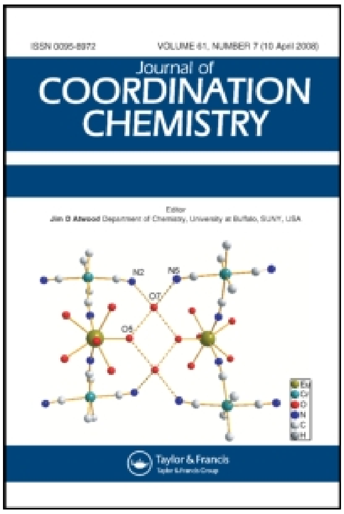

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Syntheses and crystal structures of two Cu(II) complexes based on a fused heterocycle ligand containing 1,3,4-thiadiazole

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Syntheses and crystal structures of two Cu(II) complexes based on a fused heterocycle ligand containing 1,3,4-thiadiazole

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By refluxing a mixture of $CuCl_2$ and 3-methyl-6-phenyl-[1,2,4]-triazolo[3,4-b][1,3,4]thiadiazole (TRTZ) with addition of acetic acid and KSCN, respectively, the complexes $[Cu(TRTZ)_2(OAc)_2(H_2O)] \cdot 1.5H_2O$ (**1**) and $[Cu(TRTZ)_2(SCN)_2(H_2O)_2] \cdot 2DMF$ (**2**) were obtained. Single-crystal structure of both complexes was determined and their thermal behaviour and IR spectra examined.

Keywords: 1,3,4-Thiadiazole; Copper complex; Crystal structure; Properties

1. Introduction

Structures and properties of thiadiazoles, their derivatives and related compounds is of great interest owing to their plant growth regulating effects, antimicrobial activity and industrial applications [1–4]. In theory, *N*,*N′*-ligands such as 1,3,4-thiadiazoles are very versatile in that they are able to bridge a wide range of metals [5] and can coordinate to many metal ions through nitrogen or sulfur. Transition metal complexes of 1,3,4-thiadiazoles derivatives are intriguing from both theoretical and practical viewpoints and are the subject of several industrial applications [6]. Although a series of mono-thiadiazole complexes were reported [7–9], complexes of fused ring 1,3,4-thiadiazoles have not been extensively studied. Here we report the syntheses and crystal structures of $[Cu(TRTZ)_2(OAc)_2(H_2O)] \cdot 1.5H_2O$ (**1**) and $[Cu(TRTZ)_2(SCN)_2(H_2O)_2] \cdot 2DMF$ (**2**)

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(TRTZ = 3-methyl-6-phenyl-[1,2,4]-triazole[3,4-b][1,3,4] thiadiazole). IR spectra and thermal analyses in an N_2 atmosphere are also reported.

2. Experimental

2.1. *Materials and measurements*

All chemicals were of analytical grade and used without further purification. The ligand, TRTZ, was prepared by a modified method described in the literature [10]. Single-crystal data were measured on a Rigaku-Raxis-IV X-ray diffractometer. Thermal behaviour was measured on a Netzsch TG209 system under nitrogen with a flow rate of $20\,\mathrm{cm^3\,min^{-1}}$. IR spectra were recorded on a Nicolet IR-470 spectrophotometer (KBr pellets) in the range 4000–400cm^{-1}.

2.2. *Syntheses*

TRTZ (0.5 mmol, 0.108 g) in DMF/H_2O (20 cm^3, 1 : 1, v : v) was added to an aqueous solution (10 cm^3) of $CuCl_2 \cdot 2H_2O$ (0.5 mmol, 0.085 g) with stirring for 30 min, then 0.5 cm^3 of glacial acetic acid was added. After reflux for 1h, the resulting solution was allowed to stand at ambient temperatures for several weeks, yielding blue crystals of **1** (Yield, 45%). Complex **2** was obtained under the same procedure except using KSCN (1 mmol, 0.097 g) instead of glacial acetic acid. Green crystals of **2** were obtained in 50% yield. Anal. Calcd for $C_{48}H_{58}Cu_2N_{16}O_{15}S_4$ (1) (%): C, 42.53; H, 4.28; N, 16.54. Found: C, 42.39; H, 4.26; N, 16.48. Calcd for $C_{28}H_{34}CuN_{12}O_4S_4$ (**2**) (%): C, 42.29; H, 4.28; N, 21.15. Found: C, 42.25; H, 4.27; N, 21.11%.

