Mononuclear, dinuclear, hexanuclear, and one-dimensional polymeric silver complexes having ligand-supported and unsupported argentophilic interactions stabilized by pincer-like 2,6-bis(5-pyrazolyl)pyridine ligands†‡

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The mononuclear complexes $[Ag(H_2L^1)(Py)_2](NO_3)\cdot H_2O(1, H_2L^1 = 2,6-bis(5-methyl-1$ *H*-pyrazol- $3-yl)pyridine) and <math>[Ag(NO_3)(L^2)](2, L^2 = 2,6-bis(5-methyl-1-isopropyl-1$ *H*-pyrazol-3-yl)pyridine), $dinuclear complex <math>[Ag_2(H_2L^3)_2(HL^4)_2](3, H_2L^3 = 2,6-bis(5-phenyl-1$ *H*-pyrazol-3-yl)pyridine, HL⁴ =6-(5-phenyl-1*H* $-pyrazolyl-3-yl)picolinate), one-dimensional polymer <math>\{[Ag_2(H_2L^1)_2](NO_3)_2\cdot H_2O\}_n$ (4), and hexanuclear clusters $[Ag_6(HL^1)_4](X)_2$ (X = NO₃⁻, **5**; BF₄⁻, **6**; ClO₄⁻, **7**) stabilized by pincer-like bispyrazolyl ligands have been prepared and characterized using ¹H NMR spectroscopy, elemental analysis, IR spectroscopy, luminescence spectroscopy and X-ray diffraction. In complex **3**, there is a ligand unsupported Ag–Ag bond between the two silver atoms. Complex **4** displays a one-dimensional polymer consisting of an infinite Ag–Ag chain and every two adjacent silver ions are bridged by an H₂L¹ ligand. Complexes **5** and **7** have the same Ag₆ cores in which six silver atoms are held together by four HL¹ and five Ag–Ag bonds, while complex **6** was held together by six Ag–Ag bonds. The silver–silver distances in these complexes are found in the range of 2.874(1)–3.333(2) Å for ligand supported, and 3.040(1) Å for ligand unsupported Ag–Ag bonds, respectively. Complexes **3–7** are strongly luminescent due to either intraligand or metal–ligand charge transfer processes.

Introduction

Direct metal-metal interactions are important because they are often associated with many potentially useful chemical and physical properties of materials such as catalytic behavior, or magnetic, optical, or electronic properties.¹ The attractive interactions between closed-shell and pseudo closed-shell d¹⁰, s², and d⁸ metal centers have been becoming familiar and are termed as *metallophilicity*.^{1e,2} The attraction between the closed-shell metals promotes the aggregation of the metal centers having d¹⁰ d⁸, s² configurations, which has been supported by spectroscopic and structural evidence.^{2e,3} The weak interactions often lead to materials with interesting properties and structural motifs.

Metallophilicity of an order-of-magnitude comparable to hydrogen bonds in the case of gold or weaker for other metals has been used as an element for the construction of various coordination polymers. Many metallic aggregates and coordination polymers containing Au–Au,⁴ Ag–Ag^{5,6}, Ag–Au⁷ and Cu– Cu⁸ bonds have recently been reported. The strengths of the interactions have an order-of-magnitude comparable to those of hydrogen bonds.^{2a,9} Compared with gold–gold interactions, silver–silver interactions have been calculated to be relatively weaker.¹⁰ However, there are still many examples of argentophilic interactions; most are ligand supported,⁵ while few are ligand-unsupported.⁶

Pyrazolyl ligands are a kind of multifunctional organic ligand that often display an *exo*-bidentate coordination mode. The structure and properties of closed-shell d¹⁰ coinage metal pyrazolates are of significant interest.¹¹⁻¹⁶ Numerous closedshell d¹⁰ coinage metal complexes with a variety of structures stabilized by monopyrazole ligands ranging from dimers,¹² trimers,¹³ tetramers,^{13h,14} hexamers^{7b,c,15} to polymers^{131,14d,16} have been reported. When silver(1) pyrazolate is considered, several trimers,^{6b,13k,n} two tetramers,^{13h,14h} and a one-dimensional polymer¹³¹ have been structurally characterized using X-ray diffraction. However, hexanuclear or higher nuclearity clusters are not known so far.^{14h}

Bispyrazolyl ligands, as a kind of potentially anionic multidentate linker, would be expected to be suitable candidates to connect transition metals into aggregates. Surprisingly, coinage metal complexes stabilized by bispyrazolyl ligands have scarcely been reported. To our knowledge, only a flexible porous silver(1) coordination polymer^{17a} and a copper(1) coordination polymer^{17b} supported by 3,3',5,5'-tetramethyl-4,4'-bipyrazole have been recently reported.

We have been interested in the synthesis and reactivity of multinuclear complexes and coordination polymers, and a number of complexes containing Pt–Pt,^{18a} Pt–Tl,^{18b,c} Pt–Ag,^{18d} Au–Au^{18e}, and Ag–Ag^{18f} interactions have been recently presented. As an continuation of our studies on metal–metal interactions, in this paper we report the synthesis and characterization of a family

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^bDepartment of Chemistry, Liaocheng University, Liaocheng 252059, China † Structural parameters of the complexes 1–7. CCDC reference numbers 655894–655901. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b710916d

[‡] Electronic supplementary information (ESI) available: Molecular structures of H_2L^1 , **2**, **6** and **7**, and emission spectral data for 3–7. See DOI: 10.1039/b710916d

of interesting silver complexes and a coordination polymer with ligand-supported and ligand-unsupported silver–silver interactions. These complexes are stabilized by the pincer-like bispyrazolyl ligands, 2,6-bis(5-methyl-1*H*-pyrazol-3-yl)pyridine (H_2L^1), 2,6-bis(5-methyl-1-isopropyl-1*H*-pyrazol-3-yl)pyridine (L^2), 2,6-bis(5-phenyl-1*H*-pyrazol-3-yl)pyridine (H_2L^3), and 6-(5-phenyl-1*H*-pyrazolyl-3-yl)picolinate (HL⁴) generated *in situ* (see ESI[‡]).

Experimental

All chemicals were of reagent grade quality obtained from commercial sources and used as received, unless stated otherwise. 1,1'-(2,6-Pyridyl)bis-1,3-butanedione^{19a} and 2,6-bis(5-methyl-1*H*-pyrazol-3-yl)pyridine^{19b,c} (H₂L¹) were prepared according to the reported procedures. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Bruker Avance (400 MHz) spectrometer. Elemental analyses were determined with a Perkin-Elmer 2400C instrument. IR spectra were measured as KBr pellets using a Nicolet 5DX FX-IR spectrophotometer. Mass spectra (EI, 70 eV) were recorded on a HP5989B mass spectrometer. The photoluminescence study was carried out on powdered samples in the solid-state at room temperature using a SHIMADZU RF-540 spectrometer.

Preparations

2,6-Bis(5-methyl-1*H***-pyrazol-3-yl)pyridine hemihydrate (H₂L¹. 0.5H₂O).** 2,6-Bis(5-methyl-1*H*-pyrazol-3-yl)pyridine was prepared from 2,6-bis(1,3-dioxobutyl)pyridine and hydrazine hydrate. Anal. calcd for C₁₃H₁₄N₅O_{0.5}: C, 62.89; H, 5.68; N, 28.21. Found: C, 63.07; H, 5.81; N, 28.37%. ¹H NMR (CDCl₃): δ 12.57 (br, 2H), 7.54 (t, J = 7.6, 1H), 7.25 (d, J = 7.6, 2H), 6.27 (s, 2H), 2.18 (s, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 149.5, 149.0, 141.9, 139.7, 121.0, 103.5, 10.8. MS (*m*/*z*): 239 (M⁺, 100%), 210, 167, 154, 141, 129, 77. IR data (KBr pellet, cm⁻¹): 3185 s, 3127 s, 2976 s, 2927 s, 1574 s, 1475 s, 1302 s, 1160 s, 1007 s, 804 s, 691 w.

