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Four novel linear trinuclear assemblies containing bridging triazole ligands. Crystal structure, magnetic, semiconducting and fluorescent properties

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Abstract

Four homotrinuclear linear coordination compounds with bridging ligand of (m-phenol)-1,2,4-triazole, $[Mn_3(L)_6(H_2O)_6](ClO_4)_6$ (1), $[Ni_3(L)_6(H_2O)_6](BF_4)_6$ (2), $[Cd_3(L)_6(H_2O)_6](ClO_4)_6$ (2H₂O·2DMF·2EtOH (3), $[Zn_3(L)_8(H_2O)_4](BF_4)_4(SiF_6)$ (2EtOH·12H₂O (4), have been synthesized and structurally determined. The structures consist of three metal ions in linear arrangements, linked to each other by two pairs of three N1, N2 bridging triazole ligands. The negative value of *J* suggests that antiferromagnetic interaction exists in 1. Green fluorescence of 2 and 4 with emissions at 518 nm for 2 and 524 for 4 is possibly assigned to LMCT. The energy gaps of the compounds 2 and 4 are 1.82 and 1.97 eV, respectively, which suggests that the two materials behave as semiconductors. © 2006 Elsevier B.V. All rights reserved.

Keywords: Crystal structure; Diffuse reflectance spectra; Fluorescence; Magnetism; Linear trinuclear; 1,2,4-Triazole

1. Introduction

Since the first crystal structure of the trinuclear complex $[Ni_3(Htrz)_6(H_2O)_6](NO_3)\cdot 2H_2O$ (Htrz = 1,2,4-triazole) reported in [1], the knowledge of the 1,2,4-triazole complexes and their structures and properties has developed rapidly. However, not many compounds in this class have been described and only a small number of X-ray structural determinations of 1,2,4-triazole complexes are known. The triazoles with donor atoms in the five-membered ring possess the capability of linking metal centers to constitute a bridge between the metal centers. The geometrical similarity of the 1,2,4-triazoles to imidazoles makes the triazoles and their complexes sought after compounds to mimic natural processes, which are devoted to

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mimicking the enzymatic reactions by functionalized models [2]. The coordination complexes of 1,2,4-triazoles possess a great diversity of structures, which is connected to the di- or trinucleating properties of the neutral and anionic triazole ring. The 1,2,4-triazoles have attracted great and growing interest in coordination chemistry because of the fact that they can give transition metal coordination polymers with the two closely adjacent bridging nitrogen atoms, and can effectively transmit magnetic interaction between paramagnetic centers [3]. The chelating nitrogen donor atoms can support the very strong ligand field in ferrous complexes to induce a transition from the HS to the LS state on cooling or increasing pressure [4]. Such systems are also applicable for information storage [5]. Herein, we focus on the linear arrangements containing 4-substituted (m-phenol)-1,2,4triazole. Four novel linear trinuclear complexes, $[Mn_3(L)_6(H_2O)_6](ClO_4)_6$ (1), $[Ni_3(L)_6(H_2O)_6](BF_4)_6$ (4DMF

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2. Experimental section

2.1. General

All chemicals were used as purchased without further purification except that (*m*-phenol)-1,2,4-triazole (L) was prepared by literature methods [6] with some modifications of prolonging the reaction time at 170 °C to enhance the yield. $ZnSiF_6$ and $Zn(BF_4)_2$ were prepared by Zn₂(OH)₂CO₃ reacting with H₂SiF₆ and HBF₄, respectively. $Mn(ClO_4)_2$, $Cd(ClO_4)_2$ were, respectively, obtained from HClO₄ reacting with MnCO₃ and Cd₂(OH)₂CO₃. Ni₂(OH)₂CO₃ reacted with HBF₄ to synthesize Ni(BF₄)₂. The IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellets in the range $4000-400 \text{ cm}^{-1}$ and elemental analyses of C, H and N were carried out on a Vario EL III elemental analyzer. The electronic emission and excitation spectra recorded at room temperature were obtained on an Edinburgh FL/FS 920 TCSPC fluorescence spectrophotometer at room temperature with excitation and emission slit at 5.0 nm, increment 1.0 nm and integration time 0.1 s. Optical diffuse reflectance spectra were measured at room temperature with a Lambda 35 UV-vis spectrophotometer. Variable-temperature, solid-state direct current (DC) magnetic susceptibility data down to 2 K were collected on a Quantum Design PPMS60000 magnetometer in our institute. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants.