2.3. *X-ray crystallography*

Selected crystals of **1** and **2** were mounted on a Rigaku-Raxis-IV X-ray diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 291(2) K. Some 4351 reflections were measured over the ranges $0 \le h \le 13$, $-8 \le k \le 8$, $-23 \le l \le 22$, yielding 2531 unique reflections for **1** and 4648 reflections over the ranges $-22 \le h \le 13$, $-13 \le k \le 16$, $-15 \le l \le 16$, yielding 2787 unique reflections for **2**. Raw data were corrected and the structure was solved using the SHELX-97 program. Non-hydrogen atoms were located by direct phase determination and subjected to anisotropic refinement [11]. Full-matrix least-squares calculations on F^2 were applied in the final refinement. Details of crystal structure determinations of **1** and **2** are summarized in table 1.

3. Results and discussion

3.1. *Crystal structures of 1 and 2*

Selected bond distances and angles for **1** and **2** are listed in tables 2 and 3. ORTEP drawings of them are presented in figures 1 and 2, respectively.

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

	1	**2**
Empirical formula	$C_{48}H_{58}Cu_2N_{16}O_{15}S_4$	$C_{28}H_{34}CuN_{12}O_4S_4$
M	1354.42	794.50
Crystal system	Monoclinic	Monoclinic
Space group	$P2/n$	$C2/c$
a (Å)	11.626(2)	19.256(4)
b (Å)	6.8820(14)	14.227(3)
c (Å)	19.560(3)	13.726(3)
β (°)	100.18(3)	105.69(3)
V (Å^3)	1540(5)	3620.2(14)
Z	1	4
D_c (g cm^{-3})	1.460	1.458
$F(000)$	700.0	1644
Crystal size (mm^3)	$0.17 \times 0.18 \times 0.20$	$0.17 \times 0.18 \times 0.20$
θ range (°)	1.90 to 25.0	1.8 to 25.0
S	1.112	1.045
Reflections collected/unique	4351/2531 [R(int) = 0.0420]	4648/2787 [R(int) = 0.140]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0487$, $wR_2 = 0.1525$	$R_1 = 0.0722$, $wR_2 = 0.1965$

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2**.

Complex **1**			
Cu1–O1	1.947(4)	N3–Cu1–N3#1	174.14(15)
Cu1–O1#1	1.947(4)	O1–Cu1–O1#1	175.21(15)
Cu1–N3	1.989(3)	O1–Cu1–N3	92.81(14)
Cu1–N3#1	1.989(3)	O1#1–Cu1–O3	92.40(11)
Cu1–O3	2.545(5)	Cu1–O1–C11	118.10(3)
O1–C11	1.286(6)	O1–Cu1–N3	92.81(14)
Complex **2**			
Cu1–O1	2.540(5)	O1–Cu1–N1	86.44(17)
Cu1–N1	1.993(4)	O1–Cu1–N5	83.30(2)
Cu1–N5	1.965(5)	O1–Cu1–O1#1	180.00
Cu1–N1#1	1.993(4)	N1–Cu1–N1#1	180.00
N5–C11	1.136(8)	Cu1–N5–C11	176.4(5)
S2–C11	1.642(7)	S2–C11–N5	179.4(5)

Symmetry transformations used to generate equivalent atoms #1: $-x+3/2$, y, $-z+1/2$.

Table 3. Hydrogen bond data for **1** and **2** (Å, °).

