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Structure and photoluminescence of
silver(I) trinuclear halopyrazolato complexes

Yui Morishima^a, David James Young^b, Kiyoshi Fujisawa^{a*}

^a Department of Chemistry, Ibaraki University, Mito
310-8512, Japan

^b School of Science, Monash University, 47500 Bandar Sunway,
Selangor D.E., Malaysia

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* Corresponding author :

Kiyoshi Fujisawa: Department of Chemistry, Ibaraki University, Mito 310-8512, Japan.

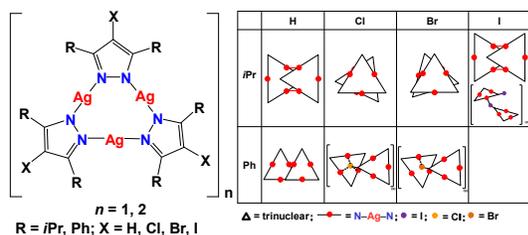
E-mail: kiyoshif@mx.ibaraki.ac.jp

† Electronic supplementary information (ESI) available: X-ray crystallographic and refinement data for complexes [Ag(L1Cl)]₂, [Ag(L1I)], [Ag(L1D)]₂, and [Ag(L5Cl)] (Table S1); experimental details for [Ag(L1Br)]₂, [Ag(L5H)]₂, and [Ag(L5Br)]; IR, far-IR and Raman spectra for L1 and L5 complexes (Fig. S1); emission wavelengths at variable temperatures (Table S2). CCDC 993077, 993079, 993080, and 993082. For ESI and crystallographic data in CIF and other electronic formats see DOI: 101039/***.

Abstract

Five halogen substituted pyrazolates, 4-chloro-3,5-diisopropylpyrazole (4-Cl-3,5-*i*Pr₂pzH), 4-bromo-3,5-diisopropylpyrazole (4-Br-3,5-*i*Pr₂pzH), 4-iodo-3,5-diisopropylpyrazole (4-I-3,5-*i*Pr₂pzH), 4-chloro-3,5-diphenylpyrazole (4-Cl-3,5-Ph₂pzH), and 4-bromo-3,5-diphenylpyrazole (4-Br-3,5-Ph₂pzH) were conveniently prepared by halogenation of the appropriate pyrazoles with *N*-halosuccinimides (NXS) (X = Cl, Br, and I) followed by complexation of the pyrazolate anions with silver(I) nitrate. Single crystal X-ray analysis revealed either dimeric trinuclear {[Ag(μ-4-X-3,5-R₂pz)]₃}₂ (R = *i*Pr, X = Cl, Br, and I) or trinuclear [Ag(μ-4-X-3,5-R₂pz)]₃ (R = *i*Pr, X = I; R = Ph, X = Cl, R = Ph, X = Br) structures, the latter held together with argentophilic interactions (Ag⋯Ag interactions) that could also be observed in the Raman spectra. The electronegativity of the halogen substituent could be correlated with the strength of the Ag⋯Ag interaction and the wavelength of solid-state photoluminescence. All complexes were emissive on UV irradiation at low temperatures, with the colour of emission from the diisopropyl substituted analogues red shifted by the halogens in the order Cl (red) > Br (orange) > I (yellow). Emission from the diphenyl substituted analogues was dominated by the extended aromatic system and was largely invariant to the halogens.

TOC



Graphical abstract

Luminescent silver(I) complexes of substituted halopyrazolate anions are either dimeric trinuclear or trinuclear structures held together with weak interactions.

Introduction

Metal pyrazolato complexes have been studied for over 100 years.^{1,2} Early studies suggested that silver(I) pyrazolate existed as a polymeric 1D chain $[\text{Ag}(\text{pz})]_n$ (pz = pyrazolate anion, $\text{C}_3\text{H}_3\text{N}_2^-$).³ Subsequent *ab-initio* powder XRD evidence indicated that silver(I) pyrazolate could exist as either a coordination polymer $[\text{Ag}(\text{pz})]_n$ with an intermolecular $\text{Ag}\cdots\text{Ag}$ distance of 3.27 Å or as a dimeric trinuclear $\{[\text{Ag}(\text{pz})]_3\}_2$ structure with an intermolecular $\text{Ag}\cdots\text{Ag}$ distance of 3.43 Å, depending on the method of synthesis.⁴ The pyrazolate ligand bridges silver(I) ions in a N–Ag–N linear coordination mode,^{1,5} with additional stabilization of the silver(I) ions provided by argentophilic interactions ($\text{Ag}\cdots\text{Ag}$ interactions).⁶

Silver(I) pyrazolato complexes form polynuclear, trinuclear, and tetranuclear structures, depending on the method of synthesis and the nature of the substituents on the pyrazolate ring (Fig. 1).^{7–9} The first single crystal X ray diffraction characterization of a dimeric trinuclear complex with the 3,5-diphenylpyrazolate ligand ($\{[\text{Ag}(\mu\text{-}3,5\text{-Ph}_2\text{pz})]_3\}_2$) was reported by Fackler and co-workers in 1989.¹⁰ Since then, many silver(I) pyrazolato structures have been characterized (See Table 1).^{9–21} The dimeric trinuclear (hexanuclear) structure is stabilized by intermolecular argentophilic interaction(s).^{4,9–13,15–17,19–21}

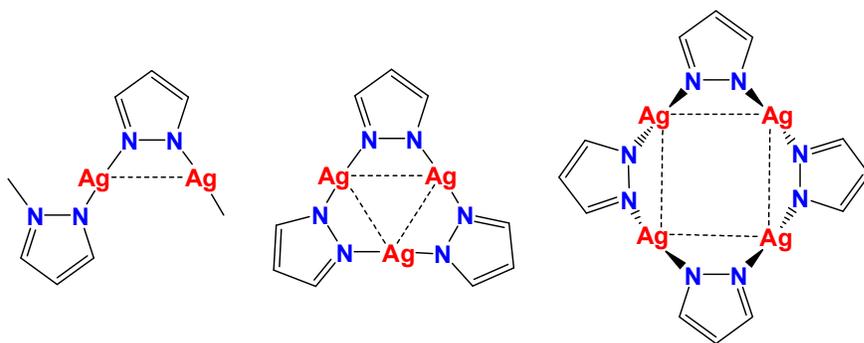


Fig. 1 Different structures of silver(I) pyrazolato complexes; left: polynuclear, center: trinuclear, right: tetranuclear.^{7–9}

The silver(I) 3,5-diisopropylpyrazolato complex ($\{[\text{Ag}(\mu\text{-}3,5\text{-}i\text{Pr}_2\text{pz})]_3\}_2$) displays two intermolecular argentophilic interactions (Fig. 2, left).¹¹ Introducing a bromine at the 4-position of the pyrazolate ligand yields the silver(I) 4-bromo-3,5-diisopropylpyrazolato complex ($\{[\text{Ag}(\mu\text{-}4\text{-Br-}3,5\text{-}i\text{Pr}_2\text{pz})]_3\}_2$) with three intermolecular argentophilic interactions (Fig. 2, middle).¹¹

Nitration of the 4-position of the pyrazolate ion and subsequent complexation yields the trinuclear silver(I) 3,5-diisopropyl-4-nitropyrazolato complex ($[\text{Ag}(\mu\text{-4-NO}_2\text{-3,5-}i\text{Pr}_2\text{pz})]_3$) without any intermolecular argentophilic interactions.¹¹ In this case, the oxygen atoms of the NO_2 coordinate with an adjacent silver(I) ion, forming a dimeric structure (Fig. 2, right).

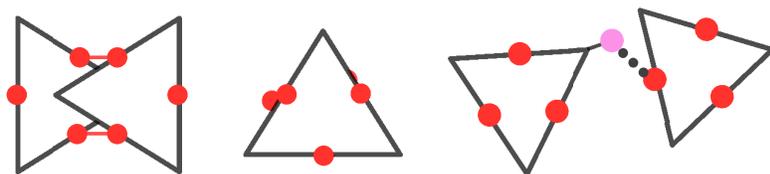


Fig. 2. Schematic diagram of trinuclear complexes indicating interactions¹¹; left: $\{[\text{Ag}(\mu\text{-3,5-}i\text{Pr}_2\text{pz})]_3\}_2$, center: $\{[\text{Ag}(\mu\text{-4-Br-3,5-}i\text{Pr}_2\text{pz})]_3\}_2$, right: $\{[\text{Ag}(\mu\text{-4-NO}_2\text{-3,5-}i\text{Pr}_2\text{pz})]_3\}_2$.
 ●: silver(I) ion, ◻: pyrazolate ion, ●: O atom of NO_2 substituent.

Silver(I) pyrazolato trinuclear complexes (Ag_3) can exhibit luminescence,^{16,22} self-assembly,²³ and remarkable π acid/base interactions.²⁴⁻²⁵ Luminescent transition-metal complexes are an attractive research area because of their potential applications in display devices and chemosensors.²⁶ The silver(I) 3,5-bis(trifluoromethyl)pyrazolato complex ($\{[\text{Ag}(\mu\text{-3,5-(CF}_3)_2\text{pz})]_3\}_2$) exhibits efficient UV \rightarrow blue internal conversion attributable to $^1\text{LMMCT}$ absorption below 290 nm at 77 K and ^3MM emission from a $\text{Ag}\cdots\text{Ag}$ excited state.¹⁶ This emission is highly temperature dependent and influenced by π - π interaction with aromatic solvents.²⁵ There are, however, relatively few published investigations of luminescent silver(I) pyrazolato complexes correlating emission with the nature of the substituents on the pyrazolate ring. Silver(I), is the most stable of the Group 11 ions (standard reduction potential E^0 (V versus NHE (normal hydrogen electrode)); $\text{Cu}^{2+} + \text{e}^- = \text{Cu}^+$: 0.159 V, $\text{Ag}^{2+} + \text{e}^- = \text{Ag}^+$: 1.98 V, $\text{Au}^+ + \text{e}^- = \text{Au}$: 1.83 V and $\text{Au}^{3+} + 3\text{e}^- = \text{Au}$: 1.52 V)²⁷ and luminescent silver(I) materials are, therefore, an attractive target with potential applications in light-emitting devices.

