Mn1–N4	2.3634(16)
Mn1–N4 ^A	2.1270(14)	Mn1–N7	2.1530(17)
Mn1 ^A –N4–Mn1	103.45(6)		
2			
Mn1–N4	2.378(3)	N3–Mn1	2.274(3)
Mn1–N4 ^B	2.126(3)	N2–Mn1	2.213(3)
N1–Mn1	2.272(3)	N7–Mn1	2.180(4)
Mn1 ^B –N4–Mn1	103.13(12)		
3			
Mn1–N1	2.331(3)	Mn1–N4	2.168(3)
Mn1–N7	2.135(3)	Mn1–N13	2.290(3)
Mn1–N14	2.223(2)	Mn1–N15	2.294(3)
Mn2–N1	2.191(3)	Mn2–N4	2.279(3)
Mn2–N10	2.147(5)	Mn2–N16	2.287(3)
Mn2–N17	2.239(2)	Mn2–N18	2.291(3)
Mn3–N28	2.244(3)	Mn3–N29	2.107(3)
Mn3–N30	2.248(3)	Mn3–N31	1.982(3)
Mn3–N34	1.951(3)	Mn3–N37	1.977(3)
Mn4–N19	2.279(3)	Mn4–N20	2.209(3)
Mn4–N21	2.296(3)	Mn4–N22	2.341(3)
Mn4–N22 ^C	2.143(3)	Mn4–N25	2.138(4)
Mn1–N4–Mn2	106.72(12)	Mn2–N1–Mn1	104.20(11)
Mn4 ^C –N22–Mn4	105.11(13)		

Figure 1. Crystal structure of complex **1**.Figure 2. Crystal structure of complex **2**.Figure 3. Crystal structure of complex **3** showing three cocrystallized moieties.

In complex **2**, each Mn cation exhibits a distorted octahedral coordination sphere and the Mn–N bond lengths range from 2.126(3) $\text{\AA}$ [Mn1–N4A (A: $1-x$, $1-y$, $1-z$)] to 2.378(2) $\text{\AA}$ (Mn1–N4). In this dimeric unit, the Mn cations are separated from each other by 3.532(4) $\text{\AA}$ with a bridging Mn–N4–Mn1A angle of 103.1°. The bridging and terminal azido ligands are quasilinear [177.29 and 179.90°].

The structure of complex **3** comprises three doubly end-on azide-bridged Mn^{II} dimers and two Mn^{III} monomers. One dimer exhibits a centrosymmetric structure and the

other is asymmetric. The dimeric structure is very similar to that of complexes **1** and **2**. In the asymmetric dimer comprised of Mn1 and Mn2, the nitrogen atoms of one terminal azido group [Mn1–N7: 2.135(3) Å] and one bridging group [Mn1–N1: 2.331(3) Å] are situated in the axial positions. The intradimer Mn1...Mn2 distance is 3.569(6) Å, and the bridging Mn1–N1–Mn2 and Mn1–N4–Mn2 bond angles are 104.2 and 106.73°, respectively. In the inversion center related unit, the Mn–N distances are in the range 2.138(4) (Mn4–N25) to 2.341(3) Å (Mn4–N22). In this dimeric unit, the Mn cations are separated from each other by 3.562(3) Å. The bridging azides slightly deviate (up and down) from that plane and the bridging Mn–N4–Mn1A angle is 105.1°. In the neutral Mn^{III} monomer Mn(tpp-N₃)(N₃)₃, the Mn–N bond lengths range from 1.951(3) to 2.248(3) Å, which is consistent with a Mn^{III} ion with a Jahn–Teller effect for the d⁴ electronic configuration. The bond lengths and coordination geometry are very similar to those of [Mn(terpy)(N₃)₃].^[18]

