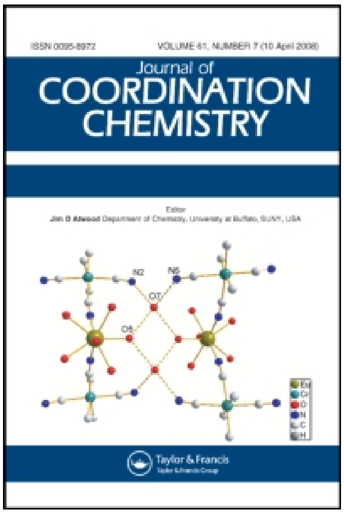

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

In situ synthesis, crystal structures, and luminescence of two new tetrazole complexes

Yun-Zhi Tang[a]; Zan Cao[a]; He-Rui Wen[a]; Su-Lan Liao[a]; Shuai Huang[a]; Chang-Lin Yu[a]
[a] School of Material & Chemistry Engineering, Jiangxi University of Science and Technology, Ganzhou, 341000, P.R. China

To cite this Article Tang, Yun-Zhi , Cao, Zan , Wen, He-Rui , Liao, Su-Lan , Huang, Shuai and Yu, Chang-Lin(2010) '*In situ* synthesis, crystal structures, and luminescence of two new tetrazole complexes', Journal of Coordination Chemistry, 63: 17, 3101 — 3107, First published on: 09 August 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.508515

URL: http://dx.doi.org/10.1080/00958972.2010.508515

Journal of Coordination Chemistry
Vol. 63, No. 17, 10 September 2010, 3101–3107

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In situ synthesis, crystal structures, and luminescence of two new tetrazole complexes

YUN-ZHI TANG*, ZAN CAO, HE-RUI WEN, SU-LAN LIAO,
SHUAI HUANG and CHANG-LIN YU

School of Material & Chemistry Engineering,
Jiangxi University of Science and Technology, Ganzhou, 341000, P.R. China

(*Received 11 November 2009; in final form 13 May 2010*)

The synthesis, crystal structures, and luminescent properties of two new complexes containing tetrazolyl ligands are described. Refluxing a mixture of fipronil (fipronil = (±)-5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]-1H-pyrazole-3-carbonitrile), sodium azide, and $CuCl_2$ in ethanol and water gives complex **1**, $[M(L)_2](H_2O)_2] \cdot 2H_2O$ (HL = (±)-5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]-1H-pyrazole-3-tetrazole, M = Cu). Hydrothermal reaction of fipronil, sodium azide, and $Cd(ClO_4)_2$ in the presence of water and ethanol (Demko–Sharpless tetrazole synthesis) yields **2**, $[M(L)_2](H_2O)_2] \cdot 2H_2O$ (M = Cd). The metals in both complexes are six coordinate from two water molecules, two nitrogens from different tetrazolyl groups, and two nitrogens from pyrazolyl groups. Photoluminescence studies reveal that **2** exhibits strong blue fluorescent emission at $\lambda_{max} = 451$ nm in solid state at room temperature.

Keywords: Tetrazole complex; *In situ* synthesis; Copper complex; Cadmium complex

1. Introduction

Tetrazole has found a wide range of applications in coordination chemistry as ligands, in medicinal chemistry as metabolically stable surrogates for carboxylic acids, and in materials science as high-density energetic materials [1–6]. Recently, Ren-Gen Xiong and co-workers [7–12] reported a series of supramolecular motifs formed during Demko–Sharpless [2 + 3] cycloaddition under hydrothermal conditions. The structural characterizations of such supramolecular motifs provide important clues to the mechanistic role of the metal and offer invaluable insight to the reaction mechanism that may, in turn, allow synthetic chemists to further optimize reaction conditions [11, 12]. Most tetrazole complexes are non-oxidative metals, such as Zn^{2+}, with few copper tetrazole complexes from Demko–Sharpless [2 + 3] cycloaddition reported [13, 14]; in those reported copper complexes containing tetrazolyl, the copper valence is mostly +1 [13, 14]. Cu^{II} complex generated from Demko–Sharpless [2 + 3]