We now report the influence of halogen substituents at the 4-position of the pyrazolate ligands on the structures and luminescence properties of corresponding silver(I) complexes. We also report a convenient and versatile synthetic route to these ligands. Halogenation of pyrazoles can be achieved with Cl_2 , $\text{NaOCl}/\text{CH}_3\text{COOH}$, Br_2 , $\text{Br}_2/\text{CH}_3\text{COOH}$, $\text{I}_2/\text{KI}/\text{Na}_2\text{CO}_3$, $\text{I}_2/\text{NaI}/\text{CH}_3\text{COONa}$, $\text{I}_2/(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$, $\text{I}_2/\text{LiN}(\text{CH}(\text{CH}_3)_2)_2$, $\text{I}_2/\text{H}_2\text{O}_2$, KICl_2 , $\text{I}_2/\text{NaI}/\text{Na}_2\text{CO}_3$, $\text{I}_2/\text{NaI}/\text{K}_2\text{CO}_3$, I_2/HIO_3 ,

and ICl.^{28–30} These reagents are, however, toxic and corrosive and halogenations often require high temperatures and long reaction times. We therefore investigated the use of the more conveniently handled *N*-halosuccinimides³¹ as an alternative and achieved good yields at room temperature with simple product isolation.

Silver(I) 3,5-diisopropylpyrazolato complexes bearing Chlorine ($[\text{Ag}(\text{L1Cl})]_2$), and Iodine ($[\text{Ag}(\text{L1I})]_n$ ($n = 1$ or 2)) at the 4-position were synthesized together with the corresponding 3,5-diphenyl analogue bearing Chlorine ($[\text{Ag}(\text{L5Cl})]$). The structures of $[\text{Ag}(\text{L1H})]_2$, $[\text{Ag}(\text{L1Br})]_2$, $[\text{Ag}(\text{L5H})]_2$, and $[\text{Ag}(\text{L5Br})]$ have been previously reported.^{10–13} Their resynthesis here allows a systematic study of the influence of halogen at the 4-position on the structural and emissive properties of these complexes.

Experimental

Materials

The preparation and handling of all the complexes was performed under an argon atmosphere using standard Schlenk tube techniques. Dichloromethane was carefully purified by distillation from phosphorous pentoxide under an argon atmosphere.³² Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl under an argon atmosphere.³² Super-dehydrated *n*-hexane was purchased from Wako Pure Chemical Ind. Ltd. and deoxygenated by purging with argon gas. Deuteriochloroform was obtained from Cambridge Isotope Laboratories, Inc. Other reagents are commercially available and were used without further purification. The 3,5-diisopropyl-1-pyrazole (3,5-*i*Pr₂pzH = **L1H-H**) and 3,5-diphenyl-1-pyrazole (3,5-Ph₂pzH = **L5H-H**) were prepared by published methods.³³ The 4-halo-3,5-diphenyl-1-pyrazoles (4-X-3,5-Ph₂pzH = **L5X-H**) were synthesized by halogenation of the corresponding pyrazole using *N*-halosuccinimides (NXS) by a modification of a literature method.³¹ Although the synthesis of 4-halo-3,5-dimethyl-1-pyrazoles using *N*-halosuccinimides have been reported, the synthesis of the corresponding 4-halo-3,5-diisopropyl-1-pyrazoles (4-X-3,5-*i*Pr₂pzH = **L1X-H**) using these reagents have not previously been published.^{31g} Some of the chemical properties of $[\text{Ag}(\text{L1H})]_2$, $[\text{Ag}(\text{L1Br})]_2$, $[\text{Ag}(\text{L5H})]_2$, and $[\text{Ag}(\text{L5Br})]$ have been previously reported.^{10–13} These compounds were remade here to permit a more detailed comparison of their spectroscopic properties with those of the new members in the series. Pyrazolate anions were obtained by the reaction of the corresponding

pyrazoles with 1 equiv. of sodium hydride in diethyl ether at room temperature for 1-2 hours.⁹

Measurements

IR spectra (4000 – 400 cm^{-1}) were recorded on KBr pellets, using a JASCO FT/IR-6300 spectrophotometer. Raman spectra (4000 – 50 cm^{-1}) were measured in solid-disks on a JASCO RFT600 spectrophotometer with YAG laser 500 mW. Far-IR spectra (800 – 150 cm^{-1}) were recorded on CsI pellets, using a JASCO FT/IR 6200 spectrophotometer. Abbreviations used in the description of vibration data are as follows: vs, very strong; s, strong; m, medium; w, weak. ^1H and ^{13}C NMR (500 MHz and 125 MHz respectively) were obtained on a Bruker AVANCE-500 NMR spectrometer at room temperature (298 K) in CDCl_3 . ^1H and ^{13}C chemical shifts were reported as δ values relative to residual solvent peaks. Some ^{13}C NMR signals for **[Ag(L5Br)]** were not observed due to the low solubility of this complex. Electronic absorption spectra (solution and solid, 200 – 800 nm) were recorded on a JASCO V-560 spectrophotometer. Solid samples (mulls) for spectroscopy that were prepared by finely grinding microcrystalline material into powders with a mortar and pestle and then adding mulling agents (poly(dimethylsiloxane), viscosity 10,000) (Aldrich)) were uniformly spread between quartz plates. Luminescence spectra were recorded on a JASCO FP-6500 (solid, 300 – 750 nm) spectrofluorometer. Low temperature electronic absorption and luminescence spectra were recorded using solid samples cooled with a liquid nitrogen cooled cryostat (CoolSpeK) from Unisoku Scientific Instruments (Osaka, Japan). The elemental analyses (C, H, and N) were performed by the Chemical Analysis Center of Ibaraki University.

Preparation of Ligands

4-Cl-3,5-*i*Pr₂pzH (L1Cl-H)

A solution of *N*-chlorosuccinimide (5.28 g, 39.5 mmol) in acetone (60 cm^3) was added dropwise to a solution of **L1H-H** (5.00 g, 32.8 mmol) in dichloromethane (20 cm^3) over 15 min. After stirring for 5 hours, the solvent was evaporated under vacuum and the resulting solid was extracted with hexane (100 cm^3) to remove succinimide. The filtrate was then washed with H_2O , dried over anhydrous magnesium sulfate and evaporated under vacuum to provide a white powder that was recrystallized from acetonitrile at 0 °C. Colorless crystals (4.98 g, 26.7 mmol, yield 81%) were filtered and dried under vacuum. IR (KBr, cm^{-1}): 3166vs (N–H), 3094vs (N–H), 2973vs (C–H,

aliphatic), 2932vs (C–H, aliphatic), 2884vs (C–H, aliphatic), 2811vs (C–H, aliphatic), 1574s (C=N), 1487s, 1469s, 1447s, 1422w, 1387m, 1366s, 1335m, 1310m, 1276vs, 1170m, 1143m, 1112s, 1078vs, 1051m, 1011vs, 961w, 923w, 884m, 733w, 711w, 682w, 621w, 588m, 539w, 500w, 469w. Raman (solid, cm^{-1}): 3170w (N–H), 3090w (N–H), 2975vs (C–H, aliphatic), 2912vs (C–H, aliphatic), 2873vs (C–H, aliphatic), 2758w, 2719w, 2587w, 1569w (C=N), 1484m, 1466m, 1450s, 1421s, 1388w, 1368w, 1336m, 1307s, 1278m, 1182w, 1145w, 1113m, 1081m, 1062m, 1001w, 962m, 926w, 881s, 685w, 635s, 588w, 543s, 503m, 460w, 429w, 359w, 281m, 239m, 190w. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ 1.30 (d, $J = 7.0$ Hz, 12H, CHMe_2), 3.07 (sept, $J = 7.0$ Hz, 2H, CHMe_2), 10.19 (s, br, 1H, NH). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ 21.4 (CHMe_2), 25.9 (CHMe_2), 104.9 (C–Cl), 150.3 (pz- $\text{C}_{3,5}$). Anal. Calc. for $\text{C}_9\text{H}_{15}\text{ClN}_2$: C 57.90, H 8.10, N 15.01; Found: C 57.78, H 8.17, N 14.96.

4-Br-3,5-*i*Pr₂pzH (L1Br-H)

This ligand was prepared by a procedure analogous to that used for **L1Cl-H** using 2.28 g (15.0 mmol) of **L1H-H**. Colorless crystals (2.33 g, 10.1 mmol, yield 67%) were isolated from acetonitrile at 0 °C. IR (KBr, cm^{-1}): 3158vs (N–H), 3085vs (N–H), 2968vs (C–H, aliphatic), 2932vs (C–H, aliphatic) 2873vs (C–H, aliphatic) 2810vs (C–H, aliphatic), 2362w, 1570s (C=N), 1484s, 1468s, 1420w, 1382m, 1364s, 1334m, 1309m, 1299m, 1270s, 1169m, 1143m, 1111s, 1071s, 1051m, 1041s, 1009vs, 925w, 883m, 835m, 731w, 703w, 620w, 581m, 490w. Raman (solid, cm^{-1}): 3167w (N–H), 2972vs (C–H, aliphatic), 2913vs(C–H, aliphatic), 2871vs(C–H, aliphatic), 2765w, 2716w, 1570w(C=N), 1465s, 1447s, 1420s, 1390w, 1369w, 1335w, 1306m, 1272m, 1181w, 1112m, 1076m, 1053w, 1002w, 961m, 882s, 625s, 515m, 494m, 368m, 277m, 224m. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ 1.30 (d, $J = 7.0$ Hz, 12H, CHMe_2), 3.06 (sept, $J = 7.0$ Hz, 2H, CHMe_2), 10.92 (s, br, 1H, NH). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ 21.6 (CHMe_2), 26.5 (CHMe_2), 91.0 (C–Cl), 151.5 (pz- $\text{C}_{3,5}$). Anal. Calc. for $\text{C}_9\text{H}_{15}\text{BrN}_2$: C 46.77, H 6.54, N 12.12; Found: C 46.50, H 6.53, N 12.03.

