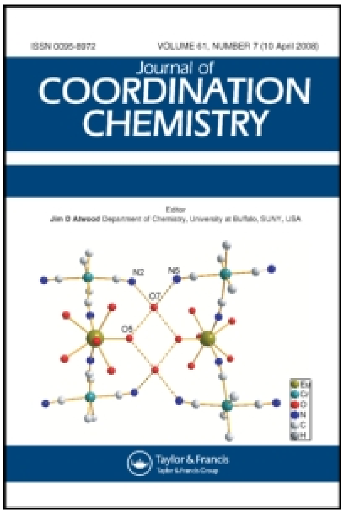

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structure and properties of a silver(I) complex with 2-(1H-1,2,4-triazol-1-yl) acetic acid

Lixia Xie[a]; Aimin Ning[a]; Xin Li[a]
[a] College of Sciences, Henan Agricultural University, Zhengzhou, P.R. China

To cite this Article Xie, Lixia , Ning, Aimin and Li, Xin(2009) 'Synthesis, crystal structure and properties of a silver(I) complex with 2-(1H-1,2,4-triazol-1-yl) acetic acid', Journal of Coordination Chemistry, 62: 10, 1604 — 1612
To link to this Article: DOI: 10.1080/00958970802672994
URL: http://dx.doi.org/10.1080/00958970802672994

Journal of Coordination Chemistry
Vol. 62, No. 10, 20 May 2009, 1604–1612

Synthesis, crystal structure and properties of a silver(I) complex with 2-(1H-1,2,4-triazol-1-yl) acetic acid

LIXIA XIE*, AIMIN NING and XIN LI

College of Sciences, Henan Agricultural University, Zhengzhou, P.R. China

(*Received 26 June 2008; in final form 27 August 2008*)

The treatment of 2-(1H-1,2,4-triazol-1-yl) acetic acid (Htza) with $AgClO_4$ resulted in $[Ag_3(tza)_2(ClO_4)]_n$. Its crystal structure was characterized by X-ray crystallography. Each pair of adjacent Ag1 atoms, separated at 2.954 Å, is bridged by the bidentate carboxylate. Each Ag2 is coordinated in an exactly linear geometry by two triazole nitrogens from two tza^- ligands. Solid state fluorescent measurements have a ligand-based emission at 415 nm. Thermal properties were also investigated.

Keywords: Ag(I) metal ion; Crystal structure; Fluorescent properties

1. Introduction

Design and self-assembly of metal coordination polymers has received attention [1–5] for crystallographic diversity and a myriad of applications [6, 7]. Although a variety of hybrid polymers have been synthesized with intriguing architectures and physical properties, it is still a challenge to prepare advanced luminescent materials with predictable structures and properties through combination of organic ligands with metal ions. Judicious selection of organic ligands and suitable metal ions bearing the right coordination geometries is pivotal for designing fluorescent complexes [8–17]. Because silver(I) possesses variable coordination geometries and their complexes have extraordinary fluorescence properties [18–26], much research has focused on silver inorganic–organic hybrid materials. Organic ligands also play a crucial role in control of fluorescent characteristics of metal-organic complexes, through tuning their structural dimensionalities and stereochemistry with different coordination sites. As a ligand with multiple coordination sites, 1,2,4-triazole can bridge different metal centers to afford coordination polymers that exhibit extraordinary structural diversity and new fluorescent materials [27, 28]. 2-(1H-1,2,4-triazol-1-yl) acetic acid (Htza) is selected to react with Ag(I) in this article providing $[Ag_3(tza)_2(ClO_4)]_n$ with 2-D puckered layers made up of Ag centers and tza^- bridges which exhibits blue fluorescent emission.

---

*Corresponding author. Email: toxielix@163.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802672994

2. Experimental

2.1. *Materials and methods*

All chemicals were of reagent grade quality obtained from commercial sources and used as received. Htza was prepared according to the reported procedures [29]. Elemental analyses (C, H, and N) were carried out on a Perkin–Elmer 240C analytical instrument. Infrared (IR) spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000−400 cm^{-1} regions. Thermogravimetric analyses were carried out with a Netzsch Sta 409 unit at a heating rate of 5°C min^{-1} under nitrogen. Powder X-ray diffraction (PXRD) patterns were recorded using Cu-Kα1 radiation on a PANalytical X'Pert PRO diffractometer. Luminescence spectra for the solid samples were recorded with a Hitachi 850 fluorescence spectrophotometer.

