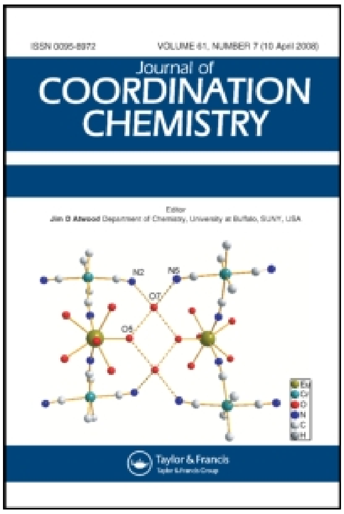

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and characterization of an anion triazole framework containing μ_3-Cl and μ_2-Cl bridges

Yuan Yuan Liu[a]; Bin Ding[a]; En-Cui Yang[a]; Xiao-Jun Zhao[a]; Xiu Guang Wang[a]
[a] College of Chemistry and Life Chemistry, Tianjin Normal University, Tianjin 300387, PR China

To cite this Article Liu, Yuan Yuan , Ding, Bin , Yang, En-Cui , Zhao, Xiao-Jun and Wang, Xiu Guang(2009) 'Synthesis and characterization of an anion triazole framework containing μ_3-Cl and μ_2-Cl bridges', Journal of Coordination Chemistry, 62: 10, 1623 — 1629

To link to this Article: DOI: 10.1080/00958970802680690

URL: http://dx.doi.org/10.1080/00958970802680690

Journal of Coordination Chemistry
Vol. 62, No. 10, 20 May 2009, 1623–1629

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Synthesis and characterization of an anion triazole framework containing μ_3-Cl and μ_2-Cl bridges

YUAN YUAN LIU, BIN DING*, EN-CUI YANG, XIAO-JUN ZHAO
and XIU GUANG WANG

College of Chemistry and Life Chemistry, Tianjin Normal University,
Tianjin 300387, PR China

(*Received 18 July 2008; in final form 18 August 2008*)

Using 3,5-dimethyl-4-amino-1,2,4-triazole (L) and corresponding Ag(I), K(I) salts under ammonia solution and hydrothermal conditions, a triazole–silver(I)–potassium(I) complex $\{K[Ag_2L_2(\mu_3\text{-Cl})(\mu_2\text{-Cl})_2]\}_n$ (**1**) has been isolated. In **1**, μ_3-Cl, μ_2-Cl and L bridge Ag^I ions forming a rare 1-D $[Ag_2L_2(\mu_3\text{-Cl})(\mu_2\text{-Cl})_2]^-$ anion while K^+ cations are located between neighboring anion chains. Strong solid-state fluorescence spectrum of **1** was also investigated showing that the excited peak is located at 320 nm while the maximum emission peak is located at 440 nm.

Keywords: 3,5-Dimethyl-4-amino-1,2,4-triazole; μ_3-Cl; μ_2-Cl; Anion chains; Fluorescence

1. Introduction

Metal-organic coordination polymers have great interest due to versatile coordination motifs and potential applications in light-emitting diodes (LEDs), catalysis and magnetic properties [1–4]. Although a variety of frameworks with beautiful topologies and interesting electronic, magnetic and optical properties have been synthesized, rational control in the construction of polymeric networks remains a challenge in crystal engineering. In general, judicious selection of ligand, central metal, solvent, and reaction environment dramatically affect structural motifs of coordination frameworks [5].

1,2,4-Triazole and its derivatives combine the coordination geometries of pyrazoles and imidazoles with regard to the arrangement of their three heteroatoms [6]. Previously, we reported a series of 3,5-substituted triazole–cadmium coordination polymers from 0-D to 3-D tuned via different triazole ligands and anions. We also reported the first right-handed helical triazole–metal complexes, some triazole–Zn(II) complexes with blue fluorescence properties, and triazole–Fe(II) complexes with spin-crossover properties [7]. Recently, using ammonia as solvent under hydrothermal conditions has proven to be an efficient strategy for preparing metal–triazole frameworks [8]. Herein using 3,5-dimethyl-4-amino-1,2,4-triazole (L) and Ag(I),

