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Journal of Solid State Chemistry 172 (2003) 45–52

JOURNAL OF  
SOLID STATE  
CHEMISTRY

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# Effect of synthetic conditions on the structures of silver(I)-hexamethylenetetramine coordination polymers: crystal structures of two three-dimensional frameworks featuring new topological motifs

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Received 30 June 2002; received in revised form 19 September 2002; accepted 24 September 2002

## Abstract

Two novel coordination complexes,  $[\text{Ag}_3(\mu_4\text{-hmt})_2(\mu\text{-ssa})(\text{H}_2\text{O})](\text{NO}_3) \cdot 3\text{H}_2\text{O}$  **1**, and  $[\text{Ag}_8(\mu_3\text{-hmt})_2(\mu_4\text{-hmt})_2(\mu\text{-pma})_2(\mu\text{-H}_2\text{O})_3] \cdot 18\text{H}_2\text{O}$  **2** (hmt = hexamethylenetetramine, ssa = sulfosalicylate and pma = 1,2,4,5-benzenetetracarboxylate), have been prepared and structurally characterized. Crystal data: **1**  $\text{C}_{19}\text{H}_{33}\text{Ag}_3\text{N}_9\text{O}_{13}\text{S}$ , orthorhombic,  $Pna2_1$ ,  $a = 20.483(7) \text{ \AA}$ ,  $b = 21.890(1) \text{ \AA}$ ,  $c = 6.493(2) \text{ \AA}$ ,  $V = 2911.3(13) \text{ \AA}^3$ ,  $Z = 4$ ; **2**  $\text{C}_{44}\text{H}_{94}\text{Ag}_8\text{N}_{16}\text{O}_{37}$ , monoclinic,  $C2/c$ ,  $a = 32.099(10) \text{ \AA}$ ,  $b = 12.916(3) \text{ \AA}$ ,  $c = 21.431(8) \text{ \AA}$ ,  $\beta = 126.74(1)^\circ$ ,  $V = 7120(4) \text{ \AA}^3$ ,  $Z = 4$ . Both complexes exhibit unprecedented and different topological motifs of Ag-hmt networks. Complex **1** is a novel three-dimensional cationic network with two types of channels, in which the larger one is the largest one in Ag-hmt networks; while **2** is a three-dimensional network with cylindrical channels, consisting of mixed  $\mu_3$ - and  $\mu_4$ -hmt ligands. The results demonstrate that under different synthetic conditions, such as the presence of multiple small counter anions or different pH values, different Ag-hmt linkages may be formed to generate new three-dimensional networks.

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**Keywords:** Silver(I); Coordination polymer; Microporosity; Inclusion compound; Supramolecular chemistry

## 1. Introduction

Crystal engineering and design of solid-state architectures of coordination polymers are very attractive fields in recent years [1,2]. Assembly of such extended supramolecular architectures by selecting the chemical structure of organic ligands and the coordination geometry of metal ions may yield a large number of new networks exhibiting interesting topologies and potential properties as new materials [3–7]. We and others have found that combination of hexamethylenetetramine (hmt,  $\text{C}_6\text{H}_{12}\text{N}_4$ ) as a polydentate ligand and silver(I) can produce a wide variety of supramolecular architectures in different one-, two- and three-dimensional topological motifs [5–13]. In these structurally characterized three-dimensional architectures, hmt

usually acts in a unique bridging mode, and only two mixed bridging modes have been found in a one-dimensional ribbon-like coordination polymer  $[\text{Ag}_2(\mu\text{-hmt})(\mu_3\text{-hmt})(\text{H}_2\text{O})(\text{SbF}_6)]$  and a two-dimensional coordination polymer  $[\text{Ag}_2(\mu\text{-hmt})(\mu_3\text{-hmt})(\text{ssa})]$  (ssa = sulfosalicylate,  $\text{C}_7\text{H}_4\text{O}_6\text{S}$ ) [6,11]. On the other hand, the self-assembly of silver(I) atoms with hmt in different conditions, such as different Ag(I)/hmt molar ratios, different counter anions, and/or different anionic organic ligands, may lead to different molecular architectures. For example, both metal salts  $\text{AgClO}_4$  and  $\text{AgNO}_3$  gave 1:1 adducts that contain quite similar two-dimensional hexagonal  $[\text{Ag}(\mu_3\text{-hmt})]$  layers; while in the presence of excessive silver ions, three-dimensional frameworks featuring  $\mu_4$ -hmt ligands are recovered for both metal salts, showing different stoichiometries [7–9].

As a sequel work of our systematic investigation on Ag-hmt coordination networks, we report herewith two

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new coordination polymers, namely  $[\text{Ag}_3(\mu_4\text{-hmt})_2(\mu\text{-ssa})(\text{H}_2\text{O})](\text{NO}_3) \cdot 3\text{H}_2\text{O}$  **1** and  $[\text{Ag}_8(\mu_3\text{-hmt})_2(\mu_4\text{-hmt})_2(\mu\text{-pma})_2(\mu\text{-H}_2\text{O})_3] \cdot 18\text{H}_2\text{O}$  **2** (pma = 1,2,4,5-benzenetetracarboxylate,  $\text{C}_{10}\text{H}_2\text{O}_8$ ). Although the organic ligands were employed previously [11,13], however, novel structural motifs are resulted from different synthetic methods in this work. Complex **1** is a novel three-dimensional cationic network with two types of channels, in which the larger one, containing eight Ag(I) atoms and eight hmt ligands, is the largest one among the Ag-hmt networks. While **2** is another new type of three-dimensional non-interpenetrated network with cylindrical channels that is the first example constructed by mixed  $\mu_3$ - and  $\mu_4$ -bridging hmt ligands in Ag-hmt networks.

## 2. Experimental

The  $\text{Ag}_2(\text{ssa})$  and  $\text{Ag}_4(\text{pma})$  were prepared according to the literature method [14]. The reagents and solvents employed were commercially available and used as received without further purification. The C, H, N microanalyses were carried out with a Perkin-Elmer 240 elemental analyser. The FT-IR spectra were recorded from KBr pellets in range  $4000\text{--}400\text{ cm}^{-1}$  on a Nicolet SDX spectrometer.