2.2. Synthesis

2.2.1. Synthesis of (m-phenol)-1,2,4-triazole (L)

The reaction was carried out by heating the diformylhydrazine (6 mmol, 0.56 g) with *m*-amino-phenol (6 mmol, 0.53 g) at 443 K for three days. The orange product was purified by recrystallization from ethanol. Yield based on *m*-amino-phenol: 0.79 g, 82%. Elemental analysis (%), Found (calcd): C, 59.80 (59.62); H, 4.45(4.38); N, 26.07 (25.90) Scheme 1.

2.2.2. Synthesis of $[Mn_3(L)_6(H_2O)_6](ClO_4)_6$ (1)

To a solution of (*m*-phenol)-1,2,4-triazole (64 mg, 0.4 mmol) in a minimum of water was added aqueous solu-



Scheme 1. The synthesis of (m-phenol)-1,2,4-triazole.

tion of 0.2 mmol Mn(ClO₄)₂ (about 52 mg) yielding yellow suspension. The suspension was filtered and the filtrate was placed to naturally evaporate. The orange block crystals were isolated by slow evaporation of the aqueous solution at room temperature for a couple of weeks. Yield on L: 53 mg, 43%. Elemental analysis (%), Found (calcd): C, 31.42(31.39); H, 2.92(2.96); N, 13.68(13.73). IR data (in KBr, cm⁻¹): 3433 (s), 3125 (m), 2975 (m), 2896 (w), 1616 (s), 1544 (w), 1496 (w), 1462 (w), 1382 (w), 1301 (w), 1207 (m), 1113 (s), 1090 (s), 1012 (m), 1000 (m), 870 (m), 781 (m), 650 (m), 625 (m), 458 (w).

2.2.3. Synthesis of $[Ni_3(L)_6(H_2O)_6](BF4)_6 \cdot 4DMF(2)$

The 10 mL aqueous solution of Ni(BF₄)₂ (about 46 mg, 0.2 mmol) was added dropwise to a solution of (*m*-phenol)-1,2,4-triazole (64 mg, 0.4 mmol) in a minimum of water. The reaction mixture was stirred at room temperature for 6 h producing green precipitate. The green precipitate was filtered, washed with water and ethanol in turn and added to DMF. Evaporation of DMF solution yielded green prismatic crystals suitable for X-ray diffraction. Yield on L: 52 mg, 38%. Elemental analysis (%), Found (calcd): 34.89(34.91); H, 3.95(4.00); N, 14.97(14.93). IR data (in KBr, cm⁻¹): 3410 (s), 2974 (m), 2927 (m), 1629 (m), 1455 (w), 1381 (w), 1326 (w), 1271 (w), 1089 (s), 1050 (s), 881 (s), 804 (s), 669 (w), 433 (w).

2.2.4. Synthesis of $[Cd_3(L)_6(H_2O)_6](ClO_4)_6 \cdot 2H_2O \cdot 2DMF \cdot 2EtOH(3)$

To a stirring aqueous solution (10 mL) containing (*m*phenol)-1,2,4-triazole (64 mg, 0.4 mmol) was added dropwise an aqueous solution of Cd(ClO₄)₂ (about 62 mg, 0.2 mmol). The resulting yellow mixture was filtered, washed with water and added to mixture of DMF and EtOH (v/v, 10:5). The yellow prismatic crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the solution at room temperature for several weeks. Yield on L: 42 mg, 27%. Elemental analysis (%), Found (calcd): 30.55(30.51); H, 3.75(3.71);N, 12.31(12.27). IR data (in KBr, cm⁻¹): 3435 (s), 3121 (m), 2977 (m), 2898 (w), 1616 (s), 1542 (w), 1492 (w), 1460 (w), 1380 (w), 1303 (w), 1205 (m), 1089 (s), 1010 (m), 1005 (m), 871 (m), 781 (m), 652 (m), 623 (m), 457 (w).