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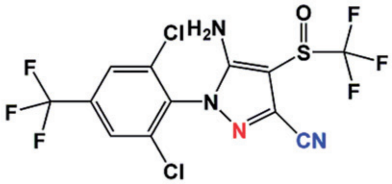
*Corresponding author. Email: tangyunzhi75@163.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.508515



Scheme 1. The structure of fipronil ligand.

cycloaddition reaction has not been reported. As part of our continuous interest in understanding the mechanism of the Demko–Sharpless tetrazole reaction and the synthetic usefulness of *in situ* reactions, we changed the synthetic condition and carried out the Demko–Sharpless reaction system in an atmosphere of oxygen and prepared a Cu^{II} complex, **1**. Under hydrothermal condition, by *in situ* reaction of fipronil (scheme 1), sodium azide, and $Cd(ClO_4)_2$ in the presence of water and ethanol (Demko–Sharpless tetrazole synthesis methods), we get a new cadmium complex, **2**.

In this article, we describe the synthesis and structural characterizations by X-ray crystallography of **1** and **2** as well as their luminescence.

2. Experimental

2.1. *Synthesis of* $[M(L)_2](H_2O)_2]\cdot 2H_2O$ *(M = Cu for 1 and Cd for 2)*

As shown in scheme 1, **1** was synthesized according to the Sharpless reaction [1, 2] by the following procedure. A flask with a mixture of fipronil (0.876 g, 2 mmol), sodium azide (0.650 g, 10 mmol), and $CuCl_2$ (0.270 g, 2 mmol) with molar ratio 1 : 5 : 1 in ethanol and water (V : V = 2 : 1) was filled with oxygen and stirred while refluxing for 4 h. Beautiful green block-like crystals were obtained from the filtrate about 2 weeks later. For **1**, yield: 0.701 g (32%) on the basis of fipronil. Calcd for $C_{24}H_{16}Cl_4F_{12}N_{14}O_6S_2Cu$ (%): C, 27.06; H, 1.46; N, 17.92. Found (%): C, 27.03; H, 1.49; N, 17.89. IR (KBr, cm^{-1}) 3429.5(m), 3139.9(m), 1621.7(s), 1501.3(s), 1512.2(vs), 1420.1(s), 1346.7(s), 1211.0(m), 1113.6(m), 1069.3(m), 891.2(m), 850.6(m), 693.7(m), 639(m), 605(w), 480(w).

Compound **2** was synthesized as follows (scheme 1). A heavy-walled Pyrex tube containing a mixture of fipronil (0.0876 g, 0.2 mmol), $Cd(ClO_4)_2\cdot 6H_2O$ (0.0840 g, 0.2 mmol), NaN_3 (0.065 g, 1 mol), water (2 mL), and ethanol (0.5 mL) was frozen and sealed under vacuum, then placed inside an oven at 120°C. Pale yellow block-like crystals for **2** were obtained after 48 h of heating. Yield: 0.167 g (73%) on the basis of fipronil. Calcd for $C_{24}H_{16}Cl_4F_{12}N_{14}O_6S_2Cd$ (%): C, 25.20; H, 1.40; N, 17.15. Found (%): C, 26.23; H, 1.39; N, 17.17. IR (KBr, cm^{-1}) 3412.3(m), 3123.1(m), 1622.8(s), 1517.2(vs), 1424.1(s), 1337.7(s), 1211.1(w), 1118.7(s), 1105(w), 912.5(s), 889.2(m), 850(m), 746(m), 641(m), 607(w), 478(w).

2.2. *Single crystal structure determination*

A green crystal of **1** with dimensions 0.170 mm × 0.110 mm × 0.105 mm was selected on a Bruker P4 diffractometer with graphite-monochromated Mo-Kα radiation

Table 1. Crystal data and structure refinement for **1** and **2**.