### 2.1. Syntheses of $[\text{Ag}_3(\mu_4\text{-hmt})_2(\mu\text{-ssa})(\text{H}_2\text{O})](\text{NO}_3) \cdot 3\text{H}_2\text{O}$ **1**

An aqueous solution ( $5\text{ cm}^3$ ) of hmt (0.140 g, 1.0 mmol) was added dropwise to a stirred ethanolic suspension ( $5\text{ cm}^3$ ) of  $\text{Ag}_2(\text{ssa})$  (0.216 g, 0.5 mmol) at  $50^\circ\text{C}$  for 15 min. The solution was adjusted to  $\text{pH} \approx 4.5$  by the addition of dilute  $\text{HNO}_3$  solution. The resulting yellowish solution was allowed to stand in air at room temperature for a week, yielding pale yellow crystals (56%). Anal. calc. for  $\text{C}_{19}\text{H}_{33}\text{Ag}_3\text{N}_9\text{O}_{13}\text{S}$  **1**: C, 23.99; H, 3.50; N, 13.25; S, 3.37%. Found: C, 24.01; H, 3.46; N, 13.28; S, 3.39%. IR ( $\text{cm}^{-1}$ ): 3429m, br, 2959m, 2890m, 2882w, 1637m, 1588s, 1482s, 1440s, 1384vs, 1300m, 1236vs, 1187s, 1159s, 1117m, 1082m, 1032s, 1004vs, 899w, 814s, 737m, 674s, 596s, 512w, 414w.

### 2.2. Syntheses of $[\text{Ag}_8(\mu_3\text{-hmt})_2(\mu_4\text{-hmt})_2(\mu\text{-pma})_2(\mu\text{-H}_2\text{O})_3] \cdot 18\text{H}_2\text{O}$ **2**

It was prepared as for **1** (yield ca. 68%) using a molar Ag:hmt ratio of 2:1. Anal. calc. for  $\text{C}_{44}\text{H}_{94}\text{Ag}_8\text{N}_{16}\text{O}_{37}$  **2**: C, 22.95; H, 4.12; N, 9.73%. Found: C, 22.91; H, 4.08; N, 9.71%. IR ( $\text{cm}^{-1}$ ): 3436s, br, 2952m, 2880m, 1567vs, 1480m, 1460m, 1418s, 1374vs, 1323m, 1236s, 1137w, 1052w, 1007vs, 920w, 864w, 812m, 691m, 666m, 603w, 544w, 512w, 460w.

### 2.3. Crystal structure determination

Diffraction intensities for the two complexes were collected at  $21^\circ\text{C}$  on a Siemens R3m diffractometer operating in the  $\omega$ -scan technique. Lorentz-polarization and absorption corrections were applied [15]. The structures were solved and refined by SHELX-97 [16]. Carbon-bound hydrogen atoms were generated geometrically (C–H 0.96 Å). In **1**, the ssa anion is disordered in two positions approximately along a line passing through the C(4)–C(7) atoms. The rings were refined as rigid hexagons, and a combination of temperature and distance restraints were used to treat the disorder. The disorder affected the other parts of the structure, and similar restraints were applied to them. The disorder precluded finding the water hydrogen atoms. For **2**, the O(1w) is disordered and was refined with 1/2 site occupancies, the water hydrogen atoms were located from difference maps and refined. The absolute structure parameter was refined to 0.0(2) for **1** [17]. Crystal data as well as details of data collection and refinement for the complexes are summarized in Table 1. Atomic coordinates and equivalent isotropic displacement parameters and selected interatomic distances and angles are given in Tables 2 and 3. Drawings were produced with SHELXTL [18].

CCDC-##### contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internet) +44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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

Complex	<b>1</b>	<b>2</b>
Formula	$\text{C}_{19}\text{H}_{33}\text{Ag}_3\text{N}_9\text{O}_{13}\text{S}$	$\text{C}_{44}\text{H}_{94}\text{Ag}_8\text{N}_{16}\text{O}_{37}$
$F_w$	951.21	2302.31
Crystal system	Orthorhombic	Monoclinic
Space group	$Pna2_1$ (No. 33)	$C2/c$ (No. 15)
$a$ (Å)	20.483(7)	32.099(10)
$b$ (Å)	21.890(1)	12.916(3)
$c$ (Å)	6.493(2)	21.431(8)
$\beta$ (deg)	90	126.74(1)
Volume (Å <sup>3</sup> )	2911.3(13)	7120(4)
$Z$	4	4
$\lambda(\text{MoK}\alpha)$ (Å)	0.71073	0.71073
$T$ (K)	293(2)	293(2)
$\rho_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	2.170	2.148
$\mu$ ( $\text{MoK}\alpha$ ) ( $\text{mm}^{-1}$ )	2.150	2.258
No. of unique reflections	3277	9627
No. of observed [ $I \geq 2\sigma(I)$ ]	3109	9470
Crystal size (mm)	$0.34 \times 0.18 \times 0.14$	$0.48 \times 0.38 \times 0.36$
$R_1$ [ $I > 2\sigma(I)$ ] <sup>a</sup>	0.0670	0.0617
$wR_2$ (all data) <sup>b</sup>	0.1624	0.2012