2.2.5. Synthesis of $[Zn_3(L)_8(H_2O)_4](BF_4)_4(SiF_6)$ 2EtOH·12H₂O (4)

A 20 mL aqueous solution of (m-phenol)-1,2,4-triazole (96 mg, 0.6 mmol) was added to mixture of aqueous solution containing Zn(BF₄)₂ (24 mg, 0.1 mmol) and ZnSiF₆ (20 mg, 0.1 mmol) yielding a yellow suspension. The yellow suspension was filtered and the filtrate was placed to naturally evaporate. The orange prismatic crystals were isolated by slow evaporation of the solution at room temperature for several weeks. Yield on L: 38 mg, 22%. Elemental analysis (%), Found (calcd): 34.72(34.68); H, 4.25(4.28); N, 14.32(14.27). IR data (in KBr, cm⁻¹): 3433 (s), 3125 (m), 2975 (m), 2896 (w), 1616 (s), 1544 (w), 1496 (w), 1462

(w), 1382 (w), 1301 (w), 1207 (m), 1113 (s), 1090 (s), 1012 (m), 1000 (m), 870 (m), 781 (m), 650 (m), 625 (m), 458 (w).

2.3. Structural determination and refinement of 1-4

A summary of the crystal data and data collection and refinement parameters for the complexes 1–4 is given in Table 1. Data were collected on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293(2) K. The intensity data were collected by the ω scan technique and were reduced using CrystalClear program [7]. The structures were solved by direct methods using SHELXTLTM package of crystallographic software [8] and refined by full-matrix least-squares technique on F^2 . All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in the final stage of the refinement on calculated positions bonded to their carrier atoms.

3. Results and discussion

3.1. Description of structures of 1-4

Attempts to synthesize linear chain compounds with triazole functionalities in conjunction with non-coordinating anions resulted in a series of polynuclear cations of composition $[M_3(trz)_6(H_2O)_6]$ [9] (trz = 1,2,4-triazoles). Though the reactions of 4-substituted 1,2,4-triazoles with the metal salts of non-coordinating anions, such as CIO_4^- , BF_4^- ,

Table 1 Crystallographic and experimental data for 1–4

 PF_6^{2-} and SiF_6^{2-} , yield either 1-D chain [10] or linear trinuclear entities, the existence of the non-coordinating anions has no direct effect on the geometries of the polynuclear complexes. The structures of 1-4 are very similar, therefore are discussed together. Figs. 1 and 2 give the principal structural features of polynuclear cations of 1-3 and 4, respectively, and Tables 2–5, respectively, list the selected bond distances and bond angles of compounds 1-4. The trinuclear cations have the same overall structure: three metal cations with +6 charges are arranged in linear geometries with crystallographic inversion centers located on the center metal atoms, linking to each other by two pairs of three bridging triazole ligands as bidentate ligands by 1and 2-positioned N atoms; the coordination spheres of all metal atoms are (4+2) octahedral geometries: the center metal atoms are surrounded by six N atoms to form almost perfect ML₆ octahedra; the terminal metal atoms are coordinated to three water molecules and three N atoms for 1-3 and one more monodentate L takes the place of one water molecule in the distorted octahedral environment of each terminal metal atom of 4. Namely, the terminal metal atoms are surrounded by four N atoms from four separate L ligands and two water molecules (Fig. 2). The bond angles around the center metal atoms are all very close to 90° [89.74(9)–90.26(9)° for 1; 89.41(7)–90.59(7)° for 2; 87.48(6)-92.52(6)° for 3; 89.67(7)-90.33(7)° for 4], which is in accord with their almost perfect ML₆ octahedra. As expected, the ranges of those around the terminal ones are larger: 87.62(8)-92.54(9)° for 1; 85.76(5)-92.00(6)° for