4-I-3,5-*i*Pr₂pzH (L1I-H)

This ligand was prepared by a procedure analogous to that used for **L1Cl-H**, using 1.27 g (8.34 mmol) of **L1H-H**. Colorless crystals (1.34 g, 4.82 mmol, yield 58%) were isolated from acetonitrile at 0 °C. IR (KBr, cm^{-1}): 3151vs (N–H), 3068vs (N–H), 2966vs (C–H, aliphatic), 2930 vs (C–H, aliphatic), 2870vs (C–H, aliphatic), 2802 vs (C–H, aliphatic), 1560m (C=N), 1480s, 1463s, 1416w,

1382m, 1364s, 1330w, 1294w, 1265s, 1167w, 1110m, 1071s, 1032s, 1007vs, 960w, 924w, 885m, 730w, 701w, 617w, 574m, 486w. Raman (solid, cm^{-1}): 3155w (N–H), 2968vs (C–H, aliphatic), 2928 vs (C–H, aliphatic), 2909vs (C–H, aliphatic), 2870vs (C–H, aliphatic), 2758w, 2716w, 1556w (C=N), 1462s, 1446s, 1416s, 1388m, 1369m, 1333m, 1305m, 1267m, 1251m, 1186w, 1149w, 1112m, 1075m, 1042w, 1000w, 960m, 927w, 881s, 688w, 620s, 575w, 499s, 473w, 446w, 386w, 351m, 304m, 277m, 208m. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ 1.30 (d, $J = 7.0$ Hz, 12H, CHMe_2), 3.03 (sept, $J = 7.0$ Hz, 2H, CHMe_2), 11.32 (s, br, 1H, NH). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ 21.9 (CHMe_2), 27.7 (CHMe_2), 59.2 (C-Cl), 153.9 (pz- $\text{C}_{3,5}$). Anal. Calc. for $\text{C}_9\text{H}_{15}\text{IN}_2$: C 38.86, H 5.44, N 10.07; Found: C 38.70, H 5.42, N 10.08.

4-Cl-3,5-Ph₂pzh (L5Cl-H)

N-Chlorosuccinimide (1.81 g, 13.6 mmol) and **L5H-H** (3.00 g, 13.6 mmol) were dissolved in acetonitrile (20 cm^3) and stirred for 3 hours at 70 °C. The solvent was evaporated under vacuum and the resulting solid extracted with chloroform (40 cm^3) to remove succinimide. The filtrate was washed with H_2O , dried with anhydrous magnesium sulfate and evaporated to provide a white powder that was recrystallized from chloroform at 0 °C. Colorless crystals (0.645 g, 2.53 mmol, yield 19%) were filtered and dried under vacuum. IR (KBr, cm^{-1}): 3197m (N–H), 3158m (C–H, aliphatic), 1604w, 1581w, 1561m, 1492m(C=N), 1472m, 1440m, 1385m, 1311w, 1293w, 1257m, 1210w, 1134s, 1074m, 1025m, 1003w, 990m, 957vs, 915m, 767vs, 721m, 693vs, 659m, 581m, 539m, 482w. Raman (solid, cm^{-1}): 3067m (C–H, aromatic), 1606vs, 1556m (C=N), 1517m, 1448m, 1427m, 1395m, 1296w, 1262w, 1221w, 1180w, 1161m, 1033w, 1003m, 993s, 845w, 770w, 706w, 671m, 618w, 553w, 506w, 485w, 405w, 361w, 347w, 287m, 245m, 220m. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ 7.41 (t, $J = 7.2$ Hz, 2H, *p*-Ph), 7.46 (t, $J = 7.2$ Hz, 4H, *m*-Ph), 7.81 (s, br, 4H, *o*-Ph), 10.93 (s, br, 1H, NH). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ 106.3 (pz- C_4), 126.0 (*p*-Ph), 127.9 (*m*-Ph), 129.1 (*o*-Ph). Anal. Calc. for $\text{C}_{15}\text{H}_{11}\text{ClN}_2$: C 70.73, H 4.35, N 11.00; Found: C 71.07, H 4.41, N, 11.06.

4-Br-3,5-Ph₂pzh (L5Br-H)

This ligand was prepared by a procedure analogous to that used for **L5Cl-H**, using 3.00 g (13.6 mmol) of **L5H-H** (3.00 g, 13.6 mmol). Colorless crystals (1.63 g, 5.45 mmol, yield 40%) were isolated from chloroform at 0 °C. IR (KBr, cm^{-1}): IR (KBr, cm^{-1}): 3200m (N–H), 3059w (C–H,

aromatic), 1604w, 1580m, 1560m, 1489s (C=N), 1468s, 1449s, 1392m, 1332w, 1312w, 1293w, 1255s, 1219w, 1210w, 1150w, 1121s, 1074m, 1025m, 1001w, 981m, 958vs, 917m, 757vs, 718m, 695vs, 660m, 575s, 513s. Raman (solid, cm^{-1}): 3068m (C–H, aliphatic), 1607vs, 1553m (C=N), 1517m, 1447m, 1423m, 1396m, 1294w, 1258w, 1186w, 1158m, 1032w, 1002s, 984s, 844w, 768w, 669m, 618w, 525w, 479w, 405w, 361w, 324w, 258m, 241m, 221w. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ 7.42 (t, $J = 6.9$ Hz, 2H, *p*-Ph), 7.46 (t, $J = 6.9$ Hz, 4H, *m*-Ph), 7.78 (s, br, 4H, *o*-Ph), 11.05 (s, br, 1H, NH). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ 91.7 (*pz-C}_4*), 128.2 (*m*-Ph), 129.0 (*o*-Ph), 129.2 (*p*-Ph), Anal. Calc. for $\text{C}_{15}\text{H}_{11}\text{BrN}_2 \cdot 1/4(\text{CHCl}_3)$: C 55.65, H 3.48, N 8.51; Found: C 55.64, H 3.50, N 8.65.

Preparation of Complexes

$\{[\text{Ag}(\mu\text{-4-Cl-3,5-}i\text{Pr}_2\text{pz})]_3\}_2$ ($[\text{Ag}(\text{L1Cl})]_2$).

A solution of NaL1Cl (265 mg, 1.27 mmol) in tetrahydrofuran (10 cm^3) was added dropwise to a suspension of silver(I) nitrate (217 mg, 1.28 mmol) in tetrahydrofuran (10 cm^3) over 15 min. The reaction was protected from light and after stirring for 16 hours, the solvent was evaporated under vacuum. The resulting solid was extracted with dichloromethane (40 cm^3) to remove sodium nitrate. The filtrate was evaporated under vacuum to provide a white powder that was recrystallized from hexane at $-15 \text{ }^\circ\text{C}$. Colorless crystals (154 mg, 0.0874 mmol, yield 41%) were filtered and dried under vacuum. IR (KBr, cm^{-1}): 2965vs (C–H, aliphatic), 2929 (C–H, aliphatic), 2868s (C–H, aliphatic), 1505m (C=N), 1455m, 1383s, 1364s, 1299w, 1280m, 1261m, 1146s, 1115m, 1092s, 1044m, 1034m, 921w, 880w, 802m, 558w. Far-IR (CsI, cm^{-1}): 670w, 658w, 598m, 579s (C–Cl), 559s, 511m (Ag–N), 441w, 375vs, 350s, 293vs, 276s, 256vs, 194w, 176w. Raman (solid, cm^{-1}): 2971vs (C–H, aliphatic), 2912vs (C–H, aliphatic), 2869vs (C–H, aliphatic), 2758w, 2714w, 1495m (C=N), 1445s, 1430m, 1368s, 1304m, 1283m, 1182w, 1152w, 1110m, 1053w, 958m, 882s, 745w, 729w, 707w, 655m, 599w, 573s (C–Cl), 511m (Ag–N), 427w, 337w, 269m, 197m (Ag...Ag). $^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ 1.41 (d, $J = 7$ Hz, 72H, CHMe_2), 3.13 (sept, $J = 7$ Hz, 12H, CHMe_2). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ 22.2 (CHMe_2), 28.4 (CHMe_2), 103.9 (C–Cl), 155.6 (*pz-C}_{3,5}*). UV–Vis (solution, cyclohexane, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{cm}^{-1}\text{mol}^{-1}\text{dm}^3$)): 226 (30400). UV–Vis (solid, nujol, nm): 225. Emission (solid, 299 K, $\lambda_{\text{max}}/\text{nm}$): 312, 373.5, 620, 721 (ex. 280 nm). Anal. Calc. for $\text{C}_{54}\text{H}_{84}\text{Ag}_6\text{Cl}_6\text{N}_{12}$: C 36.82, H 4.81, N 9.54; Found: C 36.68, H 4.70, N 9.46.

[Ag(μ -4-I-3,5-*i*Pr₂pz)]₃ ([Ag(L1I)]) and **{[Ag(μ -4-I-3,5-*i*Pr₂pz)]₃}₂ ([Ag(L1I)]₂).**

This complex was prepared by a procedure analogous to that used for [Ag(L1C)]₂, substituting NaL1I (540 mg, 1.80 mmol). Colorless crystals (376 mg, 0.326 mmol, yield 54%) were isolated from dichloromethane/hexane at -15 °C. Both [Ag(μ -4-I-3,5-*i*Pr₂pz)]₃ and {[Ag(μ -4-I-3,5-*i*Pr₂pz)]₃}₂ were obtained from the same solution. Attempts to separate these complexes from one other were not successful (see section 3-1). These colorless crystals were filtered and dried under vacuum. IR (KBr, cm⁻¹): 2963vs (C-H, aliphatic), 2925vs (C-H, aliphatic), 2864s (C-H, aliphatic), 1498s (C=N), 1456s, 1429m, 1381m, 1362s, 1301m, 1276m, 1169m, 1141s, 1104s, 1089s, 1038s, 922w, 877w, 724w, 583w, 551m, 503w. Far-IR (CsI, cm⁻¹): 653w, 641w, 598w, 582w, 554w, 534m (C-I), 499m (Ag-N), 483w, 454m, 387s, 364w, 337m, 246vs, 192vs. Raman (solid, cm⁻¹): 2961s(C-H, aliphatic), 2907v (C-H, aliphatic), 2877s(C-H, aliphatic), 2864s(C-H, aliphatic), 2751w, 2710w, 1478m (C=N), 1442s, 1368s, 1306m, 1276m, 1174m, 1146m, 1110m, 1085m, 1037s, 958m, 879s, 711w, 636s, 531s (C-I), 498m (Ag-N), 456w, 373m, 338w, 269m, 227m, 196w(Ag...Ag). ¹H-NMR (CDCl₃, 500 MHz): δ 1.43 (d, *J* = 7.1 Hz, 36H, CHMe₂), 3.20 (sept, *J* = 7.1 Hz, 6H, CHMe₂). ¹³C-NMR (CDCl₃, 125 MHz): δ 22.7 (CHMe₂), 29.7 (CHMe₂), 56.3 (C-I), 159.6 (pz-C_{3,5}). UV-Vis (cyclohexane, λ_{\max}/nm ($\epsilon/\text{cm}^{-1}\text{mol}^{-1}\text{dm}^3$)): 229.5 (35000). UV-Vis (nujol, nm): 230.5. Emission (solid, 299 K, λ_{\max}/nm): 314, 363.5, 621, 700 (ex. 280 nm). Anal. Calc. for C₂₇H₄₂Ag₃I₃N₆: C 28.08, H 3.67, N 7.28; Found: C 27.85, H 3.53, N 7.28.

