

Two Mononuclear d¹⁰ Metal Coordination Compounds with *m*-phenol-1,2,4-triazole: Crystal Structures and Properties of Fluorescence and Diffuse Reflectance Spectrum

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Although coordination compounds of 1,2,4-triazoles have been known for more than a century,¹ the chemistry of the triazole complexes and the knowledge of their structures and properties have increased rather quickly since the early 1980s. The geometry of 1,2,4-triazole is similar to those of pyrazoles and imidazoles, which is a six-electron aromatic system of five-membered ring. Compared with pyrazoles and imidazoles, the bonding of the 1,2,4-triazole ring with metal complexes has one link more, thus resulting in more rich coordination modes. The triazole ring tends to adopt bidentate (bridging) or tridentate for triazolate anions to construct polynuclear or extending structures.² Therefore, mononuclear metal-triazole complexes are rare especially for first-row transition metals. To our knowledge, there exist only a few papers about mononuclear metal-triazole complexes.³ Besides the coordination chemistry, triazoles have other applications in the wide fields, such as photography,⁴ agriculture, medicine and industry. As a readily available and inexpensive resource, 1,2,4-triazole is also a good candidate to synthesize suitable nitrenium ion precursors,⁵ and synthetic applications⁶ and implication as "ultimate carcinogens" from aromatic amines.⁷ In view of coordination character of 1,2,4-triazole, herein two mononuclear coordination compounds, [Cd(HCOOH)(ptr)₂]₂·H₂NCH₂NH₂ (**1**) and [ZnCl₂(ptr)₂]₂·H₂O (**2**) (ptr = *m*-phenol-1,2,4-triazole), were synthesized and the crystal structures and properties of fluorescence and diffuse reflectance spectrum were characterized.

Experimental Section

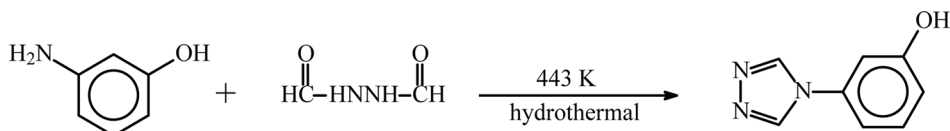
Materials and physical measurements. All chemicals were used as purchased without further purification except that *m*-phenol-1,2,4-triazole (ptr) was prepared by literature methods⁸ with some modifications of prolonging the reaction time at 170 °C to enhance the yield. The IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellets in the range 4000-400 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 with excitation and emission slit at 5.0 nm, increment 1.0 nm and integration time 0.1 s. Optical diffuse reflectance spectrum was measured at room temperature with a Lambda 35 UV-vis spectrophotometer.

***m*-phenol-1,2,4-triazole (ptr).** *m*-phenol-1,2,4-triazole was prepared by reacting the diformylhydrazine (6 mmol, 0.528 g) and *m*-amino-phenol (6 mmol, 0.654 g) in a Teflon-lined stainless steel autoclave in a furnace at 443 K for 3 days, and then cooled to 293 K. The product was isolated and washed with hot water and hot ethanol. Yield based on *m*-amino-phenol: 0.754g, 78%. Elemental analysis (%) for C₈H₇N₃O, Found (calcd): C, 59.61 (59.62); H, 4.29 (4.38); N, 26.18 (25.90). IR (cm⁻¹, KBr): 3136 (w), 3120 (w), 2954 (w), 2846 (w), 2743 (w), 1613 (s), 1533 (vs), 1494 (s), 1388 (w), 1381 (m), 1293 (s), 1204 (s), 1093 (m).