	1	2	3	4
Empirical formula Color and habit	C ₄₈ H ₅₄ Cl ₆ Mn ₃ N ₁₈ O ₃₆ Orange Block	$C_{60}H_{82}B_6F_{24}N_{22}Ni_3O_{16}$ Green Block	C ₅₈ H ₈₄ Cd ₃ Cl ₆ N ₂₀ O ₄₂ Yellow Block	C ₆₈ H ₁₀₀ B ₄ F ₂₂ N ₂₄ O ₂₆ SiZn ₃ Orange Prism
Crystal size (mm)	$0.4 \times 0.34 \times 0.34$	$0.2 \times 0.2 \times 0.15$	$0.23 \times 0.2 \times 0.1900$	$0.4 \times 0.35 \times 0.22$
Crystal system	Rhombohedral		Monoclinic	Monoclinic
space group	<i>R</i> -3	<i>P</i> 1	<i>P2</i> ₁ /c	C2/c
$a(\dot{\mathbf{A}})$	12.716(3)	12.141(6)	13.480(14)	38.248(11)
$b(\dot{A})$	12.716(3)	12.443(6)	18.519(18)	14.480(4)
<i>c</i> (Å)	12.716(3)	15.539(7)	18.007(18)	21.805(6)
α (°)	76.845(17)	93.923(3)		_
β (°)	76.845(17)	108.081(3)	108.891(9)	120.333(2)
γ (°).	76.845(17)	104.480(5)		
$V/(\dot{A})^3$	1915.8(7)	2133.4(17)	4253(7)	10423(5)
Ζ	1	1	2	4
Fw	1836.61	2064.47	2283.35	2355.16
$D_{\rm calcd} ({\rm Mgm^{-3}})$	1.592	1.607	1.783	1.501
$\mu (\mathrm{mm}^{-1})$	0.795	0.782	1.038	0.814
<i>F</i> (000)	933	1054	2308	4824
θ (°)	4.01 to 24.99	3.22 to 25.00	3.17 to 25.02	3.04 to 25.03
Reflections measured	12010	13548	25382	32421
Independent Refs	2240 ($R_{\rm int} = 0.0526$)	7432 ($R_{\rm int} = 0.0590$)	7439 ($R_{\rm int} = 0.0735$)	9152 ($R_{\rm int} = 0.0507$)
Observed Refs	989	5467	5927	6690
Final R_1 , $wR_2 [I \ge 2\sigma(I)]$	0.0959, 0.2516	0.0622, 0.1365	0.0862, 0.1982	0.0873, 0.2380
R_1 , wR_2 (all data)	0.1433, 0.2843	0.0909, 0.1545	0.1096, 0.2177	0.1164, 0.2658
S	1.029	1.004	1.064	1.073
$(\Delta/\sigma)_{\rm max/min}$	0.015, 0.001	0.000, 0.000	1.363, 0.016	0.030, 0.002
Largest difference peak/ $e(Å)^{-3}$	0.761, -0.600	1.243, -0.523	1.126, -1.575	1.411, -0.547

 $R_1 = \left(\sum \|F_o| - |F_c\| / \sum |F_o|\right). \quad wR_2 = \left[\sum (w(F_o^2 - F_c^2)^2) / \sum (w|F_o^2|^2)\right]^{1/2}.$



Fig. 1. The linear arrangement of polynuclear cations $[M_3(L)_6(H_2O)_6]^{6+}$ [M=Mn (1), Ni (2), Cd (3)]. Hydrogen atoms are omitted.

2; 83.91(8)–94.93(6)° for 3; 87.05(7)–91.73(7)° for 4. The M–N distances are in normal ranges and the center average M–N distances are about 0.03–0.05 Å longer than those terminal ones [M–N_{center} = 2.264 for 1; 2.100 for 2; 2.332 for 3; 2.176 for 4. M–N_{terminal} = 2.232 for 1; 2.052 for 2; 2.2937 for 3; 2.133 for 4], which is related to the reason that the center metal atoms need longer bond distances to overcome the more steric hindrance.