2,6-Bis(5-methyl-1-isopropyl-1*H*-pyrazol-3-yl)pyridine (L²). A mixture of 2,6-bis(5-methyl-1H-pyrazol-3-yl)pyridine (0.48 g, 2 mmol) and 60% NaH (0.32 g, 8 mmol) in dry DMF (15 mL) was stirred for 2 h at room temperature. To the solution was added 2-bromopropane (0.98 g, 8 mmol). After stirring at 60 °C for two days, the resulting solution was concentrated to 3 mL. Addition of H₂O (15 mL) precipitated a pale yellow powder. Column chromatography involved elution with ethyl acetate-petroleum ether (1:5) which separated the compound as a white powder (0.40 g). Yield: 61.0%. Anal. calcd for C₁₉H₂₅N₅: C, 70.56; H, 7.79; N, 21.65. Found: C, 70.52; H, 7.82; N, 21.57%. ¹H NMR (CDCl₃): δ 7.82 (d, J = 7.6, 2H), 7.68 (t, J = 7.6, 1H), 6.72 (s, 2H), 4.45 (m, 2H), 2.33 (s, 6H), 1.52 (d, J = 6.8, 12H). ¹³C NMR (100 MHz, $CDCl_3$): δ 152.2, 150.4, 138.1, 136.7, 118.0, 104.0, 49.9, 22.5, 11.1. MS (m/z): 323 (M⁺, 100%), 294, 279, 239, 210, 129, 77. IR data (KBr pellet, cm⁻¹): 2977 s, 2931 s, 1595 s, 1572 s, 1548 m, 1505 m, 1432 s, 1403 m, 1345 m, 1256 s, 990 m, 825 w, 792 s, 742 w, 694 w.

2,6-Bis(1'-phenyl-1',3'-dioxopropyl)pyridine. Under a dinitrogen atmosphere, to a 100 cm³ Schlenk flask charged with sodium (0.77 g, 33.4 mmol), dry ethanol (15 mL) was added and the

mixture was stirred until all sodium was consumed. Ethanol was eliminated in vacuo. To the freshly prepared sodium ethoxide, acetophenone (4.5 mL) in dry toluene (30 mL) was added, followed quickly by dimethyl pyridine-2,6-dicarboxylate (2.50 g, 12.8 mmol). The mixture was stirred for 8 h and a yellowish sodium salt precipitated out of the solution. After stirring at 60 °C for 4 h, the mixture was filtered and washed with diethyl ether before drying. The dry solid was slowly added to a vigorously stirred solution of acetic acid (15 mL), water (25 mL), and ice (50 g), and the resulting solid was collected by filtration. The yellow solid was dissolved in CH₂Cl₂ (150 mL) and filtered. The resulting solution was washed with aqueous sodium bicarbonate solution (6%, 2 \times 30 mL) and distilled water (30 mL), then dried over anhydrous magnesium sulfate. A yellow solid was obtained after removal of CH₂Cl₂. Yield: 3.3 g, 69.9%. Anal. calcd for C₂₃H₁₇NO₄: C, 74.38; H, 4.61; N, 3.77. Found: C, 74.42; H, 4.68; N, 3.75%. ¹H NMR (DMSO- d_6): δ 16.54 (br), 16.50 (br), 8.29–8.21 (m), 8.10-8.07 (m), 7.72 (s), 7.69 (t), 7.61-7.53 (m), 7.19 (s), 4.97 (s), 4.50 (s). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 196.4, 195.8, 185.5, 183.0, 182.9, 151.5, 151.4, 139.8, 136.2, 134.4, 133.9, 133.4, 129.1, 129.0, 128.4, 127.5, 127.0, 125.6, 124.9, 124.4, 93.9, 92.9, 49.4, 41.2. MS (m/z): 371 (M⁺), 266, 224, 105 (100%), 77. IR data (KBr pellet, cm⁻¹): 3743 w, 3085 w, 1610 s, 1565 s, 1550 s, 1485 s, 1304 m, 1262 m, 1230 s, 1070 s, 837 w, 805 m, 774 s, 685 m, 618 m.

2,6-Bis(5-phenyl-1*H***-pyrazol-3-yl)pyridine (H_2L^3).** A mixture of 2,6-bis(1'-phenyl-1',3'-dioxopropyl)pyridine (3.71 g, 10 mmol), hydrazine hydrate (85%, 10 mL), and a few drops of concentrated HCl in methanol (200 mL) was refluxed for 36 h. The resulting solution was concentrated to ca. 20 mL. Addition of H₂O (50 mL) to the above solution resulted in a pale yellow precipitate. The product was purified by recrystallization from CH₃CH₂OH and CH₂Cl₂ (1 : 1). Yield: 2.1 g, 57.2%. Anal. calcd for C₂₃H₁₇N₅: C, 76.01; H, 4.71; N, 19.27. Found: C, 75.87; H, 4.82; N, 19.32%. ¹H NMR (400 MHz, DMSO- d_6): δ 13.61 (br, 2H), 8.04 (t, J = 7.6, 1H), 7.92 (d, J = 8.0, 4H), 7.82 (d, J = 7.6, 2H), 7.52 (s, 2H), 7.46 (t, J = 7.6, 4H), 7.34 (t, J = 7.6, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 152.1, 147.5, 143.7, 143.1, 139.4, 133.9, 129.5, 129.2, 128.7, 128.1, 125.6, 118.9, 101.2. MS (*m*/*z*): 363 (M⁺, 100%), 334, 304, 239, 190, 129, 97, 71. IR data (KBr pellet, cm⁻¹): 3200 s, 3030 m, 1602 m, 1566 s, 1453 s, 1313 m, 1219 m, 1186 m, 1156 m, 1074 m, 810 m, 765 s, 691 s.

[Ag(H₂L¹)(Py)₂](NO₃)·H₂O (1). A solution of 2,6-bis(5methyl-1*H*-pyrazol-3-yl)pyridine (H₂L¹) (48 mg, 0.2 mmol) and AgNO₃ (34 mg, 0.2 mmol) in pyridine (5 mL) was stirred in the dark at room temperature for 24 h. Then the mixture was filtered through a short plug of Celite. Slow evaporation of diethyl ether into the filtrate afforded colorless crystals suitable for X-ray single diffraction. Yield: 87.1%. Anal. calcd for C₂₃H₂₅AgN₈O₄: C, 47.19; H, 4.30; N, 19.14. Found: C, 47.02; H, 4.42; N, 19.26%. ¹H NMR (400 MHz, DMSO-*d*₆): δ 13.21 (s, 2H), 8.59 (d, *J* = 7.8, 4H), 8.05 (t, *J* = 8.0, 1H), 7.88 (d, *J* = 7.2, 2H), 7.84 (t, *J* = 7.8, 2H), 7.43 (t, *J* = 7.8, 4H), 6.86 (s, 2H), 2.30 (s, 6H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 150.8, 149.8, 149.3, 142.0, 139.9, 137.9, 125.0, 120.9, 103.6, 11.0. IR data (KBr pellet, cm⁻¹): 3446 s, 3200 s, 3138 m, 2985 w, 2929 w, 1578 s, 1501 m, 1382 s, 1323 m, 1227 w, 1160 m, 1019 m, 790 s, 735 w. [Ag(L²)(NO₃)] (2). A solution of 2,6-bis(5-methyl-1-isopropyl-1*H*-pyrazol-3-yl)pyridine (L²) (65 mg, 0.2 mmol) and AgNO₃ (34 mg, 0.2 mmol) in THF (2 mL) was stirred, in darkness, for *ca.* two days. The resulted precipitate was filtered and washed with diethyl ether. Slow evaporation of diethyl ether into its clear DMF solution yielded colorless crystals suitable for X-ray single diffraction. Yield: 64.8%. Anal. calcd for C₁₉H₂₅AgN₆O₃: C, 46.26; H, 5.11; N, 17.04. Found: C, 46.39; H, 5.20; N, 17.25%. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.08 (t, *J* = 7.6, 1H), 7.89 (d, *J* = 8.0, 2H), 6.82 (s, 2H), 4.34 (br, 2H), 2.24 (s, 6H), 0.99 (s, 12H). ¹³C NMR (100 MHz, CDCl₃): δ 152.8, 150.7, 138.4, 136.9, 117.9, 103.9, 49.8, 22.4, 11.0. IR data (KBr pellet, cm⁻¹): 2974 s, 2930 m, 1600 m, 1575 s, 1495 m, 1410 s, 1384 s, 1293 s, 1260 m, 803 m, 731 w.