2.2. *Preparation of* $[Ag_3(tza)_2(ClO_4)]_n$

A mixture of $Ag(ClO_4) \cdot 6H_2O$ (0.2 mmol, 0.0630 g), Htza (0.2 mmol, 0.0254 g) and NaOH (0.2 mmol, 0.0080 g) in 10 mL H_2O was stirred thoroughly for several minutes, then filtered. The filtrate was allowed to stand undisturbedly at room temperature. Colorless prisms in ca 51% yield were collected after 1 week. Anal. Calcd for $C_8N_6H_8O_8Ag_3Cl$ (675.25): C, 14.23; H, 1.19; N, 12.45%. Found: C, 14.32; H, 1.05; N, 12.51%. IR (solid KBr pellet): 3439(m), 3131(w), 1625(s), 1517(w), 1386(s), 1312(m), 1104(s), 798(w), 683(w), 624(w).

2.3. *X-ray crystallography*

The intensities of the complex were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation using SMART and SAINT programs [30]. Forty-five frames of data were collected at 298 K with an oscillation range of 1° per frame and an exposure time of 10 s per frame. Indexing and unit cell refinement were based on all observed reflections from those 45 frames. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares with SHELXTL version 5.1 [31]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were added geometrically and refined using the riding model. Crystal data and structure determination summaries for the complex are listed in table 1. Selected bond distances and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structure of* $[Ag_3(tza)_2(ClO_4)]_n$

Single crystal structural analysis reveals that the complex crystallizes in the monoclinic space group *C2/c* and consists of 2-D puckered layers made up of Ag centers and tza$^-$ bridges. As shown in figure 1, the asymmetric unit consists of one and a half crystallographically independent Ag(I) ions, one tza$^-$, and half of a ClO_4^-; Ag(I) exhibits two coordination geometries. Each Ag1 atom is ligated by two carboxyl

Table 1. Crystallographic data.

Formula	$C_4H_4Ag_{1.5}Cl_{0.5}N_3O_4$
Molecular weight	337.63
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cells and dimensions (Å,°)	
a	15.870(3)
b	7.884(1)
c	13.436(3)
α	
β	111.85(1)
γ	
V^3	1560(1)
Z	8
$F(000)$	1280
μ (mm^{-1})	3.956
Number of reflections measured	3934
Number of unique reflections.	1284
R_{int}	0.0455
R_1	0.0338
wR_2 (all data)	0.0939
Goodness-of-fit	1.047

Note: $R_1 = \|F_0| - |F_c\|/|F_0|$; $wR_2 = \left[\sum w(F_0^2 - F_c^2)^2 / \sum w(F_0^2)^2\right]^{1/2}$.

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

Ag(1)–O(1)#1	2.250(3)	Ag(2)–N(3)	2.180(3)
Ag(1)–O(2)#2	2.298(3)	Ag(2)–N(3)#4	2.180(3)
Ag(1)–N(2)	2.340(3)	O(1)–Ag(1)#1	2.250(3)
Ag(1)–Ag(1)#3	2.9543(9)	O(2)–Ag(1)#5	2.298(3)
O(1)#1–Ag(1)–O(2)#2	141.08(14)	O(2)#2–Ag(1)–Ag(1)#3	84.79(9)
O(1)#1–Ag(1)–N(2)	110.89(13)	N(2)–Ag(1)–Ag(1)#3	177.62(10)
O(2)#2–Ag(1)–N(2)	96.37(12)	N(3)–Ag(2)–N(3)#4	180.00(7)
O(1)#1–Ag(1)–Ag(1)#3	69.09(10)		

Note: Symmetry transformations used to generate equivalent atoms: #1: $-x+1,\ y,\ -z+1/2$; #2: $x,\ -y+1,\ z-1/2$; #3: $-x+1,\ -y+1,\ -z$; #4: $-x,\ -y+1,\ -z$; #5: $x,\ -y+1,\ z+1/2$.