3.2. Magnetic property of 1

The magnetic behavior of $[Mn_3(L)_6(H_2O)_6](ClO_4)_6$ (1) is shown in Fig. 3 in the form of χ_m vs T and χ_m T vs T plots. The produce $\chi_m T$ decreases on cooling and 1 follows the Curie-Weiss law $\chi_m = 179.1/(T + 6.56)$ in the temperature range of 50-300 K, whose magnetic behaviors indicate weak antiferromagnetic interactions between adjacent manganese(II) ions. Compound 1 is a symmetrical linear trinuclear complex, thus the corresponding magnetic susceptibility data are represented by Eq. (1) [the Hamiltonian being $H = -2J[S_1 \cdot S_2 + S_2 \cdot S_3]$, assuming that the exchange integrals between the neighboring manganese(II) are identical $(J_{12} = J_{23} = J)$ and the integral between the terminal manganese(II) is zero $(J_{13} = 0)$ [11], where χ_m is magnetic susceptibility per tri manganese(II); N is Avogadro's number; β is Bohr's magneton; k is Boltzmann's constant and J is the isotropic exchange parameter. The best least-squares fit of the theoretical equation to experimental data leads to g = 2.03, J/k = -0.446 K and the agreement factor R = $1.06 \times 10^{-2} [R = \sum |(\chi_m)_{obs} - (\chi_m)_{calc}|^2 / \sum (\chi_m)_{obs}^2].$ The negative J value suggests that antiferromagnetic interaction existing in 1 is in agreement with the result of the fit obtained from the Curie-Weiss law.

$$\chi_{\rm m} = \frac{2Ng^2\beta^2}{KT} \cdot \frac{A}{B} \tag{1}$$

where

$$A = 14x^{44} + 5x^{40} + 31x^{36} + 14x^{34} + 5x^{32} + x^{30} + 105x^{26} + 5x^{22} + 19x^{20} + 30x^{18} + 69x^{16} + 91x^{14} + 30x^{12} + 55x^8 + 91x^4 + 140$$



Fig. 2. The linear arrangement of polynuclear cations $[Zn_3(L)_8(H_2O)_4]^{6+}$. Hydrogen atoms are omitted.

Table 2 $\begin{pmatrix} \\ A \end{pmatrix}$ and bond angles (°) for 1

Mn(1) - N(12)	2.264(2)
Mn(2) - O(1W)	2.195(2)
Mn(2)—N(11)	2.232(2)
N(12)#1-Mn(1)-N(12)#2	89.74(9)
N(12)#2-Mn(1)-N(12)	90.26(9)
O(1W)#2-Mn(2)-O(1W)	88.76(10)
O(1W)#2-Mn(2)-N(11)	176.13(8)
O(1W) - Mn(2) - N(11)	92.54(9)
O(1W)-Mn(2)-N(11)#2	87.62(8)
N(11)-Mn(2)-N(11)#2	91.16(9)
C(15) - N(11) - Mn(2)	128.4(2)
N(12) - N(11) - Mn(2)	124.94(16)
C(13) - N(12) - Mn(1)	128.0(2)
N(11) - N(12) - Mn(1)	124.58(16)

Symmetry code: #1 = -x, -y, -z; #2 = y, z, x; #3 = -y, -z, -x.

$$B = 7x^{44} + 5x^{40} + 12x^{36} + 7x^{34} + 6x^{32} + 3x^{30}$$

+ $35x^{26} + 5x^{22} + 12x^{20} + 9x^{18} + 18x^{16} + 13x^{14}$
+ $9x^{12} + 11x^8 + 13x^4 + 15$
 $x = \exp(-J/KT)$

The superexchange integral J between adjacent metal ions comes from the contributions of the sum of both ferromagnetic (J_F) and antiferromagnetic (J_{AF}). There mainly exist two factors to control the value of J. First, the σ -overlap density between the Mn(II) ions and ligand molecular orbitals is the main pathway to govern the superexchange interaction. When metal atoms are bridged by polyatomic extended ligands like 1,2,4-triazoles, J_{AF} will hold the predominance increasing with the ratio to the square of the overlap integral between magnetic orbitals centered on

Table 3 (A) Selected bond distances (A) and bond angles (°) for 2

nearest neighbor metal ions [12]. Therefore, the 1,2,4-triazole rings twisting out of the equatorial plane formed by the two Mn(II) ions involved are also expected to decrease the overlap of the magnetic orbitals in the bridging region [13]. Second, the Mn–N–N angles play an important role in the exchange interaction: a symmetric bridging model with the M–N–N angles deviating from 135° allows a less antiferromagnetic interaction than the more symmetric bridging model in a M(N-N)₂M framework. It is consistent with the calculation made by A. Escuer [14], showing that the antiferromagnetic component of J reaches its maximum for the parameters M-N-N 135° and N-M-N 90°. Though the N-Mn-N angles are around 90°, the Mn-N-N angles in large deviations from 135° decrease the value of J_{AF} . The overall result of 1 shows very weak antiferromagnetic interaction between adjacent Mn(II) centers. Both antiferromagnetic and ferromagnetic interactions are reported in the complexes containing triazole ligands, indicating additional structural factors determining the sign and magnitude of J should be taken into consideration.