Magnetic Behavior of Complexes **1**, **2**, and **3**

The $\chi_m T$ vs. T plots (2–300 K) of complexes **1**, **2**, and **3** are shown in Figures 4, 5, and 6, respectively. At 300 K, the $\chi_m T$ values per dimer are 8.762 and 8.904 emu K mol^{−1} for **1** and **2**, respectively, which are both close to the expected value (8.75 emu K mol^{−1}) for two uncoupled spin $S_{Mn} = 5/2$ systems. With decreasing temperature, $\chi_m T$ increases sharply to reach a maximum value of 6.43 emu K mol^{−1} at 8 K for complex **1** and 14.34 emu K mol^{−1} at 9 K for complex **2**; it then decreases because of weak intermolecular antiferromagnetic interaction and/or zero-field splitting of the ground spin state of $S = 5$. Magnetic susceptibility could be fit to a Curie–Weiss law with Curie constant $C = 8.96$ emu K mol^{−1} and a positive Weiss constant $\theta = 8.68$ K for complex **1** and $C = 4.08$ emu K mol^{−1} and $\theta = 7.89$ K for complex **2**. These results indicate that the overall magnetic behavior of **1** and **2** is ferromagnetic, which should be attributed to the dinuclear superexchange mediated through the $\mu_{1,1}$ -azido bridges. The expression for the magnetic susceptibility (χ_d) of a Mn^{II} dimer derived from Van Vleck's equation (the spin Hamiltonian $\hat{H} = -2J\hat{S}_{Mn1}\hat{S}_{Mn2}$) is expressed in Equation (1), in which $A = 55 + 30\exp(-10J/kT) + 14\exp(-18J/kT) + 5\exp(-24J/kT) + \exp(-28J/kT)$ and $B = 11 + 9\exp(-10J/kT) + 7\exp(-18J/kT) + 5\exp(-24J/kT) + 3\exp(-28J/kT) + \exp(-30J/kT)$.

$$\chi_d = \frac{2Ng^2\beta^2}{kT} \frac{A}{B} \quad (1)$$

Considering weak intermolecular antiferromagnetic coupling, the final molar magnetic susceptibility takes the form of Equation (2), where zJ' is the interaction between molecules, and the N , g , β , and θ parameters have their usual meaning.

$$\chi_M = \frac{\chi_d}{1 - \chi_d(2zJ'/Ng^2\beta^2)} \quad (2)$$

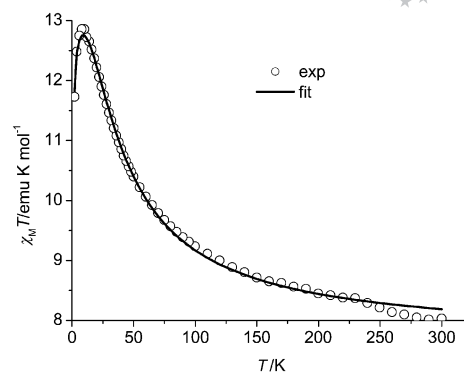


Figure 4. $\chi_m T$ vs. T plot for complex **1**. The solid line represents the best fit.

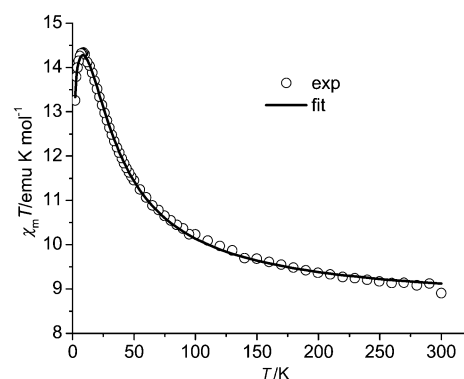


Figure 5. $\chi_m T$ vs. T plot for complex **2**. The solid line represents the best fit.

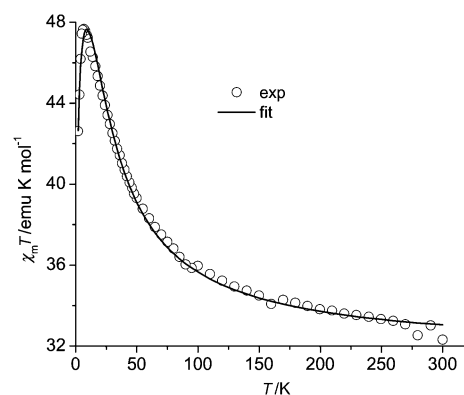


Figure 6. $\chi_m T$ vs. T plot for complex **3**. The solid line represents the best fit.

The best-fit parameters obtained are $J = 2.46(4)$ cm^{−1}, $g = 1.99(1)$, and $zJ' = -0.0078$ cm^{−1} with an agreement factor of $R = \sum(\chi_{\text{obsd}}T - \chi_{\text{calcd}}T)^2 / \sum(\chi_{\text{obsd}}T)^2 = 4.24 \times 10^{-5}$ for complex **1** and $J = 2.25(2)$ cm^{−1}, $g = 1.98(1)$, $zJ' = -0.0072(3)$ cm^{−1} and $R = 2.03 \times 10^{-5}$ for complex **2**.

