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An Ion Crystal Based on Silver Double Helicates and Keggin Polyanions[1]

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Abstract—An ion crystal $[Ag_2L_2][(n\text{-}C_4H_9)_4N][PMo_{12}O_{40}] \cdot H_2O \cdot 0.5CH_3OH \cdot 0.25DMF$ (**I**) (DMF is *N*,*N*-dimethylformamide) has been synthesized by the complexation of metal double helix and Keggin polyanions in a DMF–CH_3OH solution and structurally characterized by elemental analysis, IR spectra, and single-crystal X-ray diffraction. In compound **I** $[PMo_{12}O_{40}]^{3-}$ anions and $[(n\text{-}C_4H_9)_4N]^+$ ions alternately arrange themselves in a special order in consistence with that of $[Ag_2L_2]^{2+}$ metal helicates based on π–π stacking interactions, yielding a packing of complex cations and Keggin anions.

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INTRODUCTION

As nanosized metal–oxygen macroanions, polyoxometalates are suitable building blocks of ionic crystals in combination with appropriate macrocations [1–5]. Metal helicates as an important model for studing chiral recognition and transmission [6–15] should be suitable macrocations matching with polyanions. In metal helical structures, the metal ions display the same absolution configurations, while the basic features of the design necessary to assemble a double helix are now fairly well established, the design and control of assembly of the helical units into a multi-helical array represents a considerable synthetic challenge [6–15]. It is expected that by modulating the forming and the packing mode of the helicand to form a special packing based on the macroanionic effect of polyoxometalates (**POM**), the chirality of the metal centers would be able to extend to higher dimensionality. To test this approach, we first selected Schiff-base ligands with two N–N single bond units to build double metal helicates based on transmitting the chirality from one metal center to another and selected high-charged Keggin-type polyoxometalates to facilitate and control the forming of special structures. Here, we primarily researched the synergistic effect among silver metal helicates and Keggin-type $[PMo_{12}O_{40}]^{3-}$ anions in crystal $[Ag_2L_2][(n\text{-}C_4H_9)_4N][PMo_{12}O_{40}] \cdot H_2O \cdot 0.5CH_3OH \cdot 0.25DMF$ (**I**).

[1] The article is published in the original.

EXPERIMENTAL

All organic solvents and materials used for synthesis were of reagent grade and used without further purification. Complex $\alpha\text{-}[(n\text{-}C_4H_9)_4N]_3PMo_{12}O_{40} \cdot H_2O$ was prepared according to a literature method [16] and characterized by IR spectra and TG analyses. Elemental analyses (C, H, and N) were carried out on a Perkin–Elmer 240C analyzer. IR spectra were recorded on a VECTOR 22 Bruker spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. ^{1}NMR spectral measurements were performed on a Bruker DRX-500 NMR spectrometer at room temperature with TMS as an internal reference.

Synthesis of ligand L was carried out according a literature method [11].

For $C_{26}H_{20}N_6$			
anal. calcd, %:	C, 75.00;	H, 4.80;	N, 20.19.
Found, %:	C, 75.12;	H, 4.72;	N, 20.30.

^{1}H NMR (DMSO-d_6; δ, ppm): 8.59(d., 2H, Py), 8.55 (m., 2H, –CH–), 7.93 (d., 4H, Ph), 7.84 (d., 2H, Py), 7.60 (t., 2H, Py), 7.46 (d., 2H, Py), 7.43 (d., 4H, Ph), 7.46 (t., 2H, Py).