oxygens and a nitrogen from three equivalent tza$^-$ ligands in a noncoplanar, highly skew mode [Ag1–N2 2.340(3) Å; Ag1–O2B 2.298(3) Å; Ag1–O1A 2.250(3) Å; torsion angle Ag1–O2B–C4B–C3B 42.8(3)°], completing a triangular coordination geometry around the metal center ($\sum_{\text{Ag1}}$ 348.4°). Each Ag2 is coordinated in exactly linear geometry by two triazole nitrogens from two tza$^-$ ligands [Ag2–N3 2.180(3) Å; N3–Ag2–N3D 180.00(7)°]. With its bridging carboxyl groups and triazole moieties, each tza$^-$ ligand is bound to four Ag atoms. Two adjacent Ag1 ions are joined via O1 and O2 from carboxyl to generate a bimetallic unit $[Ag_2(CO_2)_2]$. Each pair of adjacent Ag1 atoms, [Ag1–Ag1C] 2.954 Å, is bridged by the bidentate-bridging carboxylate. The Ag $\cdots$ Ag distance is proportional to the bite size of the carboxylate. The distance is longer than the Ag $\cdots$ Ag separation of 2.88 Å in the metal [32] and is shorter than the sum of van der Waals radii of two silver atoms (3.44 Å). Consequently, a weak Ag–Ag bond is formed between each adjacent pair of Ag1 atoms [13]. These bimetallic units are further connected through the N2 from triazole moieties affording a 1-D $\{Ag(tza)\}_n$ chain propagating along the [001] direction. Neighboring chains are fused through coordination of Ag2 to N3 along the a-axis, resulting in 2-D puckered

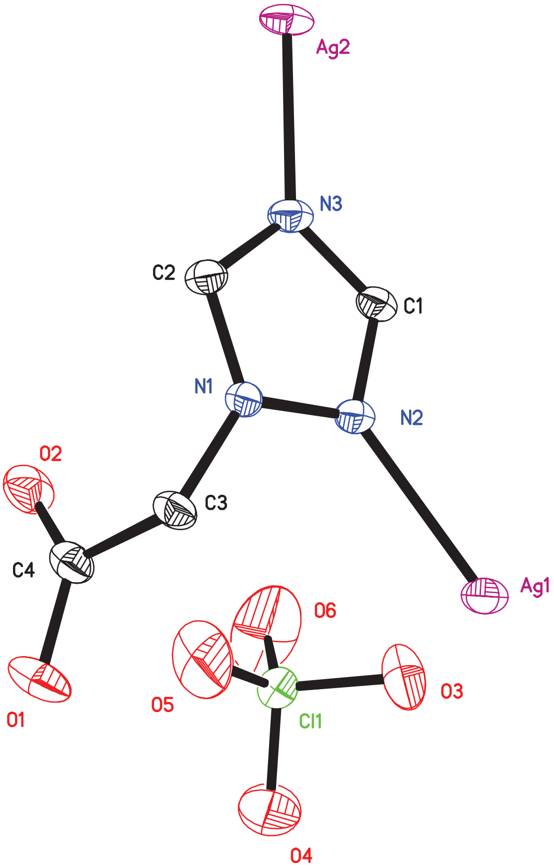

Figure 1. Asymmetric unit of $[Ag_3(tza)_2(ClO_4)]_n$ with thermal ellipsoids at 30% probability. H atoms are omitted.

layers (figure 2). In addition, ClO_4^- counterions are located above and below the plane. The 2-D layer lies in the *ac* crystallographic plane and contains openings of a minimum $7.04 \times 4.04\,Å^2$ size as defined by the shortest transannular distance factoring in van der Waals radii. The layers are noninterpenetrated despite the large cavity size. Adjacent layers are stacked offset with respect to each other in an ABAB fashion by van der Waals' interactions into a 3-D supramolecular network.

3.2. *IR spectroscopy*

The absence of strong peaks around $1700\,cm^{-1}$ indicates that all carboxylates are deprotonated [33]. The ClO_4^- was monitored by appearance of the band at $1104\,cm^{-1}$ [34]. IR data are consistent with the crystal data of the complex.