3.3. Fluorescent properties of 2 and 4

In contrast to the studies of magnetic properties, very limited fluorescent studies on 1,2,4-triazole coordination complexes are reported. The solid-state electronic emission spectra of the compounds 2 and 4 at room temperature show luminescence features as given in Fig. 4. Very strong green fluorescence for 2 and 4 both can be observed. The maximum emission wavelength at 518 nm for 2 by excited the solid sample under violet light at $\lambda_{ex} = 397$ nm. Excitation of the solid sample of 4 with UV light at 375 nm

Selected bond distances (A) and bond angles (1) for 2					
Ni(1)—N(22)	2.0791(17)	Ni(2)—N(21)	2.0629(18)		
Ni(1)—N(11)	2.1109(15)	Ni(2)—O(2W)	2.0772(14)		
Ni(1)—N(31)	2.1112(17)	Ni(2)—O(3W)	2.0807(16)		
Ni(2)—N(12)	2.0456(17)	Ni(2)—O(1W)	2.0958(16)		
Ni(2)—N(32)	2.0475(16)				
N(22)-Ni(1)-N(11)#1	89.88(6)	N(32)—Ni(2)—O(1W)	88.58(6)		
N(22)-Ni(1)-N(11)	90.12(6)	N(21)-Ni(2)-O(1W)	176.09(5)		
N(22)-Ni(1)-N(31)#1	90.59(7)	O(2W)— $Ni(2)$ — $O(1W)$	89.83(6)		
N(11)-Ni(1)-N(31)#1	89.67(6)	O(3W)-Ni(2)-O(1W)	85.76(5)		
N(22)-Ni(1)-N(31)	89.41(7)	C(11) - N(11) - Ni(1)	130.32(13)		
N(11)-Ni(1)-N(31)	90.33(6)	N(12)-N(11)-Ni(1)	122.79(10)		
N(12)-Ni(2)-N(32)	91.30(6)	C(12)-N(12)-Ni(2)	126.33(13)		
N(12)-Ni(2)-N(21)	91.91(6)	N(11)-N(12)-Ni(2)	126.62(9)		
N(32)— $Ni(2)$ — $N(21)$	91.11(6)	C(21)— $N(21)$ — $Ni(2)$	129.19(13)		
N(12)-Ni(2)-O(2W)	90.10(5)	N(22)-N(21)-Ni(2)	123.26(12)		
N(32)-Ni(2)-O(2W)	177.92(6)	C(22)— $N(22)$ — $Ni(1)$	126.39(12)		
N(21)-Ni(2)-O(2W)	90.38(6)	N(21)-N(22)-Ni(1)	126.57(12)		
N(12)-Ni(2)-O(3W)	176.06(5)	C(31) - N(31) - Ni(1)	128.74(13)		
N(32)-Ni(2)-O(3W)	91.89(5)	N(32) - N(31) - Ni(1)	124.31(10)		
N(21)-Ni(2)-O(3W)	90.35(6)	C(32)— $N(32)$ — $Ni(2)$	127.72(13)		
O(2W)-Ni(2)-O(3W)	86.65(5)	N(31)-N(32)-Ni(2)	125.02(11)		
N(12)—Ni(2)—O(1W)	92.00(6)				

Symmetry code: #1 = -x, -y, -z.