The decrease in $\chi_m T$ at low temperature could be alternatively interpreted by the presence of zero-field splitting (ZFS) of the spin ground state $S_T = 5$. The data were fit to a model that includes the energy splitting of the ground spin state. By using a modified term of the Heisenberg spin Hamiltonian of a dinuclear system ($\hat{H} = -2J\hat{S}_1\hat{S}_2$) as $\hat{H}_{ZFS}$

$= D[\hat{S}_{\text{Tz}}^2 - S_{\text{T}}(S_{\text{T}}+1)/3]$, the expression for the magnetic susceptibility of ferromagnetically coupled Mn^{II} dimer is depicted in Equation (3),^[15c] where $A = 6\exp(9D/kT) + 24\exp(6D/kT) + 54\exp(D/kT) + 96\exp(-6D/kT) + 150\exp(-15D/kT) + 180\exp(-10J/kT) + 84\exp(-18J/kT) + 30\exp(-24J/kT) + 6\exp(-28J/kT)$, $B = \exp(10D/kT) + 2\exp(9D/kT) + 2\exp(6D/kT) + 2\exp(D/kT) + \exp(-6D/kT) + 2\exp(-15D/kT) + 9\exp(-10J/kT) + 7\exp(-18J/kT) + 5\exp(-24J/kT) + 3\exp(-28J/kT) + \exp(-30J/kT)$.

$$\chi_M = \frac{Ng^2\beta^2}{3kT} \frac{A}{B} \quad (3)$$

The least-square fit of the experimental data to the above expression gives the following parameters: $J = 2.46(2) \text{ cm}^{-1}$, $g = 1.99(1)$, $D = 0.019(1) \text{ cm}^{-1}$, and $R = 4.10 \times 10^{-5}$ for complex **1** and $J = 2.26(2) \text{ cm}^{-1}$, $g = 1.98(1)$, $D = 0.017(1) \text{ cm}^{-1}$, and $R = 2.02 \times 10^{-5}$ for complex **2**.

The best-fit results including intermolecular interaction or zero-field splitting are very similar. Both effects are likely operative with similar strength, and it is impossible to distinguish between them.^[15c]

At 300 K, the $\chi_{\text{m}}T$ value of complex **3** is ca. $33.0 \text{ emu K mol}^{-1}$, which is close to that ($32.25 \text{ emu K mol}^{-1}$) expected for an uncoupled system ($6\text{Mn}^{\text{II}} + 2\text{Mn}^{\text{III}}$). With a decrease in the temperature, the $\chi_{\text{m}}T$ values increase sharply to reach a maximum value of $47.66 \text{ emu K mol}^{-1}$ at 7 K, and then they decrease to $42.62 \text{ emu K mol}^{-1}$ at 2 K due to weak antiferromagnetic interaction and/or zero-field splitting. These results indicate that the overall behavior of **3** corresponds to a ferromagnetic interaction, which should be attributed to the dinuclear superexchange mediated through the $\mu_{1,1}$ -azido bridges. Magnetic susceptibility could be fit to a Curie–Weiss law with Curie constant $C = 32.57 \text{ emu K mol}^{-1}$ and a positive Weiss constant $\theta = 6.25 \text{ K}$. The positive θ value and the shape of the $\chi_{\text{m}}T$ curves for **3** indicate the existence of ferromagnetic interactions between double EO azido-bridged Mn^{II} ions.

Taking the contributions of intermolecular interaction and the Mn^{III} monomers into account and using one J value for simplicity, the final molar magnetic susceptibility is in the form of Equation (4), where χ_{dimer} is the expression including both J and zJ' for complexes **1** and **2**.

$$\chi_M = 3\chi_{\text{dimer}} + \frac{4Ng^2\beta^2}{kT} \quad (4)$$

The least-square fit of the experimental data gives the following parameters: $J = 1.92(4) \text{ cm}^{-1}$, $g = 1.98(1)$, $zJ' = -0.0019(4) \text{ cm}^{-1}$, and $R = 5.47 \times 10^{-5}$ for complex **3**.

Field dependence of the magnetization at 2 K of complexes **1**, **2**, and **3** are shown in the Supporting Information. Experimental data fit well to the Brillouin function value for $S = 5$, and are well above that for two noncoupling $S = 5/2$ Mn^{II} ions, which indicates the existence of ferromagnetic interactions between double EO azido-bridged Mn^{II} ions. For complex **3**, the Mn^{III} monomers ($S_{\text{Mn}^{\text{III}}} = 2$) should be included when calculating the Brillouin curve, that is, $S = 5 \times 3 + 2 \times 2$ and noninteracting $S = 6 \times 5/2 + 2 \times 2$, respectively. The experimental data for **3** are above the Brillouin curve for $S = 6 \times 5/2 + 2 \times 2$ at low magnetic field ($< 20 \text{ kOe}$), and they are below that for $S = 5 \times 3 + 2 \times 2$. The discrepancy in **3** compared with complexes **1** and **2** is assigned to the presence of Mn^{III} ions, and it is usually difficult to reach magnetic saturation because of magnetic anisotropy.^[19]