[Ag₂(H₂L³)₂(HL⁴)₂] (3). A mixture of 2,6-bis(5-phenyl-1*H*-pyrazol-3-yl)pyridine (H₂L³) (36 mg, 0.1 mmol) and AgOAc (35 mg, 0.1 mmol) in 20 mL of water in a sealed stainless vial was heated at 170 °C for 48 h. Cooling the vial slowly afforded colorless crystals. Yield: 32%. Anal. calcd for $C_{76}H_{54}Ag_2N_{16}O_4$: C, 62.05; H, 3.70; N, 15.23. Found: C, 62.17; H, 3.83; N, 15.31%. IR data (KBr pellet, cm⁻¹): 3246 s, 3062 s, 1656 s, 1596 s, 1569 s, 1452 s, 1217 m, 1117 m, 1076 m, 809 m, 757 s, 693 m, 652 w.

 $[Ag_2(H_2L^1)_2](NO_3)_2 \cdot H_2O$ (4). A solution of 2,6-bis(5-methyl-1H-pyrazol-3-yl)pyridine (H₂L¹) (48 mg, 0.2 mmol) and AgNO₃ (34 mg, 0.2 mmol) in DMF (5 mL) was stirred at room temperature in the dark for ca. two days, then it was filtered through a short plug of Celite. To the resulting clear solution, diethyl ether was added, and the resulting precipitate was filtered and washed with acetone. Complex 4 was obtained as a white powder. Yield: 78.6%. Crystals suitable for X-ray single diffraction were obtained from slow evaporation of diethyl ether into its DMF solution. Anal. calcd for C₂₆H₂₈Ag₂N₁₂O₇: C, 37.34; H, 3.37; N, 20.10. Found: C, 37.39; H, 3.44; N, 19.94%. ¹H NMR (400 MHz, DMSO- d_6): δ 13.18 (s, 2H), 8.07 (t, J = 8.0, 1H), 7.88 (d, J = 8.0, 2H), 6.86 (s, 2H), 2.30 (s, 6H). ¹³C NMR (100 MHz, DMSO- d_6): δ 149.8, 149.4, 142.2, 140.0, 121.2, 103.7, 11.0. IR data (KBr pellet, cm⁻¹): 3525 s, 3189 s, 3139 s, 2981 s, 1578 s, 1502 m, 1437 m, 1370 s, 1321 s, 1282 m, 1021 m, 787 s.

[Ag₆(HL¹)₄](NO₃)₂·(CH₃)₂CO (5). A solution of 4 (84 mg, 0.1 mmol) and AgNO₃ (34 mg, 0.2 mmol) in DMF (10 mL) and acetone (0.3 mL) was stirred at room temperature in the dark for *ca*. two days, then it was filtered off through a short plug of Celite. Diethyl ether was slowly evaporated into the resulting clear solution, and colorless crystals suitable for X-ray single diffraction were obtained after several days. Yield: 68.2%. Anal. calcd for C₅₅H₅₄Ag₆N₂₂O₇: C, 37.06; H, 3.05; N, 17.29. Found: C, 36.89; H, 3.06; N, 17.39%. IR data (KBr pellet, cm⁻¹): 3198 s, 3136 s, 2922 s, 1672 s, 1573 s, 1483 m, 1384 s, 1372 s, 1275 m, 1150 m, 1097 m, 1018 m, 811 m, 791 s.

 $[Ag_6(HL^1)_4](BF_4)_2$ (6). A solution of 2,6-bis(5-methyl-1*H*-pyrazol-3-yl)pyridine (H₂L¹) (48 mg, 0.2 mmol) and AgBF₄ (78 mg, 0.4 mmol) in DMF (8 mL) was stirred at room temperature in the dark for *ca*. two days, then it was filtered through a short plug of Celite. Diethyl ether was slowly evaporated into the resulting clear solution, and colorless crystals suitable for X-ray single diffraction were obtained after several days. Yield: 34.3%. Anal.

calcd for $C_{52}H_{48}Ag_6B_2F_8N_{20};$ C, 35.21; H, 2.73; N, 15.79. Found: C, 35.46; H, 2.82; N, 15.92%. IR data (KBr pellet, cm^-1): 3354 s, 3144 m, 2928 w, 1577 s, 1477 m, 1438 m, 1384 m, 1293 w, 1082 s, 792 s.

 $\label{eq:complex} \begin{array}{l} \textbf{[Ag_6(HL^1)_4](ClO_4)_2} \cdot Et_2O~(7). \quad \mbox{Complex 7 was prepared by an analogous method to that used for 6 from 2,6-bis(5-methyl-1H-pyrazol-3-yl)pyridine~(H_2L^1) (48 mg, 0.2 mmol) and AgClO_4$ (83 mg, 0.4 mmol) in CH_3CN (8 mL). Yield: 42.2\%. Anal. calcd for $C_{56}H_{58}Ag_6C_{12}N_{20}O_9$: C, 35.90; H, 3.12; N, 14.95. Found: C, 35.73; H, 3.21; N, 15.12\%. IR data (KBr pellet, cm^{-1}): 3287 s, 3145 m, 2924 w, 1575 s, 1481 m, 1434 m, 1383 m, 1115 s, 791 s. \end{array}$

X-Ray crystallography

Single-crystal X-ray diffraction data for the complexes were collected at 298(2) K on a Siemens Smart/CCD area-detector diffractometer with MoK α radiation ($\lambda = 0.71073$ Å) using an ω -2 θ scan mode. Unit-cell dimensions were obtained with leastsquares refinement. Data collection and reduction were performed using the SMART and SAINT software.20 All structures were solved by direct methods and refined against F^2 by the fullmatrix least squares techniques.^{21a} All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in their calculated positions. Disordered solvent molecules for 6 and 7 could not be modeled successfully and were removed from their reflection data with SQUEEZE^{21b} (total potential solvent accessible void volume 270.0 Å³ for 6 and solvent accessible void volume 118.00 Å³ for 7). The structure of $H_2L^1 \cdot 0.5H_2O$ was checked for missing symmetry using the ADDSYM function of PLATON,^{21b} and this treatment resulted in a new space group Pbna replacing the original space group Pnna. Its water hydrogen cannot be located in a sensible position and has been left out of the refinement model. Details of the X-ray experiments and crystal data are summarized in Table 1. Selected bond distances and angles are given in Tables 2-4.

Results and discussion

Synthesis

1,1'-(2,6-Pyridyl)bis-1,3-butanedione and ligand 2,6-bis(5-methyl-1*H*-pyrazol-3-yl)pyridine (H_2L^1) were synthesized according to the known procedures. As shown in Scheme 1, 2,6-bis(1'-phenyl-1',3'-dioxopropyl)pyridine was prepared from dimethyl pyridine-2,6-dicarboxylate, acetophenone, and freshly prepared EtONa. 2,6-Bis(5-phenyl-1*H*-pyrazol-3-yl)pyridine (H₂L³) was prepared from the condensation reaction of the 2,6-bis(1'-phenyl-1',3'dioxopropyl)pyridine with hydrazine hydrate. The pincer ligand 2,6-bis(5-methyl-1-isopropyl-1*H*-pyrazol-3-yl)pyridine (L^2) was prepared by using 2,6-bis(5-methyl-1H-pyrazol-3-yl)pyridine, NaH, and 2-bromopropane. All the compounds were characterized by elemental analyses, IR, MS, 1H NMR and 13C NMR spectroscopy. ¹H NMR spectra of 2,6-bis(diketonyl)pyridine compounds are complicated since several tautomers exist in their solutions including bis(keto-enol), enol-enol, bis(keto), and keto-(keto-enol). The broad signals at *ca*. 16 ppm are assignable to the enol OH protons. The resonance signals of acidic NH protons appear at 12.6 and 13.6 ppm for H_2L^1 and H_2L^3 respectively.