3.3. *Thermogravimetric analysis*

Thermogravimetric (TG) data show that the polymer is thermally stable to 255°C. Subsequently, decomposition occurs in two steps with a total weight loss of 49.4% by

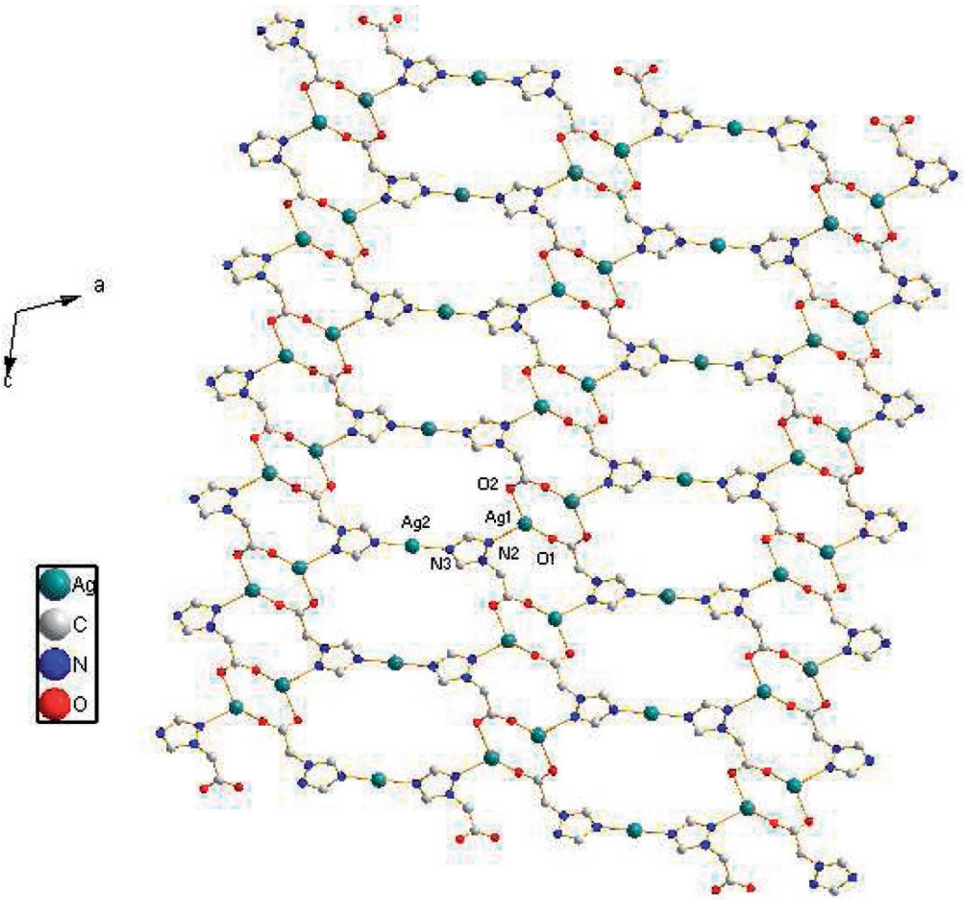

Figure 2. 2-D network structure of $[Ag_3(tza)_2(ClO_4)]_n$ extended along the *ac* plane. H atoms and ClO_4^- counterions are omitted for clarity.

790°C (figure 3). The first stage, which occurs from 255 to 335°C, is attributed to loss of the $C_2H_2N_3$–CH_2–CO unit of the ligand. The observed weight loss (33.22%) is in agreement with the calculated value (32.8%). The second stage, occurring between 335 and 730°C, corresponds to the loss of ClO_4^- and decomposition of the complex. The residual percentage weight (observed 50.6%) is consistent with the formation of Ag_2O (expected 51.5%). The PXRD patterns of the sample pretreated at 255°C for 2 h is in agreement with the simulated one based on the single crystal X-ray diffraction data of the complex (see Supplementary Material, figure S1), indicating that the framework of the complex remains intact upon heating to 255°C.

3.4. *Luminescent properties*

Metal-organic polymeric complexes with a d^{10} closed-shell electronic configuration exhibit fluorescent properties. Here, the fluorescent properties of tza^- ligand and the complex in solid state at room temperature are investigated (figure 4). Excitation at

