



Paper

Modifying silver(I) coordination frameworks containing a flexible dithioether ligand by variation of counter anions

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Two silver(I) coordination architectures with the flexible ligand 1,6-bis(phenylthio)hexane (**L**) have been synthesized and their crystal structures determined by X-ray diffraction analysis. Different frameworks were observed in the two complexes due to variation of the counter anions. The dinuclear complex $[\text{Ag}(\text{L})(\text{ClO}_4)]_2$ (**1**) has a cage structure with the perchlorate anions coordinated to the two silver(I) ions in a rare η^2 bridging mode. However, in the complex $[\text{Ag}(\text{L})(\text{NO}_3)]_n$ (**2**) there is a 2D network with monatomic bridging nitrate anions. The results show the great influence of counter anions on building metal–organic supramolecular structures. In addition, the different conformations of the flexible ligand **L** in the frameworks of **1** and **2** indicate its ready adaptability to various coordination environments.

Introduction

There has been current significant interest in the rational design and synthesis of new polymeric metal–organic coordination architectures for their potential use as functional materials.¹ Besides its formation of numerous complexes with rigid polyfunctional *N*-donor ligands to construct network structures,² the soft metal silver(I) has a high affinity for sulfur ligands, such as thioether, and so such compounds can be used as building blocks to construct coordination frameworks. For example, $\text{Ag}_7(\text{tpst})_6(\text{ClO}_4)_2(\text{NO}_3)_5(\text{dmf})_2$ which shows a coordination polymer chain containing nanosized tubes (tpst = 2,4,6-tris[(4-pyridyl)methylsulfanyl]-1,3,5-triazine)³ and the two-dimensional (2D) sheet structure of a $\text{AgC}_2\text{F}_5\text{CO}_2$ complex with 2,3,5,6-tetrakis(methylsulfanyl)pyridine⁴ were reported recently. We have also observed some interesting structures, such as a chiral (10,3)-a net⁵ and a resilient honeycomb structure⁶ in some silver(I) complexes with a series of flexible dithioether ligands. For these complexes, the choice of length of the spacer unit in the ligands, anions, and solvents, and the ratio of metal salt to ligand is crucial to the structure of the final network.

As a continuation of the above-mentioned series of research, we report herein the silver(I) perchlorate (**1**) and silver(I) nitrate complexes (**2**), which form different frameworks by using a flexible dithioether ligand 1,6-bis(phenylthio)hexane **L** as a building block, in order to evaluate the influence of counter anions on the resultant frameworks. Interestingly, it is also shown that **L** can modify its conformation in the presence of different counter anions.

Experimental

Materials and general methods

Most of the starting materials and solvents for the syntheses and characterization were obtained commercially and used without further purification. 1,6-Bis(phenylthio)hexane (**L**) was prepared according to literature methods.⁷ Elemental

analyses were performed on a Perkin-Elmer 240C analyzer. IR spectra (KBr pellets) were taken on a FT-IR 170 SX (Nicolet) spectrometer. The X-ray powder diffraction (XRPD) patterns of **1** and **2** were registered with a Rigaku D/Max-2500 diffractometer, operated at 40 kV and 100 mA, using a Cu-target tube and a graphite monochromator. Fixed scatter and divergence slits of 0.5° and a 0.15 mm receiving slit were used. The intensity data were recorded by continuous scan in a 2 θ mode from 2° to 50° with a step size of 0.02° and a scan speed of 4° min⁻¹. Simulation of the XRPD spectra was carried out by the single-crystal data and diffraction-crystal module of the commercially available Cerius2 program.⁸

Synthesis of complexes $[\text{Ag}(\text{L})(\text{ClO}_4)]_2$ **1** and $[\text{Ag}(\text{L})(\text{NO}_3)]_n$ **2**

The ligand **L** (45 mg, 0.15 mmol) dissolved in CHCl_3 (2 mL) was added to a solution of $\text{AgClO}_4 \cdot 6\text{H}_2\text{O}$ (15 mg, 0.04 mmol) in acetone (2 mL). Colorless single crystals suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into the mixed solution. Yield: 30%. Anal. calcd. for $\text{C}_{18}\text{H}_{22}\text{S}_2\text{AgClO}_4$ **1**: C, 42.41; H, 4.35. Found: C, 42.47; H, 4.12%. IR (cm^{-1}): 2927m, 1474m, 1439s, 1269m, 1159m, 1071s, 1023s, 752m, 739s, 688m, 623s.