[Ag(μ -4-Cl-3,5-Ph₂pz)]₃ ([Ag(L5Cl)]).

This complex was prepared by a procedure analogous to that used for [Ag(L5H)]₂, substituting NaL5Cl (107 mg, 0.385 mmol). Colorless crystals (61.4 mg, 0.0566 mmol, yield 44%) were isolated from dichloromethane at -25 °C. IR (KBr, cm⁻¹): 3063m (C-H, aromatic), 3025m (C-H, aromatic), 2963m, 1950w, 1883w, 1807w, 1760w, 1685w, 1603m, 1577m, 1463s (C=N), 1438s, 1407w, 1323m, 1297m, 1261s, 1191m, 1144s, 1096s, 1073s, 1030s, 916m, 867w, 800s, 766s, 731m, 696vs, 604m, 586m, 509w (Ag-N), 477m, 436w. Far-IR (CsI, cm⁻¹): 619m, 605vs, 588m (C-Cl), 556w, 509s (Ag-N), 498w, 479s, 434s, 404m, 389m, 357m, 320m, 299m, 290m, 265s, 236w, 223s, 154m. Raman (solid, cm⁻¹): 3068m (C-H, aromatic), 1605vs, 1578w, 1521s, 1466w (C=N), 1440s, 1409s, 1324m, 1299m, 1276w, 1182w, 1158w, 1034w, 1004s, 991s, 969w, 844w, 768w, 698w, 675m, 619m, 582w (C-Cl), 510w (Ag-N), 406w, 360w, 287w. ¹H-NMR (CDCl₃, 500 MHz): δ 7.18

(t, $J = 7$ Hz, 12H, *m*-Ph), 7.31 (t, $J = 7$ Hz, 6H, *p*-Ph), 7.58 (d, $J = 7$ Hz, 12H, *o*-Ph). ^{13}C -NMR (CDCl₃, 125 MHz): δ 106.2 (*pz-C*₄), 127.9 (*o*-Ph), 129.0 (*m*-Ph), 128.9 (*p*-Ph), 131.8 (Ph-*C*₁), 151.2 (*pz-C*_{3,5}). UV-Vis (solution, CH₂Cl₂, λ_{max} /nm ($\epsilon/\text{cm}^{-1}\text{mol}^{-1}\text{dm}^3$): 242 (93100). UV-Vis (solid, nujol, nm): 249. Emission (solid, 299 K, λ_{max} /nm): 320.5, 634.5 (ex. 280 nm). Anal. Calc. for C₄₅H₃₀Ag₃Cl₃N₆: C 49.83, H 2.79, N 7.75; Found: C 49.72, H 2.75, N 7.69.

Crystal Structure Determination

Single crystals of [Ag(L1Cl)]₂, [Ag(L1I)], and [Ag(L1I)]₂ for X-ray analysis were obtained by recrystallization at -15 °C from hexane and dichloromethane/hexane solutions, respectively. Single crystals of [Ag(L5Cl)] for X-ray analysis were obtained from dichloromethane at -25 °C. Crystal data and refinement parameters are given in Table S1 for [Ag(L1Cl)]₂, [Ag(L1I)], [Ag(L1I)]₂, and [Ag(L5Cl)].

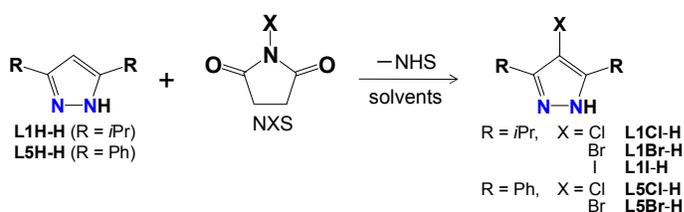
Diffraction data were measured on a Rigaku Mercury diffractometer using graphite monochromated Mo K α ($\lambda = 0.71070$ Å) radiation at low temperature (-65 °C for [Ag(L1Cl)]₂, -83 °C for [Ag(L1I)] and [Ag(L1I)]₂, and at -70 °C for [Ag(L5Cl)]). All crystals were mounted on the tip of glass fibers using highly viscous oil. The unit cell parameters of each crystal were determined using CrystalClear from 6 images. The crystals to detector distance was ca. 45 mm. Data were collected using 0.5° intervals in φ and ω to a maximum 2θ value of 55.0° . A total of 744 oscillation images were collected. The highly redundant data sets were reduced using CrystalClear and corrected for Lorentz and polarization effects.^{34,35} An empirical absorption correction was applied for each complex. Structures were solved by direct methods (SIR97³⁶ or SIR92³⁷). The position of the silver(I) ions and their first coordination sphere were located from a direct method *E*-map; other non-hydrogen atoms were found in alternating difference Fourier syntheses,³⁸ and least-squares refinement cycles and during the final cycles were refined anisotropically (CRYSTALSTRUCTURE).^{34,39} Refinement was carried out by a full matrix least-squares method on F^2 . All calculations were performed by the CrystalStructure program. Crystallographic data and structure refinement parameters including the final discrepancies (R and R_w) are listed in Tables S1 (Supplementary Information). Solvent molecules were highly disordered in the structure of [Ag(L1Cl)]₂ and these atoms were refined isotropically. There were also some disorder in the isopropyl groups (C31 and C41) of [Ag(L1Cl)]₂ and (C21 and C39) in [Ag(L1I)]₂. Large solvent

accessible voids were observed in the structure of $[\text{Ag}(\text{L1I})]$. They are presumably filled with severely disordered isopropyl groups, which could not be modeled by the present analysis. Observed reflections were too low for $[\text{Ag}(\text{L5Cl})]$ and so a 2 sigma cutoff was applied for this calculation. The absolute structures were deduced based on Flack parameters⁴⁰ of 0.25(8) refined using 3956 Friedel pairs for $[\text{Ag}(\text{L1I})]$, 0.06(3) refined using 3170 Friedel pairs for $[\text{Ag}(\text{L5Cl})]$. Additional refinements details are contained in the CIF files (ESI †). Instrument parameters, crystal data, and data collection parameters for all the complexes are summarized in Table S1. Selected bond distances are listed in Tables 1 and 2.

Results and Discussion

Synthesis

The ligand syntheses are depicted in Scheme 1 and gave pure product in each case. The reactions of **L1H-H** and **L5H-H** with the three different *N*-halosuccinimides (NXS, X = Cl, Br, and I), in appropriate solvents led to isolation of only the desired products **L1Cl-H**, **L1Br-H**, **L1I-H**, **L5Cl-H**, and **L5Br-H**. This method is more convenient than using the traditional reagents listed above and more straight forward than ultrasonic halogenation with NXS which requires specialized instrumentation.^{30d,30e,30f}

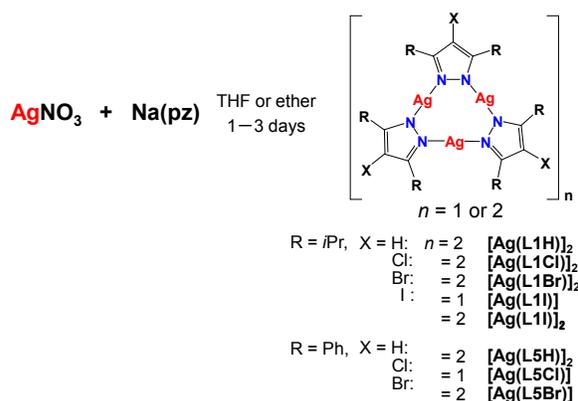


Scheme 1. Ligand synthesis.

All of the seven complexes, prepared as depicted in Scheme 2, gave satisfactory elemental analyses. The reactions of silver(I) nitrate with the sodium salts of the five different halogen substituted pyrazoles **NaL1Cl**, **NaL1Br**, **NaL1I**, **NaL5Cl**, **NaL5Br**, and two different non-substituted pyrazoles **NaL1H** and **NaL5H** in appropriate solvents led to the isolation of products $[\text{Ag}(\text{L1Cl})]_2$, $[\text{Ag}(\text{L1Br})]_2$, $[\text{Ag}(\text{L1I})]_n$, $[\text{Ag}(\text{L5Cl})]$, $[\text{Ag}(\text{L5Br})]$, and $[\text{Ag}(\text{L1H})]_2$ and

$[\text{Ag}(\text{L5H})]_2$, respectively. $[\text{Ag}(\text{L1I})]_n$ was obtained in two polymorphs. Both complexes were obtained by recrystallization from the same solvent and could not be separated. All complexes were stable when shielded from light.

There are alternative, published protocols for synthesizing silver(I) pyrazolato complexes. One method involves using silver(I) oxide.^{8,11,15–18,21,23} However, this reaction needs to be heated for some hours. The reaction of sodium pyrazolate with silver(I) nitrate was therefore selected for our study.



Scheme 2. Synthesis of complexes.