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

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

Table 2  
Atomic coordinates ( $\times 10^4$ ) and isotropic thermal parameters ( $\times 10^3$ )  
for **1** and **2**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
<b>Complex 1</b>				
Ag(1)	7331(1)	3158(1)	5159(8)	28(1)
Ag(2)	9977(1)	2832(1)	10191(9)	34(1)
Ag(3)	11603(1)	4708(1)	5192(10)	43(1)
S(1)	5594(5)	6593(5)	5240(3)	39(3)
O(1)	6381(10)	3792(8)	5150(14)	40(3)
O(2)	7024(9)	4559(9)	5320(11)	40(3)
O(3)	5101(9)	6837(10)	6660(3)	40(3)
O(4)	5506(11)	6806(11)	3110(3)	40(3)
O(5)	6265(7)	6660(9)	5990(4)	40(3)
O(6)	5137(11)	3929(9)	5060(10)	40(3)
C(1)	6478(10)	4343(9)	5130(15)	29(3)
C(2)	5890(11)	4765(11)	5490(6)	19(2)
C(3)	5264(14)	4517(15)	5290(19)	19(2)
C(4)	4707(14)	4988(13)	5300(11)	19(2)
C(5)	4807(17)	5581(13)	5130(14)	19(2)
C(6)	5448(11)	5787(6)	5150(6)	19(2)
C(7)	5999(14)	5393(12)	5080(12)	19(2)
N(1)	7947(10)	3376(11)	8390(3)	18(2)
N(2)	8920(5)	3278(5)	10120(6)	18(2)
N(3)	8352(5)	4270(5)	10110(5)	18(2)
N(4)	7857(10)	3404(11)	12150(3)	18(2)
C(8)	8533(13)	3054(9)	8410(4)	21(1)
C(9)	7969(15)	4029(10)	8440(4)	21(1)
C(10)	7532(6)	3217(6)	10320(5)	21(1)
C(11)	8998(6)	3946(5)	10160(8)	21(1)
C(12)	8563(13)	3152(10)	12100(4)	21(1)
C(13)	7990(15)	4109(10)	12110(4)	21(1)
N(5)	10563(12)	2973(11)	7150(4)	17(2)
N(6)	10611(13)	3019(11)	3390(4)	17(2)
N(7)	11547(5)	2644(4)	5300(5)	17(2)
N(8)	11262(5)	3720(5)	5100(5)	17(2)
C(14)	10192(6)	2886(6)	5150(7)	21(1)
C(15)	11136(16)	2591(11)	7010(5)	21(1)
C(16)	10862(14)	3657(11)	6980(5)	21(1)
C(17)	11151(16)	2520(11)	3390(5)	21(1)
C(18)	10828(14)	3581(11)	3330(5)	21(1)
C(19)	11789(6)	3273(5)	5250(7)	21(1)
N(9)	10499(8)	5191(7)	10160(6)	58(6)
O(7)	9921(9)	5043(11)	10210(9)	124(9)
O(8)	10644(6)	5728(5)	10110(6)	46(4)
O(9)	10899(13)	4803(8)	9640(4)	119(13)
O(1W)	12768(11)	4533(11)	4210(5)	123(13)
O(2W)	12064(12)	4521(10)	9110(4)	83(7)
O(3W)	12431(11)	3363(8)	9900(5)	83(8)
O(4W)	13482(13)	3443(10)	4600(10)	190(3)
<b>Complex 2</b>				
Ag(1)	10000	6799(1)	7500	98(1)
Ag(2)	10000	3222(1)	7500	93(1)
Ag(3)	6737(1)	4812(1)	4155(1)	98(1)
Ag(4)	7702(1)	4855(1)	6064(1)	78(1)
Ag(5)	11104(1)	7996(1)	11020(1)	96(1)
O(1W)	10049(6)	5012(8)	7993(10)	118(4)
O(2W)	7686(2)	5166(3)	4979(3)	81(1)
O(1)	8350(2)	5826(4)	7125(3)	110(2)
O(2)	7781(2)	7082(4)	6687(3)	100(2)
O(3)	7891(2)	9304(4)	8750(3)	85(1)
O(4)	8248(2)	8395(5)	9833(3)	100(2)
O(5)	9401(2)	9033(5)	10532(3)	107(2)
O(6)	9497(2)	7393(4)	10920(3)	92(1)

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
O(7)	9505(2)	5414(4)	8586(4)	100(2)
O(8)	9436(2)	6905(4)	8006(3)	89(1)
N(1)	10764(2)	7363(4)	8684(3)	70(1)
N(2)	11176(2)	7805(4)	10041(3)	69(1)
N(3)	11453(2)	8681(4)	9329(3)	68(1)
N(4)	11669(2)	6864(3)	9688(3)	70(1)
C(1)	11361(2)	8790(4)	9920(3)	71(1)
C(2)	11579(2)	7003(4)	10280(3)	73(2)
C(3)	10689(2)	7489(5)	9287(3)	74(1)
C(4)	10957(2)	8334(5)	8590(3)	74(1)
C(5)	11171(2)	6565(4)	8939(3)	73(1)
C(6)	11842(2)	7860(5)	9579(3)	74(2)
N(5)	8793(2)	2352(4)	7863(3)	70(1)
N(6)	9227(2)	2875(4)	7281(3)	70(1)
N(7)	8517(2)	1615(4)	6623(3)	68(1)
N(8)	8336(2)	3428(4)	6690(3)	69(1)
C(7)	8594(2)	1422(4)	7366(3)	70(1)
C(8)	9293(2)	2670(5)	8010(3)	71(1)
C(9)	8418(2)	3211(5)	7433(3)	74(1)
C(10)	8833(2)	3709(4)	6861(3)	70(1)
C(11)	8140(2)	2480(5)	6216(3)	71(1)
C(12)	9018(2)	1933(4)	6792(3)	72(1)
C(13)	8184(2)	6616(4)	7224(3)	73(1)
C(14)	8197(2)	8620(5)	9227(3)	74(1)
C(15)	9325(3)	8075(6)	10412(3)	79(2)
C(16)	9335(2)	6323(5)	8355(4)	76(2)
C(17)	8490(2)	7060(4)	8033(3)	67(1)
C(18)	8243(2)	7669(4)	8250(3)	70(1)
C(19)	8497(2)	7999(4)	9015(3)	69(1)
C(20)	9018(2)	7717(5)	9572(3)	72(1)
C(21)	9265(2)	7132(5)	9351(3)	72(1)
C(22)	9015(2)	6798(4)	8586(3)	71(1)
O(3W)	10594(3)	9800(5)	10554(4)	120(2)
O(4W)	12066(3)	8903(7)	11955(4)	140(3)
O(5W)	10066(2)	9898(4)	11933(3)	100(2)
O(6W)	10753(3)	10967(5)	11837(3)	105(2)
O(7W)	11882(3)	9169(5)	8128(4)	123(2)
O(8W)	13171(4)	11180(7)	9715(7)	173(4)
O(9W)	9290(6)	4294(7)	9439(8)	211(6)
O(10W)	13006(7)	9973(9)	8479(8)	246(8)
O(11W)	9358(8)	5331(10)	10687(10)	313(13)