Caution: perchlorate compounds are potentially explosive and should be handled carefully.

Complex **2** was obtained by stirring a solution of AgNO_3 (170 mg, 1 mmol) in methanol (5 mL) and a solution of **L** (604 mg, 2 mmol) in CHCl_3 (5 mL) at 50 °C for 30 minutes. Colorless needle crystals formed over 10 minutes. Single crystals suitable for X-ray analysis were obtained by recrystallization from DMF. Yield: 16%. Anal. calcd. for $\text{C}_{18}\text{H}_{22}\text{S}_2\text{AgNO}_3$ **2**: C, 45.77; H, 4.69; N, 2.96. Found: C, 45.53; H, 4.49; N, 2.72%. IR (cm^{-1}): 2925m, 1471m, 1438m, 1383s, 1367s, 1290s, 1023m, 752m, 740s, 732m, 688m.

X-Ray crystallographic data collection and structure determination

Single crystal X-ray diffraction measurements of **1** and **2** were carried out on a Bruker Smart 1000 CCD diffractometer at

Table 1 Crystallographic data and structure refinement summary for complexes **1** and **2**

Formula	C ₁₈ H ₂₂ AgClO ₄ S ₂	C ₁₈ H ₂₂ AgNO ₃ S ₂
<i>M</i>	509.80	472.36
Crystal size/mm	0.20 × 0.20 × 0.25	0.35 × 0.20 × 0.20
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	10.051(2)	12.5416(7)
<i>b</i> /Å	10.334(1)	9.1826(5)
<i>c</i> /Å	11.187(2)	17.461(1)
α /°	66.406(3)	90
β /°	89.958(3)	99.573(1)
γ /°	71.145(2)	90
<i>V</i> /Å ³	996.5(2)	1982.9(2)
<i>Z</i>	2	4
<i>D</i> _{calc} /g cm ⁻³	1.699	1.582
μ /mm ⁻¹	1.375	1.243
<i>F</i> (000)	516	960
Total reflections	4111	7912
Independent reflections	3568	3499
<i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	0.0543, 0.1229	0.0252, 0.0698
Goodness-of-fit on <i>F</i> ²	0.943	1.076
Residual electron densities/e Å ⁻³	0.938 to -0.391	0.304 to -0.536

293(2) K with Mo-K α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refinements on *F*² were carried out by full-matrix least squares method. The oxygen atoms of the perchlorate ions were refined isotropically. All other non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the ligands were introduced and allowed to ride on their parent atoms and refined with fixed thermal factors. Crystallographic data and experimental details are summarized in Table 1.

CCDC reference numbers 204846 and 204847.

See <http://www.rsc.org/suppdata/ce/b3/b302208k/> for crystallographic data in CIF or other electronic format.

Results and discussion

Description of the crystal structures

In complex **1**, two distant silver(i) ions are linked by two distinct **L** ligands *via* their sulfur donors to form a centrosymmetric 18-membered macrocycle (Ag...Ag separation is 4.76 Å) (Fig. 1). Two perchlorate anions are located above and below the plane formed by S(1), S(2), S(1A), and S(2A) with a deviation distance of 2.19 Å (from the chloride atom to the plane). It is known that in most reported AgClO₄ complexes with dithioether ligands the perchlorate anions usually take the role of a monodentate ligand or intercalating anion. However, the anions in **1** coordinate to two silver(i) ions in the rare η^2

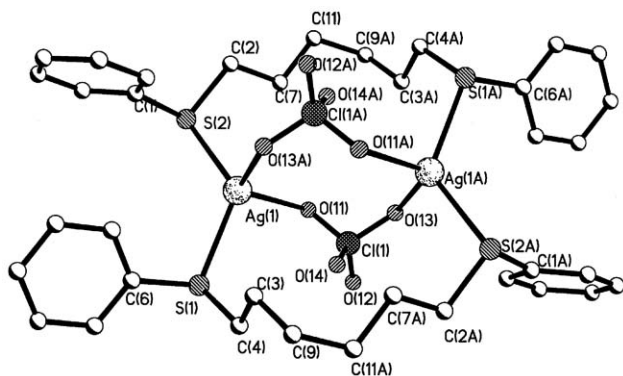


Fig. 1 The dinuclear cage structure of **1** featuring η^2 bridging perchlorate ligands. Click here to access a 3D representation.