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*Corresponding author. Email: qsdingbin@yahoo.com.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802680690

K(I) salts in ammonia solution and hydrothermal conditions, a triazole–silver(I)–potassium(I) complex $\{K[Ag_2L_2(\mu_3\text{-Cl})(\mu_2\text{-Cl})_2]\}_n$ (**1**) is isolated. In **1**, μ_3-Cl, μ_2-Cl and L bridges extend neighboring Ag^I ions forming a rare 1-D $[Ag_2L_2(\mu_3\text{-Cl})(\mu_2\text{-Cl})_2]^-$ anion chain while K^+ is located between neighboring anion chains. Solid-state fluorescence spectrum of **1** was also investigated showing that the excited peak is located at 320 nm while the maximum emission peak is at 440 nm.

2. Experimental

2.1. *Materials and general methods*

Reagents were purchased commercially and used without purification. The 3,5-dimethyl-4-amino-1,2,4-triazole (L) was prepared according to the literature method [9]. Solvents were distilled from appropriate drying agents prior to use. Elemental analyses of carbon, hydrogen and nitrogen were carried out with a CE-440 (Leeman-Labs) analyzer. FT-IR spectrum (KBr pellets) was taken on an AVATAR-370 (Nicolet) spectrometer from 4000 to 400 cm^{-1}. The luminescence spectrum was measured by a MPF-4 fluorescence spectrophotometer with a xenon arc lamp as the light source.

2.2. *Synthesis of $\{K[Ag_2L_2(\mu_3\text{-Cl})(\mu_2\text{-Cl})_2]\}_n$ (1)*

A mixture of AgCl (0.1 mmol), KCl (0.05 mmol), L (0.1 mmol) and ammonia (15 mL) was placed in a 25-mL Teflon-lined steel vessel and heated to 140°C for 5 days and cooled to room temperature, giving colorless block crystals which were collected and washed by H_2O and diethyl ether. The yields are 35% based on Ag. Elemental analysis (%) Calcd for **1**: C, 16.41; H, 2.75; N, 19.14. Found: C, 16.52; H, 2.68; N, 19.30. Hydrothermal conditions and the use of ammonia solution were essential for the synthesis of **1**. AgCl is not very soluble in water and use of ammonia helps to make AgCl soluble. On the other hand, it also helps to adjust the pH of the starting solutions, which is key for preparing metal–triazole frameworks. FT-IR (KBr): 3112 m, 3022 m, 1612 s, 1583 m, 1551 s, 1491 m, 1459 s, 1384 m, 1326 m, 1311 m, 1282 m, 1227 s, 1091 w, 1057 s, 956 s, 793 m, 765 m, 737 w, 721 m, 703 m, 635 m cm^{-1}.

2.3. *X-ray crystallography*

Structure measurement of **1** was performed on a computer controlled Bruker APEX-II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation (0.71073 Å) by using a ω-scan technique. Semi-empirical absorption corrections using SADABS were applied. The structure was solved by direct methods and refined with full-matrix least-squares using SHELXS-97 and SHELXL-97 [10]. Anisotropic thermal parameters were assigned to all nonhydrogen atoms. The organic hydrogen atoms were generated geometrically. Analytical expressions of neutral-atom scattering factors were employed and anomalous dispersion corrections were incorporated. The crystallographic data and selected bond lengths and angles are listed in tables 1 and 2, respectively.

Table 1. Crystallographic data and structure refinement summary.

Formula	$C_8N_8H_{16}Ag_2KCl_3$
Fw (g mol^{-1})	585.48
Wavelength (Å)	0.71073
Crystal size (mm^3)	$0.10 \times 0.10 \times 0.10$
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions (Å)	
a	13.143(3)
b	12.128(2)
c	10.858(2)
β	91.36(3)
V (Å^3)	1730.2(6)
Z	4
θ range (°)	2.29–25.02
Limiting indices	$-15 \le h \le 11$ $-13 \le k \le 13$ $-12 \le l \le 11$
ρ (g cm^{-3})	2.248
μ (mm^{-1})	2.974
Reflections collected/Unique	4680/1479
R_{int}	0.0570
Data/restraints/parameters	1479/0/105
Goodness of Fitness	1.037
F(000)	1136
$R_1{}^a/wR_2{}^b$ [$I > 2\sigma(I)$]	0.0562/0.0899
R_1/wR_2 (all data)	0.0940/0.0997
Largest diff. peak and hole (e Å^{-3})	1.023 and −1.127