Synthesis of compound I. Ligand L (0.1 mmol, 45 mg) and $AgNO_3$ (0.1 mmol, 18 mg) were added to 20 ml of CH_3OH. A mixture was stirred and refluxed for 2 h at 90°C to give a resulting yellow solution. The compound **I** was prepared by the layering method. A buffer layer of a solution (8 ml) of methanol–water (1 : 1, v/v) was carefully layered over a solution of $\alpha\text{-}[(n\text{-}C_4H_9)_4N]_3PMo_{12}O_{40} \cdot H_2O$ (0.013 mmol, 22 mg) in

Table 1. Crystallographic data and refinement parameters for compound **I**

Parameter	Value
Crystal size, mm	0.40 × 0.34 × 0.30
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	14.201(3)
b, Å	16.314(3)
c, Å	23.614(4)
α, deg	105.456(4)
β, deg	91.668(4)
γ, deg	100.872(4)
V, Å^3	5159.8(16)
Z	2
ρ_{calcd}, g cm^{-3}	2.04
μ, mm^{-1}	1.88
Data collection θ range, deg	1.76–25
F(000)	3074
Range of intensity measurement	$-15 \le h \le 16$, $-19 \le k \le 19$ $-23 \le l \le 28$
Measured reflections	24723
Independent reflections	17006
R_{int}	0.1129
Refinement parameters	1299
R factor ($I \ge 2\sigma(I)$)	$R_1 = 0.0714$, $wR_2 = 0.1254$
R factor (for the whole array)	$R_1 = 0.1709$, $wR_2 = 0.1399$
GOOF	0.944
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, *e* Å^{-3}	1.16 and –0.85

5 ml of DMF and 0.1 ml of water. Then 5 ml of the resulting yellow solution was carefully layered over the buffer layer. Yellow block crystals appeared after a month. The yield was 76% based on α-[(*n*-$C_4H_9)_4N]_3PMo_{12}O_{40} \cdot H_2O$.

For $C_{69.25}H_{81.75}N_{13.25}O_{41.75}PAg_2Mo_{12}$ (M = 3165.72)			
anal. calcd, %:	C, 26.27;	H, 2.60;	N, 5.86.
Found, %:	C, 26.45;	H, 2.72;	N, 5.67.

IR spectrum (KBr; ν, cm^{-1}): 808 ν(Mo–Oc), 879 ν(Mo–Ob), 957 ν(Mo = Ot), 1063 ν(P–Oa) (four characteristic vibrations resulting from heteropolyanions with the Keggin structure) and 1616, 1585, 1473, 1439, 1384, 1304, 1252, and 1156 cm^{-1} (the vibrations resulting from the ligand).

X-ray diffraction analysis. The crystal structure of complex **I** was determined from single-crystal X-ray diffraction data. Intensity data were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated MoK_a radiation (λ = 0.71073 Å using the SMART and SAINT programs [17]. The structure was solved by direct methods and refined on F^2 by using full-matrix least-squares methods with the SHELXTL version 5.1 [18]. All non-hydrogen atoms except solvent molecules were refined anisotropically. Hydrogen atoms of ligand L and the $[(n\text{-}C_4H_9)_4N]^+$ ion were localized in their calculated positions and refined using a riding model. Hydrogen atoms of the solvent organic molecules were localized by difference Fourier maps and refined by fixing the isotropic displacement factors at 1.2 times that of the mother atoms attached. Hydrogen atoms of the solvent water molecules were not treated. The completeness of the data is 0.94, if the θ_{min} is 25° and lower, if the θ_{max} is larger than 25°. This may be due to the low crystal structure quality resulting from the easy losing of solvent molecules. In addition, a large number of heavy atoms (P, Mo, Ag), and likewise accommodating light atoms like C and N, resulted in large differences in thermal parameters of some light atoms. Thus, 144 restrains were used to solid some non-positive definite atoms and the solvent DMF in the refinement. The crystal parameters, data collection, and refinement results for compound **I** are summarized in Table 1. The selected bond lengths and bond angles are listed in Table 2.