D–H	(D–H)	d(H···A)	∠DHA	d(D···A)	A
Complex **1**					
O3–H3C	0.850	2.280	127.00	2.877(5)	O2 [$3/2-x$, $1+y$, $1/2-z$]
O3–H3D	0.850	2.590	101.00	2.877(5)	O2 [x, $-y$, $z-1/2$]
O5–H5B	0.850	2.540	102.00	2.842(7)	O2 [$3/2-x$, $1+y$, $1/2-z$]
O5–H5E	0.850	2.410	123.00	2.959(7)	O1 [$x+1/2$, $-y+1/2$, $z+1/2$]
Complex **2**					
O1–H1B	0.8500	2.8200	129.00	3.415(6)	S1 [$3/2-x$, $1/2-y$, $-z$]
O1–H1C	0.8500	2.1200	135.00	2.793(7)	O2 [$3/2-x$, $1/2-y$, $-z$]

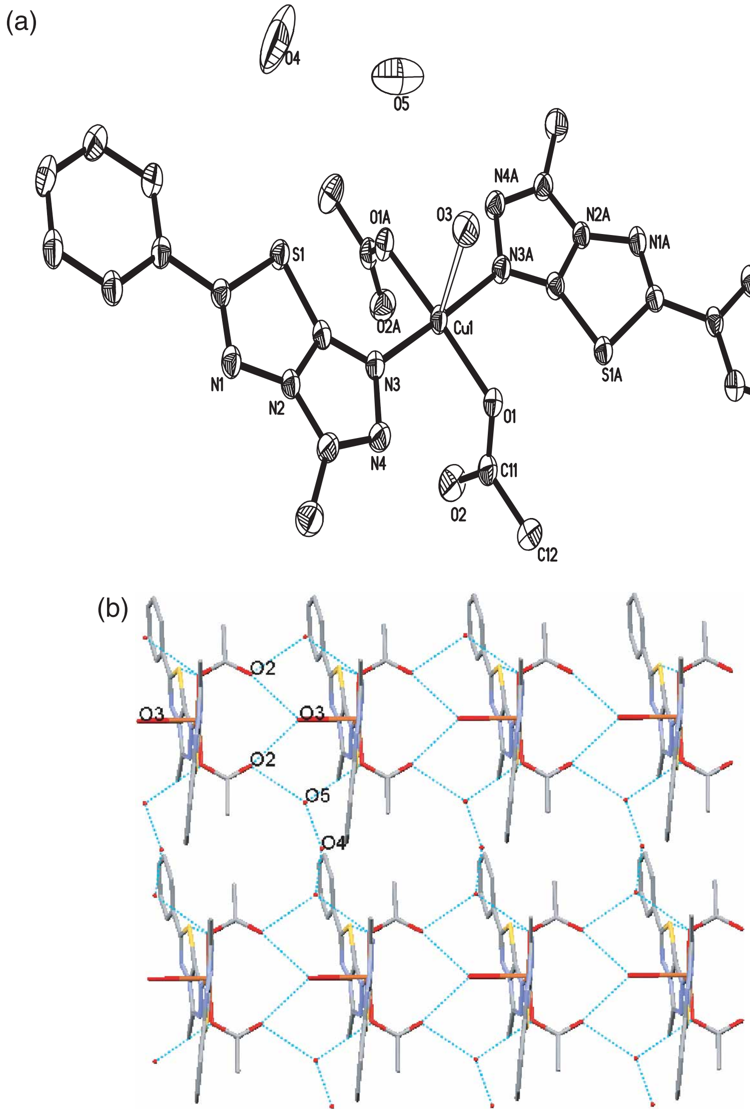


Figure 1. (a) ORPTEP drawing of **1** (50% probability displacement ellipsoids); (b) the 2D hydrogen bond network in 1; (c) packing of **1** along the *a* axis.