Identification code	**1**	**2**
Empirical formula	$C_{24}H_{16}Cl_4CuF_{12}N_{14}O_6S_2$	$C_{24}H_{16}CdCl_4F_{12}N_{14}O_6S_2$
Formula weight	1093.97	1142.83
Temperature (K)	296(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*C2*/*c*	*C2*/*c*
Unit cell dimensions (Å, °)		
a	20.434(3)	19.7583(15)
b	13.254(2)	13.3531(10)
c	14.685(2)	15.2969(12)
β	98.442(2)	96.3840(10)
Volume (Å^3), Z	3934.0(10), 4	4010.8(5), 4
Calculated density (mg m^{-3})	1.847	1.893
μ(Mo-Kα) (mm^{-1})	1.050	1.030
F(000)	2172	2248
Crystal size (mm^3)	0.17 × 0.11 × 0.105	0.16 × 0.14 × 0.11
θ range for data collection (°)	1.84–24.99	1.84–27.73
Index ranges	$-24 \le h \le 24$, $-15 \le k \le 15$, $-17 \le l \le 17$	$-14 \le h \le 25$, $-14 \le k \le 16$, $-19 \le l \le 17$
Reflections collected	11491	11496
Independent reflections	3427 [R(int) = 0.0615]	4336 [R(int) = 0.0270]
Data/restraints/parameters	3427/72/305	4336/0/293
Goodness-of-fit on F^2	1.088	1.129
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0538$, $wR_2 = 0.1354$	$R_1 = 0.0557$, $wR_2 = 0.1629$
R indices (all data)	$R_1 = 0.1182$, $wR_2 = 0.1664$	$R_1 = 0.0828$, $wR_2 = 0.1771$
Min., Max. ρ (e Å^3)	0.400, −0.511	0.720, −0.654

($\lambda = 0.71073$ Å) at 293 K using the θ–2θ scan technique. The data were corrected for Lp and absorption effects. The crystal structure was solved by direct methods with SHELXS-97 [15]. Subsequent difference Fourier synthesis enabled all heavier atoms to be located. After several cycles of refinement, all hydrogens were located from successive difference Fourier synthesis. All non-hydrogen atoms were finally refined with anisotropic displacement parameters by full-matrix least-squares techniques [16]. Hydrogen positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The same manipulations for **2** were conducted as described above. Detailed information about the crystal data and structure determination for both compounds are summarized in table 1. Their selected distances and bond angles are given in table 2.

3. Results and discussion

Compared with IR spectra of fipronil and sodium azide, peaks around 2300 cm^{-1} of the cyano group in fipronil and 2100 cm^{-1} of the azide disappeared, while a series of new peaks appeared around 1624–1424 cm^{-1} in both complexes, indicating that the [2 + 3] cycloaddition between cyano and azide occurred [7–12]. A broad absorption around 3400 cm^{-1} suggests the existence of water in both complexes. For **1**, the color of the crystals is green, totally different from that of other copper tetrazole complexes

Table 2. Selected bond distances and angles for **1** and **2**.

1		**2**	
Cu(1)–N(1)#1	1.938(4)	Cd(1)–N(1)#1	2.278(4)
Cu(1)–N(1)	1.938(4)	Cd(1)–N(1)	2.278(4)
Cu(1)–O(1)#1	2.153(4)	Cd(1)–O(1 W)#1	2.291(4)
Cu(1)–O(1)	2.153(4)	Cd(1)–O(1W)	2.291(4)
Cu(1)–N(5)#1	2.282(4)	Cd(1)–N(3)	2.431(4)
Cu(1)–N(5)	2.282(4)	Cd(1)–N(3)#1	2.431(4)
N(1)#1–Cu(1)–N(1)	169.5(2)	N(1)#1–Cd(1)–N(1)	162.25(19)
N(1)#1–Cu(1)–O(1)#1	93.74(16)	N(1)#1–Cd(1)–O(1W)#1	96.60(13)
N(1)–Cu(1)–O(1)#1	93.98(16)	N(1)–Cd(1)–O(1W)#1	96.19(14)
N(1)#1–Cu(1)–O(1)	93.98(16)	N(1)#1–Cd(1)–O(1W)	96.19(14)
N(1)–Cu(1)–O(1)	93.74(16)	N(1)–Cd(1)–O(1W)	96.60(13)
O(1)#1–Cu(1)–O(1)	85.6(2)	O(1W)#1–Cd(1)–O(1W)	87.5(2)
N(1)#1–Cu(1)–N(5)#1	76.20(16)	N(1)#1–Cd(1)–N(3)	97.19(13)
N(1)–Cu(1)–N(5)#1	96.68(16)	N(1)–Cd(1)–N(3)	70.61(13)
O(1)#1–Cu(1)–N(5)#1	168.64(14)	O(1W)#1–Cd(1)–N(3)	166.16(13)
O(1)–Cu(1)–N(5)#1	89.76(15)	O(1W)–Cd(1)–N(3)	89.84(14)
N(1)#1–Cu(1)–N(5)	96.68(15)	N(1)#1–Cd(1)–N(3)#1	70.61(13)
N(1)–Cu(1)–N(5)	76.20(16)	N(1)–Cd(1)–N(3)#1	97.19(13)
O(1)#1–Cu(1)–N(5)	89.76(15)	O(1W)#1–Cd(1)–N(3)#1	89.84(14)
O(1)–Cu(1)–N(5)	168.64(14)	O(1W)–Cd(1)–N(3)#1	166.16(13)
N(5)#1–Cu(1)–N(5)	96.6(2)	N(3)–Cd(1)–N(3)#1	95.81(19)