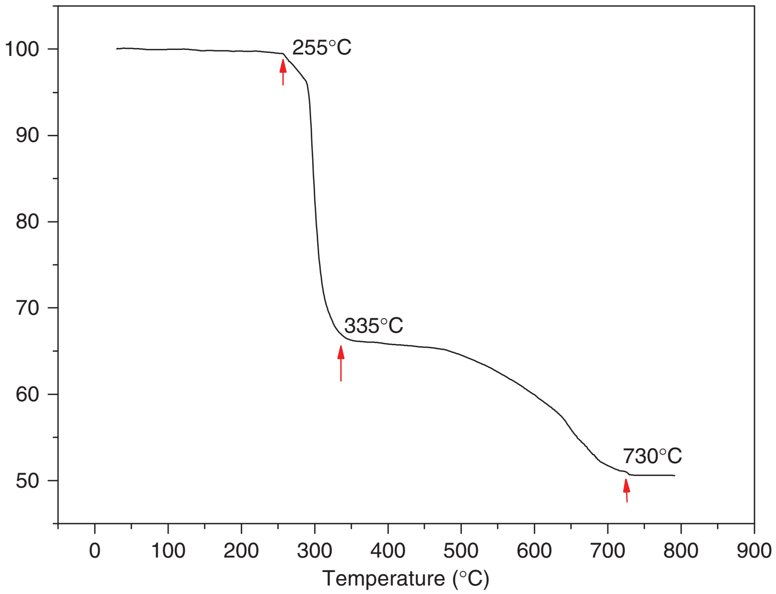

Figure 3. TGA curves of $[Ag_3(tza)_2(ClO_4)]_n$ in 30–790°C.

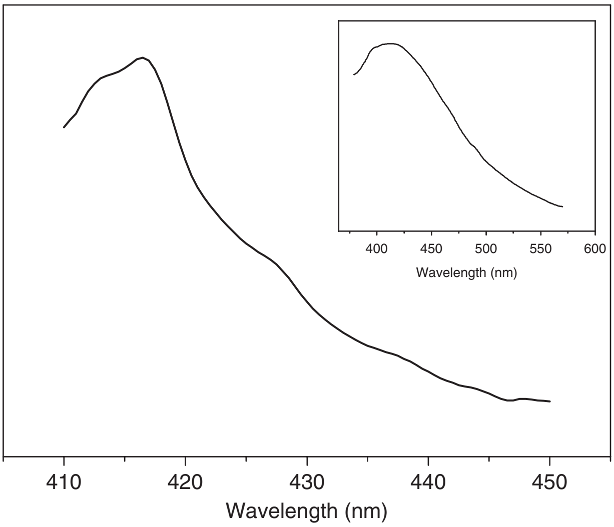

Figure 4. Emission spectra of $[Ag_3(tza)_2(ClO_4)]_n$ and Htza (insert) at 298 K in solid state.

380 nm leads to blue fluorescent emission at 415 nm for the complex. The emission is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature since the Ag^+ ions are difficult to oxidize or to reduce due to the d^{10} configuration. The emission can be assigned to the intraligand (π–π^*) fluorescent emission; the free ligand displays fluorescent properties in solid state with the emission maxima located at 410 nm. The shift of emission in the complex is probably due to the

different configuration of ligand. Photoluminescence behavior is closely associated with the local environment around metal ions [35].

4. Conclusion

We prepared a crystalline product from reaction of Htza with Ag(ClO_4) in water and characterized its structure. Two crystallographically distinct Ag's exhibit two coordination geometries. With its bridging carboxylates and triazoles, each tza$^-$ ligand is bound to four Ag atoms, constructing a 2-D puckered layered motif. The elemental analyses and IR data are consistent with the X-ray analysis results. A blue fluorescent emission band at 415 nm for the complex can be observed (excitation at 380 nm).

Supplementary Data

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC 692816). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +(1223)336-033; Email: teched@chemcrys.cam.ac.uk).

Acknowledgment

We gratefully acknowledge the financial support of the Start-Up Fund of the Henan Agricultural University (30700061).

References

[1] (a) J.M. Lehn. *Supramolecular Chemistry: Concepts, Perspectives*, chap. 9, VCH, Weinheim, Germany (1995); (b) H.L. Li, A. Laine, M. O'Keeffe, O.M. Yaghi. *Science*, **283**, 1145 (1999); (c) M. Kondo, M. Shimamura, S.I. Noro, S. Minakoshi, A. Asami, K. Seki, S. Kitagawa. *Chem. Mater.*, **12**, 1288 (2000); (d) E.J. Schelter, J.K. Bera, J. Bacsa, J.R. Galan-Mascaros, K.R. Dunbar. *Inorg. Chem.*, **42**, 4256 (2003); (e) H.J. Kim, W.C. Zin, M. Lee. *J. Am. Chem. Soc.*, **126**, 7009 (2004); (f) D.M. Ciurtin, N.G. Pschirer, M.D. Smith, U.H.F. Bunz, H.C. zur Loye. *Chem. Mater.*, **13**, 2743 (2001).