[Cd(HCOOH)(ptr)₂]₂·H₂NCH₂NH₂ (1**).** The mixture of CdI₂ (73 mg, 0.2 mmol), *m*-phenol-1,2,4-triazole (32 mg, 0.2 mmol), HCOOH (9 mg, 0.2 mmol) and H₂NCH₂NH₂·2HCl (23 mg, 0.2 mmol) (to prepare another kind of 1,2,4-triazole) with 10 mL mixed-solvent of water and EtOH (V/V = 1 : 1) in a Teflon-lined stainless steel autoclave at 443 K for 72 h resulted orange block crystals. Yield on ptr: 32 mg, 21%. Elemental analysis (%), Found (calcd): C, 27.72 (27.69); H, 2.80 (2.84); N, 14.32 (14.35). IR data (in KBr, cm⁻¹): 3436 (s), 3128 (s), 3103 (s), 1605 (s), 1559 (s), 1532 (s), 1519 (m), 1471 (m), 1333 (m), 1203 (s), 1098 (s), 1034 (w), 999 (m), 869 (s), 829 (m), 778 (s), 688 (s), 650 (m), 616 (s).

[ZnCl₂(ptr)₂]₂·H₂O (2**).** The 10 mL aqueous solution of ZnCl₂ (14 mg, 0.1 mmol) was dropwise to a solution of *m*-phenol-1,2,4-triazole (32 mg, 0.2 mmol) in a minimum of water. The reaction mixture was stirred at room temperature for 6 h producing red suspension. The red suspension was filtered and the filtrate was placed for natural evaporation. Evaporation of the filtrate at room temperature for several weeks yielded red prismatic crystals suitable for X-ray diffraction. Yield on ZnCl₂: 18 mg, 38%. Elemental analysis



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

Table 1. Crystal and experimental data

	1	2
Empirical formula	C ₁₈ H ₂₂ CdI ₂ N ₈ O ₄	C ₁₆ H ₁₆ Cl ₂ N ₆ O ₃ Zn
Color and Habit	Orange Block	Red Prism
Crystal Size (mm)	0.3 × 0.24 × 0.2	0.25 × 0.25 × 0.15
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	P2 ₁ /c
<i>a</i> (Å)	9.735(5)	7.9410(11)
<i>b</i> (Å)	14.162(7)	14.4271(15)
<i>c</i> (Å)	18.789(9)	16.494(2)
β (°)	95.114(5)	100.045(5)
<i>V</i> (Å ³)	2580(2)	1860.7(4)
<i>Z</i>	4	4
<i>F</i> _w	780.64	476.62
<i>D</i> _{calc} (Mgm ⁻³)	2.010	1.701
μ (mm ⁻¹)	3.279	1.639
<i>F</i> (000)	1488	968
θ (°)	3.08 to 25.03	3.04 to 25.02
Reflections measured	7848	11731
Independent reflections	2258 (<i>R</i> _{int} = 0.0333)	3262 (<i>R</i> _{int} = 0.0484)
Observed Reflection	2121	2397
Final <i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0270, 0.0697	0.0478, 0.1241
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b indices (all)	0.0292, 0.0710	0.0670, 0.1377
<i>GOF</i> on <i>F</i> ²	1.042	0.998
(Δ / σ) _{max/min}	0.001, 0.000	0.004, 0.000
Largest difference peak/ eÅ ⁻³	0.921, -0.678	0.843, -0.762

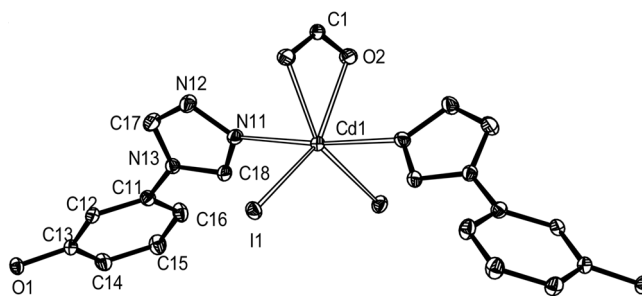
$$R_1^a = (\sum ||F_o| - |F_c|| / \sum |F_o|). wR_2^b = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w|F_o|^2)]^{1/2}$$

(%), Found (calcd): 40.29 (40.32); H, 2.41 (3.38); N, 17.61 (17.63). IR data (in KBr, cm⁻¹): 3430 (s), 2973 (m), 2923 (m), 1605 (s), 1496 (w), 1379 (w), 1292 (w), 1205 (m), 1087 (s), 1049 (s), 1012 (w), 871 (m), 773 (m), 684 (w), 648 (w), 603 (w).