Structural characterization

Single-crystal X-ray structural analyses were performed on compounds, $[\text{Ag}(\text{L1Cl})]_2$, $[\text{Ag}(\text{L1I})]$, $[\text{Ag}(\text{L1I})]_2$, and $[\text{Ag}(\text{L5Cl})]$. Diffraction data for the known silver(I) complexes $[\text{Ag}(\text{L1H})]_2$, $[\text{Ag}(\text{L1Br})]_2$, $[\text{Ag}(\text{L5H})]_2$, and $[\text{Ag}(\text{L5Br})]$ complexes were used for comparison.^{10–13} The perspective drawings of these complexes are given in Fig. 3 for $[\text{Ag}(\text{L1Cl})]_2$, Fig. S1 for $[\text{Ag}(\text{L1Br})]_2$, Fig. 4 for $[\text{Ag}(\text{L1I})]$, Fig. 5 for $[\text{Ag}(\text{L1I})]_2$, Fig. S2 for $[\text{Ag}(\text{L5H})]_2$, Fig. 6 for $[\text{Ag}(\text{L5Cl})]$, and Fig. S3 for $[\text{Ag}(\text{L5Br})]$. Selected bond distances, intramolecular and intermolecular Ag \cdots Ag distances, and bond angles are summarized in Tables 1 and 2.

$\{[\text{Ag}(\mu\text{-4-Cl-3,5-}i\text{Pr}_2\text{pz})]_3\}_2$ $[\text{Ag}(\text{L1Cl})]_2$ exists as a dimeric trinuclear with three intermolecular argentophilic interactions (Ag1 \cdots Ag4, 3.1003(17); Ag2 \cdots Ag5, 3.1298(15); Ag3 \cdots Ag6, 3.1051(16) Å). These distances are significantly shorter than twice Bondi's van der Waals radius (3.44 Å = 1.72 Å \times 2), indicating Ag \cdots Ag interaction.⁴¹ Moreover, the planes formed by the two Ag₃N₆ metallacycles completely overlap. The short distances between C₄ atoms of adjacent pyrazolates (referred to as pz-C₄ \cdots pz-C₄) for this dimer are in the range 4.99(3) to 5.39(2)

Å (Fig. 3 and Table 2). By comparison, the parent $[\text{Ag}(\text{L1H})]_2$ has two intermolecular argentophilic interactions ($\text{Ag}\cdots\text{Ag}$, 2.9870(4) Å) and the planes are only slightly overlapped.¹¹ The $\text{pz-C}_4\cdots\text{pz-C}_4$ distances in this complex are 5.52 and 5.91 Å - much longer than those of $[\text{Ag}(\text{L1Cl})]_2$ (Table 2) despite the relative bulk of Chlorine versus Hydrogen. We attribute this to the relatively high electronegativity of Chlorine that withdraws electron density from the coordinating N and thus strengthens the intermolecular argentophilic interactions.

$\{[\text{Ag}(\mu\text{-4-Br-3,5-}i\text{Pr}_2\text{pz})]_3\}_2$ $[\text{Ag}(\text{L1Br})]_2$ also exists as a dimeric trinuclear with three intermolecular argentophilic interactions.¹¹ The intramolecular argentophilic interactions in $[\text{Ag}(\text{L1Cl})]_2$ are only slightly weaker than those in $[\text{Ag}(\text{L1Br})]_2$ (average of three distances (Å) for $[\text{Ag}(\text{L1Cl})]_2$ is 3.47 (ranging from 3.3927(16) to 3.5445(16)), while for $[\text{Ag}(\text{L1Br})]_2$ is 3.45 (ranging from 3.413 to 3.489) but the intermolecular argentophilic interactions in $[\text{Ag}(\text{L1Cl})]_2$ are significantly stronger than those in $[\text{Ag}(\text{L1Br})]_2$ (average value of three distances (Å) for $[\text{Ag}(\text{L1Cl})]_2$ is 3.11 (ranging from 3.1003(17) to 3.1298(15)), while for $[\text{Ag}(\text{L1Br})]_2$ is 3.23 (ranging from 3.044 to 3.408) (Table 1). The dimeric trinuclear units of $[\text{Ag}(\text{L1Cl})]_2$ and $[\text{Ag}(\text{L1Br})]_2$ are structurally very similar. However, the packing of these dimers is quite different with $[\text{Ag}(\text{L1Cl})]_2$ units packed parallel to one another (Fig. 3), and $[\text{Ag}(\text{L1Br})]_2$ dimers packed perpendicular to adjacent dimers and parallel to diagonal dimers (data not shown).

Two polymorphs of $\{[\text{Ag}(\mu\text{-4-I-3,5-}i\text{Pr}_2\text{pz})]_3\}_n$ $[\text{Ag}(\text{L1I})]_n$ ($n = 1$ or 2) were prepared from the same reaction. $\{[\text{Ag}(\mu\text{-4-I-3,5-}i\text{Pr}_2\text{pz})]_3\}_n$ exists as a mixture of trinuclear metallacycle ($[\text{Ag}(\text{L1I})]$) (Fig. 4) with no close $\text{Ag}\cdots\text{Ag}$ contacts and the corresponding dimeric trinuclear metallacycle ($[\text{Ag}(\text{L1I})]_2$) (Fig. 5) with two argentophilic interactions ($\text{Ag1}\cdots\text{Ag2}'$, 3.2049(7) Å) (Table 1). The structure of $[\text{Ag}(\text{L1I})]_2$ is similar to that of $[\text{Ag}(\text{L1H})]_2$ but with additional weak $\text{Ag}\cdots\text{I}$ interactions to neighbouring dimers. Similarly, one of the silver(I) ions of monomeric $[\text{Ag}(\text{L1I})]$ interacts with one of the Iodine substituents of an adjacent $[\text{Ag}(\text{L1I})]$ unit, yielding a 1D polymer of trinuclear metallacycles. The distance between Ag1 and I1' (symmetry operators: $X+1/2$, $-Y+1/2$, Z) is 3.3677(12) Å (Fig. 4 and Table 2) is shorter than the sum of Bondi's van der Waals radii of Ag and I atoms ($1.72 + 1.98 = 3.70$ Å)⁴¹ and can be considered as a soft acid (Ag(I) ion), soft base (I substituent) interaction. The distance between Ag and I on adjacent $[\text{Ag}(\text{L1I})]_2$ dimers are 3.5043(7) (Ag2-I2') and 3.5698(8) (Ag3-I2') Å (symmetry operators: $-X+2$, $Y+1/2$, $-Z++1/2$) (Fig. 5 and Table 2). Therefore, $[\text{Ag}(\text{L1I})]_2$ also exists as a loosely bonded 1D polymer in the solid state.

Not unexpectedly, as the 4-position halogens increase in size (Bondi's van der Waals radii Cl (1.75 Å) < Br (1.85 Å) < I (1.98 Å))⁴¹ the overlap between Ag₃N₆ planes decreases. The three short pz-C₄⋯pz-C₄ distances in [Ag(L1Cl)]₂, [Ag(L1Br)]₂, and [Ag(L1I)]₂, range from 4.99(3) to 5.39(2) Å, from 5.31 to 5.53 Å, and from 6.13(1) to 7.56(1) Å, respectively (Table 2). Finally, a comparison of Ag⋯Ag contacts as the halogens become larger, reveals that the intermolecular argentophilic interactions weaken, and distortion of the trinuclear structure is reduced. This is in contrast to the better overlap and shorter Ag⋯Ag contacts observed when comparing the parent [Ag(L1H)]₂ with the bulkier [Ag(L1Cl)]₂.

The solid-state structures of 3,5-diphenylprazolato silver(I) complexes {[Ag(μ-4-X-3,5-Ph₂Pz)]₃]_n (n = 1 or 2) (X = H and Br) have been reported by Fackler, Raptis, and co-workers.^{10,12,13} {[Ag(μ-3,5-Ph₂Pz)]₃]₂ ([Ag(L5H)]₂) has only one intermolecular argentophilic interaction and exists as a dimeric trinuclear (Ag⋯Ag', 2.9712(14) Å). By comparison, only soft-soft, Ag⋯X interactions are observed for [Ag(μ-4-Cl-Ph₂Pz)]₃ ([Ag(L5Cl)]) and [Ag(μ-4-Br-3,5-Ph₂Pz)]₃ ([Ag(L5Br)]) which exist as weakly bound 1D polymers (Fig. 6). No intermolecular argentophilic interactions were observed for these halogenated analogues, as was the case for [Ag(L1I)]. The intermolecular distances in [Ag(L5Cl)] are 3.345(4) Å (Ag1⋯Cl141), 3.395(4) Å (Ag2⋯Cl141), and 3.448(4) Å (Ag3⋯Cl141). The corresponding (Ag⋯Br) intermolecular distance in [Ag(L5Br)] is 3.208 Å (Table 2). Again, these Ag⋯X contacts are shorter than the sum of Bondi's van der Waals radii of Ag and Cl (1.72 + 1.75 = 3.47 Å) and Ag and Br (1.72 + 1.85 = 3.57 Å). Raptis and co-workers suggest that the Bromine substituent in [Ag(L5Br)] increases the π-acidity of the Ag₃ face¹³ and it seems reasonable to us that this effect would be even greater for the Chlorine analogue. The electron withdrawing phenyl substituents of L5 also enhance this π-acidity as opposed to the electron release isopropyl substituents of L1.¹³

In summary, a comparison of the four dimeric trinuclear L1 complexes ([Ag(L1H)]₂, [Ag(L1Cl)]₂, [Ag(L1Br)]₂, and [Ag(L1I)]₂) revealed two intermolecular argentophilic interactions for the complexes in which the substituent X = H and I, and three intermolecular argentophilic interactions for X = Cl and Br. This pattern does not correlate with the size of the halogen substituents, but can be explained by the influence of the more electronegative halogens on the metal. Only in [Ag(L1I)]₂ were Ag⋯I interactions observed. By contrast, the solid-state structures of the 3,5-diphenylpyrazolato complexes [Ag(L5Cl)] and [Ag(L5Br)], are dominated by Ag⋯X,

rather than Ag...Ag interactions. Only in [Ag(L5H)]₂ was Ag...Ag intermolecular interactions observed. These results point to the subtle interplay of electronic, more so than steric influences of the 3, 5 and 4 substituents that promote one weak interaction over another.