[2] (a) J.M. Lehn. *Chem. Eur. J.*, **6**, 2097 (2000); (b) H. Doumanidis. *Nanotechnology*, **13**, 248 (2002); (c) S. Banfi, L. Carlucci, E. Caruso, G. Ciani, D.M. Proserpio. *J. Chem. Soc., Dalton Trans.*, 2714 (2002).

[3] (a) G.R. Desiraju. *Angew. Chem. Int. Ed. Engl.*, **34**, 2311 (1995); (b) L.R. MacGillivray, J.L. Atwood. *Nature*, **389**, 469 (1997); (c) J.M. Lehn. *Science*, **295**, 2400 (2002); (d) S. Forster. T. Plantenberg. *Angew. Chem., Int. Ed.*, **41**, 688 (2002); (e) M. Antonietti. *Nature Mater.*, **2**, 9 (2003); (f) I.W. Hamley. *Angew. Chem., Int. Ed.*, **42**, 1692 (2003).

[4] (a) S. Leininger, B. Olenyuk. P.J. Stang. *Chem. Rev.*, **100**, 853 (2000); (b) B.J. Holliday. C.A. Mirkin. *Angew. Chem. Int. Ed.*, **40**, 2022 (2001); (c) M. Fujita. *Acc. Chem. Res.*, **32**, 53 (1999); (d) G.F. Swiegers, T.J. Malefetse. *Chem. Rev.*, **100**, 3483 (2000); (e) S.R. Seidel, P.J. Stang. *Acc. Chem. Res.*, **35**, 972 (2002).

[5] (a) D.J. Hill, M.J. Mio, R.B. Prince, T.S. Hughes, J.S. Moore. *Chem. Rev.*, **101**, 3893 (2001); (b) N. Yoshida, K. Ichikawa. *Chem. Commun.*, 1091 (1997); (c) L.J. Childs, M. Pascu, A.J. Clarke, N.W. Alcock, M.J. Hannon. *Chem. Eur. J.*, **10**, 4291 (2004); (d) S.R. Batten, R. Robson. *Angew. Chem. Int. Ed.*, **37**, 1460 (1998); (e) K. Kasai, M. Aoyagi, M. Fujita. *J. Am. Chem. Soc.*, **122**, 2140 (2000).

[6] (a) M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi. *Acc. Chem. Res.*, **34**, 319 (2001); (b) O.M. Yaghi, H. Li, C. Davis, D. Richardson, T.L. Groy. *Acc. Chem. Res.*, **31**, 474 (1998); (c) G. Férey. *Chem. Mater.*, **13**, 3084 (2001); (d) O.R. Evans, W. Lin. *Acc. Chem. Res.*, **35**, 511 (2002); (e) M.J. Zaworotko. *Chem. Commun.*, 1 (2001); (f) P.J. Hagrman, D. Hagrman, J. Zubieta. *Angew. Chem., Int. Ed.*, **38**, 2638 (1999).

[7] (a) X.M. Zhang, M.L. Tong, X.M. Chen. *Angew. Chem. Int. Ed.*, **41**, 1029 (2002); (b) J. Tao, Y. Zhang, M.L. Tong, X.M. Chen, T. Yuen, C.L. Lin, X. Huang, J. Li. *Chem. Commun.*, 1342 (2002); (c) R. Cao, D. Sun, Y. Liang, M. Hong, K. Tatsumi, Q. Shi. *Inorg. Chem.* **41**, 2087 (2002); (d) R.G. Xiong, X. Xue, H. Zhao, X.Z. You, B.F. Abrahams, Z. Xue. *Angew. Chem. Int. Ed.*, **41**, 3800 (2002); (e) P.M. Forster, A.K. Cheetham. *Angew. Chem. Int. Ed.*, **41**, 457 (2002); (f) N. Guillou, S. Pastre, C. Livage, G. Férey. *Chem. Commun.*, 2358 (2002); (g) Y. Kim. *Chem. Commun.*, 908 (2002); (h) Z. Shi, S. Feng, Y. Sun, J. Hua. *Inorg. Chem.*, **40**, 5312 (2001); (i) Z. Shi, L. Zhang, S. Gao, G. Yang, J. Hua, L. Gao, S. Feng. *Inorg. Chem.*, **39**, 1990 (2000); (J) L.R. MacGillivray, R.H. Groeneman, J.L. Atwood. *J. Am. Chem. Soc.*, **120**, 2676 (1998); (k) A. Corma, M.E. Davis. *Chem. Phys. Chem.*, **5**, 304 (2004).