X-ray crystallography. A summary of the crystallographic data for compounds **1** and **2** is given in Table 1. The data were collected on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo-*K* α 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.⁹ The structures were solved by direct methods using SHELXTLTM package of crystallographic software¹⁰ 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.

Results and Discussion

Description of crystal structures. Compound **1** crystallizes in the space group C2/c with a crystallographic inversion center locating on the Cd(II) atom. As the molecular structure shown in Figure 1, the Cd(II) center in compound **1** is in a distorted (4 + 2) octahedral geometry, whose equatorial plane is built by O2, O2A (A = 1-x, y, 0.5-z)

**Figure 1.** The molecular structure of compound **1**.**Table 2.** Selected Bond Distances (Å) and Angles (°) for **1** and **2**

1		2	
Cd1-N11	2.393(3)	Zn1-N12	2.0338(12)
Cd1-O2	2.427(3)	Zn1-N22	2.0581(12)
Cd1-I1	2.8393(9)	Zn1-Cl2	2.2038(6)
		Zn1-C11	2.2180(6)
N11-Cd1-N11A	173.61(14)	N12-Zn1-N22	105.06(5)
N11-Cd1-O2	88.75(10)	N12-Zn1-Cl2	114.01(4)
N11A-Cd1-O2	85.54(10)	N22-Zn1-Cl2	109.70(4)
O2-Cd1-O2A	53.63(13)	N12-Zn1-C11	108.83(4)
N11-Cd1-I1	90.97(8)	N22-Zn1-C11	102.11(4)
N11A-Cd1-I1	92.62(8)	Cl2-Zn1-C11	115.94(2)
O2-Cd1-I1	150.91(6)	C13-N12-Zn1	131.39(11)
O2A-Cd1-I1	97.35(7)	N11-N12-Zn1	120.28(9)
I1-Cd1-I1A	111.72(3)	C23-N22-Zn1	124.99(11)
C18-N11-Cd1	120.7(2)	N21-N22-Zn1	126.09(9)
N12-N11-Cd1	130.8(2)		
C1-O2-Cd1	92.8(2)		

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

from a same HCOOH ligand and two iodine anions I1 and I1A, and the axial positions are occupied by two nitrogen atoms from two separate ptr ligands. The Cd(II) locates in the equatorial plane with maximum deviation from the best least-squares plane being 0.0239 Å. The Cd-I, Cd-O and Cd-N bond distances as shown in Table 2 are in normal range and similar to those of mononuclear Cd(II) complexes reported by Salas and Dillen.³ The range of double bonds C=N distances of the triazole rings in **1** is between 1.299(5) and 1.291(4) Å, similar to those found in the ligand ptr between 1.2984(17) and 1.2967(17) Å,¹¹ indicating the coordination of N_{Triazole} having little effect on the π - π conjugation of triazole ring.

The minimum centroid-to-centroid distance of phenyl rings is 4.860 Å, indicating no $\pi \cdots \pi$ stacking interactions in the crystal structures. Interestingly, the most important action of the hydrogen bonding O1-H \cdots O2B (2.589(7) Å, 170.2°, B = x, 2-y, -0.5+z) is to respectively form right- and left-handed helical supramolecular chains with pitch heights of *l*_p = 18.789 Å. Both the helical supramolecular chains interlace each other at the Cd(II) center along the *c* direction to form a double helical structure of supramolecular chain (Figure 2), which acts as a foundational block to further construct the 3-D supramolecular pack of **1** by hydrogen

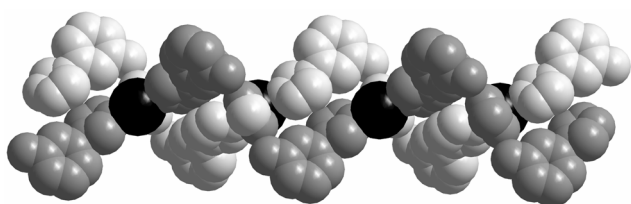


Figure 2. The space-filling representation of the double helical supramolecular chain along the *c* axis in **1** constructed from hydrogen bonding O1-H...O2. The hydrogen and iodine atoms are omitted for clarity.

bonding C18-H...O1C (3.107(9) Å, 133.8°; C = 1.5-x, 1.5-y, -z). The 3-D framework can be regarded as -ABAB- fashion along the *c* direction. The layers A only contain the ptr ligands and the layers B comprise of [Cd(HCOOH)₂] units (Figure S1). Another interesting feature of **1** is that there exist 1-D channels along the *c* direction in the crystal structure, although compound **1** is a mononuclear complex. Omitting the guest water molecules, the total solvent-accessible volume of the channels in the unit is 395.5 Å³ accounting for 15.3% calculated by PLATON.