The atomic coordinates and other parameters of structure **I** have been deposited with the Cambridge Crystallographic Data Center (no. 670160; deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The reaction of ligand L (Fig. 1a) with $AgNO_3$ in the presence of $[PMo_{12}O_{40}]^{3-}$ anions afforded compound **I**,

$[Ag_2L_2][(n\text{-}C_4H_9)_4N][PMo_{12}O_{40}] \cdot H_2O \cdot 0.5CH_3OH \cdot 0.25DMF$. The single-crystal structure analysis exhibits the crystallization of center-symmetrical space group $P\bar{1}$. Each molecular unit consists of one $[Ag_2L_2]^{2+}$ polymer, one $[(n\text{-}C_4H_9)_4N]^+$ ion, two halves of $[PMo_{12}O_{40}]^{3-}$ polyanions and one solvent water molecule, a half of methanol molecule, and a quarter of DMF. In the $[Ag_2L_2]^{2+}$ polymer (Fig. 1b), each Ag^+ ion is coordinated in a distorted tetrahedral geometry by two nitrogen atoms from two imine groups and two nitrogen atoms from two pyridine rings. The bond lengths of Ag–N are 2.229(5)–2.485(5) Å. These bond lengths are comparable to 2.166(11)–2.469(9) Å of Ag–N in the silver helical compound $Ag_2L_2 \cdot 2ClO_4$ (**II**) with the chiral space group $P3_221$ [11]. Each ligand spans both the silver ions but does not wrap around the metal–metal axis. One of the two ligands passes above the Ag(1)–Ag(2) axis and the other goes beneath, with the $[Ag_2L_2]^{2+}$ cation appearing more like a box than a double helix. All these structural characters are similar to those in silver helical compound **II**. The atropisomer chiral bridging mode of the ligands translates the chirality of the first metal center to the second one, resulting in the formation of the chiral helicate. The two silver centers, being of the same chirality, are coordinated by two coupled ligands with an Ag···Ag separation of 3.88 Å, leading to the replication of the conformational chirality of the first ligand to the second. The π–π stacking interactions between benzene ring A and pyridine ring B, as well as between benzene ring C and pyridine ring D are found to stabilize the helical mode with the dihedral angle of the stacked pair both being 4.5° and the centroid distances of 3.93 Å between the A and B rings, as well as 4.00 Å between the C and D rings. The torsion angles of C(13)–N(1)–N(2)–C(15), C(14)–N(4)–N(5)–C(21), C(39)–N(7)–N(8)–C(41), and C(40)–N(10)–N(11)–C(47) are 154.5°, 166.1°, 155.5°, and 165.5°, respectively.

As shown in Fig. 2, two centrosymmetrically related $[Ag_2L_2]^{2+}$ double helicates form a shoulder-by-shoulder dimeric double helicate cation through π–π stacking interactions between pyridine ring B and symmetry-related pyridine ring B(1) with a centroid distance of 3.50 Å. Each dimeric double helicate cation has a parellelly stacked tetraaromatic ring ABB(1)A(1). These dimers further form 1D dichain along the *x* axis through π–π stacking interactions between the benzene ring F and benzene ring E(2), as well as benzene ring F(3) and benzene ring E(1), belonging to two adjacent $[Ag_2L_2]^{2+}$ units, with the centroid distance being 3.87 Å. These dichains are further parallelly arranged to form layers. In the same manner, the charge-compensating $[PMo_{12}O_{40}]^{3-}$ anions and $[(n\text{-}C_4H_9)_4N]^+$ ions alternately arrange themselves in a special order in consistence with that of $[Ag_2L_2]^{2+}$ metal helicates to form layers (Figs. 2, 3), which position themselves at the two sides