### 3. Results and discussion

#### 3.1. Synthesis chemistry

Complex **1** was first synthesized by the reaction of ethanolic solution of Ag<sub>2</sub>(ssa) and hmt in molar ratio of 1:2 with the addition of dilute HNO<sub>3</sub> solution, which is somewhat out of our anticipation. However, a crystalline product was also obtained from the reaction system of Ag<sub>2</sub>(ssa), AgNO<sub>3</sub> and hmt in molar ratio of 1:1:2 in ethanolic solution, and proved to be identical to **1** by elemental analysis, IR spectra and crystallographic unit-cell parameters within experimental errors (orthorhombic, *a* = 20.51(1) Å, *b* = 21.82(1) Å, *c* = 6.55(1) Å, *V* = 2848(4) Å<sup>3</sup>). Such phenomenon is similar to that of another coordination polymer, namely

Table 3

Selected bond lengths (Å) and bond angles (deg) for **1** and **2**

Complex 1			
Ag(1)–N(4a)	2.29(2)	Ag(2)–O(3c)	2.38(2)
Ag(1)–N(7b)	2.38(1)	Ag(2)–N(6d)	2.49(2)
Ag(1)–O(1)	2.39(2)	Ag(3)–N(3e)	2.24(1)
Ag(1)–N(1)	2.49(2)	Ag(3)–N(8)	2.27(1)
Ag(2)–N(5)	2.33(2)	Ag(3)–O(1W)	2.50(2)
Ag(2)–N(2)	2.38(1)		
N(4a)–Ag(1)–N(7b)	121.5(9)	N(2)–Ag(2)–O(3c)	108.8(6)
N(4a)–Ag(1)–O(1)	104(2)	N(5)–Ag(2)–N(6d)	114.7(3)
N(7b)–Ag(1)–O(1)	83.1(5)	N(2)–Ag(2)–N(6d)	115(1)
N(4a)–Ag(1)–N(1)	115.6(4)	O(3c)–Ag(2)–N(6d)	81.4(7)
N(7b)–Ag(1)–N(1)	116.7(9)	N(3e)–Ag(3)–N(8)	164.2(4)
O(1)–Ag(1)–N(1)	108(2)	N(3e)–Ag(3)–O(1W)	96.2(7)
N(5)–Ag(2)–N(2)	113(1)	N(8)–Ag(3)–O(1W)	98.1(7)
N(5)–Ag(2)–O(3c)	119.7(8)		
Complex 2			
Ag(1)–N(1)	2.353(5)	Ag(3)–N(7c)	2.283(4)
Ag(1)–N(1a)	2.353(5)	Ag(3)–O(2W)	2.482(5)
Ag(1)–O(1W)	2.50(1)	Ag(4)–O(3d)	2.279(5)
Ag(2)–N(6)	2.277(5)	Ag(4)–O(1)	2.325(5)
Ag(2)–N(6a)	2.277(5)	Ag(4)–O(2W)	2.329(5)
Ag(2)–O(1W)	2.51(1)	Ag(4)–N(8)	2.464(5)
Ag(3)···Ag(4)	3.344(1)	Ag(5)–N(2)	2.257(5)
Ag(3)–N(3b)	2.274(5)	Ag(5)–N(5e)	2.258(5)
N(1)–Ag(1)–N(1a)	144.0(2)	N(7d)–Ag(3)–O(2W)	114.8(2)
N(1)–Ag(1)–O(1W)	93.9(4)	O(3d)–Ag(4)–O(1)	110.5(2)
N(1a)–Ag(1)–O(1W)	120.1(4)	O(3d)–Ag(4)–O(2W)	134.9(2)
N(6)–Ag(2)–N(6a)	157.3(2)	O(1)–Ag(4)–O(2W)	110.9(2)
N(6)–Ag(2)–O(1W)	93.1(4)	O(3d)–Ag(4)–N(8)	100.0(2)
N(6a)–Ag(2)–O(1W)	108.0(4)	O(1)–Ag(4)–N(8)	84.7(2)
N(3c)–Ag(3)–N(7d)	143.8(2)	O(2W)–Ag(4)–N(8)	101.0(2)
N(3c)–Ag(3)–O(2W)	99.6(2)	N(2)–Ag(5)–N(5e)	158.8(2)

Symmetry codes: (a)  $x, y, z - 1$ ; (b)  $x - \frac{1}{2}, -y + \frac{1}{2}, z$ ; (c)  $-x + \frac{3}{2}, y - \frac{1}{2}, z + \frac{1}{2}$ ; (d)  $x, y, z + 1$ ; (e)  $-x + 2, -y + 1, z - \frac{1}{2}$  for **1**; (a)  $-x + 2, y, -z + \frac{3}{2}$ ; (b)  $x - \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$ ; (c)  $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$ ; (d)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (e)  $-x + 2, -y + 1, -z + 2$  for **2**.

[Ag<sub>4</sub>(μ<sub>4</sub>-hmt)<sub>3</sub>(H<sub>2</sub>O)](SO<sub>4</sub>)(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O [10]. Both cases indicate that the Ag-hmt complexes containing multiple counterions may exhibit different topological motifs compared to those containing a single type of counterions [8–11].

On the other hand, from the reaction system of ethanolic Ag<sub>4</sub>(pma) and hmt in molar ratio of 1:2 upon addition of dilute HNO<sub>3</sub>, **2** was obtained; while upon dropwise addition of an aqueous NH<sub>3</sub> solution, another complex [Ag(μ<sub>3</sub>-hmt)]<sub>2</sub>[Ag(NH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>(pma) · 3H<sub>2</sub>O consisting of two-dimensional hexagonal [Ag(μ<sub>3</sub>-hmt)] layers and unique dimeric [Ag(NH<sub>3</sub>)<sub>2</sub>]<sub>2</sub><sup>+</sup> species was isolated [13]. This fact, together with that found in the pair of complexes [Ag<sub>2</sub>(μ<sub>4</sub>-hmt)(SO<sub>4</sub>)(H<sub>2</sub>O)] · 4H<sub>2</sub>O and [Ag<sub>3</sub>(μ<sub>4</sub>-hmt)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](SO<sub>4</sub>)(HSO<sub>4</sub>) · 2H<sub>2</sub>O reported previously [10], demonstrates that with the same ligand, different Ag-hmt linkages may result at different pH values, and hence generate different stable frameworks.