The molecule structure of **2** is similar to that of **1**, except no HCOOH molecule surrounding the metal center. Compound **2** crystallizes in the space group *P2₁/c*. As the molecular structure shown in Figure 3, the Zn(II) center is coordinated by two nitrogen atoms from two separate monodentate ptr and two chlorine atoms to form a greatly distorted tetrahedron geometry. The lattice water molecule O1W play an important role in the hydrogen bondings. O1W acts as a triple bridge to link the [ZnCl₂(ptr)₂] units into a zigzag chain along the *b* direction via hydrogen bondings (O1W...Cl2A = 3.064(4) Å, A = 1-x, 0.5+y, 0.5-z; C13-H...O1WB = 2.974(5) Å, 161.8°, B = 1-x, -0.5+y, 0.5-z; O2-H...O1W = 2.930(5) Å, 172.5°) as shown in Figure 4. The zigzag chains are further linked into a 2-D layered structure *via* hydrogen bonding O1W...Cl1C (2.928(5) Å, C = 1-x, 1-y, 1-z) (Figure S3).

Fluorescent properties of 1 and 2. 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 **1** and **2** show luminescence features as given in Figure 5. Very strong green fluorescence of **1** can be observed. The maximum emission wavelength at 580 nm

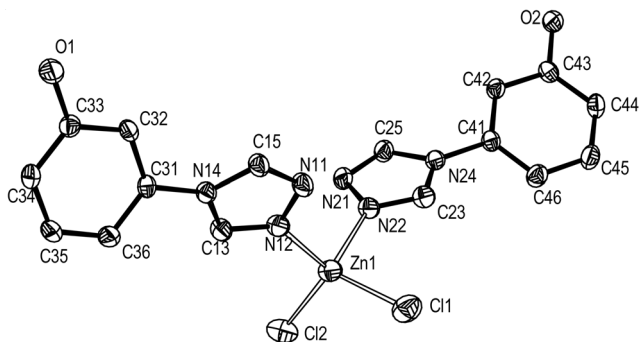


Figure 3. The molecular structure of compound **2**.

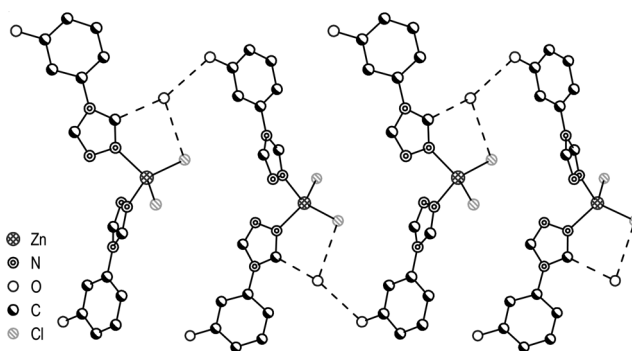


Figure 4. The 1-D zigzag chain in compound **2** constructed from hydrogen bondings.