Symmetrical code for **1**, #1 $-x+1$, y, $-z+3/2$; for **2**, #1 $-x$, y, $-z+1/2$.

(pale yellow) indicating copper valence may be +2. In order to confirm the valence of copper, we have measured solid-state fluorescence spectrum of crystalline sample of **1** by Perkin-Elmer LS50B spectrofluorophotometer at room temperature and did not detect any fluorescence, suggesting the copper valence should be +2.

Crystallographic data of **1** (table 1) show monoclinic crystal system, space group $C2/c$ and $Z=4$. As shown in figure 1, **1** lies on a twofold rotation axis made up of double tetrazole ligands and two coordinated water molecules. Each tetrazole loses one proton to maintain the electric charge balance, so the copper valence in **1** is also obviously +2 representing the first $\mathrm{Cu^{II}}$ complex from *in situ* [2 + 3] cycloaddition [13, 14]. Outside of each $[\mathrm{Cu(L)_2\cdot(H_2O)_2}]$ unit, there are two co-crystallized water molecules.

The $\mathrm{Cu^{II}}$ ion in **1** has a distorted octahedral geometry defined by two water molecules, two nitrogens from different tetrazolyl groups, and two nitrogens from pyrazolyl groups, respectively. Each tetrazole provides one N (β site) from tetrazolyl and one N (β site) from pyrazole to bind $\mathrm{Cu^{II}}$, thus, resulting in the formation of a stable five-membered ring (figure 1). The Cu(1)–N(5) distance (2.282(4) Å) is longer than that of Cu(1)–N(1) (1.938(4) Å), and the angle of O(1)–Cu(1)–N(5) is 168.64(14)°, deviating from 180°, suggesting that Cu of **1** is highly unsymmetrical (as shown in table 2). All the Cu–O distances (2.153(4) Å) in **1** are similar to analogous literature values [17, 18].

The central cadmium in **2** also adopts a distorted octahedral coordination mode with two water molecules, two nitrogens from different tetrazolyl groups, and two nitrogens from pyrazolyl groups (as shown in figure 2). All the Cd–O (2.291(4) Å) and Cd–N (2.431(4) and 2.278(4) Å) (table 2) bond distances in **2** agree with normal distances [10, 19].

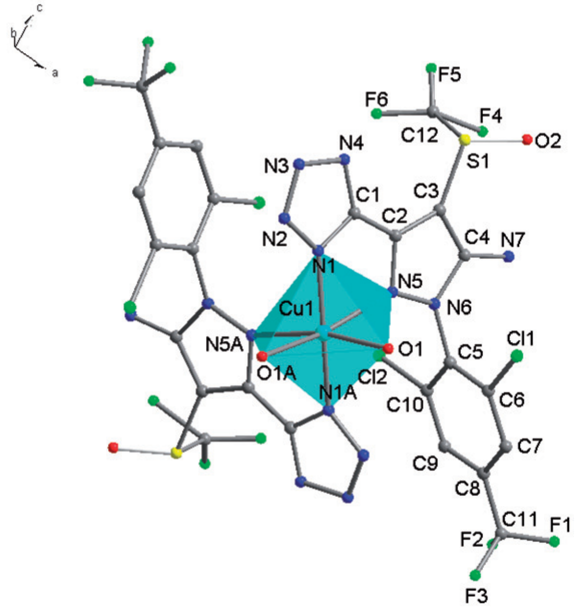


Figure 1. The coordination of **1**.