The above results could be interpreted by the theoretical point of view for dinuclear complexes by using the spin-polarization model and hybrid density functional theory (DFT). Kahn et al. first explained the ferromagnetic interactions between EO azido-bridged dinuclear complexes on the basis of the spin-polarization effect. This model considers that the electron of a bridging nitrogen atom (α spin) of the in-plane π_{g} orbital (HOMO) is partially delocalized toward the two metal orbitals; the unpaired electrons occupying the orbitals are likely to have β spins, which favors ferromagnetic interactions. The interaction through the

Table 3. Comparison of structural parameters and magnetic data for end-on azido-bridged complexes.^[a]

Complex	Mn–N _{azido} / Å	Δd / Å	θ / °	J / cm^{-1}
$\text{Mn}_2(\text{N}_3)_4(\text{ttp})_2$	2.245(2)	0.236	103.45(6)	2.46(4)
$\text{Mn}_2(\text{N}_3)_4(\text{ttp-N}_3)_2$	2.252(3)	0.252	103.13(12)	2.25(2)
$[\text{Mn}_2(\text{N}_3)_4(\text{ttp-N}_3)_2][\text{Mn}(\text{ttp-N}_3)(\text{N}_3)_3]$	2.242(3)	0.150	105.29(12)	1.92(4)
$[\text{Mn}(\text{terpy})(\text{N}_3)_2]_2 \cdot 2\text{H}_2\text{O}^{[14a]}$	2.227(3)	0.090	104.6(1)	2.43
$[\text{Mn}_2(\text{L}^1)_2(\mu_{1,1}\text{-N}_3)_2](\text{ClO}_4)_2^{[15a]}$	2.249(3)	0.030	102.12	0.77(1)
$[\text{Mn}_2(\text{L}^2)_2(\mu_{1,1}\text{-N}_3)_2](\text{ClO}_4)_2^{[15a]}$	2.240(3)	0.072	104.29	2.04(3)
$[\text{Mn}_2(\text{L}^3)_2(\mu_{1,1}\text{-N}_3)_2](\text{ClO}_4)_2^{[15a]}$	2.248(5)	0.053	103.58	1.75(2)
$[\text{Mn}_2(\text{phen})_4(\mu_{1,1}\text{-N}_3)_2][\text{Co}(\text{bpb})(\text{CN})_2]_2 \cdot \text{H}_2\text{O}^{[15b]}$	2.229(6)	0.002	102.6(4)	1.27
$[\text{Mn}_2(\text{phen})_4(\mu_{1,1}\text{-N}_3)_2][\text{Cr}(\text{bpb})(\text{CN})_2]_2 \cdot \text{H}_2\text{O}^{[15b]}$	2.226(2)	0.003	102.55(12)	1.10
$[\text{Mn}_2(\text{phen})_4(\mu_{1,1}\text{-N}_3)_2][\text{Fe}(\text{bpb})(\text{CN})_2]_2 \cdot \text{H}_2\text{O}^{[15b]}$	2.288(5)	0.006	101.4(3)	1.20
$[\text{Mn}_2(2,2'\text{-dpa})_2(\text{N}_3)_2(\mu_{1,1}\text{-N}_3)_2]^{[14b]}$	2.237(3)	0.059	103.11(10)	1.12
$[\text{Mn}(\text{tptz})(\mu_{1,1}\text{-N}_3)_2]_n^{[16]}$	2.273(1)	0.0017	106.16(4)	2.03
$[\text{Mn}(\text{pyz})(\mu_{1,1}\text{-N}_3)_2]_n^{[20a]}$	2.234(2)	0	98.8(5)	0.61
$[\text{Mn}(2\text{-bzpy})(\mu_{1,1}\text{-N}_3)_2]_n^{[20b]}$	2.197(4)	0.032	100.5(2)	0.40

[a] Average values. $\Delta d = d(\text{Mn–N}_{\text{azido}}) - d(\text{Mn–N}'_{\text{azido}})$. $\text{L}^1 = [N,N\text{-bis}(\text{pyridine-2-yl})\text{benzylidene}] \text{ethane-1,2-diamine}$, $\text{L}^2 = [N,N\text{-bis}(\text{pyridine-2-yl})\text{-benzylidene}] \text{propane-1,3-diamine}$, $\text{L}^3 = [N,N\text{-bis}(\text{pyridine-2-yl})\text{-benzylidene}] \text{butane-1,4-diamine}$, $\text{bpb}^{2-} = 1,2\text{-bis}(\text{pyridine-2-carboxamido})\text{benzenate}$, $2,2'\text{-dpa} = 2,2'\text{-dipicolylamine}$, $\text{tptz} = 2,4,6\text{-tris}(2\text{-pyridyl})\text{-1,3,5-triazine}$, $\text{pyz} = \text{pyrazine}$, $2\text{-bzpy} = 2\text{-benzoylpyridine}$.