Table 2. Selected bond lengths and bond angles for compound **I***

Bond	*d*, Å	Bond	*d*, Å
P(1)–O(2)	1.484(7)	P(1)–O(23)	1.480(9)
P(1)–O(1)	1.531(7)	P(1)–O(26)	1.518(7)
P(1)–O(4)	1.533(8)	P(2)–O(25)	1.549(6)
P(1)–O(3)	1.550(8)	P(2)–O(24)	1.590(7)
Mo(1)–O(19)	1.640(5)	Mo(7)–O(38)	1.642(5)
Mo(1)–O(7)	1.858(5)	Mo(7)–O(34)	1.872(4)
Mo(1)–O(9)	1.894(5)	Mo(7)–O(27)	1.894(5)
Mo(1)–O(10)	1.920(5)	Mo(7)–O(30)	1.943(5)
Mo(1)–O(8)	1.960(4)	Mo(7)–O(36)	1.950(5)[a]
Mo(1)–O(4)	2.430(7)	Mo(7)–O(26)	2.451(7)[a]
Mo(1)–O(1)	2.471(7)	Mo(7)–O(23)	2.455(8)
Ag(1)–N(12)	2.230(5)	Ag(2)–N(6)	2.249(5)
Ag(1)–N(3)	2.295(5)	Ag(2)–N(9)	2.266(6)
Ag(1)–N(2)	2.430(5)	Ag(2)–N(8)	2.452(5)
Ag(1)–N(11)	2.430(5)	Ag(2)–N(5)	2.485(5)
Angle	**deg**	**Angle**	**deg**
O(2)P(1)O(1)	114.5(4)	O(10)Mo(1)O(4)	64.7(2)
O(2)P(1)O(4)[b]	109.0(4)	O(7)Mo(1)O(1)	67.1(2)
O(1)P(1)O(4)[b]	110.9(4)	O(10)Mo(1)O(1)	90.6(3)
O(2)P(1)O(3)	111.1(4)	O(8)Mo(1)O(1)	62.9(2)
O(1)P(1)O(3)	103.9(4)	N(8)Ag(2)N(5)	124.7(2)
O(4)[b]P(1)O(3)	107.0(4)	N(9)Ag(2)N(5)	126.3(2)
O(9)Mo(1)O(4)	64.0(2)	N(6)Ag(2)N(5)	73.0(2)
O(10)Mo(1)O(8)	86.1(2)	N(9)Ag(2)N(8)	71.0(2)
O(7)Mo(1)O(8)	87.5(2)	N(6)Ag(2)N(8)	135.0(2)
O(9)Mo(1)O(10)	86.2(2)	N(6)Ag(2)N(9)	136.2(2)
N(12)Ag(1)N(3)	136.7(2)	N(12)Ag(1)N(11)	72.6(2)
N(12)Ag(1)N(2)	132.7(2)	N(3)Ag(1)N(11)	125.8(2)
N(3)Ag(1)N(2)	72.9(2)	N(2)Ag(1)N(11)	125.5(2)

* Symmetry transformations: [a] $-x+1, -y, -z+1$, [b] $-x+2, -y, -z+2$.