Table 4	,				
Selected bond distances	(Å) an	d bond	angles	(°)	for 3

Cd(1) - N(21)	2.3054(16)	Cd(2) - N(31)	2.2760(17)
Cd(1) - N(11)	2.337(2)	Cd(2)—O(2W)	2.2933(16)
Cd(1) - N(32)	2.3543(17)	Cd(2)—N(22)	2.3205(17)
Cd(2)—O(3W)	2.2716(16)	Cd(2)—O(1W)	2.368(2)
N(21)-Cd(1)-N(11)	91.13(7)	N(31)-Cd(2)-O(1W)	86.18(6)
N(21)-Cd(1)-N(11)#1	88.87(7)	O(2W)— $Cd(2)$ — $O(1W)$	89.58(7)
N(21)#1-Cd(1)-N(32)	91.12(8)	N(12)#1-Cd(2)-O(1W)	175.49(4)
N(21)— $Cd(1)$ — $N(32)$	88.88(8)	N(22)-Cd(2)-O(1W)	86.95(7)
N(11)-Cd(1)-N(32)	87.48(6)	C(17) - N(11) - Cd(1)	130.07(10)
N(11)-Cd(1)-N(32)#1	92.52(6)	N(12) - N(11) - Cd(1)	123.43(7)
O(3W)-Cd(2)-N(31)	174.10(3)	C(18)-N(12)-Cd(2)#1	127.51(10)
O(3W)-Cd(2)-O(2W)	83.91(8)	N(11)-N(12)-Cd(2)#1	125.17(9)
N(31)-Cd(2)-O(2W)	90.23(8)	C(27) - N(21) - Cd(1)	123.55(9)
O(3W)-Cd(2)-N(12)#1	86.23(7)	N(22)-N(21)-Cd(1)	129.59(8)
N(31)-Cd(2)-N(12)#1	94.93(6)	C(28) - N(22) - Cd(2)	132.21(10)
O(2W)-Cd(2)-N(12)#1	94.78(7)	N(21)-N(22)-Cd(2)	120.25(8)
O(3W)-Cd(2)-N(22)	94.82(8)	C(37)—N(31)—Cd(2)	126.97(10)
N(31)-Cd(2)-N(22)	90.98(8)	N(32) - N(31) - Cd(2)	126.56(7)
O(2W)-Cd(2)-N(22)	176.24(3)	C(38) - N(32) - Cd(1)	130.41(9)
N(12)#1-Cd(2)-N(22)	88.66(7)	N(31)-N(32)-Cd(1)	122.54(8)
O(3W)-Cd(2)-O(1W)	93.11(7)		

Symmetry code: #1 - x, -y + 2, -z + 2.

Table 5 Selected bond distances (Å) and bond angles (°) for **4**

Zn(1)—N(12)	2.1545(14)	Zn(2)—N(41)	2.128(2)
Zn(1) - N(32)	2.1846(19)	Zn(2) - N(11) #1	2.133(2)
Zn(1) - N(21)	2.190(2)	Zn(2) - N(31)	2.1525(18)
Zn(2) - N(22)	2.1203(18)	Zn(2)— $O(2W)$	2.1554(17)
Zn(2)— $O(1W)$	2.1240(18)		
N(12)-Zn(1)-N(32)#1	88.91(6)	N(41)-Zn(2)-O(2W)	87.34(8)
N(12)— $Zn(1)$ — $N(32)$	91.09(6)	N(11)#1-Zn(2)-O(2W)	88.89(7)
N(12)— $Zn(1)$ — $N(21)$	89.73(7)	N(31)-Zn(2)-O(2W)	89.18(7)
N(32)— $Zn(1)$ — $N(21)$	89.67(7)	C(18)-N(11)-Zn(2)#1	128.29(15)
N(12)— $Zn(1)$ — $N(21)$ #1	90.27(7)	N(12)-N(11)-Zn(2)#1	124.38(11)
N(32)— $Zn(1)$ — $N(21)$ #1	90.33(7)	C(17) - N(12) - Zn(1)	126.33(14)
N(22)-Zn(2)-O(1W)	89.05(7)	N(11) - N(12) - Zn(1)	126.69(14)
N(22)— $Zn(2)$ — $N(41)$	94.49(8)	C(28) - N(21) - Zn(1)	129.41(14)
O(1W)-Zn(2)-N(41)	89.76(8)	N(22)-N(21)-Zn(1)	123.56(14)
N(22)— $Zn(2)$ — $N(11)$ #1	89.28(8)	C(27)— $N(22)$ — $Zn(2)$	126.18(15)
O(1W)-Zn(2)-N(11)#1	90.44(7)	N(21)-N(22)-Zn(2)	127.04(16)
N(41)— $Zn(2)$ — $N(11)$ #1	176.23(7)	C(38)— $N(31)$ — $Zn(2)$	125.68(13)
N(22)— $Zn(2)$ — $N(31)$	91.73(7)	N(32) - N(31) - Zn(2)	126.55(14)
O(1W)-Zn(2)-N(31)	179.20(7)	C(37)— $N(32)$ — $Zn(1)$	128.54(15)
N(41)— $Zn(2)$ — $N(31)$	90.01(8)	N(31) - N(32) - Zn(1)	123.19(13)
N(11)#1-Zn(2)-N(31)	89.74(7)	C(48)— $N(41)$ — $Zn(2)$	132.69(15)
N(22)-Zn(2)-O(2W)	177.96(7)	N(42) - N(41) - Zn(2)	120.95(15)
O(1W)-Zn(2)- $O(2W)$	90.05(7)		