azido bridge does not depend on the surroundings of the metal ions but only on the fashion of azido bridges.^[9] DFT calculations show that the value of J is mainly dependent on the energy gap between the molecular orbitals associated with the unpaired electrons (SOMOs). Aromí et al. recently gave a rough relationship between the exchange coupling constant (J) and the Mn–N–Mn bridging angle (θ), which was afterwards improved to $J = 0.614\theta - 61.9$ on the basis of eight complexes.^[15a,15b] The magnet data of this work and available EO azido-bridged dinuclear complexes are in good agreement with the fact that the exchange coupling constant increase with the Mn–N–Mn bridging angle (Table 3), which is consistent with theoretical predictions.^[9a] The J – θ relationship can be now improved on the basis of 15 data sets listed in Table 3 to give the equation $J = 0.276\theta - 26.9$, as shown in Figure 7. In addition, an increase in the asymmetry of the azido bridging (Δd in Table 3) was shown to bring about a decrease in antiferromagnetic interactions (J_{AF}), and consequently an increase in the global magnetic exchange constant ($J = J_{\text{AF}} + J_{\text{F}}$).^[14a] Careful examination of the data in Table 3 shows that the J values for the dimeric complexes generally increase with an increase in Δd , which is in agreement with the above prediction.

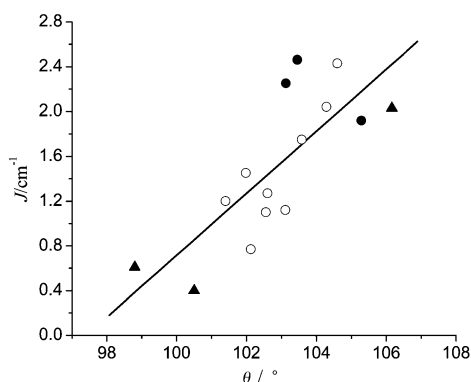


Figure 7. Plot of J vs. Mn–N–Mn bond angle (θ) for EO azido-bridged Mn^{II} compounds (● this work, ▲ 1D complexes). The straight line represents the best fit.

Conclusions

We successfully prepared three doubly EO azido-bridged dinuclear Mn^{II} complexes. The ferromagnetic properties of dinuclear superexchange mediated through the $\mu_{1,1}$ -azido bridges were confirmed in all complexes. Consideration of the intermolecular antiferromagnetic coupling of Mn^{II} or the presence of zero-field splitting (ZFS) of the molecular spin ground state allows the magnetic coupling constants to be evaluated. On the basis of the results of this work and the available $\mu_{1,1}$ -azido-bridged Mn^{II} complexes, a clearer magnetostructural correlation was reached.

Experimental Section

Materials: 4'-*p*-Tolyl-2,2':6',2''-terpyridine (ttp) and 4'-(*p*-bromomethylphenyl)-2,2':6',2''-terpyridine (ttp-Br) were prepared as

previously reported.^[21] All other reagents were commercial grade materials and used as received.

Measurements: Elemental analyses were determined with an Elemental Vario EL elemental analyzer. IR spectra were measured as KBr pellets with a Magna-IR 750 spectrophotometer in the 4000–400 cm^{-1} region. Variable-temperature magnetic susceptibility was measured with a SQUID magnetometer with an applied magnetic field of 2000 Oe for **1**, **2**, and **3**.

Caution! Perchlorate and azide salts are potentially explosive and should be handled carefully in small amounts.

4'-*p*-Tolyl-2,2':6',2''-terpyridine (ttp): Yield: 8%. ^1H NMR (400 MHz, CDCl_3): δ = 8.73 (s, 2 H), 8.69–8.60 (m, 4 H), 7.89–7.80 (m, 4 H), 7.51 (d, J = 6.3 Hz, 2 H), 7.32 (ddd, J = 7.2, 4.6, 1.2 Hz, 2 H), 2.45 (s, 3 H) ppm. $\text{C}_{22}\text{H}_{17}\text{N}_3$ (323.40): calcd. C 81.71, H 5.30, N 12.99; found C 81.53, H 5.47, N 12.50.