Table 1 Bond distances (Å) and angles (°) for trinuclear and dimeric trinuclear complexes $\{[\text{Ag}(\mu\text{-pz})]_3\}_{1 \text{ or } 2}$

	Ag–N (range)	N–Ag–N (range)	intra Ag⋯Ag (range)	inter Ag⋯Ag (shortest)	references
$\{[\text{Ag}(\mu\text{-3,5-}i\text{Pr}_2\text{pz})]_3\}_2$	2.048(3)-2.088(3)	170.21(13)-177.68(13)	3.324-3.489	2.9870(4)	11
$\{[\text{Ag}(\mu\text{-4-Cl-3,5-}i\text{Pr}_2\text{pz})]_3\}_2$	2.055(12)-2.097(11)	169.4(5)-172.0(5)	3.3927(16)-3.5445(16)	3.1003(17)	this work
$\{[\text{Ag}(\mu\text{-4-Br-3,5-}i\text{Pr}_2\text{pz})]_3\}_2$	2.053(4)-2.094(4)	168.61(16)-172.89(16)	3.413-3.489	3.0438(5)	11
$[\text{Ag}(\mu\text{-4-I-3,5-}i\text{Pr}_2\text{pz})]_3$	2.064(8)-2.117(7)	173.4(3)-179.2(3)	3.3975(12)-3.4461(18)	—	this work
$\{[\text{Ag}(\mu\text{-4-I-3,5-}i\text{Pr}_2\text{pz})]_3\}_2$	2.061(6)-2.116(6)	171.3(2)-172.9(3)	3.4007(8)-3.4428(10)	3.2049(7)	this work
$\{[\text{Ag}(\mu\text{-3,5-Ph}_2\text{pz})]_3\}_2$	2.073(4)-2.106(4)	171.17(17)-172.30(16)	3.35-3.52	2.9712(14)	12
$[\text{Ag}(\mu\text{-4-Cl-3,5-Ph}_2\text{pz})]_3$	2.088(8)-2.101(8)	176.3(3)-177.2(3)	3.4547(18)-3.5421(14)	—	this work
$[\text{Ag}(\mu\text{-4-Br-3,5-Ph}_2\text{pz})]_3$	2.054(10)-2.122(10)	170.1(4)-178.4(4)	3.43-3.63	—	13
$\{[\text{Ag}(\mu\text{-pz})]_3\}_2$	2.13(2)-2.24(2)	172.1(7)-177(1)	3.414(6)-3.449(6)	3.431(4)	4
$\{[\text{Ag}(\mu\text{-3,5-Me}_2\text{pz})]_3\}_2$	2.028(51)-2.049(46)	—	3.318(9)-3.388(11)	3.230(13)	14
$\{[\text{Ag}(\mu\text{-3-Ph-5-Me-pz})]_3\}_2$	2.058(11)-2.111(10)	174.5(4)-178.7(4)	3.333-3.470	3.2027(16)	13
$\{[\text{Ag}(\mu\text{-3-}o\text{-Cl-Phpz})]_3\}_2$	2.095(7)-2.147(6)	176.5(3)-178.4(3)	3.458-3.585	3.524(1)	13
$[\text{Ag}(\mu\text{-4-NO}_2\text{-3,5-}i\text{Pr}_2\text{pz})]_3$	2.072(5)-2.128(5)	170.52(19)-178.20(18)	3.296-3.529	—	11
$[\text{Ag}(\mu\text{-3-}i\text{Pr-5-}t\text{Bupz})]_3$	2.081(5)-2.095(6)	177.5(2)-179.2(2)	3.3719(7)-3.4586(8)	—	9
$\{[\text{Ag}(\mu\text{-4-Br-3-}t\text{Bupz})]_3\}_2$	2.097(7)-2.138(6)	171.7(3)-176.7(3)	3.382-3.458	3.142(3)	13
$\{[\text{Ag}(\mu\text{-3,5-(CF}_3)_2\text{pz})]_3\}_2$	2.081(3)-2.096(3)	172.01(12)-177.69(13)	3.440-3.541	3.2037(4)	15-17
$\{[\text{Ag}(\mu\text{-3-(CF}_3)_5\text{-Me-pz})]_3\}_2$	2.076(3)-2.084(3)	177.78(10)-178.62(10)	3.392-3.493	3.3553(4)	17
$\{[\text{Ag}(\mu\text{-3-(CF}_3)_5\text{-}t\text{Bu-pz})]_3\}_2$	2.086(3)-2.093(4)	166.94(16)-172.99(15)	3.413-3.489	3.4804(7)	17
$[\text{Ag}(\mu\text{-3-(C}_3\text{F}_7)_5\text{-}t\text{Bupz})]_3$	2.084(8)-2.095(8)	174.1(4)-179.3(3)	3.394-3.448	—	17
$[\text{Ag}(\mu\text{-4-Cl-3,5-(CF}_3)_2\text{pz})]_3$	2.098(4)-2.112(4)	177.7(2)-178.5(1)	3.460-3.498	—	18
$[\text{Ag}(\mu\text{-4-Br-3,5-(CF}_3)_2\text{pz})]_3$	2.102(3)-2.115(3)	176.8(1)-178.9(1)	3.443-3.491	—	18
$\{[\text{Ag}(\mu\text{-2-(3(5)-pz-6-py})]_3\}_2$	2.087(11)-2.142(10)	166.1(4)-176.1(4)	3.655-3.702	3.227(2)	19
$\{[\text{Ag}(\mu\text{-3,5-(}i\text{PrSCH}_2)_2\text{pz})]_3\}_2$	2.074(6)-2.120(6)	170.7(2)-174.9(2)	3.453-3.700	3.041(1)	20
$[\text{Ag}(\mu\text{-3,5-(}p\text{-F-PhSCH}_2)_2\text{pz})]_3$	2.073(9)-2.092(9)	172.3(4)-178.2(4)	3.468-3.564	—	21
$\{[\text{Ag}(\mu\text{-4-Ph-3,5-(PhSCH}_2)_2\text{pz})]_3\}_2$	2.013(2)-2.101(2)	171.26(9)-173.86(9)	3.486-3.629	3.2435(3)	21

Table 2Selected distances (Å) for {[Ag(L1X)]_{1or2}} and {[Ag(L5X)]_{1or2}} complexes

	pz-C ₄ ···pz-C ₄ short distances ^a	Ag···X short distances	references
{[Ag(μ-3,5- <i>i</i> Pr ₂ pz)] ₃ } ₂ {[Ag(L1H)] ₂ }	5.52-5.91		11
{[Ag(μ-4-Cl-3,5- <i>i</i> Pr ₂ pz)] ₃ } ₂ {[Ag(L1Cl)] ₂ }	4.99(3)-5.39(2)		this work
{[Ag(μ-4-Br-3,5- <i>i</i> Pr ₂ pz)] ₃ } ₂ {[Ag(LBr)] ₂ }	5.31-5.53		11
[Ag(μ-4-I-3,5- <i>i</i> Pr ₂ pz)] ₃ [Ag(LI)]		3.3677(12) (X = I)	this work
{[Ag(μ-4-I-3,5- <i>i</i> Pr ₂ pz)] ₃ } ₂ {[Ag(LI)] ₂ }	6.13(1)-7.56(1)	3.5043(7), 3.5698(8) (X = I)	this work
{[Ag(μ-3,5-Ph ₂ pz)] ₃ } ₂ {[Ag(L5H)] ₂ }	5.18-6.27		12
[Ag(μ-4-Cl-3,5-Ph ₂ pz)] ₃ [Ag(L5Cl)]		3.345(4), 3.395(4), 3.448(4) (X = Cl)	this work
[Ag(μ-4-Br-3,5-Ph ₂ pz)] ₃ [Ag(L5Br)]		3.208 (X = Br)	13

^a pz-C₄···pz-C₄ short distance: the distance between C4 of adjacent pyrazolates

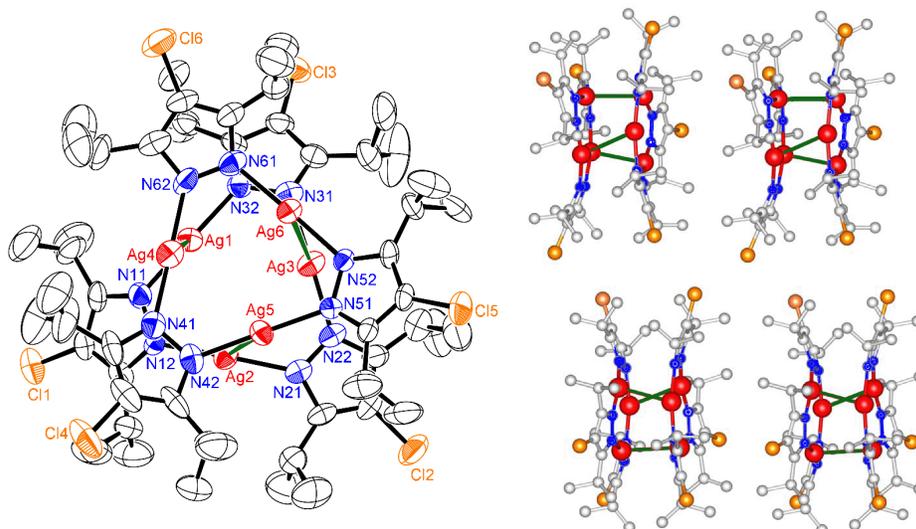


Fig. 3. Left side: molecular structure of $[\text{Ag}(\text{L1Cl})]_2$, showing $\text{Ag}\cdots\text{Ag}$ intermolecular interactions (green lines), 50% displacement ellipsoids, and the selected atom labeling scheme. Right side: packing diagram (ball and stick) of $[\text{Ag}(\text{L1Cl})]_2$, showing $\text{Ag}\cdots\text{Ag}$ intermolecular interactions (green lines). Hydrogen atoms and solvent molecules are omitted for clarity. Color code: Ag, red; N, blue, Cl, orange.