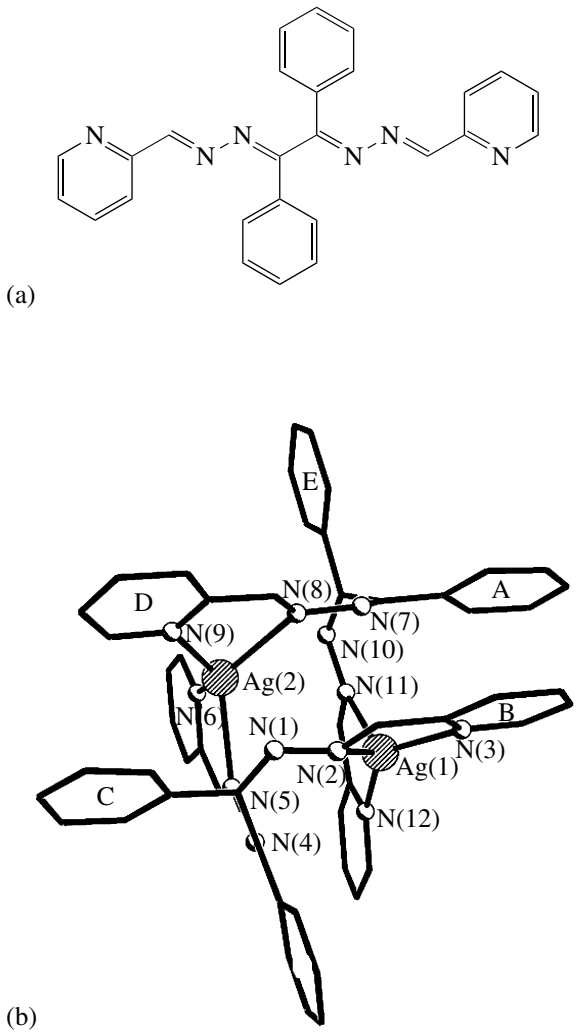

Fig. 1. Ligand L (a) and the $[Ag_2L_2]^{2+}$ polymer (b). Hydrogen atoms are omitted for clarity.

of the layers constructed by $[Ag_2L_2]^{2+}$ metal helicates and connect adjacent layers together featuring an ion crystal. In addition, there is a short contact between Ag(1) and O(22) belonging to polyanions with the distance being 3.53 Å.

In compound **I**, there are two types of $[PMo_{12}O_{40}]^{3-}$ anions due to different spacial positions. The central P atom is surrounded by a cube of eight oxygen atoms with each oxygen site half-occupied. These eight oxygen atoms are all crystallographically disorded, and this case can be found in many compounds [5]. The P–O and Mo–O distances are in a range of 1.480(9)–1.590(7) and 1.609(5)–2.503(9) Å, respectively. In addition, the OPO angles are in a range of 103.9(4)°–114.5(4)°. These results are comparable to the literatures [5] and indicate that these polyanions are distorted. These Keggin anions play not only a charge-compensating role but also serve as templates during the assembly so that the metal helicates are aggregated around them, modulating the forming and the packing mode of the helicand to form an ion crystal. It is possible that because the $[PMo_{12}O_{40}]^{3-}$ anions have a large volume and high negative charges, the chiral $[Ag_2L_2]^{2+}$ metal helicates could not efficiently pack in a special direction to form a chiral 3D polymer. Thus, to extend the chirality of the metal centers of the helicates to higher dimensionality, it is necessary to further find matchable polyanions with the $[Ag_2L_2]^{2+}$ units or to find matchable chiral metal helicates with the $[PMo_{12}O_{40}]^{3-}$ anions. It is hopeful to control the assembly of the helical units into a multihelical array based