Table 1 (Crystallographic da	ta for H ₂ L ¹ .0.5H ₂ C) and complexes 1–	7						
		$H_2L^1 \cdot 0.5 H_2O$	1	2	3	4	5	6	7	
Fo	rmula	$C_{13}H_{14}N_5O_{0.5}$	$\mathrm{C}_{23}\mathrm{H}_{25}\mathrm{AgN}_{8}\mathrm{O}_{4}$	$\mathrm{C}_{19}\mathrm{H}_{25}\mathrm{AgN_6O_3}$	$C_{76}H_{54}Ag_2N_{16}O_4$	$\mathbf{C}_{26}\mathbf{H}_{28}\mathbf{A}\mathbf{g}_{2}\mathbf{N}_{12}\mathbf{O}_{7}$	$\mathbf{C}_{55}\mathbf{H}_{54}\mathbf{A}\mathbf{g}_6\mathbf{N}_{22}\mathbf{O}_7$	$C_{52}H_{47}Ag_6B_2F_8N_{20}$	$C_{52}H_{48}Ag_6C_{12}N_{20}O_8$	
Fw	1	248.29	585.38	493.32	1471.09	836.34	1782.42	1772.94	1799.22	
Ū	yst. syst.	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	
Sp	ace group	Pbna	Pl	$P2_1/c$	$P2_1/c$	$P2_1/n$	Pbcn	C2/c	Pbcn	
a/.	Å	8.226(2)	10.038(4)	23.981(4)	12.863(2)	13.179(2)	23.032(3)	17.219(5)	24.165(6)	
p/.	Å	24.045(6)	11.11(4)	9.1046(17)	21.723(3)	10.539(2)	12.013(2)	23.494(7)	11.793(3)	
c/r	Å	6.477(2)	12.541(4)	21.983(4)	12.774(2)	22.155(3)	22.495(3)	17.751(5)	22.190(5)	
a/	0		78.493(5)							
β/	0		71.280(5)	117.224(3)	115.749(2)	97.296(2)		109.124(4)		
77	0		86.839(6)							
$^{\prime}A$	/ų	1281.1(6)	1298.0(8)	4268.1(14)	3215.1(8)	3052.2(8)	6224.0(16)	6785(4)	6323(3)	
Ζ		4	5	8	2	4	4	4	4	
D/	2 g cm $^{-3}$	1.287	1.498	1.535	1.520	1.820	1.902	1.736	1.890	
Re	fins collected	6085	6827	21 593	16888	15613	31135	17448	31 057	
Inc	1. refins	1146	4510	7455	5660	5371	5497	5968	5507	
$R_{ m in}$		0.0972	0.0315	0.0845	0.0312	0.0249	0.1079	0.0431	0.0973	
ŭ	of on F^2	1.070	1.012	1.024	1.030	1.015	1.032	1.093	0.855	
R_1	, $wR2 \left[I > 2\sigma(I) \right]$	0.0677, 0.1724	0.0502, 0.01115	0.0616, 0.1493	0.0348, 0.0749	0.0346, 0.0829	0.0510, 0.1239	0.0524, 0.1188	0.0549, 0.1392	
R1	, wR2 (all data)	0.1266, 0.2132	0.1024, 0.1340	0.1715, 0.2201	0.0632, 0.0903	0.0481, 0.0921	0.1459, 0.1712	0.1005, 0.1335	0.0984, 0.1638	

As shown in Schemes 2 and 3, the reactions of H_2L^1 in pyridine and L² with silver nitrate in THF in 1 : 1 metal-toligand ratios yielded mononuclear silver pincer complexes with the formulae of $[Ag(H_2L^1)(Py)_2](NO_3) \cdot H_2O(1)$ and $[Ag(L^2)(NO_3)]$ (2), respectively, whereas the reaction of H_2L^1 and silver nitrate in DMF afforded $\{[Ag_2(H_2L^1)_2](NO_3)_2 \cdot H_2O\}_n$ (4). Variation of metal salt and ligand ratios from 1:3 to 1:1 did not change the composition of the products. The resonance signals in the ¹H NMR spectra of 1, 2 and 4 are similar to their corresponding ligands. Reaction of 4 with silver nitrate at a ratio of 1 : 2 afforded $[Ag_{6}(HL^{1})_{4}](NO_{3})_{2}$ (5). $[Ag_{6}(HL^{1})_{4}]X_{2}$ (X = BF₄⁻, 6, or ClO₄⁻, 7) were obtained similarly from the reactions of AgX and H_2L^1 . Variation of the ratio of the two reactants ($X = BF_4^-$ and ClO_4^-) from 1:1 to 3:1 did not change the products, and the reactions are also anion independent. Hydrothermal reaction of AgOAc and H₂L³ at 170 °C yielded complex 3 as a neutral dinuclear silver complex. Complexes 3, 5, 6, and 7 are not soluble in common organic solvents such as CHCl₃, CH₃COCH₃, CH₃CN, or DMSO, and their ¹H NMR spectra were not obtained.

Structures

The structure of $H_2L^1 \cdot 0.5H_2O$ was further characterized from Xray single crystal diffraction (see ESI[‡]). The results show that the two pyrazole rings and the pyridine ring are nearly coplanar.

Single-crystal X-ray analysis of 1 reveals that the asymmetric unit consists of one Ag center, one H_2L^1 , one uncoordinated nitrate, one water molecule and two pyridines (Fig. 1 and Table 2). H_2L^1 acts as a tridentate pincer ligand. The silver centre is pentacoordinated in a distorted bipyramidal geometry to three pyridyl nitrogen atoms and two pyrazolyl nitrogen atoms. The three equatorial Ag-N_{pyridyl} bond distances are in the range of 2.292(4)–2.382(4) Å, which are much shorter than those of the two axial Ag-N_{pyrazolyl} bonds which are 2.457(5) and 2.595(5) Å.

Compound 2 is also a discrete mononuclear complex (see ESI[‡]). The asymmetric unit of 2 is composed of two independent molecules of the formula $[Ag(L^2)(NO_3)]$ with essentially the same structure as 1. As expected, L² also acts as a tridentate pincer ligand. The silver center also displays a distorted bipyramidal geometry and is surrounded by a tridentate L² and a bidentate nitrate anion. The two axial Ag–N_{pyrazolyl} bonds (2.515(8) and 2.592(7) Å) are also much longer than the equatorial Ag–N_{pyridyl} bond (2.299(7) Å).

The asymmetric unit of complex **3** (Fig. 2) consists of one metal ion, one H_2L^3 , and one 6-(5-phenyl-1*H*-pyrazolyl-3-yl)picolinate (HL⁴) anion. Obviously HL⁴ resulted from the *in situ* oxidation of H_2L^3 . The IR spectrum shows a strong stretching band at 1656 cm⁻¹ assignable to the carboxylate group. Although H_2L^3 is potentially pentadentate, it acts as a monodentate ligand by using one of the pyrazolyl nitrogen atoms. HL⁴ acts as a chelating ligand and forms a 5-membered ring with the central silver atom. Thus the silver atom exhibits Y-shaped geometry. The Ag(1)– N(1) and Ag(1)–N(2) bond distances are 2.362(3) and 2.311(3) Å, respectively, which are much longer than that of Ag(1)–N(6) which is 2.196(3) Å. The silver ion interacts very weakly with the carboxylate group with a Ag(1)–O(1) distance of 2.864(2) Å, which is not considered to be bonding.

It is interestingly observed that there is a ligand unsupported Ag-Ag bond in the dimeric complex. The Ag-Ag distance is



Scheme 1 Synthesis of the pincer-like bispyrazolyl ligands and the pincer ligand L².



Scheme 2 Synthesis of 1, 4, 5, 6 and 7.

3.040(1) Å, which is slightly longer than the Ag–Ag separation in metallic silver (2.889 Å), but shorter than the sum of the van der Waals radii (3.44 Å). Although silver–silver interactions are a common feature in silver coordination compounds,^{5,6} only a few examples of ligand unsupported Ag(1) aggregates have been reported, such as dimeric complexes,^{6b,22} trimeric complexes,^{6b} and polymeric chains.^{6a,c,23} The preparation and structural characterization of silver complexes having ligand unsupported Ag–Ag interactions is of importance, because this has been a matter of some debate due to the scarcity of unambiguous experimental evidence of argentophilicity that is stable in the absence of stabilizing ligands. The Ag–Ag contact in this compound is comparable to those of known silver complexes having ligand unsupported Ag–Ag bonds.⁶ The structure of **4** crystallizes in the centrosymmetric space group $P2_1/n$ and features a 1-D infinite chain structure constructed through ligand supported Ag–Ag interactions. A section of the chain is shown in Fig. 3a. The asymmetric unit contains two crystallographically independent Ag atoms, two 2,6-bis(5-methyl-1*H*pyrazol-3-yl)pyridine (H₂L¹) ligands, two uncoordinated nitrate anions and one molecule of water. Both Ag(1) and Ag(2) atoms are coordinated by two pyrazolyl rings from two different H₂L¹ ligands forming a [Ag₂(H₂L¹)₂] unit. The Ag–N bond distances fall into a narrow range of 2.118(3)–2.139(3) Å. The pyrazole rings are slightly twisted from the pyridine rings which is reflected by the dihedral angles ranging from 8.8 to 21.7°. Along the chain every two adjacent Ag atoms are singly bridged by one H₂L¹, thus the compound displays a supramolecular motif consisting



Scheme 3 Synthesis of 2 and 3.