The structure of **1** is shown in figure 1(a). The copper (II) ion is four-coordinated by two nitrogen atoms of two TRTZ ligands and two oxygen atoms of OAc^- groups in a *trans* configuration. O3 is at the axial position of a tetragonal pyramid with a Cu1–O3 distance of 2.545(5) Å, which indicates a weak Cu–O (H_2O) interaction. Taking this weak interaction into account the copper(II) ion can be considered to have a $4+1$ coordination environment and may be described as lying in a distorted elongated tetragonal pyramid [12]. The basal plane has a small tetrahedral distortion (mean deviation from plane = 0.0918 Å) and the metal ion is displaced by 0.01 Å towards the axially coordinated water molecule. The two TRTZ ligands, which are almost

(c)

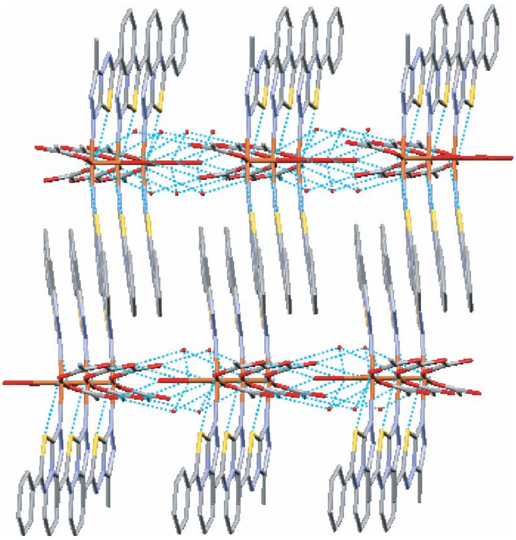


Figure 1. Continued.

planar due to conjugation (mean deviation 0.0105 Å), coordinate to copper(II) ion with a dihedral angle of 162.4° owing to repulsions involving OAc^-. Hydrogen bonds between acetate O atoms and coordinated H_2O with O3–H3 ··· O2 2.877(5) Å link the units of **1** into a 1D chain along the *b* axis. The existence of lattice water expands the hydrogen bond network along the *a* axis to construct a 2D plane with the typical hydrogen bonds O5–H5E ··· O1 2.959(7) and O5–H5B ··· O2 2.842(7) Å (figure 1b). The TRTZ rings lie of adjacent nets lie parallel to each other with a separation of 3.339 Å; the resulting π–π stacking assembles the 2D network into a 3D structure (figure 1c).

The structure of **2** is shown in figure 2(a). Like complex **1**, the Cu(II) ion is also four-coordinated by two nitrogen atoms of two TRTZ ligands and two nitrogen atoms of NCS^- ligands in a *trans* arrangement. Two water molecules are located at axial positions with a Cu–O (H_2O) distance of 2.536 Å, which is longer than the four Cu–N bonds in the equatorial plane. As a result, the copper(II) ion lies in a $4+2$ coordination environment that may be described as an elongated octahedron (Jahn-Teller effect) [13, 14]. Compared with **1**, the two TRTZ ligands coordinated to Cu(II) are coplanar. The NCS^- groups are almost linear (S2–C11–N5, 179.4(5)°) as is the Cu1–N5–C11 axis, (176.4(5)°). This situation is different to that in $[Fe(L)_2(NCS)_2][(H_2O)_2](H_2O)_2$ (L = bitrazole, Fe1–N7–C5, 154.3(5)°) [15]. In complex **2**, intermolecular hydrogen bonds form only between water and DMF molecules with O1–H1F ··· O2 of 2.793(7) Å, whereas π–π stacking exists between TRTZ rings with a separation of 3.353 Å. A packing diagram is shown in figure 2(b).