Table 2 Selective bond lengths (Å) and angles (°) for complex **1**

Ag(1)–O(13A)	2.48(1)	Ag(1)–S(1)	2.516(2)
Ag(1)–S(2)	2.523(2)	Ag(1)–O(11)	2.52(1)
O(13A)–Ag(1)–S(1)	112.2(2)	O(13A)–Ag(1)–S(2)	103.1(3)
S(1)–Ag(1)–S(2)	122.04(5)	O(13A)–Ag(1)–O(11)	119.1(3)
S(1)–Ag(1)–O(11)	98.5(2)	S(2)–Ag(1)–O(11)	102.6(2)

double-bridge mode through two oxygen atoms to form an eight-membered ring in which the plane O(11)–O(13)–O(11A)–O(13A) makes a 86.6° dihedral angle with the plane formed by S(1), S(2), S(1A), and S(2A). Both macrometallacycles make up a centrosymmetric dinuclear cage structure. Each silver(i) center adopts a tetrahedral configuration with Ag–S in the range 2.51–2.52 Å and Ag–O in the range 2.48–2.52 Å (Table 2). The length of the two almost equivalent Ag–S bonds are normal for Ag–S (thioether) complexes,⁹ while the Ag–O bond distances are shorter than those in most silver perchlorate complexes with dithioether ligands.^{4,5,10} In the silver(i) perchlorate complex with 1,3-bis(phenylthiomethyl)benzene, the anions act in a η^1 bridge mode and the Ag–O bond distances are 2.56 Å and 2.72 Å, respectively.¹¹ A similar cage with a η^2 double-bridging perchlorate anion also has been found in Ag₂(dpph₂)(ClO₄)₂ (dpph = 1,6-bis(diphenylphosphino)hexane) which has longer Ag–O bonds (2.71 and 2.64 Å) and Ag...Ag distance (5.32 Å).¹² The **L** molecule displays a *trans*-conformation with a -171.5° pseudo-torsion angle between two S–Ph groups in complex **1**. The spacer unit of **L** adopts a *gauche* geometry around the C(9A)–C(11) bond, the two segments [C(2)–C(7)–C(11)–C(9A) and C(9A)–C(3A)–C(4A)] of the alkyl chain are oriented essentially perpendicular to each other (the dihedral angle between their mean planes is 97.7°).

In complex **2**, each silver(i) ion is tetrahedrally coordinated by two sulfur donors of two distinct **L** ligands and two oxygen donors of different nitrate anions (Fig. 2), forming a 4-membered parallelogram Ag₂O₂ ring, and the important bond geometries are listed in Table 3. The Ag–O and Ag–S bond lengths are comparable with the average values of related complexes.² Each nitrate anion links two neighboring silver(i) ions in the monatomic bridge mode (Fig. 3) with a Ag...Ag non-bonded distance of 3.93 Å. The **L** molecules link two adjacent Ag₂O₂ rings (designated A and B) *via* the Ag–S bonds, and the angle between the rings is 30.7°. The Ag...Ag distance linked by **L** is 9.55 Å. The whole structure

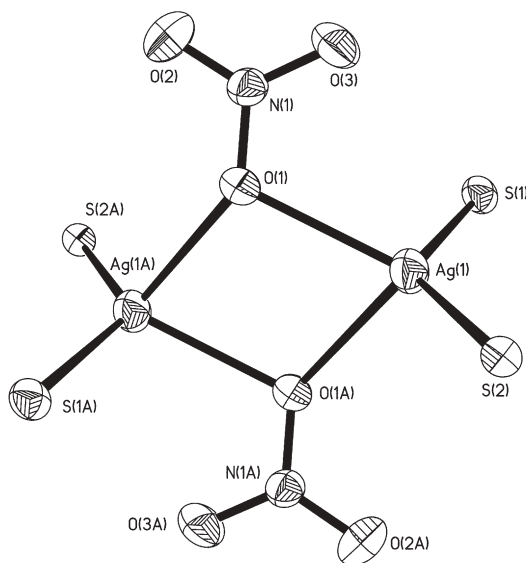


Fig. 2 The Ag₂O₂ ring: a pair of silver(i) ions are bridged by the nitrate anions in complex **2**.