Notes: $^aR = \Sigma(||F_0| - |F_C||)/\Sigma|F_0|$.
$^bwR = [\Sigma w(|F_0|^2 - |F_C|^2)^2/\Sigma w(F_0^2)]^{1/2}$.

Table 2. Selected bond distance (Å) and angles (°).[a]

Ag(1)–N(2)	2.403(8)	Ag(1)–N(2A)	2.403(8)
Ag(1)–Cl(1A)	2.580(2)	Ag(1)–Cl(1)	2.580(2)
Ag(1)–Cl(2)	2.774(4)	Ag(2)–N(3)	2.357(9)
Ag(2)–N(3B)	2.357(9)	Ag(2)–Cl(1B)	2.559(3)
Ag(2)–Cl(1B)	2.559(3)	Ag(2)–Cl(2)	2.7315(7)
Ag(2)–Cl(2A)	2.7315(7)	N(2)–Ag(1)–N(2A)	160.1(4)
N(2)–Ag(1)–Cl(1)	95.0(2)	N(2A)–Ag(1)–Cl(1A)	83.5(2)
N(2)–Ag(1)–Cl(1)	83.5(2)	Cl(1A)–Ag(1)–Cl(1)	171.25(14)
N(2)–Ag(1)–Cl(2)	80.0(2)	Cl(1)–Ag(1)–Cl(2)	85.63(7)
N(3)–Ag(2)–N(3B)	180.0(2)	N(3)–Ag(2)–Cl(1)	86.6(2)
N(3B)–Ag(2)–Cl(1)	93.4(2)	Cl(1)–Ag(2)–Cl(2)	86.91(9)
Cl(1)–Ag(2)–Cl(2A)	93.09(9)	N(3B)–Ag(2)–Cl(2A)	80.47(18)

Note: [a]Symmetry transformations used to generate equivalent atoms: A $-x+1, y, -z+1/2$; B $-x+1, -y+1, -z$.

3. Results and discussion

Single crystal X-ray analysis shows that the asymmetrical structural unit of **1** (figure 1) contains two crystallographically independent silver(I) ions (Ag1 and Ag2), one potassium(I), one μ_3-Cl, two μ_2-Cl and two Ls. The Ag–N and Ag–Cl distances vary from 2.357(9) to 2.774(4) Å, in the normal range [11]. Ag2 is octahedral with two nitrogens from two Ls, two μ_2-Cl and two μ_3-Cl forming an N_2Cl_4 donor set. Ag1 is

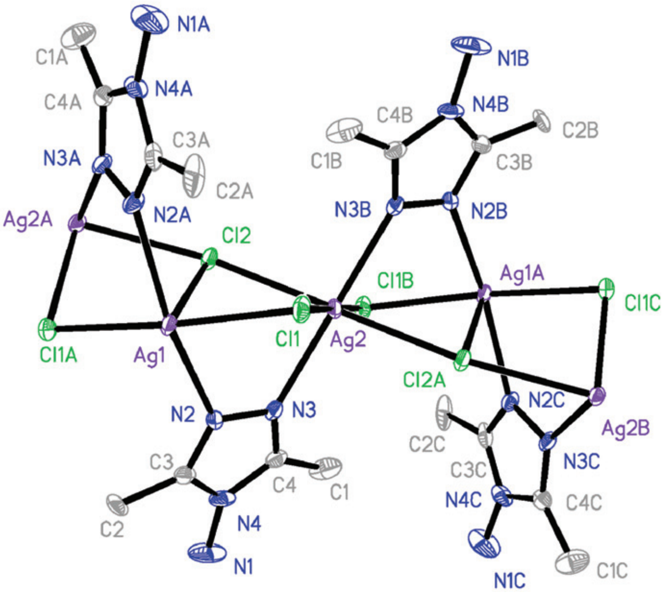

Figure 1. An ORTEP of **1** showing the coordination environment of Ag^I.