4'-(*p*-Bromomethylphenyl)-2,2':6',2''-terpyridine (ttp-Br): Yield 85%. ^1H NMR (400 MHz, CDCl_3): δ = 8.79 (s, 2 H), 8.76–8.69 (m, 4 H), 7.98–7.89 (m, 4 H), 7.61 (d, J = 6.5 Hz, 2 H), 7.41 (ddd, J = 7.5, 4.8, 1.3 Hz, 2 H) ppm. $\text{C}_{23}\text{H}_{16}\text{BrN}_3$ (414.30): calcd. C 65.68, H 4.01, N 10.44; found C 65.42, H 3.91, N 10.49.

[$\text{Mn}_2(\text{N}_3)_4(\text{ttp})_2$] (1**):** An aqueous solution (5 mL) of sodium azide (1.5 mmol) was placed in a tube to which was added a buffer layer of water/methanol (10 mL). A methanol solution (10 mL) of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) and ttp (0.5 mmol) was added to form a third layer. Orange crystals were formed on interdiffusion of the reactants in about 1 week. One suitable crystal was chosen for single-crystal X-ray diffraction. Yield: 80.9 mg (35% based on manganese). IR (KBr): $\tilde{\nu}$ = 2046 (vs) $\text{N}=\text{N}=\text{N}$, 1607 (vs), 1546 (s), 1546 (s), 1474 (s), 1329 (m), 1015 (m), 821 (m), 790 (m), 733 (w), 686 (w), 660 (w) cm^{-1} . $\text{C}_{44}\text{H}_{34}\text{Mn}_2\text{N}_{18}$ (924.77): calcd. C 57.15, H 3.71, N 27.26; found C 57.07, H 3.90, N 27.37.

[$\text{Mn}_2(\text{N}_3)_4(\text{ttp-N}_3)_2$] (2**):** A solution of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol) and ttp-Br (0.5 mmol) in methanol (10 mL) was slowly diffused into an aqueous solution (5 mL) of sodium azide (1.5 mmol) in the dark. After 1 week, well-formed orange single crystals were obtained. Yield: 75.5 mg (30% based on manganese). IR (KBr): $\tilde{\nu}$ = 2093 (vs), 2056 (vs), 1603 (vs), 1569 (s), 1546 (s), 1404 (s), 1347 (m), 1326 (m), 1246 (s), 1199 (w), 1165 (m), 1014 (s), 883 (w), 856 (w), 829 (w), 786 (s), 740 (w), 686 (w), 659 (w) cm^{-1} . $\text{C}_{44}\text{H}_{32}\text{Mn}_2\text{N}_{24}$ (1006.82): calcd. C 52.49, H 3.20, N 33.39; found C 52.11, H 3.29, N 33.85.

[$\text{Mn}_2(\text{N}_3)_4(\text{ttp-N}_3)_2$][$\text{Mn}(\text{ttp-N}_3)(\text{N}_3)_3$] (3**):** The synthetic method is slightly different from that of **2**. A solution of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.2 mmol) and ttp-Br (0.2 mmol) in methanol (10 mL) was diffused into a solution of sodium azide (1.5 mmol) in water (5 mL). After 4 weeks of exposure to light, red-brown crystals were formed. Yield: 25.7 mg (25% based on manganese). IR (KBr): $\tilde{\nu}$ = 2086 (sh), 2063 (vs), 2037 (vs), 1608 (vs), 1573 (s), 1547 (s), 1477 (s), 1431 (s), 1400 (s), 1326 (m), 1276 (m), 1246 (m), 1164 (m), 1013 (s), 891 (w), 829 (w), 790 (s), 733 (w), 690 (w), 659 (w) cm^{-1} . $\text{C}_{176}\text{H}_{128}\text{Mn}_8\text{N}_{102}$ (4111.32): calcd. C 51.42, H 3.14, N 34.75; found C 51.40, H 3.25, N 34.48.

X-ray Structure Determination: Diffraction data were collected with a Bruker Smart CCD area detector with graphite-monochromated $\text{Mo-K}\alpha$ (λ = 0.71073 Å) at room temperature. All calculations were performed by using the SHELXS-97 and SHELXL-97 programs.^[22] All structures were solved by direct method and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were located geometrically and refined by using a riding model.

CCDC-650165 to -650167 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Field dependence of magnetization at 2 K and electronic spectra in acetonitrile for complexes 1–3.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (20671055).