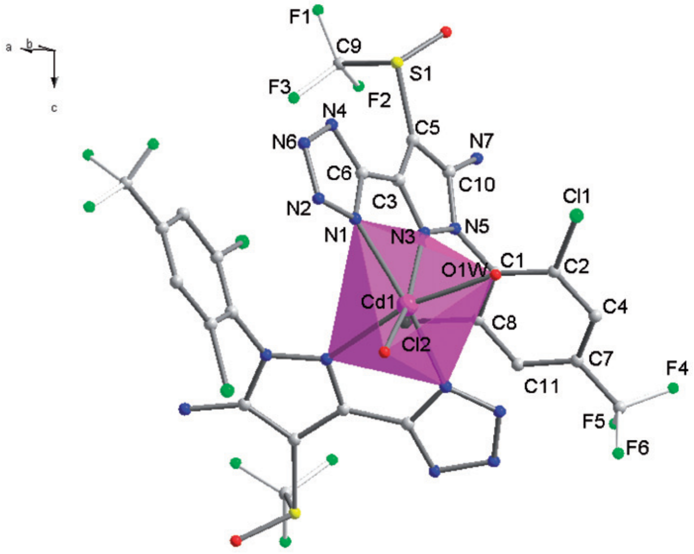


Figure 2. The coordination of **2**.

Many strong hydrogen bonds can be found in both compounds, such as between uncoordinated nitrogen of tetrazolyl and water (O1–H1A···N4 (1.994 Å), O1W–H1WA···N2 (2.196 Å)) for **1** and (O1W–H1WA···N4 (1.938 Å), O2W–H2WA···N6 (2.609 Å)) for **2**, between the amino groups and water (N7–H7A···O1W (2.036 Å)) for **1** and (N7–H7B···O2W (2.392 Å)) for **2**, as well as between lattice water and oxygen of

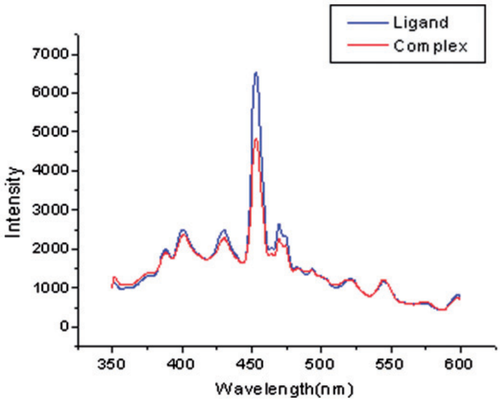


Figure 3. Fluorescent emission spectra of **2** and fipronil in solid state at room temperature.

sulfinyl groups (O1W–H1WB···O2 (1.957 Å)) for **1** and (O2W–H2WB···O1 (1.814 Å)) for **2**. Weak π–π stacking interactions between phenyl rings also can be found in both compounds, important in supramolecular assembly and stabilization of the compounds.

Solid-state fluorescence of crystalline sample for **2** and fipronil were measured by Perkin-Elmer LS50B spectrofluorophotometer at room temperature. As shown in figure 3, both **2** and fipronil show almost the same emission peaks at 451 nm. The photoluminescent mechanism is tentatively attributable to ligand-to-1igand transitions that are in reasonable agreement with the literature examples on this class of tetrazole complex previously reported [11, 20–22]. The small difference of emission intensity between ligands and **2** may be due to coordinated cadmium with little impact on fluorescence.

In conclusion, we have synthesized two new tetrazole complexes (copper and cadmium) from *in situ* Demko–Sharpless [2 + 3] cycloaddition. Complex **1** represents the first Cu^{II} tetrazole complex from [2 + 3] cycloaddition reaction. Complex **2** exhibits blue fluorescence.

Supplementary material

CCDC Nos: 739964 and 739963 contain the supplementary crystallographic data for **1** and **2**, respectively. Copies of this information can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax (int.code) +44(1223)336-033 or E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.ck).

Acknowledgments

This work was supported by the Natural Science Foundation of Jiangxi Province (2008GZH0064) and the Sustentation Fund of Education Department from Jiangxi Province (GJJ08275).

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