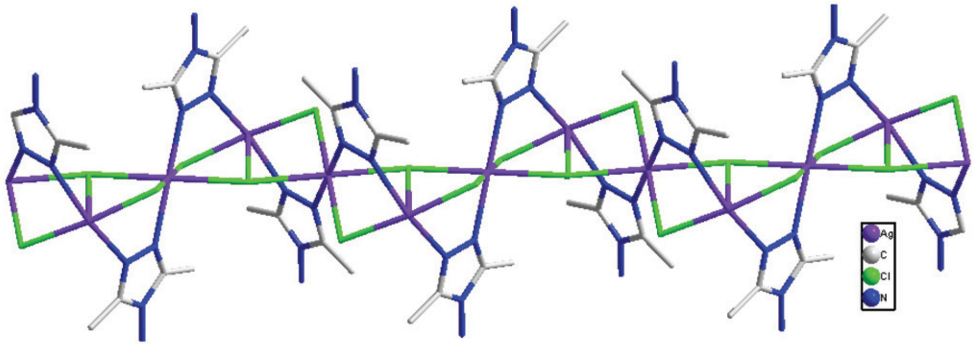

Figure 2. One-dimensional $[Ag_2L_2(\mu_2\text{-}Cl)_3]^-$ anion chains containing μ_2-Cl, μ_3-Cl and L bridges along the crystallographic *c*-axis.

square pyramidal geometry with two nitrogens from two Ls, two μ_2-Cl and one μ_3-Cl. The Ag1···Ag2 separation by μ_2-Cl and μ_3-Cl is 3.669(1) Å. The five-membered triazole ring is almost coplanar with a mean deviation of 0.0051(3) Å.

As shown in figure 2, μ_3-Cl, μ_2-Cl and L bridge Ag^I forming scarcely reported 1-D $[Ag_2L_2(\mu_3\text{-}Cl)(\mu_2\text{-}Cl)_2]^-$ anion chains along the crystallographic *c*-axis. As shown in figure 3, K^+ is located between four neighboring layers forming two linear chains. Anion chains composed of triazole derivatives are rare, revealing that hydrothermal conditions with ammonia solution is efficient for synthesizing metal–organic frameworks.

3.1. *FT-IR spectrum of 1*

FT-IR spectroscopy can be a diagnostic tool for identifying coordination modes of triazole derivatives, which can be monodentate, bidentate, or tridentate. In **1**, the medium

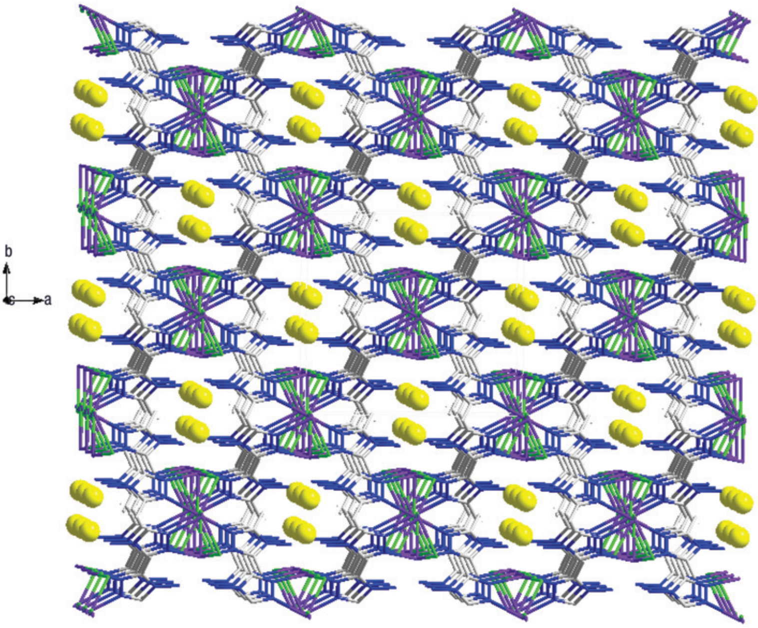

Figure 3. K^+ located between neighboring anion chains.

or weak broad bands at 3112 and 3022 cm^{-1} can be attributed to N–H stretching bands. The triazole out-of-plane ring absorption can be observed at 635 cm^{-1} [12]. The FT-IR results are in agreement with the single crystal X-ray results.