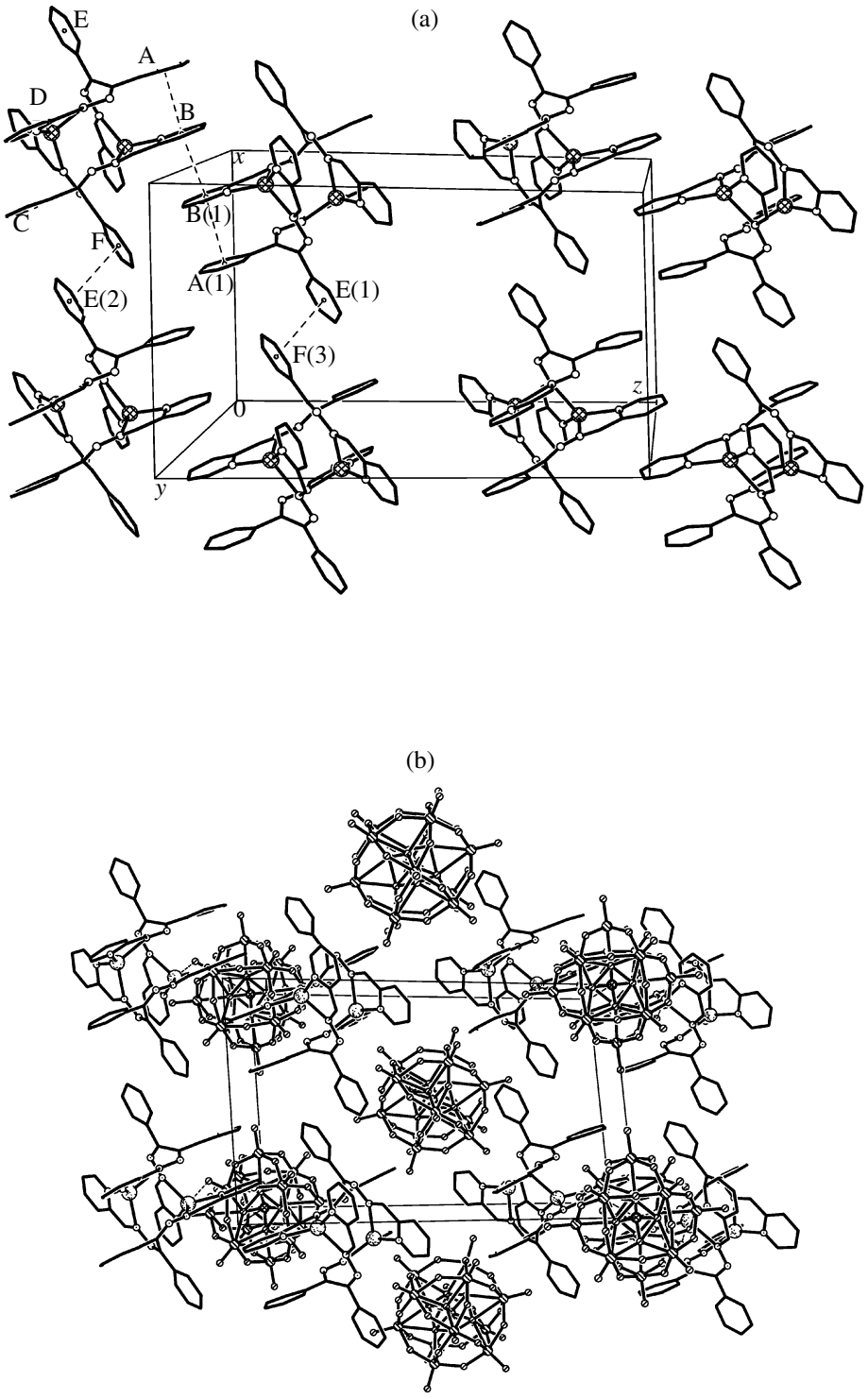

Fig. 2. Dimer constructed by two centrosymmetrically related $[Ag_2L_2]^{2+}$ double helicates, the 1D dichain along the *x* axis and the 2D layer along the *xz* plane (a), as well as the views of the layers constructed by the $[PMo_{12}O_{40}]^{3-}$ anions (b). Hydrogen atoms, solvent molecules, and the $[(n\text{-}C_4H_9)_4N]^+$ ions are omitted for clarity.