### 3.2. Crystal structures

Complexes **1** and **2** consist of different three-dimensional non-interpenetrated Ag-hmt networks, featuring two new topological motifs. **1** is a novel three-dimensional cationic network with two types of channels, as shown in Fig. 1(a). The larger ring involves eight Ag(I) atoms and eight hmt ligands, while the smaller one involves four Ag(I) atoms and four hmt ligands; each larger ring is enclosed by four larger ones and four smaller ones, and each smaller one is enclosed by four larger ones. Three crystallographically independent Ag(I) atoms have two types of coordination geometries. As illustrated in Fig. 1, both Ag(1) and Ag(2) atoms are in distorted tetrahedral geometries, each being coordinated by three nitrogen atoms from three hmt ligands [Ag–N 2.29(2)–2.49(2) Å; N–Ag–N 113(1)–121.5(9)°] and one oxygen atom from a monodentate ssa carboxylate group [Ag–O 2.39(2) Å; N–Ag–O 83.1(5)–108(2)°] or from a monodentate ssa sulfonate group oxygen atom [Ag–O 2.38(2) Å; N–Ag–O 81.4(7)–119.7(8)°]. The Ag(3) atom is ligated by two nitrogen atoms from two hmt ligands [Ag(3)–N 2.24(1) and 2.27(1) Å; N–Ag(3)–N 164.2(4)°] and one aquo oxygen atom [Ag(3)–O 2.50(2) Å; N–Ag(3)–O 96.2(7) and 98.1(7)°], resulting in a T-shaped geometry. It should be pointed out that the aromatic rings of the ssa ligands in the larger channels show the strong π–π stacking interactions in an offset fashion with the face-to-face distance of 3.21 Å. Although the larger channels are mainly occupied by the ssa ligands, a large number of lattice water molecules are located in them and hydrogen-bonded to each other and to the uncoordinated oxygen atoms of the carboxylate/sulfonate groups and aquo ligands [O···O 2.70–3.08 Å]. Moreover, the nitrate counterions are located in the smaller channels, forming strong hydrogen bonds with the lattice water molecules [O(2w)···O(9) 2.47 Å] and hmt methylene groups [C(11)···O(7) 3.05 Å and C(16)···O(9) 3.04 Å] [19].

From the topological point of view, the three-dimensional network of **1**, considering only the Ag(I)–hmt interactions, may be described as interconnection of the hexagonal (3,3)-connected Ag(hmt) layers by μ-Ag(I) atoms to furnish a three-dimensional (3,4)-connected net, comprising triconnected (silver atoms of the layers) and tetraconnected (hmt) centers in the ratio 1:1 [Fig. 2(b)]. To the best of our knowledge, such a (3,4)-connected net has not been documented so far. Two known complexes, [Ag<sub>3</sub>(μ<sub>4</sub>-hmt)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub> · 2H<sub>2</sub>O and [Ag<sub>3</sub>(μ<sub>4</sub>-hmt)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](SO<sub>4</sub>)(HSO<sub>4</sub>) · 2H<sub>2</sub>O [7,10], have the similar formulas and also consist of open three-dimensional cationic networks formed by the (3,3)-connected Ag(hmt) layers and further joined by the μ-Ag(I) atoms (or the spacers). As illustrated in Fig. 2, the different linkage of μ-Ag(I) spacers with the hmt

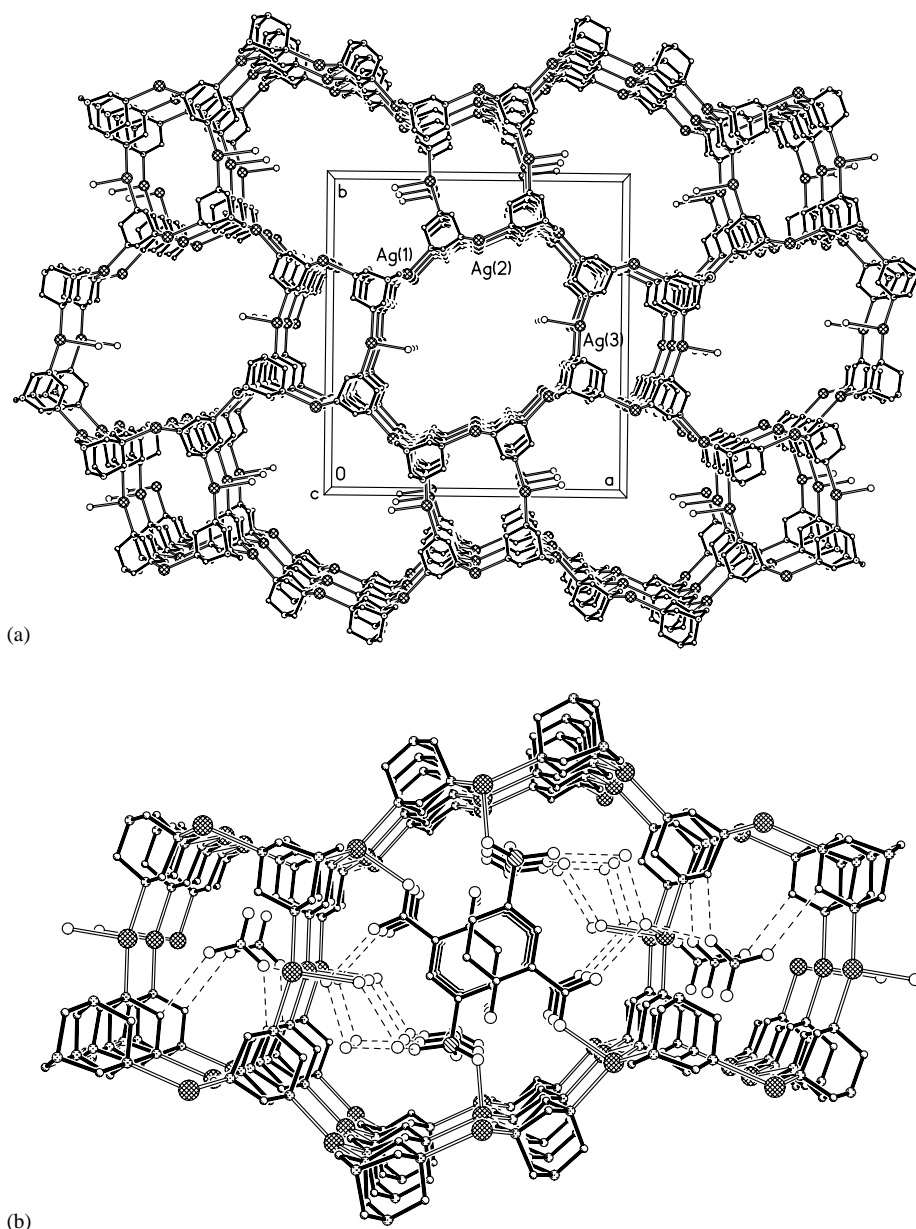


Fig. 1. Perspective views showing the three-dimensional network (a) and the structural unit (b) projected along the *c*-axis in **1**. The counter anions and lattice water molecules are omitted in (a) for clarity.