Table 3 Selective bond lengths (Å) and angles (°) for complex **2**

Ag(1)–O(1)	2.387(2)	Ag(1)–S(2)	2.4627(6)
Ag(1)–O(1A)	2.525(2)	Ag(1)–S(1)	2.5585(6)
O(1)–Ag(1)–S(2)	124.39(6)	O(1)–Ag(1)–O(1A)	74.80(7)
S(2)–Ag(1)–O(1A)	113.04(5)	O(1)–Ag(1)–S(1)	98.46(5)
S(2)–Ag(1)–S(1)	132.77(2)		

can be described as a framework formed by the 40-membered repeating units shaped like a slanted letter “I” (Fig. 3). In each unit, there are six silver(I) ions linked by four **L** molecules: four silver(I) from two complete Ag_2O_2 rings and two silver(I) ions belonging to two other rings, such that A rings and B rings alternatively appear in the “slant-I”-type unit. The units containing A rings and others including B rings are neatly packed to form a two-dimensional network (Fig. 4). Since the anions are components of the frameworks of **2**, thus, the whole structure can be thought as a self-sustaining network. A similar repeating unit, containing a bridging 4-membered Mn_2X_2 ring occurs in the $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ complex with *N,N'*-m-phenylenedimethylenebis(pyridin-2-done).¹³ In addition, the whole framework of **2** can also be described as the linkage of Ag_2O_2 rings by **L** molecules that extends to a two-dimensional network. The homologous silver nitrate complexes with 1,2-bis(phenylthio)ethane¹² and 1,4-bis(phenylthio)butane⁶ are both self-sustaining 2D networks with parallelogram repeating units and bridging anions as borders of macrometalloccycles in their structures, but in complex **2** the monatomic bridging nitrate anions form rings with silver(I) ions and the quadrangle repeating units distort to the “slant-I”-type to reduce the free space in the structure for the longer spacer unit $-(\text{CH}_2)_6-$ of **L**. In addition, the **L** molecules in **2** take a *cis*-conformation with a 27.3° pseudo-torsion angle between two S–Ph groups, the alkyl chain adopts an extended all *anti*-geometry and the carbon atoms of the spacer unit are nearly coplanar, being similar to the arrangement of those in homologous complexes.^{6,14}

The research on solvent effect

In order to get more insight into the solvent effect, we synthesized single crystals of **1** not only by the method used to prepare complex **2** but also by changing acetone for ethanol or acetonitrile. However, there is no difference in the cell data between the crystals obtained in these ways. In this respect, the influence of solvent on the final network is not directly shown in the resulting structure of **1**. We also attempted corresponding changes when synthesizing **2**, but obtain only some oil-like product.

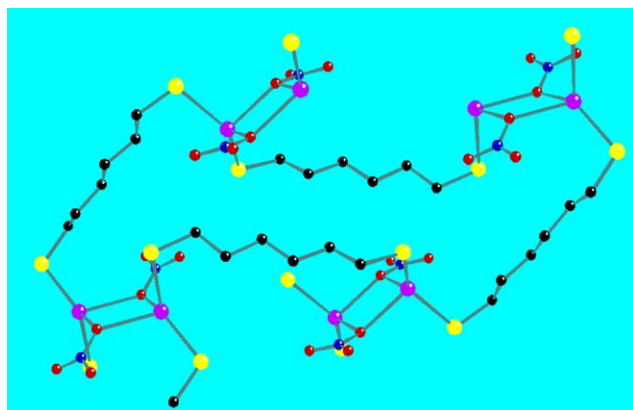


Fig. 3 The “slant-I”-type 40-membered repeating unit in complex **2** (black: C; yellow: S; red: O; purple: Ag; blue: N; phenyl groups have been omitted for clarity). A set of arbitrarily parallel rings is defined as A or B.

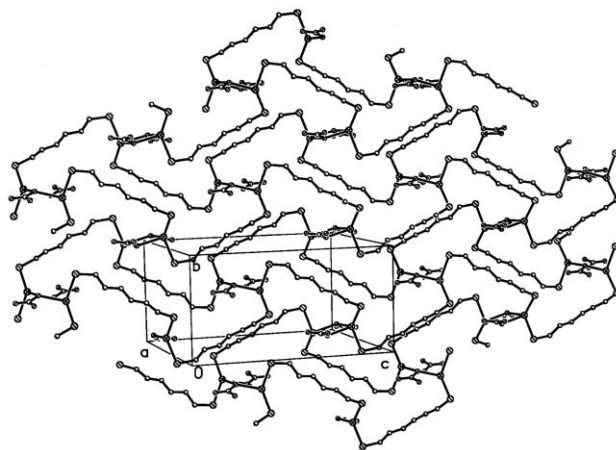


Fig. 4 The two-dimensional network in complex **2** (phenyl groups have been omitted for clarity). Click here to access a 3D representation.