- [1] a) J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortés, L. Lezama, T. Rojo, *Coord. Chem. Rev.* **1999**, *193*, 1027–1068; b) M. M. Turnbull, T. Sugimoto, L. K. Thompson (Eds.), *Molecule-Based Magnetic Materials*, American Chemical Society, Washington, **1996**.
- [2] a) M. Fettohui, M. Khaled, A. Waheed, S. Golhen, L. Ouahab, J.-P. Sutter, O. Kahn, *Inorg. Chem.* **1999**, *38*, 3967–3971; b) S. Koner, S. Saha, T. Mallah, K.-I. Okamoto, *Inorg. Chem.* **2004**, *43*, 840–842; c) Y. Song, C. Massera, O. Roubeau, P. Gamez, A. M. M. Lanfredi, J. Reedijk, *Inorg. Chem.* **2004**, *43*, 6842–6847; d) C.-M. Liu, Z. Yu, R.-G. Xiong, K. Liu, X.-Z. You, *Inorg. Chem. Commun.* **1999**, *2*, 31–34; e) J. M. Domínguez-Vera, J. Suárez-Varela, I. B. Maimoun, E. Colacio, *Eur. J. Inorg. Chem.* **2005**, 1907–1912; f) M. Murugesu, M. Habrych, W. Wernsdorfer, K. A. Abboud, G. Christou, *J. Am. Chem. Soc.* **2004**, *126*, 4766–4767.
- [3] a) F. Meyer, S. Demeshko, G. Leibel, B. Kersting, E. Kaifer, H. Pritzkow, *Chem. Eur. J.* **2005**, *11*, 1518–1526; b) M. Monfort, I. Resino, J. Ribas, X. Solans, M. Font-Bardia, H. Stoeckli-Evans, *New J. Chem.* **2002**, *26*, 1601–1606; c) D. Ghoshal, T. K. Maji, E. Zangrando, T. Mallah, É. Rivière, N. R. Chaudhuri, *Inorg. Chim. Acta* **2004**, *357*, 1031–1038.
- [4] a) M. A. S. Goher, J. Cano, Y. Journaux, M. A. M. Abu-Youssef, F. A. Mautner, A. Escuer, R. Vicente, *Chem. Eur. J.* **2000**, *6*, 778–784; b) T. K. Karmakar, S. K. Chandra, J. Ribas, G. Mostafa, T. H. Lu, B. K. Ghosh, *Chem. Commun.* **2002**, 2364–2365; c) L. Zhang, L.-F. Tang, Z.-H. Wang, M. Du, M. Julve, F. Lloret, J.-T. Wang, *Inorg. Chem.* **2001**, *40*, 3619–3622; d) D.-Q. Ma, S. Hikichi, M. Akita, Y. Moro-oka, *J. Chem. Soc. Dalton Trans.* **2000**, 1123–1134; e) M. A. Halcrow, J. S. Sun, J. C. Huffman, G. Christou, *Inorg. Chem.* **1995**, *34*, 4167–4177.
- [5] a) G. S. Papaefstathiou, S. P. Perlepes, A. Escuer, R. Vicente, M. Font-Bardia, X. Solans, *Angew. Chem. Int. Ed.* **2001**, *40*, 884–886; b) G. S. Papaefstathiou, A. Escuer, R. Vicente, M. Font-Bardia, X. Solans, S. P. Perlepes, *Chem. Commun.* **2001**, 2414–2415.
- [6] P. Mialane, A. Dolbecq, J. Marrot, E. Rivière, F. Sécheresse, *Chem. Eur. J.* **2005**, *11*, 1771–1778.
- [7] a) F. Meyer, P. Kircher, H. Pritzkow, *Chem. Commun.* **2003**, 774–775; b) S. Demeshko, G. Leibel, W. Maringgele, F. Meyer, C. Mennerich, H.-H. Klaus, H. Pritzkow, *Inorg. Chem.* **2005**, *44*, 519–528.
- [8] M.-F. Charlot, O. Kahn, M. Chaillet, C. Larrieu, *J. Am. Chem. Soc.* **1986**, *108*, 2574–2581.
- [9] a) E. Ruiz, J. Cano, S. Alvarez, P. Alemany, *J. Am. Chem. Soc.* **1998**, *120*, 11122–11129; b) M. A. Aebersold, B. Gillon, O. Plantevin, L. Pardi, O. Kahn, P. Bergerat, I. von Seggern, F. Tuczek, L. Öhrström, A. Grand, E. Lelièvre-Berna, *J. Am. Chem. Soc.* **1998**, *120*, 5238–5245.
- [10] a) P. Manikandan, R. Muthukumar, K. R. J. Thomas, B. Varghese, G. V. R. Chandramonli, P. T. Manoharan, *Inorg. Chem.* **2001**, *40*, 2378–2389; b) L. K. Thompson, S. S. Tandon, F. Lloret, J. Cano, M. Julve, *Inorg. Chem.* **1997**, *36*, 3301–3306; c) P. S. Mukherjee, T. K. Maji, G. Mostafa, T. Mallah, N. R. Chaudhuri, *Inorg. Chem.* **2000**, *39*, 5147–5150.