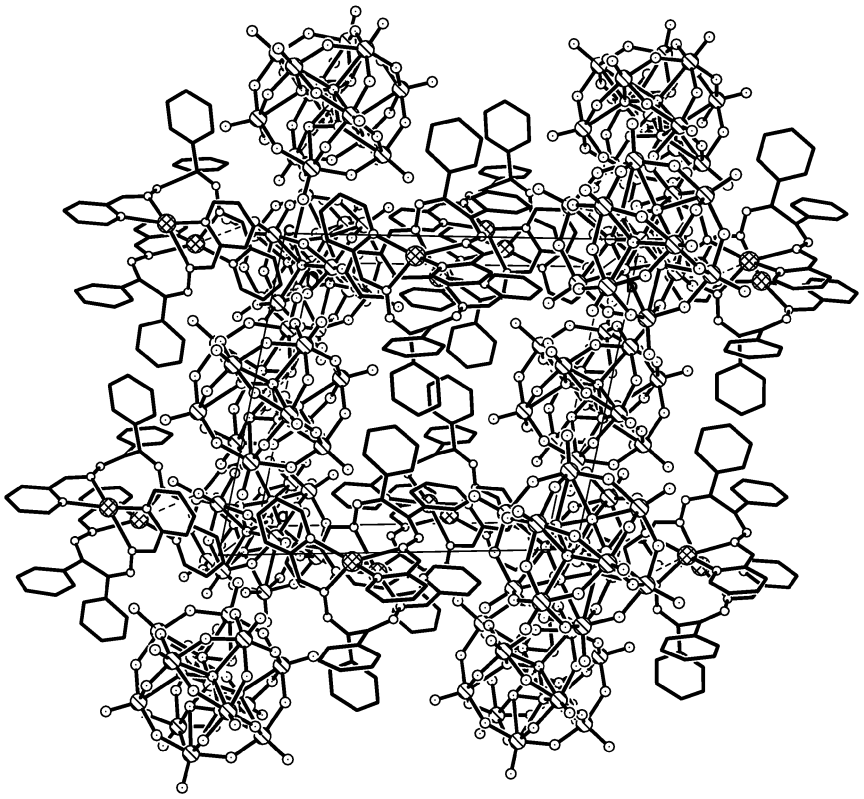

Fig. 3. Packing diagrams of the $[Ag_2L_2]^{2+}$ metal helicates and polyanions along the *xy* plane. Hydrogen atoms, solvent molecules, and the $[(n\text{-}C_4H_9)_4N]^+$ ions are omitted for clarity.

on the template effect of POM, as well as some substantially strong, selective, and directional interactions.

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REFERENCES

1. Uchida, S. and Mizuno, N., *Chem. Eur. J.*, 2003, vol. 9, p. 5850.
2. Kawamoto, R., Uchida, S., and Mizuno, N., *J. Am. Chem. Soc.*, 2005, vol. 127, p. 10560.
3. Jiang, C., Lesbani, A., Kawamoto, R., et al., *J. Am. Chem. Soc.*, 2006, vol. 127, p. 14240.
4. Kong, X.J., Ren,Y.P., Zheng, P.Q., et al., *Inorg. Chem.*, 2006, vol. 45, p. 10702.
5. Wei, M.L., He, C., Sun, Q.Z., et al., *Inorg. Chem.*, 2007, vol. 46, p. 5957.
6. Albrecht, M., *Chem. Rev.*, 2001, vol. 101, p. 3457.
7. Kitagawa, S., Kitaura, R., and Noro, S.I., *Angew. Chem. Int. Ed.*, 2004, vol. 43, p. 2334.
8. Anthony, S.P. and Radhakrishnan, T.P., *Chem. Commun.*, 2004, p. 1058.
9. Siemeling, U., Scheppelmann, I., Neumann, B., et al., *Chem. Commun.*, 2003, p. 2236.
10. Lu, W.G., Jiang, L., Feng, X.L., et al., *Cryst. Growth Des.*, 2008, vol. 8, no. 3, p. 986.
11. Sun, Q.Z., Bai, Y., He, G.J., et al., *Chem. Commun.*, 2006, p. 2777.
12. Azumaya, I., Uchida, D., Kato, T., et al., *Angew. Chem. Int. Ed.*, 2004, vol. 43, p. 1360.
13. Childs, L.J., Pascu, M., Clarke, A.J., et al., *Chem. Eur. J.*, 2004, vol. 10, p. 4291.
14. Childs, L.J., Alcock, N.W., and Hannon, M.J., *Angew. Chem.*, 2001, vol. 113, p. 1113.
15. Oh, M., Carpenter, G., and Sweigart, D.A., *Acc. Chem. Res.*, 2004, vol. 37, p. 1.
16. Sanchez, C., Livage, J., Launay, J.P., et al., *J. Am. Chem. Soc.*, 1982, vol. 104, no. 11, p. 3194.
17. *SMART and SAINT, Area Detector Control and Integration Software*, Madison (WI, USA): Siemens Analytical X-Ray Systems, Inc., 1996.
18. Sheldrick, G.M., *SHELXTL, Version 5.1, Software Reference Manual*, Madison (WI, USA): Bruker AXS, Inc., 1997.