Fig. 1 Molecular structure of $[Ag(H_2L^1)(Py)_2](NO_3) \cdot H_2O$ (1) with H atoms and the water molecule omitted.

of infinite zigzag Ag chains. The neighboring silver ions interact *via* relatively short Ag(1)–Ag(1) bonds [2.889(1) and 2.893(1) Å], which are much shorter than the unsupported one in complex **3**. The silver separations exhibited by silver complexes containing silver–silver bonds which are stabilized by bridging or capping ligands are normally in a wide range of 2.8–3.4 Å.^{5,6} The two independent Ag(1)#2–Ag(2)–Ag(1) and Ag(2)#1–Ag(1)–Ag(2) angles are 136.41(2) and 158.83(2)°, respectively, and the bent metallic axes lead to the extended zigzag chain.

Numerous Ag(I) coordination polymers with bridging ligands²⁴ have been reported; however, silver coordination polymers with infinite metallic backbones are very rare. One family of these



1		2	
Ag(1)–N(6)	2.292(4)	Ag(1)–N(1)	2.299(7)
Ag(1)-N(7)	2.330(5)	Ag(1)-N(2)	2.592(7)
Ag(1)-N(1)	2.382(4)	Ag(1)-N(4)	2.515(8)
Ag(1)-N(2)	2.457(5)	Ag(1)-O(1)	2.333(8)
Ag(1)-N(4)	2.595(5)	Ag(1)–O(2)	2.678(11)
N(6)–Ag(1)–N(7)	108.76(15)	N(1)-Ag(1)-O(1)	146.4(3)
N(6) - Ag(1) - N(1)	130.21(14)	N(1)-Ag(1)-N(4)	70.0(2)
N(7)-Ag(1)-N(1)	120.34(13)	O(1) - Ag(1) - N(4)	122.7(3)
N(6) - Ag(1) - N(2)	110.77(16)	N(1) - Ag(1) - N(2)	68.7(2)
N(7) - Ag(1) - N(2)	101.28(17)	O(1) - Ag(1) - N(2)	99.7(3)
N(1) - Ag(1) - N(2)	68.81(15)	N(4) - Ag(1) - N(2)	136.4(2)
N(6) - Ag(1) - N(4)	98.12(17)	N(1) - Ag(1) - O(2)	164.6(3)
N(7) - Ag(1) - N(4)	99.95(17)	O(1) - Ag(1) - O(2)	48.5(3)
N(1)-Ag(1)-N(4)	67.07(15)	N(4) - Ag(1) - O(2)	106.0(3)
N(2)-Ag(1)-N(4)	135.88(14)	N(2) - Ag(1) - O(2)	110.1(3)



Fig. 2 Molecular structure of $[Ag_2(H_2L^3)_2(HL^4)_2]$ (3) with H atoms omitted for clarity.



Fig. 3 (a) ORTEP drawing of a segment of the infinite Ag chain of $\{[Ag_2(H_2L^1)_2](NO_3)_2 \cdot H_2O\}_n$ (4). (b) Arrangement of the infinite chains along the crystallographic *c* axis.

Table 3Selected bond lengths (Å) and angles (°) of 3 and 4

3 ^{<i>a</i>}		4 ^b	
Ag(1) - Ag(1) #1 Ag(1) - N(6)	3.040(1)	$\begin{array}{c} Ag(1) - Ag(2) \# 1 \\ Ag(1) - Ag(2) \end{array}$	2.889(1) 2.893(1)
Ag(1) - N(2) Ag(1) - N(1)	2.311(3) 2.362(3)	Ag(1) - N(2) Ag(1) - N(9) # 1 Ag(1) - N(4)	2.118(3) 2.125(3)
Ag(1)–O(1)	2.864(2)	Ag(2)–N(7) Ag(2)–N(2)	2.125(3) 2.139(3)
N(6)-Ag(1)-N(2) N(6)-Ag(1)-N(1) N(2)-Ag(1)-N(1) N(6)-Ag(1)-Ag(1)#1 N(2)-Ag(1)-Ag(1)#1 N(1)-Ag(1)-Ag(1)#1	152.10(10) 131.99(10) 71.26(9) 116.93(7) 63.61(7) 99.62(6)	$\begin{array}{l} N(9)\#1-Ag(1)-N(4)\\ N(9)\#1-Ag(1)-Ag(2)\#1\\ N(4)-Ag(1)-Ag(2)\#1\\ N(9)\#1-Ag(1)-Ag(2)\\ N(4)-Ag(1)-Ag(2)\\ N(7)-Ag(2)-N(2)\\ N(7)-Ag(2)-Ag(1)\#2\\ N(2)-Ag(2)-Ag(1)\#2\\ N(2)-Ag(2)-Ag(1)\\ N(2)-Ag(2)-Ag(1)\\ N(2)-Ag(2)-Ag(1)\\ Ag(2)\#1-Ag(1)-Ag(2)\\ Ag(1)\#2-Ag(2)-Ag(1)\\ \end{array}$	$\begin{array}{c} 169.97(13)\\ 101.02(9)\\ 82.16(10)\\ 89.66(9)\\ 90.47(9)\\ 144.87(12)\\ 97.45(9)\\ 98.78(9)\\ 100.73(9)\\ 88.48(9)\\ 158.83(2)\\ 136.41(2) \end{array}$

^{*a*} Symmetry code: #1 - x + 1, -y, -z + 2. ^{*b*} Symmetry codes: #1 - x + 3/2, y - 1/2, -z + 3/2; #2 - x + 3/2, y + 1/2, -z + 3/2.

compounds are the silver complexes stabilized by 4'-thiomethyl-2,2':6',2"-terpyridine with short silver–silver contacts (3.03–3.15 Å),²⁵ and another one is $[Ag(\mu-pz)]_n^{131}$ with the Ag–Ag separation of 3.40 Å. Such compounds are potentially useful as nanowire materials.

The adjacent chains are connected by weak hydrogen bonding involving nitrate anions, water molecules, and the NH groups of the pyrazolyl rings. Two nitrate anions and two water molecules form four-membered rings *via* weak hydrogen bonds. These connections generate a 2-D network structure (Fig. 3b).

Although hexanuclear silver clusters **5**, **6**, and **7** have the similar formula of $[Ag_6(HL^1)_4]X_2$ (X = NO₃⁻, **5**; BF₄⁻, **6**; and ClO₄⁻, **7**), the three complexes crystallize in different space groups. Complexes **5** and **7** crystallize in an orthorhombic space group *Pbcn*, while complex **6** crystallizes in a monoclinic space group C2/c. The molecular structure of the cationic complex of **5** is depicted in Fig. 4a, and for those of **6** and **7**, see the ESI‡. Some important bond distances and angles of these are summarized in Table 4.

The asymmetric unit of **5** consists of half of the molecule with three independent Ag(I) centers, one nitrate anion, and one acetone molecule. There are two mono-deprotonated HL^1 ligands



Fig. 4 (a) Molecular structure of the cation of $[Ag_6(HL^1)_4](NO_3)_2$ (5) with H atoms omitted for clarity. (b) A simplified diagram showing the coordination geometry of the cation of $[Ag_6(HL^1)_4](NO_3)_2$ (5).

in the asymmetric unit, and both act as anionic tridentate bridging ligands with the nitrogen atoms of the pyridyl rings uncoordinated. The coordination around each Ag ion is made up of two pyrazolyl nitrogen atoms in nearly linear geometry with an average N–Ag–N angle of 170° . The Ag–N bond distances ranging from 2.081(9) to 2.126(9) Å are observed for the three independent silver ions. Because of deprotonation and complexation, the ligands become twisted and the dihedral angles between pyrazole and pyridine rings are $10.9-21.5^{\circ}$.