3.2. *IR spectra and thermal properties*

Characteristic IR data for **1** and **2** are listed in table 4. Broad absorption bands at 3472 and 3375 cm^{-1} arise from lattice water molecules in **1** and **2**. A series of strong bands

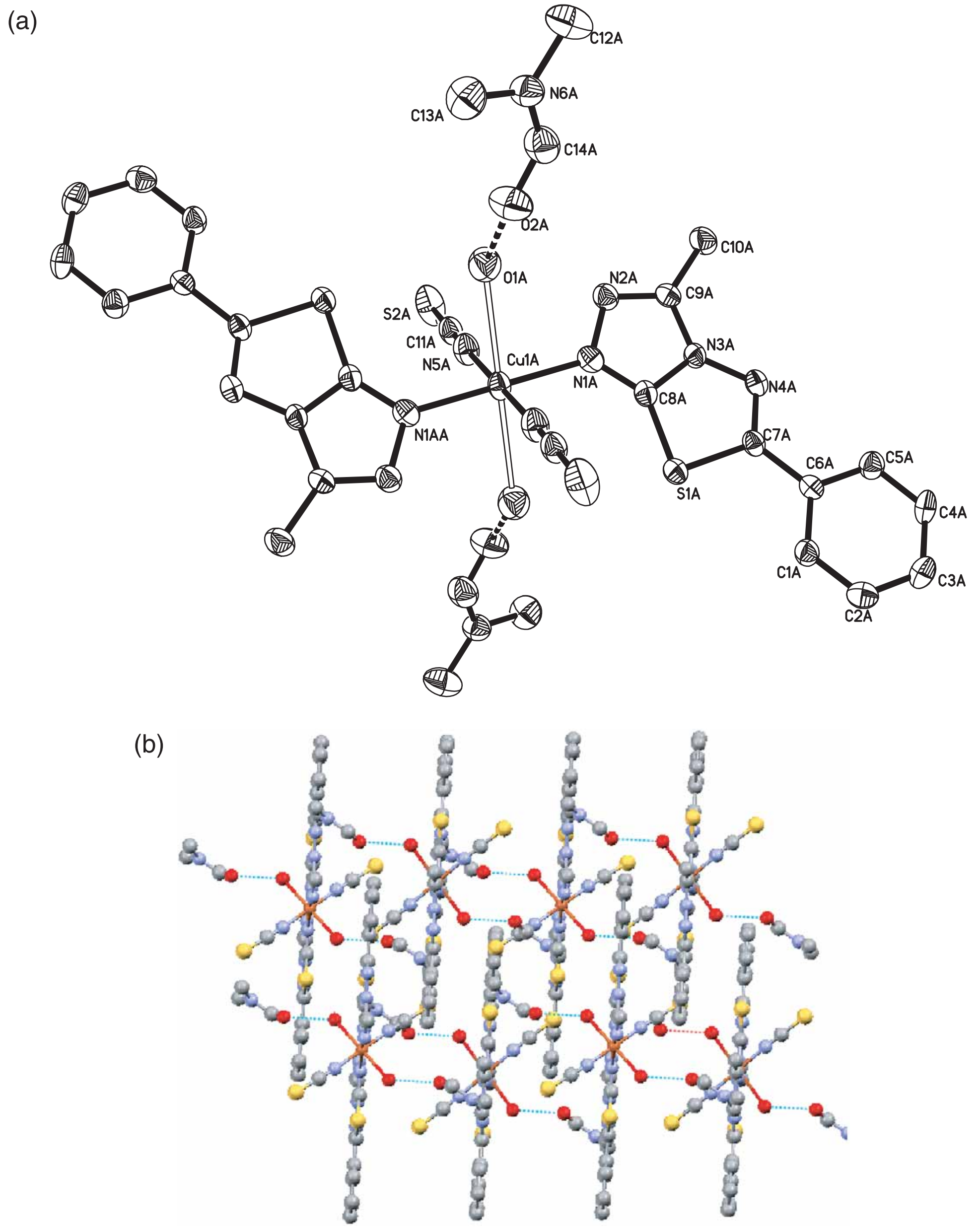
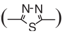


Figure 2. (a) ORPTEP drawing of **2** (50% probability displacement ellipsoids). (b) Packing of **2** along the *b* axis.

at 1485, 1445, 1235, 779 and 692 cm^{-1} in both indicate the existence of the 1,3,4-thiadiazole and benzene rings. Strong bands at about 2100 and 1655 cm^{-1} in **2** are due to terminally coordinated NCS^{-} and carbonyl (DMF), respectively, and that at 1593 cm^{-1} in **1** to OAc^{-}. IR results are thus in agreement with the X-ray studies.