Symmetry code: #1 = -x + 3/2, -y + 3/2, -z + 1.

produces the maximum emission wavelength at 524 nm. Compared to the free ligand (blue fluorescence with the emission at 450 nm with $\lambda_{ex} = 370$ nm) [15], great red shifts with about 70 nm can be found, indicating the emissions around at 520 nm possibly originate from ligand-to-metal transfer (LMCT). Interestingly, the sample of **2** can be excited by violet light at 397 nm, which is different from other 1,2,4-triazole coordination complexes excited by UV light.

3.4. Properties of diffuse reflectance spectra of 2 and 4

Optical diffuse reflectance spectra were measured at room temperature. The samples of **2** and **4** were ground into fine powder and pressed onto a thin glass slide holder. The BaSO₄ plate was used as reference. The absorption spectra were calculated from reflection spectra by the Kubelka–Munk function: $\alpha/S = (1 - R)^2/2R$, where α is the absorption coefficient, S is the scattering coefficient which



Fig. 3. Plot of χ_m vs T and $\chi_m T$ vs T over 2–300 K at a field of 1 T showing a Curie-Weiss paramagnetic behavior of **1**.



Fig. 4. The solid-state electronic spectra of **2** ($\lambda_{ex} = 397 \text{ nm}$), **4** ($\lambda_{ex} = 375 \text{ nm}$) and free (*m*-phenol)-1,2,4-triazole ($\lambda_{ex} = 370 \text{ nm}$) recorded at room temperature.

is practically wavelength independent when the particle size is larger than 5 μ m, and *R* is the reflectance. The optical properties of **2** and **4** were assessed by their optical diffuse reflectance data [16]. The Kubelka–Munk (or remission, *F*) functions converted from the diffuse reflectance data were



Fig. 5. The band gaps of **2** and **4** estimated to be 1.82, and 1.97 eV were assessed by the optical diffuse reflectance data.

plotted according to the diffuse reflectance data as shown in Fig. 5. The energy gaps of the compounds 2 and 4 determined by extrapolation from the linear portion of the absorption edge in a (α/S) vs energy plot are 1.82 and 1.97 eV, respectively, which suggests that the two materials behave as semiconductors. The energy band gaps of the present compounds are larger than those of inorganic semiconductors of CdTe (1.5 eV), GaAs (1.4 eV), CuInS₂ (1.55 eV) and CuInSe₂ (1.04 eV), all of which are highly efficient photovoltaic materials [17].

4. Conclusion

A series of homotrinuclear linear coordination compounds of general formula $[M_3L_6(H_2O)_6](anion)_6$ solvent and a trizinc $[Zn_3L_8(H_2O)_4](anion)_6$ solvent have been described, whose proposed structures agree with those reported in combination with anions that are present as non-coordinating groups, like ClO_4^- , BF_4^- and SiF_6^- , The structures consist of three metal ions in a linear arrangement, linked to each other by two pairs of three N1, N2 bridging triazole ligands. The negative J value suggests that antiferromagnetic interaction exists in 1, whose value is affected by σ -overlap density between the Mn(II) ions and ligand molecular orbitals and the parameters M-N-N 135° and N-M-N 90°. Properties of fluorescence and diffuse reflectance spectra of 2 and 4 indicate the compounds possibly have the potential applications in photoluminescence and semiconducting materials.

5. Supplementary material

Crystallographic data for the four structures reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition CCDC Nos.: 292235 for 1, 292237 for 2, 292234 for 3 and 292236 for 4). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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