groups in (3,3)-connected Ag(hmt) layers in **1** results in the different topological motif, which is therefore unprecedented. Moreover, the larger ring in **1** composed of eight Ag(I) atoms and eight hmt ligands is the largest one in the known Ag–hmt networks, as compared to the previously largest one that comprising 12 Ag(I) atoms and six hmt ligands [10].

Complex **2** consists of another new type of three-dimensional non-interpenetrated network with cylindrical channels. As depicted in Fig. 3(a), five crystallographically independent Ag(I) atoms in three types of coordination geometries have been observed. The Ag(1) and Ag(2) atoms are bridged by one twofold disordered

$\mu$ -aquo-oxygen atom [Ag–O(1w) 2.50(1) and 2.51(1) Å] with the metal–metal separation of 4.620 Å. Each of them further coordinated by two hmt nitrogen atoms [Ag–N 2.277(5)–2.353(5) Å; N–Ag–N 144.0(2)–157.3(2)°], completing a Y-shaped geometry. The Ag(3) atom also exhibit a Y-shaped geometry, being coordinated by two different hmt nitrogen atoms [Ag(3)–N 2.274(5) and 2.283(4) Å; N–Ag(3)–N 157.3(2)°] and a  $\mu$ -aquo ligand [Ag(3)–O(2w) 2.482(5) Å; N–Ag(3)–O(2w) 99.6(2) and 114.8(2)°]. The Ag(4) atom is surrounded in a greatly distorted tetrahedron, in which the metal atom is located virtually in the plane defined by two oxygen atoms from different bis-monodentate

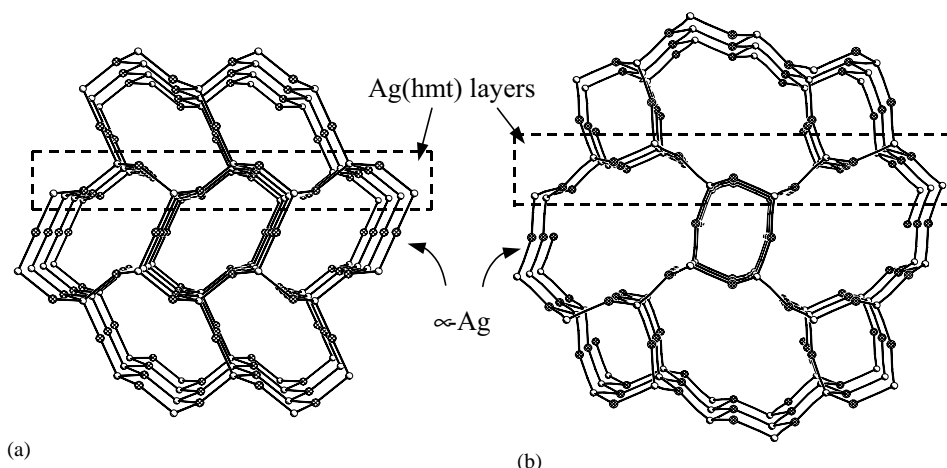


Fig. 2. The different topological motifs of three-dimensional Ag–hmt networks resulted from the interlinkages of (3,3)-connected hexagonal Ag(hmt) layers with Ag(I) connectors at different positions found in two known complexes [7,10] (a) and **1** (b). Small open balls represent centers of mass of the hmt ligands.

pma carboxylate group and one  $\mu$ -aquo ligand [Ag(4)–O 2.279(5)–2.329(5) Å; O–Ag(4)–O 110.5(2), 110.9(2) and 134.9(2)°,  $\Sigma_{\text{Ag}}$  356.3°], and the remaining position is occupied by one nitrogen atoms from hmt ligands [Ag(4)–N(8) 2.464(5) Å, N(8)–Ag(4)–O 84.7(2)–101.0(2)°]. The  $\mu$ -aquo-bridged Ag(3) and Ag(4) atoms have a metal-metal distance of 3.344(1) Å, indicating no significant Ag...Ag interaction. Each Ag(5) atom exhibits a bent 2-coordination with two nitrogen atoms from different hmt ligands [Ag(5)–N 2.257(5) and 2.258(5) Å; N–Ag(5)–N 158.8(2)°]. It should be noted that both aquo ligands in **2** are in the  $\mu$ -bridging mode, which is rarely documented in silver(I) complexes [20]. What is more, two hmt ligands exhibit different bridging modes, namely  $\mu_3$ - and  $\mu_4$ -bridging modes. To our knowledge, hmt usually acts in a unique bridging mode in the related Ag–hmt complexes, and **2** is the first example constructed by mixed  $\mu_3$ - and  $\mu_4$ -bridging hmt ligands, although the mixed  $\mu$ - and  $\mu_3$ -bridging mode has been found in two coordination polymers [Ag<sub>2</sub>( $\mu$ -hmt)( $\mu_3$ -hmt)(H<sub>2</sub>O)(SbF<sub>6</sub>) and [Ag<sub>2</sub>( $\mu$ -hmt)( $\mu_3$ -hmt)(ssa)] [6,11].