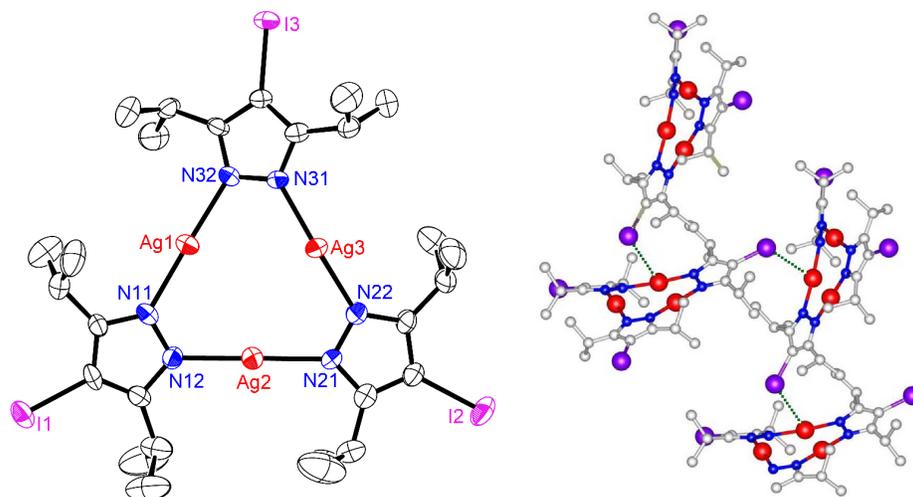


Fig. 4. Left side: molecular structure of $[\text{Ag}(\text{L1I})]$, showing 50% displacement ellipsoids and the selected atom labeling scheme. Right side: packing diagram (ball and stick) of $[\text{Ag}(\text{L1I})]$, showing $\text{Ag}\cdots\text{I}$ weak interactions (dashed green lines), Symmetry operators: $X+1/2$, $-Y+1/2$, Z . Hydrogen atoms are omitted for clarity. Color code: Ag, red; N, blue, I, violet.

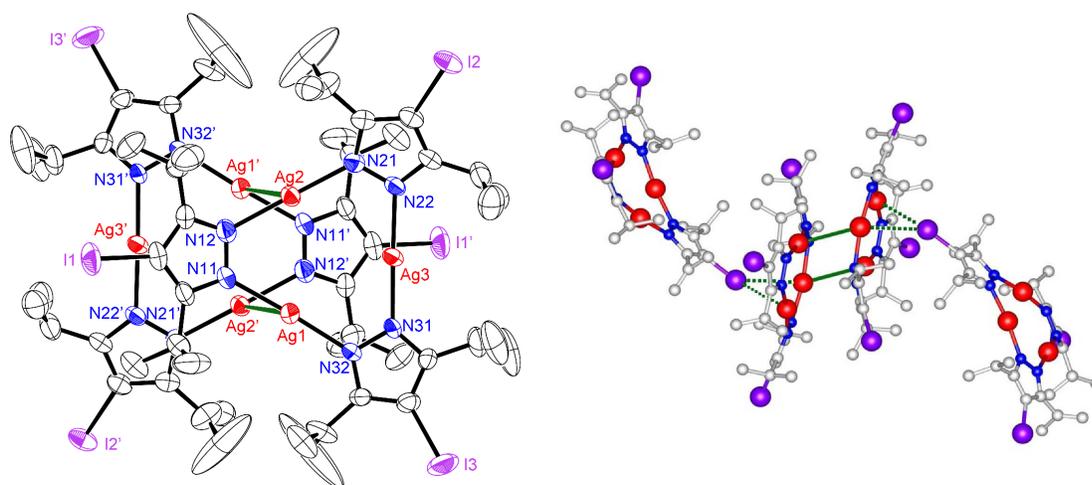


Fig. 5. Left side: molecular structure of $[\text{Ag}(\text{L11})]_2$, showing $\text{Ag}\cdots\text{Ag}$ intermolecular interactions (green lines), 50% displacement ellipsoids, and the selected atom labeling scheme. Right side: packing diagram (ball and stick) of $[\text{Ag}(\text{L11})]_2$, showing $\text{Ag}\cdots\text{I}$ weak interactions (dashed green lines), Symmetry operators: $-X+2$, $-Y+1$, $-Z+1$. Hydrogen atoms and solvent molecules are omitted for clarity. Color code: Ag, red; N, blue, I, violet.

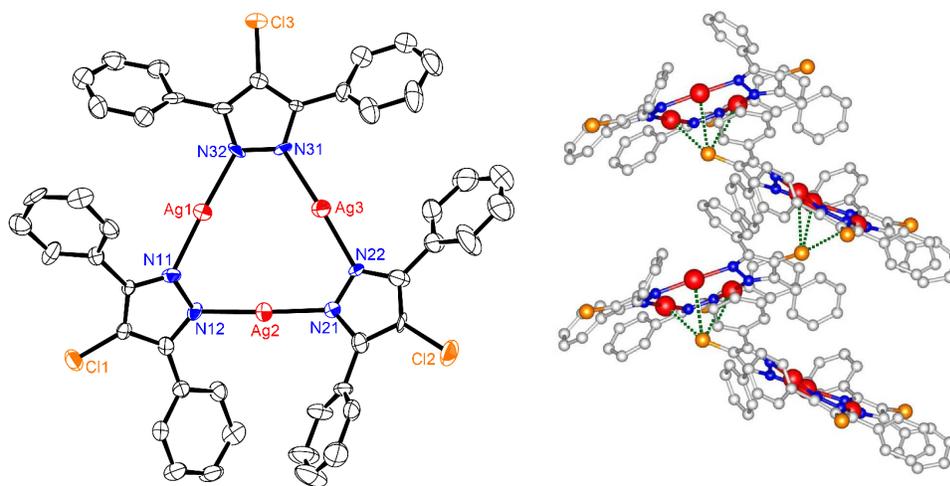


Fig. 6. Left side: molecular structure of $[\text{Ag}(\text{L5Cl})]$, showing 50% displacement ellipsoids and the selected atom labeling scheme. Right side: packing diagram (ball and stick) of $[\text{Ag}(\text{L5Cl})]$, showing $\text{Ag}\cdots\text{Cl}$ weak interactions (dashed green lines). Symmetry operators: $X+1/2$, $-Y+1/2$, Z . Hydrogen atoms and solvent molecules are omitted for clarity. Color code: Ag, red; N, blue, Cl, orange.

Spectroscopy

The ^1H and ^{13}C NMR signals of the ligands are quite different in chemical shift to those of the trinuclear metallacycle silver(I) pyrazolato complexes indicating Ag–N coordination is retained in solution. The simplicity of the latter suggest that the intermolecular Ag \cdots Ag interactions and weak Ag \cdots X interactions observed in the solid state are not retained in solution, or at least are not long lasting relative to the NMR timescale. Similarly, there were no differences in the NMR spectra of the two polymorphs of $[\text{Ag}(\text{L1I})]_n$, or between $[\text{Ag}(\text{L1I})]$ and $[\text{Ag}(\text{L1I})]_2$, again suggesting the absence (or only transitory existence) of these weak interactions in solution.

IR, far-IR, and Raman spectra of the **L1** and **L5** silver(I) complexes are reproduced in Fig. S4 (See the Supplementary Information) and selected vibrational data are listed in Table 3. The C=N stretching vibrations in the **L1** silver(I) complexes are shifted to ca. 1505 cm^{-1} ($1517 - 1498\text{ cm}^{-1}$) from ca. 1563 cm^{-1} ($1577 - 1556\text{ cm}^{-1}$) of the corresponding pyrazolate anions. The halogen substituents exhibit a relatively small influence on this vibration in the order I (1498 cm^{-1} in $[\text{Ag}(\text{L1I})]_n$) = Br (1498 cm^{-1} in $[\text{Ag}(\text{L1Br})]_2$) < Cl (1505 cm^{-1} in $[\text{Ag}(\text{L1Cl})]_2$) < H (1517 cm^{-1} in $[\text{Ag}(\text{L1H})]_2$) which does not correlate with the electronegativity of the substituents. The C–X stretching vibrations could be observed in the far-IR spectra of $[\text{Ag}(\text{L1Cl})]_2$, $[\text{Ag}(\text{L1Br})]_2$, and $[\text{Ag}(\text{L1I})]_n$, at 579 , 545 , and 534 cm^{-1} , respectively.⁴² These results are in agreement with C–X bond distances ($1.722(14)$ to $1.75(3)\text{ \AA}$ in $[\text{Ag}(\text{L1Cl})]_2$, 1.88 to 1.90 \AA in $[\text{Ag}(\text{L1Br})]_2$,¹¹ and $2.072(9)$ to $2.102(8)\text{ \AA}$ in $[\text{Ag}(\text{L1I})]_n$).

The same trend was seen in the corresponding vibrational spectra of the **L5** silver(I) complexes. The C=N stretching vibrations are shifted to ca. 1465 cm^{-1} ($1462 - 1470\text{ cm}^{-1}$) from ca. 1492 cm^{-1} ($1495 - 1489\text{ cm}^{-1}$) of the corresponding pyrazolate anions and the C=N stretching vibrations are in the order Br (1462 cm^{-1} in $[\text{Ag}(\text{L5Br})]$) \leq Cl (1463 cm^{-1} in $[\text{Ag}(\text{L5Cl})]$) < H (1470 cm^{-1} in $[\text{Ag}(\text{L5H})]_2$). Similarly, the C–X stretching vibrations were in agreement with the C–X distances, 588 cm^{-1} for $[\text{Ag}(\text{L5Cl})]_2$ ($1.742(9)$ to $1.768(11)\text{ \AA}$) and 549 cm^{-1} for $[\text{Ag}(\text{L1Br})]$ ($1.870(12)$ to $1.889(12)\text{ \AA}$)¹³.

All Ag–N stretching vibrations were observed in the region 520 cm^{-1} to 480 cm^{-1} as expected.^{9,42} The Ag–N stretching vibrations were observed in the region 520 cm^{-1} to 480 cm^{-1} ,^{19,42} and, for the **L1** complexes, in the order H (478 cm^{-1} in $[\text{Ag}(\text{L1H})]_2$) < I (499 cm^{-1} in $[\text{Ag}(\text{L1I})]_n$) <

Br (505 cm^{-1} in $[\text{Ag}(\text{L1Br})]_2$) < Cl (511 cm^{-1} in $[\text{Ag}(\text{L1Cl})]_2$) which correlates with the electronegativity of the substituent. No trend was identified for the corresponding **L5** complexes.