3.2. *Solid-state fluorescence spectrum of 1*

Syntheses of inorganic–organic coordination polymers can be an efficient method for obtaining new types of electroluminescent materials [13]. Luminescent properties of ligand and **1** were investigated in the solid state. The fluorescence spectrum of **1**, shown in figure 4, has a strong emission band centered at 440 nm upon excitation at 320 nm. No fluorescence bands can be observed for free L; therefore the emission band for **1** can be attributed to metal-to-ligand charge transfer [14]. The rigid framework structure may facilitate strong fluorescence bands of **1**.

4. Conclusion

Using 3,5-dimethyl-4-amino-1,2,4-triazole (L) and corresponding Ag(I), K(I) salts under ammonia in hydrothermal conditions gave $\{K[Ag_2L_2(\mu_3\text{-}Cl)(\mu_2\text{-}Cl)_2]\}_n$ (**1**), in which novel μ_3-Cl, μ_2-Cl and L bridges can be observed. These three bridges extend neighboring Ag^I ions forming rare 1-D $[Ag_2L_2(\mu_3\text{-}Cl)(\mu_2\text{-}Cl)_2]^-$ anion chains while K^+ located between neighboring anion chains. Solid-state fluorescence spectrum of **1** shows that with excitation at 320 nm, the maximum emission peak is located at 440 nm.

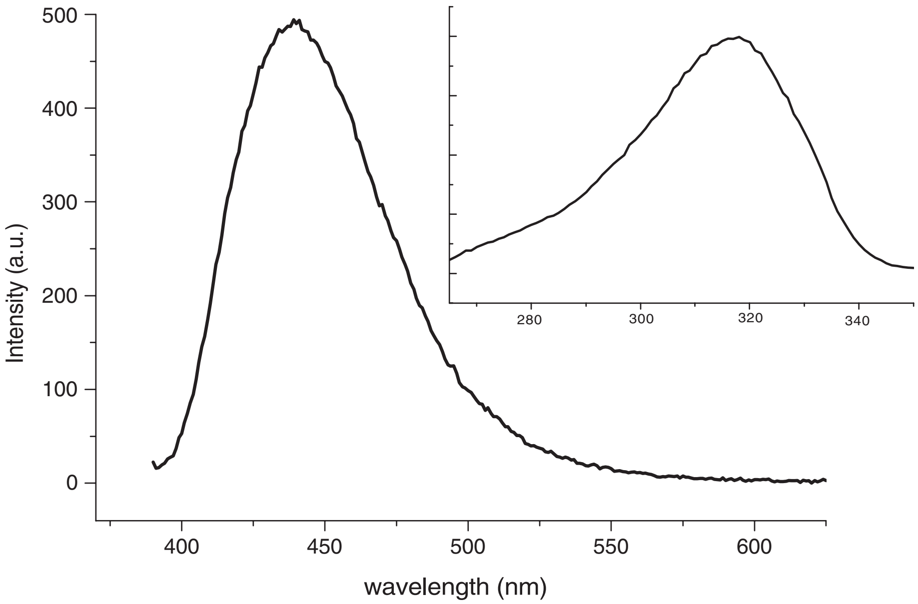

Figure 4. Solid-state fluorescence spectrum of **1**.

$[Ag_2L_2(\mu_3\text{-Cl})(\mu_2\text{-Cl})_2]^-$ reveals potential in constructing new functional polymers with triazole derivatives.

Supplementary material

The supplementary crystallographic data for this article is available from CCDC – **1** 670911. The data can be obtained free of charge via http://www.ccdc.can.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223-336033; or Email: deposit@ccdc.cam.ac.uk].

Acknowledgment

This work was supported financially by Tianjin Normal University (5RL055 and 52LX25).

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