- [11] a) S. S. Tandon, L. K. Thompson, M. E. Manuel, J. N. Bridson, *Inorg. Chem.* **1994**, *33*, 5555–5570; b) B. Kersting, G. Steinfeld, D. Siebert, *Chem. Eur. J.* **2001**, *7*, 4253–4258; c) A. Escuer, X. Vicente, M. Solans, M. Font-Bardia, *Inorg. Chem.* **1994**, *33*, 6007–6011.
- [12] a) P. S. Mukherjee, T. K. Maji, G. Mostafa, W. Hibbs, N. R. Chaudhuri, *New J. Chem.* **2001**, *25*, 760–763; b) S. K. Dey, N. Mondal, M. S. El Fallah, R. Vicente, A. Escuer, X. Solans, M. Font-Bardia, T. Matsushita, V. Gramlich, S. Mitra, *Inorg. Chem.* **2004**, *43*, 2427–2434; c) C. S. Hong, Y. Do, *Angew. Chem. Int. Ed.* **1999**, *38*, 193–195; d) P. S. Mukherjee, T. K. Maji, A. Escuer, R. Vicente, J. Ribas, G. Rosair, F. A. Mautner, N. R. Chaudhuri, *Eur. J. Inorg. Chem.* **2002**, 943–949.
- [13] a) B. Woodard, R. D. Willett, S. Haddad, B. Twamley, C. J. Gomez-Garcia, E. Coronado, *Inorg. Chem.* **2004**, *43*, 1822–1824; b) F. A. Mautner, S. Hanna, R. Cortes, L. Lezama, M. G. Barandika, T. Rojo, *Inorg. Chem.* **1999**, *38*, 4647–4652.
- [14] a) R. Cortés, J. L. Pizarro, L. Lezama, M. I. Arriortua, T. Rojo, *Inorg. Chem.* **1994**, *33*, 2697–2700; b) C.-M. Liu, S. Gao, D.-Q. Zhang, Z.-L. Liu, D.-B. Zhu, *Inorg. Chim. Acta* **2005**, *358*, 834–838.
- [15] a) T. K. Karmakar, B. K. Ghosh, A. Usman, H.-K. Fun, E. Rivière, T. Mallah, G. Aromi, S. K. Chandra, *Inorg. Chem.* **2005**, *44*, 2391–2399; b) Z.-H. Ni, H.-Z. Kou, L. Zheng, Y.-H. Zhao, L. F. Zhang, R. J. Wang, A. L. Cui, O. Sato, *Inorg. Chem.* **2005**, *44*, 4728–4736; c) T. K. Karmakar, G. Aromi, B. K. Ghosh, A. Usman, H.-K. Fun, T. Mallah, U. Behrens, X. Solans, S. K. Chandra, *J. Mater. Chem.* **2006**, *16*, 278–285.
- [16] A. Das, G. M. Rosair, M. S. El Fallah, J. Ribas, S. Mitra, *Inorg. Chem.* **2006**, *45*, 3301–3306.
- [17] R. J. Payne, E. M. M. Bulloch, A. D. Abell, C. Abell, *Org. Biomol. Chem.* **2005**, *3*, 3629–3635.
- [18] J. Limburg, J. S. Vrettos, R. H. Crabtree, G. W. Brudvig, J. C. de Paula, A. Hassan, A.-L. Barra, C. Duboc-Toia, M.-N. Collob, *Inorg. Chem.* **2001**, *40*, 1698–1703.
- [19] N. Re, E. Gallo, C. Floriani, H. Miyasaka, N. Matsumoto, *Inorg. Chem.* **1996**, *35*, 6004–6008.
- [20] a) J. L. Manson, A. M. Arif, J. S. Miller, *Chem. Commun.* **1999**, 1479–1480; b) M. A. M. Abu-Youssef, A. Escuer, D. Gatteschi, M. A. S. Goher, F. A. Mautner, R. Vicente, *Inorg. Chem.* **1999**, *38*, 5716–5723.
- [21] a) V. Uma, V. G. Vaidyanathan, B. U. Nair, *Bull. Chem. Soc. Jpn.* **2005**, *78*, 845–850; b) J. P. Collin, S. Guillerez, J. P. Sauvage, F. Barigelletti, L. D. Cola, L. Flamigni, V. Balzan, *Inorg. Chem.* **1991**, *30*, 4230–4238; c) F. Tessoro, D. Roberto, R. Ugo, M. Pizzotti, *Inorg. Chem.* **2005**, *44*, 8967–8978.
- [22] G. M. Sheldrick, *SHELX97: Programs for Crystal Structure Analysis*, University of Göttingen, Germany, **1997**.

Received: June 29, 2007

Published Online: October 29, 2007