As illustrated in Fig. 3(b), the molecular ribbons with cyclical units each involving four Ag(I) atoms and four hmt ligands are connected by the  $\mu$ -aquo-oxygen atoms, resulting in a two-dimensional infinite coordination layer. These layers are further interlinked by the biconnected Ag(5) atoms [Fig. 3(c)] to complete an open three-dimensional non-interpenetrated network having cylindrical channels with a diameter of ca. 6 Å<sup>1</sup>. Moreover, the framework is further stabilized by the bis-monodentate pma ligands between a pair of

Ag(4) atoms; therefore, the cylindrical channels are partially occupied by the uncoordinated carboxylate ends of the pma ligands, resulting in much smaller effective channels in the real solid-state structure. The free dimensions of these channels occupy 19.5% of the crystal volume [21]. The lattice water molecules are clathrated in channels and form donor hydrogen bonds with the uncoordinated carboxylate oxygen atoms [O...O 2.780(9)–2.967(12) Å].

We have successfully synthesized two new Ag–hmt coordination polymers, which exhibit unprecedented and different topological motifs in the Ag–hmt networks. Among them, one consists of the largest [Ag(hmt)]<sub>n</sub> ( $n = 8$ ) ring among the Ag–hmt networks, while the other is the first three-dimensional Ag–hmt nets constructed with mixed  $\mu_3$ - and  $\mu_4$ -bridging hmt ligands. This and the previous results suggest that different synthetic conditions for the same metal ions and ligands can yield coordination polymer architectures of different topologies through the different Ag–hmt linkages.

## Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 20001008 and 29971033) and Foundation for University Key Teachers of the Ministry of Education of China. The last author thanks the Third World Academy of Sciences for a travel grant to China. The authors also thank the Chemistry Department of the Chinese University of Hong Kong for donation of the diffractometer.

<sup>1</sup>The channel dimensions are estimated from the van der Waals radii for carbon (1.70 Å), nitrogen (1.55 Å), and oxygen (1.40 Å).

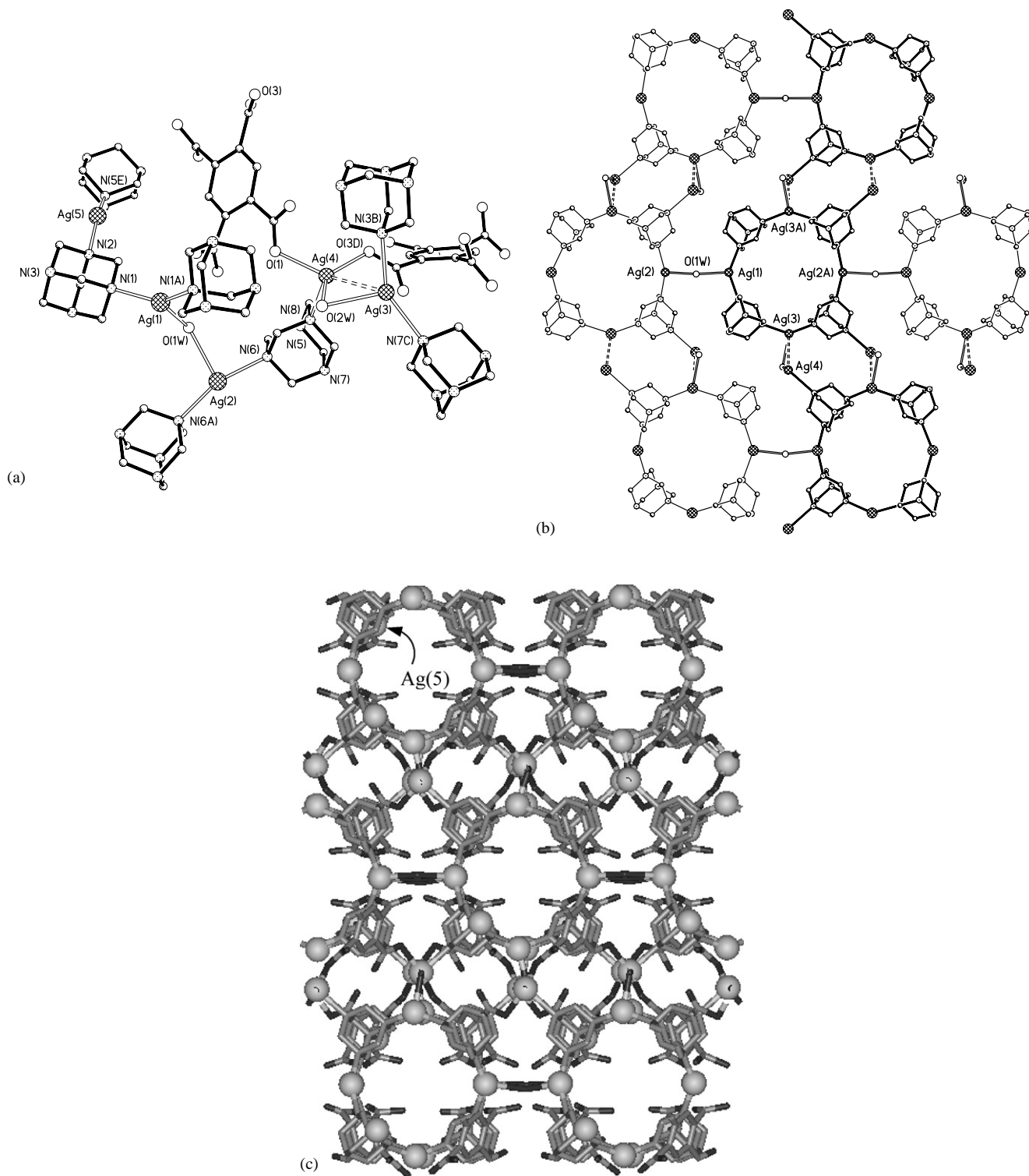


Fig. 3. Perspective views showing coordination environments of the metal atoms (a), two-dimensional layer (b) and three-dimensional network viewed along the *c*-axis (c) in **2**. The lattice water molecules, Ag...Ag interaction and hydrogen bonds are omitted in (c) for clarity.

## References

- [1] (a) J.M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, 1995 (Chapter 9).  
 (b) S.R. Batten, R. Robson, *Angew. Chem. Int. Ed.* 37 (1998) 1460.  
 (c) O.M. Yaghi, H. Li, C. Davis, D. Richardson, T.L. Groy, *Acc. Chem. Res.* 31 (1998) 474.