The silver cations in the hexanuclear core are held together with five Ag–Ag bonds through four mono-deprotonated HL¹ ligands (Fig. 4b). Three independent silver atoms are bridged by two HL¹ ligands, forming a nearly linear trimetallic chain with Ag–Ag separations of 2.905(1) and 2.908(1) Å, and an Ag–Ag– Ag angle of 167.01(4)°. Such a connection mode is quite similar to the trimetallic segment in the infinite chain complex **4**. The central silver ions of the two symmetrically related trimetallic units interact each other *via* an argentophilic attraction with a relatively short Ag(1)–Ag(1A) bond at 2.874(1) Å. In hexanuclear silver complex **6**, six Ag ions are held together with six Ag–Ag bonds. Two trimetallic units in complex **6** are connected by two Ag–Ag bonds. The distances of the three pairs of symmetrically related Ag ions (Ag1–Ag1A, Ag2–Ag2A, and Ag3–Ag3A) are 2.893(1), 3.411(2), and 3.333(2) Å, respectively. The interaction of the two central silver ions (Ag1 and Ag1A) is much stronger than those of others,

The structure of 7 consists of essentially the same Ag_6 core as 5. The separation of the two symmetrically related central ions (Ag1–Ag1A) is of 2.897(1) Å, whereas the Ag–Ag distances within the linear trimetallic chain are 2.916(1) and 2.938(1) Å, which are slightly longer than those of 5.

So far several hexanuclear silver clusters are known, displaying either a "cyclohexane-chair" conformation^{26a} or an octahedron arrangement.^{26b-e} The two linear trimetallic chains of **5–7** are arranged in a crossed fashion. This conformation for Ag₆ clusters is novel and not well modelled. These complexes also represent the first hexanuclear clusters supported by pyrazolate ligands.

The silver–silver distances in the known complexes cover a wide range depending on whether the Ag–Ag bonds are ligand bridged or ligand unsupported, the donating atoms, and the coordination geometry. For instance, Ag–Ag contacts of 2.75 Å in a trimetallic Ag(1) complex stabilized by N-heterocyclic carbenes^{27a} and 3.31 and 3.02 Å in a 3-cyanopyridine supported tetranuclear complex with linearly arranged array^{27b} were observed. The Ag–Ag contacts in these complexes are also consistent with those of our recently reported silver clusters containing multidentate N-heterocyclic carbene ligands.^{18e,f}

Emission properties

The solid-state photoluminescent spectra of complexes 3–7 and their corresponding ligands at room temperature have been measured, respectively. All the silver complexes and the ligands are intensely emissive. The solid-state emission spectra of H_2L^1 and H_2L^3 show similar single sharp bands at ~366 nm upon excitation at 338 nm. Complexes 3–7 have similar solid-state emission spectra (for emission data, see ESI‡); the solid-state excitation and emission spectra of 3, 4, and 5 are shown in Fig. 5. The unusual multiple emission bands at ~406, ~440, ~453, ~470, and ~493 nm were found upon excitation at 220 nm. The low-energy bands at around 520 nm for 3–5 were also observed as shoulder peaks in their emission spectra.

This multiple-band emission could suggest the presence of different weakly coupled relaxation channels in these complexes, as found in other compounds containing closed shell d¹⁰ metal centres.^{12,26b,28a} Vibronically structured bands with a spacing between the local maxima of the emission bands of about 1450 cm⁻¹, characteristic of the v(C=N) or v(N=N) stretch,^{14f} were also observed. The appearance of vibrational progressions is suggestive of involvement of the pyrazolate ligands in the emission process. The fact that the ligands H₂L¹ and H₂L³ are luminescent and all the silver complexes exhibit high energy emission bands at almost the same positions suggests that these emissions probably originate from the same electronic states assignable to intraligand (IL) transition and MLCT (d– π) transition.

It has been reported that for $[Ag_2(L^2)(ClO_4)_2]$ (L = 4,5diazospirobifluorene) the origin of the fluorescence at *ca*. 510 nm can be attributed to the coupling of a MLCT transition and a

Table 4Selected bond lengths (Å) and angles (°) of 5, 6, and 7

5 ^{<i>a</i>}		6 ^{<i>b</i>}		7 ^c		
$\begin{array}{l} Ag(1)-Ag(1)\#1\\ Ag(1)-Ag(2)\\ Ag(1)-Ag(3)\\ Ag(1)-N(4)\\ Ag(1)-N(7)\#1\\ Ag(2)-N(5)\#1\\ Ag(2)-N(2)\\ Ag(3)-N(8)\\ Ag(3)-N(8)\\ Ag(3)-N(9)\#1\\ \end{array}$	$\begin{array}{c} 2.874(1)\\ 2.908(1)\\ 2.905(1)\\ 2.105(8)\\ 2.126(9)\\ 2.081(9)\\ 2.092(9)\\ 2.114(9)\\ 2.092(9)\\ 2.110(11)\\ \end{array}$	$\begin{array}{c} Ag(1)-Ag(1)\#1\\ Ag(1)-Ag(2)\\ Ag(1)-Ag(3)\\ Ag(3)-Ag(3)\#1\\ Ag(1)-N(2)\\ Ag(1)-N(7)\\ Ag(2)-N(8)\#1\\ Ag(2)-N(4)\\ Ag(3)-N(3)\#1\\ Ag(3)-N(9)\\ \end{array}$ $\begin{array}{c} Ag(2)-Ag(1)-Ag(3)\\ Ag(2)-Ag(1)-Ag(1)\#1\\ Ag(1)\#1-Ag(1)-Ag(3)\\ Ag(2)-Ag(1)-Ag(1)\#1\\ N(2)-Ag(1)-Ag(2)\\ N(7)-Ag(1)-Ag(2)\\ N(7)-Ag(1)-Ag(2)\\ N(7)-Ag(1)-Ag(2)\\ N(7)-Ag(1)-Ag(3)\\ N(7)-Ag(1)-Ag(3)\\ N(7)-Ag(1)-Ag(3)\\ N(8)\#1-Ag(2)-N(4)\\ N(8)\#1-Ag(2)-N(4)\\ N(8)\#1-Ag(2)-Ag(1)\\ N(3)\#1-Ag(3)-N(9)\\ N(3)\#1-Ag(3)-Ag(3)\\ N(9)-Ag(1)-Ag(1)\\ N(3)\#1-Ag(3)-Ag(3)\\ N(9)-Ag(3)-Ag(3)\\ N(9)-Ag(3)-Ag(3)\\ N(3)\#1-Ag(3)-Ag(3)\\ N(3)\#1\\ N(3$	$\begin{array}{c} 2.893(1)\\ 2.891(1)\\ 2.918(1)\\ 3.333(2)\\ 2.120(6)\\ 2.133(6)\\ 2.082(7)\\ 2.110(7)\\ 2.084(6)\\ 2.119(7)\\ 167.34(3)\\ 84.296(19)\\ 83.04(2)\\ 75.75(2)\\ 176.4(3)\\ 98.44(16)\\ 82.91(17)\\ 92.48(17)\\ 90.96(18)\\ 82.10(16)\\ 97.31(17)\\ 173.6(3)\\ 95.96(18)\\ 89.94(18)\\ 171.9(3)\\ 96.66(18)\\ 91.13(18)\\ 75.45(18)\\ \end{array}$	$\begin{array}{c} Ag(1)-Ag(1)\#1\\ Ag(1)-Ag(2)\\ Ag(1)-Ag(3)\\ Ag(1)-N(2)\\ Ag(1)-N(7)\\ Ag(2)-N(3)\#1\\ Ag(2)-N(4)\\ Ag(3)-N(8)\#1\\ Ag(3)-N(9)\\\\ \end{array}$	$\begin{array}{c} 2.897(1)\\ 2.938(1)\\ 2.938(1)\\ 2.916(1)\\ 2.098(6)\\ 2.119(7)\\ 2.081(7)\\ 2.087(7)\\ 2.124(7)\\ 2.087(7)\\ 2.134(7)\\ \end{array}$	
		11() 116() 116()#1	101.0(2)			

^{*a*} Symmetry code: #1 - x + 1, y, -z + 1/2. ^{*b*} Symmetry code: #1 - x + 2, y, -z + 1/2. ^{*c*} Symmetry code: #1 - x + 1, y, -z + 1/2.