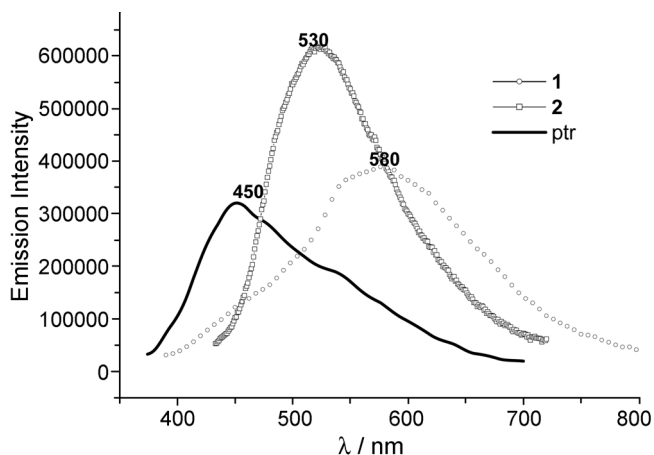


Figure 5. The solid-state electronic emission spectra of **1** ($\lambda_{\text{ex}} = 370$ nm), **2** ($\lambda_{\text{ex}} = 375$ nm) and ptr ($\lambda_{\text{ex}} = 370$ nm) recorded at room temperature.

excited the solid sample with UV ray at $\lambda_{\text{ex}} = 370$ nm. Excitation of the compound **2** with UV light at 375 nm produces pale green fluorescence with the maximum emission wavelength at 530 nm. Compared to the free ligand (blue fluorescence with the emission at 450 nm with $\lambda_{\text{ex}} = 370$ nm),⁸ great red shifts with about 130 nm and 80 nm respectively can be found, indicating the emission can be possibly original from ligand-to-metal transfer (LMCT).¹³

Property of diffuse reflectance spectrum of 2. Optical diffuse reflectance spectrum was measured at room temperature. The compound **2** was ground into fine powder and pressed onto a thin glass slide holder. The BaSO₄ plate was used as reference. The absorption spectrum was calculated from reflection spectra by the Kubelka-Munk function: $\alpha/S = (1-R)^2/2R$, α is the absorption coefficient; S is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm ; And R is the reflectance. The optical property of **2** was assessed by its optical diffuse reflectance data.¹⁴ The Kubelka-Munk (or remission, F) function converted from the diffuse reflectance data was plotted according to the diffuse reflectance data as shown in Figure 6. The energy gap of the compound **2** determined by extrapolation from the linear portion of the absorption edge in a (α/S) vs energy plot is 1.96 eV, which suggests that the compound **2** behaves as semiconductors.

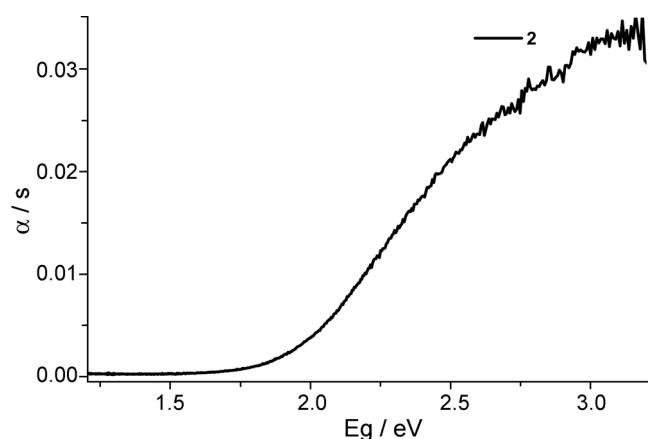


Figure 6. The band gap estimated to be 1.96 eV was assessed by the optical diffuse reflectance data.

The energy band gap of the compound **2** is a little larger than that of those 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.¹⁵

Conclusion

The syntheses, structures, and properties of fluorescence and diffuse reflectance spectrum of two mononuclear d¹⁰ complexes with 4-substituted 1,2,4-triazole ptr have been presented. Generally, it is more difficult to synthesize mononuclear complexes containing 1,2,4-triazoles, especially when the ligands coordinating with first-row transition metals. Compared with the unsubstituted triazoles, ptr loses a coordination site on the 4-positioned nitrogen, thus can only act as mono- or μ_2 -N1,N2 bridging bidentate ligands, which makes it difficult to construct extended structures. The green fluorescent properties of **1** and **2** originate from LMCT and the energy gap 1.96 eV of **2** suggests that the compound **2** behaves as semiconductors.

Supplementary material. Crystallographic data for the four structures reported here have been deposited with the Cambridge Crystallographic Data Center (Deposition CCDC Numbers: 299903-299904 for **1** and **2**, respectively). 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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