XRPD results

In order to confirm if both crystal structures are truly representative of the bulk materials, X-ray powder diffraction (XRPD) experiments have been carried out. The XRPD experimental and computer-simulated patterns of **1** and **2** are shown in Fig. 5. Although the experimental patterns, with a few unindexed diffraction lines, are slightly broadened in comparison with those simulated from the single-crystal models, it still can be considered that the bulk synthesized materials and the as-grown crystals are homogeneous both for complexes **1** and **2**.

Conclusions

The crystal structures of two silver(I) complexes with a flexible ligand **L**, **1** and **2**, reveal the profound effects of the counter anion upon the structure. Although in both complexes the silver(I) ions adopt tetrahedral S_2O_2 coordination modes, and the ratio of silver(I) to **L** is the same, the different character of the anions results in structural diversity. In **1**, the perchlorate anion acts as a η^2 double-bridging ligand and the whole structure is a bimetallic cage, whereas in **2** the nitrate anions serve as a monatomic bridge and the final framework is a 2D infinite network. This result indicates that the use of counter anions affects the solid structures and implies the possibility of modifying the metal–organic supramolecular architectures by varying the counter anions.

It is also notable that the flexible ligand **L** takes different conformations in complexes **1** and **2** according to the presence of the different counter anions. In complex **1**, the alkyl chain adopts a *gauche*-geometry, and the rotation about the C(9A)–C(11) bond facilitates the binding of the S-donors to the silver(I) ions, while the spacer unit of **L** takes a more extending, all *anti*-geometry in complex **2**. So the ligand bite (S⋯S) in complex **1** is shorter (7.18 Å) than that in complex **2** (9.43 Å). The present study shows that the flexible dithioether ligands can adjust their conformations *via* rearrangement of the backbone according to the change in coordination environment. It also indicates the ambivalence of flexible ligands: there has been difficulty in predicting their conformations when building the supramolecular architectures but they still have potential importance in constructing coordination networks.

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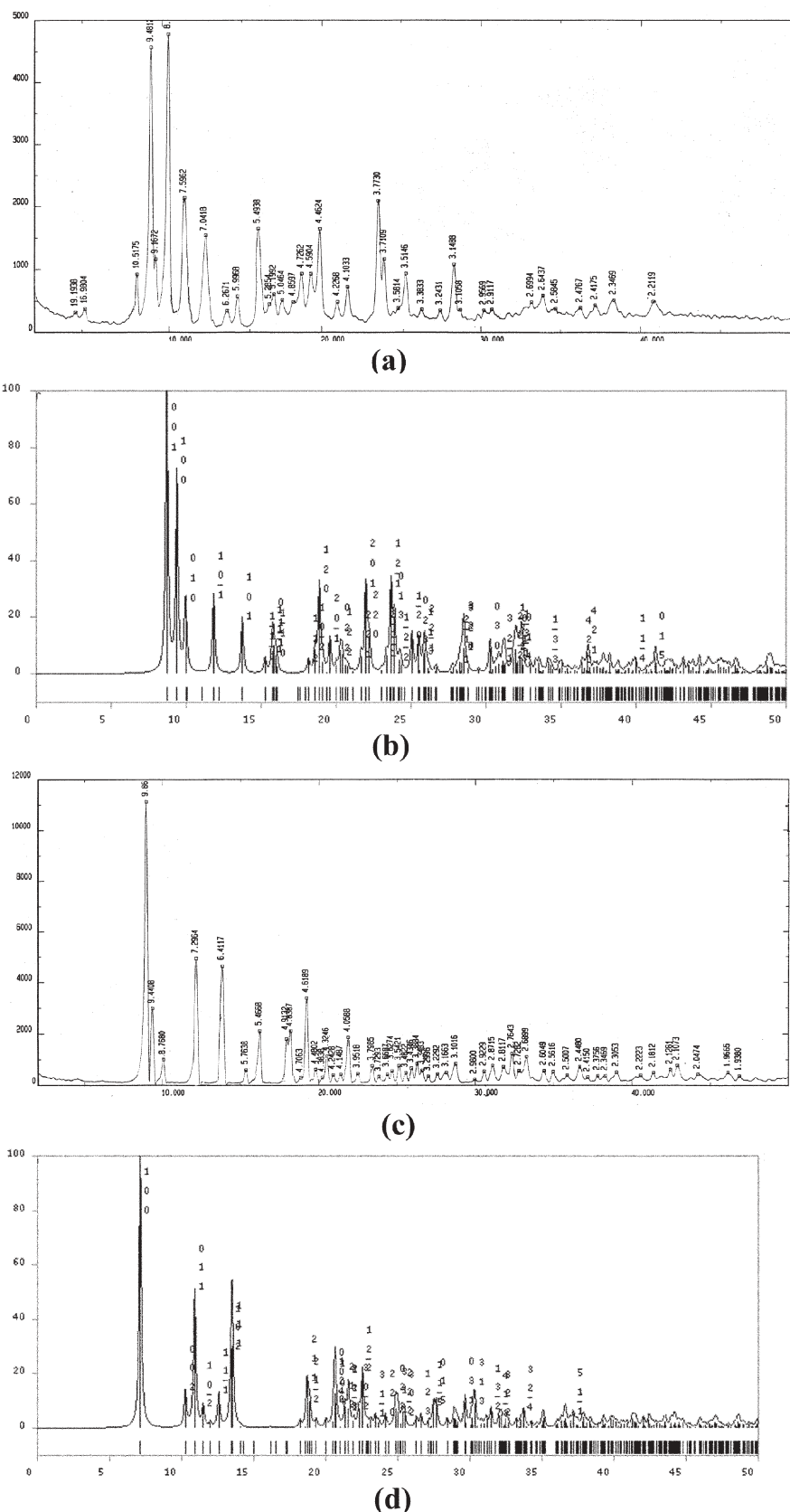