Fig. 5 Solid-state emission (right) and excitation (left) spectra of **3**, **4** and **5**.

metal-centered transition (Ag¹, ds/dp) disturbed by argentophilic interactions.^{28b} The nature of the low-energy emission bands at around 520 nm of **3**, **4**, and **5** may also be attributed to metal-centered processes.

Conclusions

Through ligand functionalities and the argentophilic attraction some new silver architectures have been made. Mononuclear pincer complexes could be prepared from both pincer-like ligands H_2L^1 and L^2 . Under different reaction conditions, three hexamer clusters and a 1-D infinite Ag chain compound are also obtained with the pincer-like ligand H_2L^1 . The hexamer clusters are the first examples supported by pyrazolate ligands. The infinite Ag chain compound featuring Ag(1)–Ag(1) interactions have Ag–Ag distances equal to the Ag–Ag separation in metallic silver. Under hydrothermal conditions, reaction of AgOAc with H_2L^3 yielded a dinuclear neutral complex having a ligand unsupported argentophilic interaction, which is relatively rare. In these complexes, the pyridine linked bis(pyrazolyl) ligands are bonded in monodentate, bidentate, or tridentate anionic fashions, respectively. In addition, these oligomeric and polymeric complexes are intensely emissive, which are potentially luminescent materials. Further studies to clarify the nature of the emissions are required.

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Notes and references

 (a) K. Campbell, C. J. Kuehl, M. J. Ferguson, P. J. Stang and R. R. Tykwinski, J. Am. Chem. Soc., 2002, **124**, 7266; (b) G. S. Papaefstathiou and L. R. MacGillivray, Angew. Chem., Int. Ed., 2002, **41**, 2070; (c) J. C. Noveron, M. S. Lah, R. E. Del Sesto, A. M. Arif, J. S. Miller and P. J. Stang, J. Am. Chem. Soc., 2002, **124**, 6613; (d) J. Stahl, J. C. Bohling, E. B. Bauer, T. B. Peters, W. Mohr, J. M. Martin-Alvarez, F. Hampel and J. A. Gladysz, *Angew. Chem., Int. Ed.*, 2002, **41**, 1872; (e) E. J. Fernandez, P. G. Jones, A. Laguna, J. M. Lopez-de-Luzuriaga, M. Monge, J. Perez and M. E. Olmos, *Inorg. Chem.*, 2002, **41**, 1056.

- 2 (a) A. Hamel, N. W. Mitzel and H. Schmidbaur, J. Am. Chem. Soc., 2001, **123**, 5106; (b) T. Grimes, M. A. Omary, H. V. R. Dias and T. R. Cundari, J. Phys. Chem. A, 2006, **110**, 5823; (c) A. Codina, E. J. Fernandez, P. G. Jones, A. Laguna, J. M. Lopez-de-Luzuriaga, M. Monge, M. E. J. Perez and M. A. Rodriguez, J. Am. Chem. Soc., 2002, **124**, 6781.
- 3 (a) P. Pyykkö, Chem. Rev., 1997, 97, 597; (b) S.-G. Wang and W. H. E. Schwarz, J. Am. Chem. Soc., 2004, 126, 1266.
- 4 (a) R. E. Bachman, M. S. Fioritto, S. K. Fetics and T. M. Cocker, J. Am. Chem. Soc., 2001, 123, 5376; (b) B.-C. Tzeng, Y.-C. Huang, W.-M. Wu, S.-Y. Lee, G.-H. Lee and S.-M. Peng, Cryst. Growth Des., 2004, 4, 63; (c) R.-Y. Liau, A. Schier and H. Schmidbaur, Organometallics, 2003, 22, 3199; (d) C. Yang, M. Messerschmidt, P. Coppens and M. A. Omary, Inorg. Chem., 2006, 45, 6592; (e) S.-Y. Yu, Z.-X. Zhang, E. C.-C. Cheng, Y.-Z. Li, V. W.-W. Yam, H.-P. Huang and R. Zhang, J. Am. Chem. Soc., 2005, 127, 17994; (f) U. Siemeling, D. Rother, C. Bruhn, H. Fink, T. Weidner, F. Trager, A. Rothenberger, D. Fenske, A. Priebe, J. Maurer and R. Winter, J. Am. Chem. Soc., 2005, 127, 1102.
- 5 (a) C.-M. Che, M.-C. Tse, M. C. W. Chan, K.-K. Cheung, D. L. Phillips and K.-H. Leung, J. Am. Chem. Soc., 2000, **122**, 2464; (b) Q.-M. Wang and T. C. W. Mak, J. Am. Chem. Soc., 2001, **123**, 7594; (c) X.-C. Huang, J.-P. Zhang and X.-M. Chen, Cryst. Growth Des., 2006, **6**, 1194; (d) G.-C. Guo, G.-D. Zhou, Q.-G. Wang and T. C. W. Mak, Angew. Chem., Int. Ed., 1998, **37**, 630; (e) G.-C. Guo and T. C. W. Mak, Angew. Chem., Int. Ed., 1998, **37**, 3183; (f) G.-C. Guo, G.-D. Zhou and T. C. W. Mak, J. Am. Chem. Soc., 1999, **121**, 3136; (g) Q.-M. Wang and T. C. W. Mak, Inorg. Chem., 2003, **42**, 1637.
- 6 (a) M. A. Omary, T. R. Webb, Z. Assefa, G. E. Shankle and H. H. Patterson, *Inorg. Chem.*, 1998, **37**, 1380; (b) K. Singh, J. R. Long and P. Stavropoulos, *J. Am. Chem. Soc.*, 1997, **119**, 2942; (c) X. Liu, G.-C. Guo, M.-L. Fu, X.-H. Liu, M.-S. Wang and J.-S. Huang, *Inorg. Chem.*, 2006, **45**, 3679; (d) Y. Kim and K. J. Seff, *J. Am. Chem. Soc.*, 1978, **100**, 175; (e) M. L. Tong, X. M. Chen, B. H. Ye and L. N. Ji, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 2237; (f) O. Kristiansson, *Inorg. Chem.*, 2001, **40**, 5058.
- 7 (a) E. J. Fernandez, A. Launa, J. M. Lopez-de-Luzuriaga, M. Monge, M. E. Olmos and R. C. Puelles, J. Phys. Chem. B, 2005, 109, 20652;
 (b) A. A. Mohamed, A. Burini and J. P. Fackler, Jr., J. Am. Chem. Soc., 2005, 127, 5012;
 (c) A. A. Mohamed, R. Galassi, F. Papa, A. Burini and J. P. Fackler, Jr., Inorg. Chem., 2006, 45, 7770;
 (d) Q.-H. Wei, L.-Y. Zhang, G.-Q. Yin, L.-X. Shi and Z.-N. Chen, J. Am. Chem. Soc., 2004, 126, 9940.
- 8 (a) A. Buljan, M. Llunell, E. Ruiz and P. Alemany, *Chem. Mater.*, 2001, **13**, 338; (b) T. Sugiura, H. Yoshikawa and K. Awaga, *Inorg. Chem.*, 2006, **45**, 7584; (c) X.-M. Zhang, Z.-M. Hao and H.-S. Wu, *Inorg. Chem.*, 2005, **44**, 7301.
- 9 (a) V. J. Catalano and M. A. Malwitz, J. Am. Chem. Soc., 2004, 126, 6560; (b) S. S. Tang, C. P. Chang, I. J. B. Lin, L. S. Liou and J. C. Wang, *Inorg. Chem.*, 1997, 36, 2294.
- 10 L. Dobrzańska, H. G. Raubenheimer and L. J. Harbour, Chem. Commun., 2005, 5050.
- 11 G. La Monica and G. A. Ardizzoia, Prog. Inorg. Chem., 1997, 46, 151.
- 12 M. A. Omary, M. A. Rawashdeh-Omary, H. V. K. Diyabalanage and H. V. R. Dias, *Inorg. Chem.*, 2003, 42, 8612.
- (a) R. G. Raptis and J. P. Fackler, Jr., *Inorg. Chem.*, 1988, 27, 4179;
 (b) G. A. Ardizzoia, S. Cenini, G. La Monica, N. Masciocchi, A. Maspero and M. Moret, *Inorg. Chem.*, 1998, 37, 4284; (c) H. V. R. Dias, H. V. K. Diyabalanage, M. A. Rawashdeh-Omary, M. A. Franzman and M. A. Omary, *J. Am. Chem. Soc.*, 2003, 125, 1207; (d) M. Enomoto, A. Kishimura and T. Aida, *J. Am. Chem. Soc.*, 2001, 123, 5608; (e) H. V. R. Dias, H. V. K. Diyabalanage, M. G. Eldabaja, O. Elbjeirami, M. A. Rawashdeh-Omary and M. A. Omary, *J. Am. Chem. Soc.*, 2005, 127, 7489; (f) M. M. Olmstead, F Jiang, S Attar and A. L. Balch, *J. Am. Chem. Soc.*, 2001, 123, 3260; (g) G Yang and R. G. Raptis, *Inorg. Chem.*, 2003, 42, 261; (h) H. V. R Dias, H. V. K. Diyabalanage and C. S. P. Gamage, *Chem. Commun.*, 2005, 1619; (i) A. Kishimura, T.