- (d) A.J. Blake, N.R. Champness, P. Hubberstey, W.-S. Li, M.A. Withersby, M. Schröder, *Coord. Chem. Rev.* 183 (1999) 117.
- (e) P.J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem. Int. Ed.* 38 (1999) 2639.
- [2] C.B. Aakeröy, K.R. Seddon, *Chem. Soc. Rev.* (1993) 397.
- [3] (a) T.L. Hennigar, D.C. MacQuarrie, P. Losier, R.D. Rogers, M.J. Zaworotko, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 972.
- (b) M.-L. Tong, B.-H. Ye, X.-M. Chen, S.W. Ng, *Inorg. Chem.* 37 (1998) 2645.
- (c) B. Moulton, J.-J. Lu, M.J. Zaworotko, *J. Am. Chem. Soc.* 123 (2001) 9224.
- [4] (a) H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, *Nature* 402 (1999) 276.
- (b) S.S.Y. Chui, S.M.F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams, *Science* 283 (1999) 1148.
- (c) S.-I. Noro, S. Kitagawa, M. Kondo, K. Seki, *Angew. Chem. Int. Ed.* 39 (2000) 2081 (and refs cited therein).
- [5] (a) L. Carlucci, G. Ciani, D.M. Proserpio, A. Sironi, *J. Am. Chem. Soc.* 117 (1995) 12861.
- (b) L. Carlucci, G. Ciani, D.M. Proserpio, S. Rizzato, *J. Solid State Chem.* 152 (2000) 211.
- [6] M. Bertelli, L. Carlucci, G. Ciani, D.M. Proserpio, A. Sironi, *J. Mater. Chem.* 7 (1997) 1271.
- [7] L. Carlucci, G. Ciani, D.W.V. Gudenberg, D.M. Proserpio, A. Sironi, *Chem. Commun.* (1997) 631.
- [8] A. Michelet, B. Voissat, P. Khodadad, N. Rodier, *Acta Crystallogr. Sect. B* 37 (1981) 2171.
- [9] O.M. Yaghi, H. Li, M. O'Keeffe, *Mater. Res. Soc. Symp. Proc.* 453 (1997) 127.
- [10] (a) M.-L. Tong, S.-L. Zheng, X.-M. Chen, *Chem. Commun.* (1999) 561.
- (b) M.-L. Tong, S.-L. Zheng, X.-M. Chen, *Chem. Eur. J.* 6 (2000) 3729.
- [11] S.-L. Zheng, M.-L. Tong, H.-L. Zhu, Y. Fang, X.-M. Chen, *J. Chem. Soc. Dalton Trans.* (2001) 2049.
- [12] (a) S.-L. Zheng, M.-L. Tong, X.-L. Yu, X.-M. Chen, *J. Chem. Soc. Dalton Trans.* (2001) 586.
- (b) S.-L. Zheng, M.-L. Tong, R.-W. Fu, X.-M. Chen, S.W. Ng, *Inorg. Chem.* 40 (2001) 3562.
- (c) S.-L. Zheng, M.-L. Tong, H.-L. Zhu, Y. Fang, X.-M. Chen, *Acta Chim. Sin. (Chin. Ed.)* 59 (2001) 1442.
- (d) S.-L. Zheng, M.-L. Tong, H.-L. Zhu, X.-M. Chen, *New J. Chem.* (2001) 1425.
- (e) S.-L. Zheng, M.-L. Tong, S.-D. Tan, Y. Wang, J.-X. Shi, Y.-X. Tong, H.K. Lee, X.-M. Chen, *Organometallics* 20 (2001) 5319.
- (f) S.-L. Zheng, M.-L. Tong, X.-M. Chen, *Chin. J. Inorg. Chem.* 18 (2002) 17.
- [13] S.-L. Zheng, M.-L. Tong, X.-M. Chen, S.W. Ng, *J. Chem. Soc. Dalton Trans.* (2002) 360.
- [14] T.C.W. Mak, W.-H. Yip, C.H.L. Kennard, G. Smith, E.J. O'Reilly, *Aust. J. Chem.* 39 (1986) 541.
- [15] A.C.T. North, D.C. Phillips, F.S. Mathews, *Acta Crystallogr. Sect. A* 24 (1968) 351.
- [16] G.M. Sheldrick, SHELX-97, Programs for Crystal Structure Analysis (Release 97-2), University of Göttingen, Germany, 1997.
- [17] D. Flack, D. Schwarzenbach, *Acta Crystallogr. Sect. A* 44 (1988) 499.
- [18] G.M. Sheldrick, SHELXTL Version 5, Siemens Analytical Instruments Inc., Madison, WI, USA, 1995.
- [19] (a) G.R. Desiraju, *Angew. Chem. Int. Ed. Engl.* 34 (1995) 2311.
- (b) R. Vargas, J. Garza, D.A. Dixon, B.P. Hay, *J. Am. Chem. Soc.* 122 (2000) 4750.
- (c) M.J. Calhorda, *Chem. Commun.* (2000) 801.
- (d) T. Steiner, *Angew. Chem. Int. Ed.* 41 (2002) 48 (and references therein).
- [20] (a) H. Schöllhorn, U. Thewalt, B. Lippert, *Inorg. Chim. Acta* 135 (1987) 155.
- (b) M. Naveke, P.G. Jones, A. Blaschette, D. Schomburg, H.K. Cammenga, M. Eppele, *Z. Anorg. Allg. Chem.* 619 (1993) 1027.
- (c) R.C. Bott, G. Smith, D.S. Sagatys, T.C.W. Mak, D.E. Lynch, C.H.L. Kennard, *Aust. J. Chem.* 46 (1993) 1055.
- (d) P.G. Jones, D. Henschel, A. Weitze, A. Blaschette, *Z. Anorg. Allg. Chem.* 620 (1994) 1514.
- (e) D.S. Sagatys, G. Smith, D.E. Lynch, C.H.L. Kennard, *J. Chem. Soc. Dalton Trans.* (1991) 361.
- (f) D. Venkataraman, G.B. Gardner, A.C. Covey, S. Lee, J.S. Moore, *Acta Crystallogr. Sect. C* 52 (1996) 2416.
- (g) G.L. Ning, L.-P. Wu, K. Sugimoto, M. Munakata, T. Kuroda-Sowa, M. Maekawa, *J. Chem. Soc. Dalton Trans.* (1996) 2529.
- [21] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1999.