Table 4. Selected IR data (cm^{-1}).

Complex	$\nu(CH_3)$	(NCS^-)	$\nu(CON)$	$\nu(COO^-)^{as}$	ν()	$\nu(ph)^s$
1	3129			1593s	1480, 1403d	779, 692
2	3216	2100s	1645s		1485, 1393d	779, 691

d, doublet; s, strong; as, antisymmetric stretching vibration.

TGA curves of both complex show two stages. For **1**, the first weight loss is about 6.7% in the range 35–90°C, corresponding to the release of water (Calcd 6.6%), and for **2**, the first weight loss of about 22.0% in the range 35–182°C is due to the release of water and DMF (Calcd 22.9%). Main weight losses, 63.9% for **1** and 55.4% for **2** in the range 203.0–320.5°C with both maximum reaction rates at 247.2°C, correspond to decomposition. Total mass losses of 88.5% for **1** and 85.8% for **2** at about 700°C are quite close to theoretical values (88.4% and 85.5%), calculated by taking CuO and $Cu(CN)_2$ as the final products [16], respectively.

Supplementary material

Supplementary crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 257842 (**1**) and 275917 (**2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] S.N. Sawhney, A. Gupta, P.K. Sharma. *Indian J. Heterocycl. Chem.*, **1**, 8 (1991).
[2] F. Bentiss, M. Lagrenée, J.P. Wignacourt. *Polyhedron*, **21**, 403 (2002).
[3] E. Shouji, H. Matsui, N. Oyama. *J. Electro. Chem.*, **417**, 17 (1996).
[4] N.S. Al-Muaike, T.I. EI-Emary. *Eur. J. Polymer Sci.*, **39**, 211 (2003).
[5] A. Gloria, B. Joaqúyń, E. Francisco, L.G. Malva. *Inorg. Chim. Acta*, **343**, 60 (2003).
[6] H. Tannai, K. Tsuge, Y. Sasaki, O. Hatozaki, N. Oyama. *J. Chem. Soc., Dalton Trans.*, 2353 (2003).
[7] C. Ma, J. Zhang, F. Li, R. Zhang. *Eur. J. Inorg. Chem.*, 2775 (2004).
[8] R.F. Song, Y.B. Xie, J.R. Li, X.H. Bu. *J. Chem. Soc., Dalton Trans.*, 4742 (2003).
[9] J.D.E.T. Wilton-Ely, A. Schier, N.W. Mitzel. *Inorg. Chem.*, **40**, 6266 (2001).
[10] M. Kritsanida, A. Mouroutsou, P. Marakos, N. Pouli, S. Papakonstantinou-Garoufalias, C. Pannecouque, M. Witvrouw, E.D. Clercq. *Il Farmaco*, **57**, 253 (2002).

[11] G.M. Sheldrick. *SHELXS-97, Program for X-ray Crystal Structure Solution*, Göttingen University, Germany (1997).

[12] H. Grove, J. Sletten, M. Julve, F. Lloret, L. Lezama, J. Carranza, S. Parsons, P. Rillema. *J. Molcu. Struc.*, **606**, 253 (2002).

[13] J. Costamagna, F. Caruso, J. Vargas, V. Manriquez. *Inorg. Chim. Acta*, **267**, 151 (1998).

[14] B. Ding, L. Yi, H.L. Gao, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang. *Inorg. Chem. Commun.*, **8**, 102 (2005).

[15] Y. Lu, Z.H. Deng. *Chemical Application of Infrared Spectroscopy*, pp. 22, 69 and 224, Science Press, Beijing (1989).

[16] X.Q. Shen, H.J. Zhong, H.Y. Zhang, H.Y. Mao, Q.A. Wu, Y. Zhu. *Polyhedron*, **23**, 876 (2004).