[8] V. Bulovic, G. Gu, P.E. Burrows, S.R. Forrest. *Nature*, **29**, 380 (1996).

[9] (a) C.W. Tang, S.A. VanSlyke. *Appl. Phys. Lett.*, **51**, 913 (1987); (b) Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami, K. Imai. *Appl. Phys. Lett.*, **65**, 807 (1994).

[10] (a) C.W. Tang, S.A. VanSlyke, C.H. Chen. *J. Appl. Phys.*, **65**, 3611 (1989); (b) Y. Hamada, T. Sano, M. Fujita, T. Fujii, Y. Nishio, K. Shibata. *Jpn. J. Appl. Phys.*, **32**, 514 (1993).

[11] Q. Wu, M. Esteghamatian, N.X. Hu, Z. Popovic, G. Enright, Y. Tao, M. D'Iorio, S. Wang. *Chem. Mater.*, **12**, 79 (2000).

[12] (a) L. Chassot, E. Müller, A. von Zelewsky. *Inorg. Chem.*, **23**, 4249 (1984); (b) J.E. McGarrah, Y.J. Kim, M. Hissler, R. Eisenberg. *Inorg. Chem.*, **40**, 4510 (2001).

[13] (a) K.T. Wan, C.M. Che, K.C. Cho. *J. Chem. Soc., Dalton Trans.*, 1077 (1991); (b) C.M. Che, K.T. Wan, L.T. He, C.K. Poon, V.W.W. Yam. *J. Chem. Soc., Dalton Trans.*, 2011 (1989).

[14] (a) W. Paw, S.D. Cummings, M.A. Mansour, W.B. Connick, D.K. Gieger, R. Eisenberg. *Coord. Chem. Rev.*, **171**, 125 (1998); (b) A. Vogler, H. Kunkely. *Coord. Chem. Rev.*, **177**, 81 (1998); (c) H. Yersin, W. Humbs, J. Strasser. *Coord. Chem. Rev.*, **159**, 325 (1997); (d) E.Y. Fung, M.M. Olmstead, J.C. Vickery, A.L. Balch. *Coord. Chem. Rev.*, **171**, 151 (1998).

[15] (a) Y. Kunugi, K.R. Mann, L. Miller, C.L. Exstrom. *J. Am. Chem. Soc.*, **120**, 589 (1998); (b) D. Song, Q. Wu, A. Hook, I. Kozin, S. Wang. *Organometallics*, **20**, 4683 (2001).

[16] (a) J.C. Vickery, M.M. Olmstead, E.Y. Fung, A.L. Balch. *Angew. Chem., Int. Ed.*, **36**, 1179 (1997); (b) G. De Santis, L. Fabbrizzi, M. Licchelli, A. Poggi, A. Taglietti. *Angew. Chem. Int. Ed.*, **35**, 202 (1996).

[17] (a) P.C. Ford, E. Cariati, J. Bourassa. *Chem. Rev.*, **99**, 3625 (1999); (b) M.L. Tong, X.M. Chen, B.H. Ye, L.N. Ji. *Angew. Chem. Int. Ed.*, **38**, 2237 (1999).

[18] R.H. Wang, Y.F. Zhou, Y.Q. Sun, D.Q. Yuan, L. Han, B.Y. Lou, B.L. Wu, M.C. Hong. *Cryst. Growth Des.*, **5**, 251 (2005).

[19] (a) S.A. Bourne, J.J. Lu, A. Mondal, B. Moulton, M.J. Zaworotko. *Angew. Chem., Int. Ed.*, **40**, 2111 (2001); (b) S.T. Wang, Y. Hou, E.B. Wang, Y.G. Li, L. Xu, J. Peng, S.X. Liu, C.W. Hu. *New J. Chem.*, **27**, 1144 (2003).

[20] (a) X.M. Zhang, M.L. Tong, M.L. Gong, X.M. Chen. *Eur. J. Inorg. Chem.*, 138 (2003); (b) X.C. Huang, S.L. Zheng, J.P. Zhang, X.M. Chen. *Eur. J. Inorg. Chem.*, 1024 (2004).