Yamashita and T. Aida, J. Am. Chem. Soc., 2005, **127**, 179; (*j*) F Fages, Angew. Chem., Int. Ed., 2006, **45**, 1680; (*k*) H. H. Murray, R. G. Raptis and J. P. Fackler, Jr., Inorg. Chem., 1988, **27**, 26; (*l*) N. Masciocchi, M. Moret, P. Cairati, A. Sironi, G. A. Ardizzoia and G. La Monica, J. Am. Chem. Soc., 1994, **116**, 7668; (*m*) M. A. Omary, M. A. Rawashdeh-Omary, M. W. A Gonser, O Elbjeirami, T Grimes and T. R. Cundari, Inorg. Chem., 2005, **44**, 8200; (*n*) H. V. R Dias and C. S. P. Gamage, Angew. Chem., Int. Ed., 2007, **46**, 2192.

- 14 (a) G. A. Ardizzoia, S. Cenini, G. La Monica, N. Masciocchi and M. Moret, *Inorg. Chem.*, 1994, 33, 1458; (b) K. Singh, J. R. Long and P. Stavropoulos, *Inorg. Chem.*, 1998, 37, 1073; (c) A. Maspero, S. Brenna, S. Galli and A. Penoni, *J. Organomet. Chem.*, 2003, 672, 123; (d) K. Fujisawa, Y. Ishikawa, Y. Miyashita and K.-i. Okamoto, *Chem. Lett.*, 2004, 33, 66; (e) G. Yang and R. G. Raptis, *Inorg. Chim. Acta*, 2003, 352, 98; (f) A. A. Mohamed, J. M. López-de-Luzuriaga and J. P. Fackler, Jr., *J. Cluster Sci.*, 2003, 14, 61; (g) H. E. Abdou, A. A. Mohamed and J. P. Fackler, Jr., *Inorg. Chem.*, 2007, 360, 2503.
- 15 R. G. Raptis, H. H. Murray and J. P. Fackler, Jr., J. Chem. Soc., Chem. Commun., 1987, 737.
- 16 S.-Z. Zhan, D. Li, X.-P. Zhou and X.-H. Zhou, *Inorg. Chem.*, 2006, **45**, 9163.
- 17 (a) J.-P. Zhang, S. Horike and S. Kitagawa, Angew. Chem., Int. Ed., 2007, **46**, 889; (b) J. He, Y.-G. Yin, T. Wu, D. Li and X.-C. Huang, Chem. Commun., 2006, 2845.
- 18 (a) F. Liu, W. Chen and D. Wang, *Dalton Trans.*, 2006, 3445; (b) W. Chen, F. Liu, K. Matsumoto, J. Autschbach, B. Le Guennic, T. Ziegler, M. Maliarik and J. Glaser, *Inorg. Chem.*, 2006, **45**, 4526; (c) W. Chen, F. Liu, D. Xu, K. Matsumoto, S. Kishi and M. Kato, *Inorg. Chem.*, 2006, **45**, 5552; (d) F. Liu, W. Chen and D. Wang, *Dalton Trans.*, 2006, 3015; (e) Y. Zhou and W. Chen, *Organometallics*, 2007, **26**, 2742; (f) B. Liu, W. Chen and S. Jin, *Organometallics*, 2007, **26**, 3660.
- (a) D. E. Fenton, J. R. Tate, U. Casellato, S. Tamburini, P. A. Vigato and M. Vidali, *Inorg. Chim. Acta*, 1984, 83, 23; (b) M. Gal, G. Tarrago, P. J. Steel and C. Marzin, *New J. Chem.*, 1985, 9, 617; (c) Y. Lin and S. A. Lang, *J. Heterocycl. Chem.*, 1977, 14, 345.
- 20 SMART-CCD Software, version 4.05, Siemens Analytical X-ray Instruments, Madison, WI, 1996.
- 21 (a) G. M. Sheldrick, SHELXS-97 and SHELXL-97, Program for Xray Crystal Structure Refinement, University of Göttingen, Germany, 1997; (b) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, University of Utrecht, The Netherlands, 1998.
- (a) M.-L. Tong, X.-M. Chen and B.-H. Ye, *Inorg. Chem.*, 1998, 37, 5278;
 (b) N. Masciocchi, M. Moret, P. Cairati, A. Sironi, G. A. Ardizzoia and G. La Monica, *J. Chem. Soc., Dalton Trans.*, 1995, 1671.
- 23 X.-M. Ming and T. C. W. Mak, J. Chem. Soc., Dalton Trans., 1991, 3253.
- 24 (a) M. A. M. Abu-Youssef, V. Langer and L. Ohrstrom, *Dalton Trans.*, 2006, 2542; (b) D. B. Cordes, L. R. Hanton and M. D. Spicer, *Inorg. Chem.*, 2006, **45**, 7651; (c) R. Horikoshi, T. Mochida and H. Moriyama, *Inorg. Chem.*, 2002, **41**, 3017; (d) K. Nomiya, S. Takahashi, R. Noguchi, S. Nemoto, T. Takayama and M. Oda, *Inorg. Chem.*, 2000, **39**, 3301; (e) H. C. Wu, P. Thanasekaran, C. H. Tsai, J. Y. Wu, S. M. Huang, Y. S. Wen and K. L. Lu, *Inorg. Chem.*, 2006, **45**, 295.
- 25 M. J. Hannon, C. L. Painting, E. A. Plummer, L. J. Childs and N. W. Alcock, *Chem.-Eur. J.*, 2002, 8, 2226.
- 26 (a) I. Tsyba, B. B. K. Mui, R. Bau, R. Noguchi and K. Nomiya, *Inorg. Chem.*, 2003, 42, 8028; (b) A. Castineiras, I. Garcia-Santos, S. Dehnen and P. Sevillano, *Polyhedron*, 2006, 25, 3653; (c) E. Block, M. Gemon, H. Kang and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1988, 27, 1342; (d) P. A. Perez-Lourido, J. A. Garcia-Vazquez, J. Romero, M. S. Louro, A. Sousa, Q. Chen, Y. Chang and J. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1996, 2047; (e) F. Sabin, C. K. Ryu, P. C. Ford and A. Vogler, *Inorg. Chem.*, 1992, 31, 1941.
- 27 (a) V. J. Catalano and M. A. Malwitz, *Inorg. Chem.*, 2003, 42, 5483;
 (b) P. Lin, R. A. Henderson, R. W. Harrington, W. Clegg, C. Wu and X. Wu, *Inorg. Chem.*, 2004, 43, 181.
- 28 (a) P. Sevillano, O. Fuhr, M. Kattannek, P. Nava, O. Hampe, S. Lebedkin, R. Ahlrichs, D. Fenske and M. M. Kappes, *Angew. Chem.*, *Int. Ed.*, 2006, **45**, 3702; (b) C.-C. Wang, C.-H. Yang, S.-M. Tseng, S.-Y. Lin, T.-Y. Wu, M.-R. Fuh, G.-H. Lee, K.-T. Wong, R.-T. Chen, Y.-M. Cheng and P.-T. Chou, *Inorg. Chem.*, 2004, **43**, 4781.