Fig. 5 XRPD patterns of complexes: (a) the experimental result of **1**; (b) the computer-simulated result of **1**; (c) the experimental result of **2**; (d) the computer-simulated result of **2**.

References

- 1 S. R. Batten and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 1460; M. J. Zaworotko, *Angew. Chem., Int. Ed.*, 2000, **39**, 3052; P. J. Hargman, D. Hargman and J. Zubietta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2639.
- 2 A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Withersby and M. Schröder, *Coord. Chem. Rev.*, 1999, **183**, 117.
- 3 M. C. Hong, Y. J. Zhao, W. P. Su, R. Cao, M. Fujita, Z. Y. Zhou and A. S. C. Chan, *Angew. Chem., Int. Ed.*, 2000, **39**, 2468.
- 4 Y. Suenaga, T. Kuroda-Sowa, M. Maekawa and M. Munakata, *J. Chem. Soc., Dalton Trans.*, 1999, 2737.

- 5 X. H. Bu, W. Chen, M. Du, K. Biradha, W. Z. Wang and R. H. Zhang, *Inorg. Chem.*, 2002, **41**, 437.
- 6 X. H. Bu, W. Chen, W. F. Hou, M. Du, R. H. Zhang and F. Brisse, *Inorg. Chem.*, 2002, **41**, 3477.
- 7 F. R. Hartey, S. G. Murray, W. Levason, H. E. Soutter and C. A. McAuliffe, *Inorg. Chim. Acta*, 1979, **35**, 265.
- 8 Cerius2, Molecular Simulation Incorporated, San Diego, CA, 2001.
- 9 S. G. Murray and F. R. Hartley, *Chem. Rev.*, 1981, **81**, 365.
- 10 J. R. Black, N. R. Champness, W. Levason and G. Reid, *J. Chem. Soc., Chem. Commun.*, 1995, 1277.
- 11 X. H. Bu, W. F. Hou, M. Du, W. Chen and R. H. Zhang, *Cryst. Growth Des.*, 2002, **2**, 303.
- 12 S. Kitagawa, M. Kondo and S. Kawata, *Inorg. Chem.*, 1995, **34**, 1455.
- 13 D. M. L. Goodgame, S. Menzer, A. M. Smith and D. J. Williams, *Inorg. Chem.*, 1994, **33**, 6409.
- 14 P. X. Shao, X. K. Yao, H. G. Wang, W. H. Wang, B. Liu, M. Li, L. W. Luo and D. H. Xu, *Gaodeng Xuexiao Huaxue Xuebao*, 1991, **12**, 143.