[21] (a) Y.J. Kang, C. Seward, D.T. Song, S.N. Wang. *Inorg. Chem.*, **42**, 2789 (2003); (b) C. Seward, J.L. Chan, D.T. Song, S.N. Wang. *Inorg. Chem.*, **42**, 1112 (2003).

[22] R.G. Lin, J.H.K. Yip. *Inorg. Chem.*, **45**, 4423 (2006).

[23] X. Liu, G.C. Guo, M.L. Fu, X.H. Liu, M.S. Wang, J.S. Huang. *Inorg. Chem.*, **45**, 3679 (2006).

[24] (a) Y.B. Dong, H.X. Xu, J.P. Ma, R.Q. Huang. *Inorg. Chem.*, **45**, 3325 (2006); (b) Y.B. Dong, G. Zhang, L. Wang, J.P. Ma, R.Q. Huang, D.Z. Shen, D.Z. Chen. *Inorg. Chem.*, **44**, 6591 (2005); (c) Y.B. Dong, J.Y. Cheng, R.Q. Huang. *Inorg. Chem.*, **42**, 5699 (2003); (d) Y.B. Dong, J.P. Ma, R.Q. Huang. *Inorg. Chem.*, **42**, 294 (2003).

[25] H.C. Wu, P. Thanasekaran, C.H. Tsai, J.Y. Wu, S.M. Huang, Y.S. Wen, K.L. Lu. *Inorg. Chem.*, **45**, 295 (2006).

[26] (a) L. Carlucci, G. Ciani, D.W.V. Gudenberg, D.M. Proserpio. *Inorg. Chem.*, **36**, 3812 (1997); (b) O.-S. Jung, S.H. Park, C.H. Park, J.K. Park. *Chem. Lett.*, **28**, 923 (1999).

[27] (a) W. Ouellette, J.R. Galan-Mascaros, K.R. Dunbar, J. Zubieta. *Inorg. Chem.*, **45**, 1909 (2006); (b) W. Ouellette, A.V. Prosvirin, V. Chieffo, K.R. Dunbar, B.S. Hudson, J. Zubieta. *Inorg. Chem.*, **45**, 9346 (2006).

[28] (a) W. Ouellette, B.S. Hudson, J. Zubieta. *Inorg. Chem.*, **46**, 4887 (2007); (b) Q.G. Zhai, C.Z. Lu, X.Y. Wu, S.R. Batten. *Cryst. Growth Des.*, **7**, 2332 (2007).

[29] R. Pellicciari. *Synth. Commun.*, 629 (1981).

[30] SMART, *SAINT, Area Detector Control, Integration Software, Siemens Analytical X-ray Systems, Inc.*, Madison, WI (1996).

[31] G.M. Sheldrick. *SHELXTL V5.1, Software Reference Manual*, Bruker AXS, Inc., Madison, WI (1997).

[32] (a) A. Bondi. *J. Phys. Chem.*, **68**, 441 (1964); (b) M. Jansen. *Angew. Chem., Int. Ed. Engl.*, **26**, 1098 (1987); (c) P. Pyykkö. *Chem. Rev.*, **97**, 597 (1997).

[33] Q. Shi, R. Cao, D.-F. Sun, M.-C. Hong, Y.-C. Liang. *Polyhedron*, **20**, 3287 (2001).

[34] (a) O.S. Jung, Y.J. Kim, Y.A. Lee, K.M. Park, S.S. Lee. *Inorg. Chem.*, **42**, 844 (2003); (b) O.S. Jung, Y.J. Kim, K.M. Park, S.N. Cho. *J. Mol. Struct.*, **657**, 207 (2003); (c) O.S. Jung, Y.J. Kim, Y.A. Lee, H.K. Chae, H.G. Jang, J. Hong. *Inorg. Chem.*, **40**, 2105 (2001); (d) D.L. Reger, R.F. Semeniuc, V. Rassolov, M.D. Smith. *Inorg. Chem.*, **43**, 537 (2004).

[35] Z.-Y. Fu, X.-T. Wu, J.-C. Dai, S.M. Hu, W.-X. Du, H.-H. Zhang, R.-Q. Sun. *Eur. J. Inorg. Chem.*, 2730 (2002).