Raman spectroscopy revealed $\text{Ag}\cdots\text{Ag}$ stretching vibrations for all complexes in which intermolecular argentophilic interactions were observed in the X-ray crystal structures, and for two **L5** complexes ($[\text{Ag}(\text{L5Cl})]$ and $[\text{Ag}(\text{L5Br})]$) for which close contacts were not observed. The frequency of these vibrations was consistent with the bond distances: 207 cm^{-1} $[\text{Ag}(\text{L1H})]_2$ (2.987 to 2.995 \AA)¹¹, 197 cm^{-1} $[\text{Ag}(\text{L1Cl})]_2$ (3.1003(17) to $3.1298(15)\text{ \AA}$), 186 cm^{-1} $[\text{Ag}(\text{L1Br})]_2$ (3.044 to 3.408 \AA)¹¹, 196 cm^{-1} $[\text{Ag}(\text{L1I})]_2$ (3.2049(7) \AA), 244 cm^{-1} $[\text{Ag}(\text{L5H})]_2$ (2.9712(14) \AA)¹².

Table 3
Selected IR, Far-IR, Raman data of the complexes (cm^{-1}).

	IR		Far-IR		Raman			reference
	$\nu(\text{C}=\text{N})$	$\nu(\text{Ag}-\text{N})$	$\nu(\text{C}-\text{X})$	$\nu(\text{C}=\text{N})$	$\nu(\text{Ag}-\text{N})$	$\nu(\text{C}-\text{X})$	$\nu(\text{Ag}\cdots\text{Ag})$	
$[\text{Ag}(\text{L1H})]_2$	1517	478	—	1516	477	—	207	9
$[\text{Ag}(\text{L1Cl})]_2$	1505	511	579	1495	511	573	197	this work
$[\text{Ag}(\text{L1Br})]_2$	1498	505	545	1499	506	533	186	this work
$[\text{Ag}(\text{L1I})]_n$	1498	499	534	1478	498	531	196	this work
$[\text{Ag}(\text{L5H})]_2$	1470	508	—	1464	510	—	244	this work
$[\text{Ag}(\text{L5Cl})]$	1463	509	588	1466	510	582	—	this work
$[\text{Ag}(\text{L5Br})]$	1462	488	549	1465	488	546	—	this work

Electronic absorption spectra for the **L1** and **L5** complexes acquired as Nujol suspensions and in solution are given in Fig. 7. These spectra were quite similar in both media. The two polymorphs of $[\text{Ag}(\text{L1I})]_n$ gave only one peak in solution or in the solid state. These results suggest that the absorption bands do not arise from the intermolecular argentophilic interactions but from chromophores in the trinuclear metallacycles. DFT calculations reported by Omary and co-workers for similar coinage metal trinuclear pyrazolato metallacycle complexes point to a transition from a filled orbital with strong ligand character to a vacant molecular orbital mainly associated with the trinuclear moiety.¹⁶ In our study, the order of the electronic absorption band maxima match the order of Ag–N bond lengths; 221 nm in $[\text{Ag}(\text{L1H})]_2$ (2.048(3) to $2.088(3)\text{ \AA}$), 225 nm in $[\text{Ag}(\text{L1Cl})]_2$ (2.055(12) to $2.097(11)\text{ \AA}$), 227.5 nm in $[\text{Ag}(\text{L1Br})]_2$ (2.053(4) to $2.094(4)\text{ \AA}$), 230.5 nm in $[\text{Ag}(\text{L1I})]_n$ (2.061(6) to $2.117(7)\text{ \AA}$) (Table 1). This correlation is consistent with Omary and co-workers proposition.¹⁶

The electronic absorption bands for the **L5** complexes were much broader, presumably because of overlapping π - π^* transition bands associated with the phenyl substituents on the ligands and little structural information could be deduced from this data.

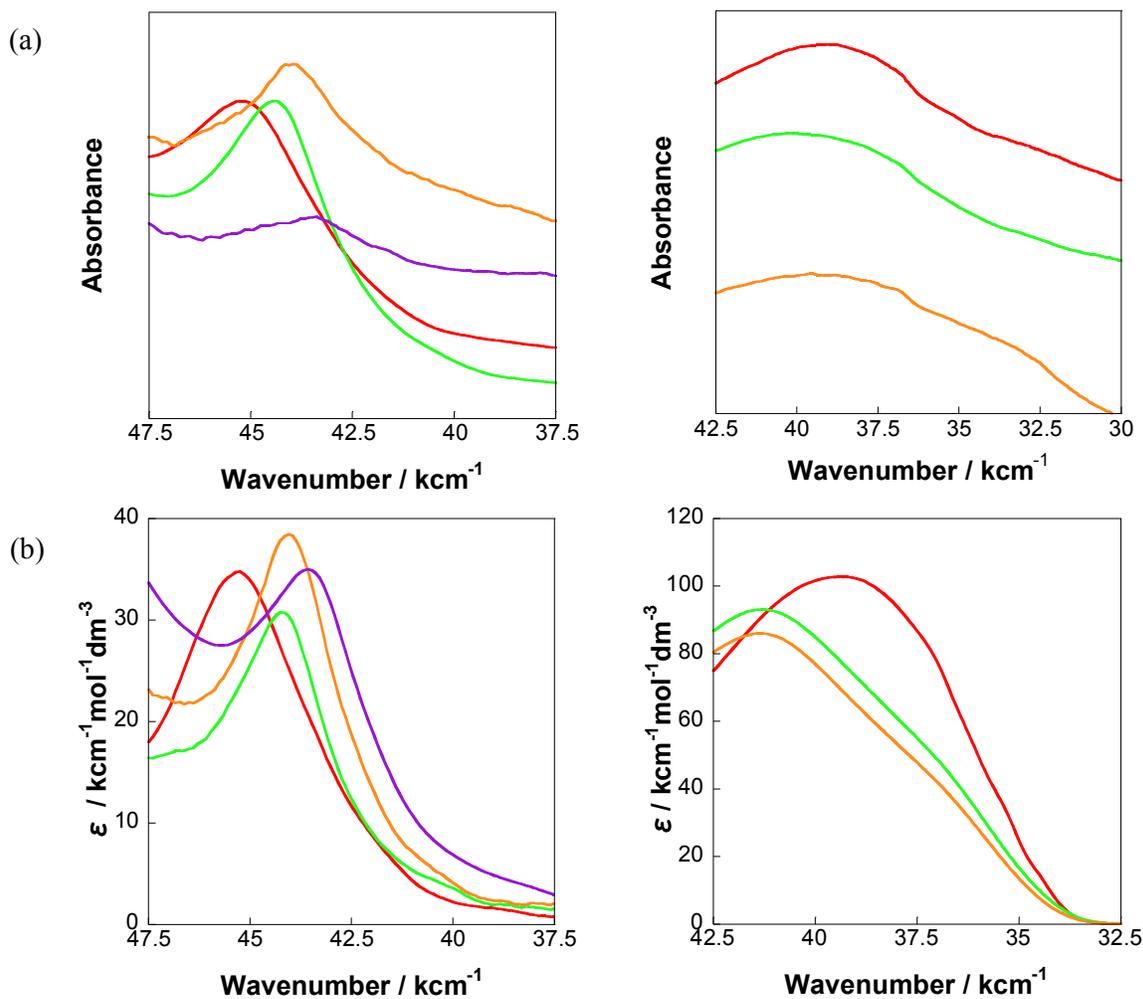


Fig. 7. Electron absorption spectra (left: **L1** complexes, right: **L5** complexes; (a) solid (nujol), (b) solution, CH_3CN : $[\text{Ag}(\text{L1H})]_2$, cyclohexane: $[\text{Ag}(\text{L1Cl})]_2$, $[\text{Ag}(\text{L1Br})]_2$, $[\text{Ag}(\text{L1I})]_n$, CH_2Cl_2 : $[\text{Ag}(\text{L5H})]_2$, $[\text{Ag}(\text{L5Cl})]$, and $[\text{Ag}(\text{L5Br})]$); red: H, green: Cl, orange: Br, purple: I).

Omary and coworkers previously reported large thermochromic shifts in the luminescence of trinuclear pyrazolato metallacycle complexes of Cu, Ag, and Au.¹⁶ New, higher energy emissions appeared in these compounds concomitant with the disappearance of lower energy bands upon cooling, resulting in dramatic colour changes from orange at 285 K to green at 77 K for the gold(I) trinuclear complex and from blue (77K) to UV emission (4 K) for the corresponding silver(I)

trinuclear complex. No such “startling” change in the emission frequency was observed with our compounds (Figs. 8, 9 and Table S2). However, temperature dependent emission at 280 nm irradiation in the solid state at variable temperatures (299, 173, and 83 K) was observed.

The emission spectrum of $[\text{Ag}(\text{L1H})]_2$ in the solid state was somewhat different to that of the halogenated analogues (Fig. 8). The more intense emission spectra of $[\text{Ag}(\text{L1H})]_2$ at 83 K exhibited vibronic structure around 345 nm and 690 nm, while no vibronic progression was observed for the halogenated analogues at the same temperature. The latter displayed visible emission on UV lamp irradiation at liquid nitrogen temperatures and the colour of this emission correlating with the electronegativity of the halogen substituent: ($[\text{Ag}(\text{L1Cl})]_2$ red, $[\text{Ag}(\text{L1Br})]_2$ orange, $[\text{Ag}(\text{L1I})]_n$ yellow).

By contrast, the emission spectra of **L5** complexes at 83 K were dominated by intense emission bands from *ca.* 400 to 600 nm with the parent $[\text{Ag}(\text{L5H})]_2$ appearing more yellowish, than blue under UV lamp irradiation at liquid nitrogen temperatures (Fig. 9). Some vibrational structure was observed in the parent and halogenated analogues and it seems reasonable to suggest that extended conjugation provided by the two phenyls groups has red shifted the intense blue band observed in the corresponding diisopropyl analogues.

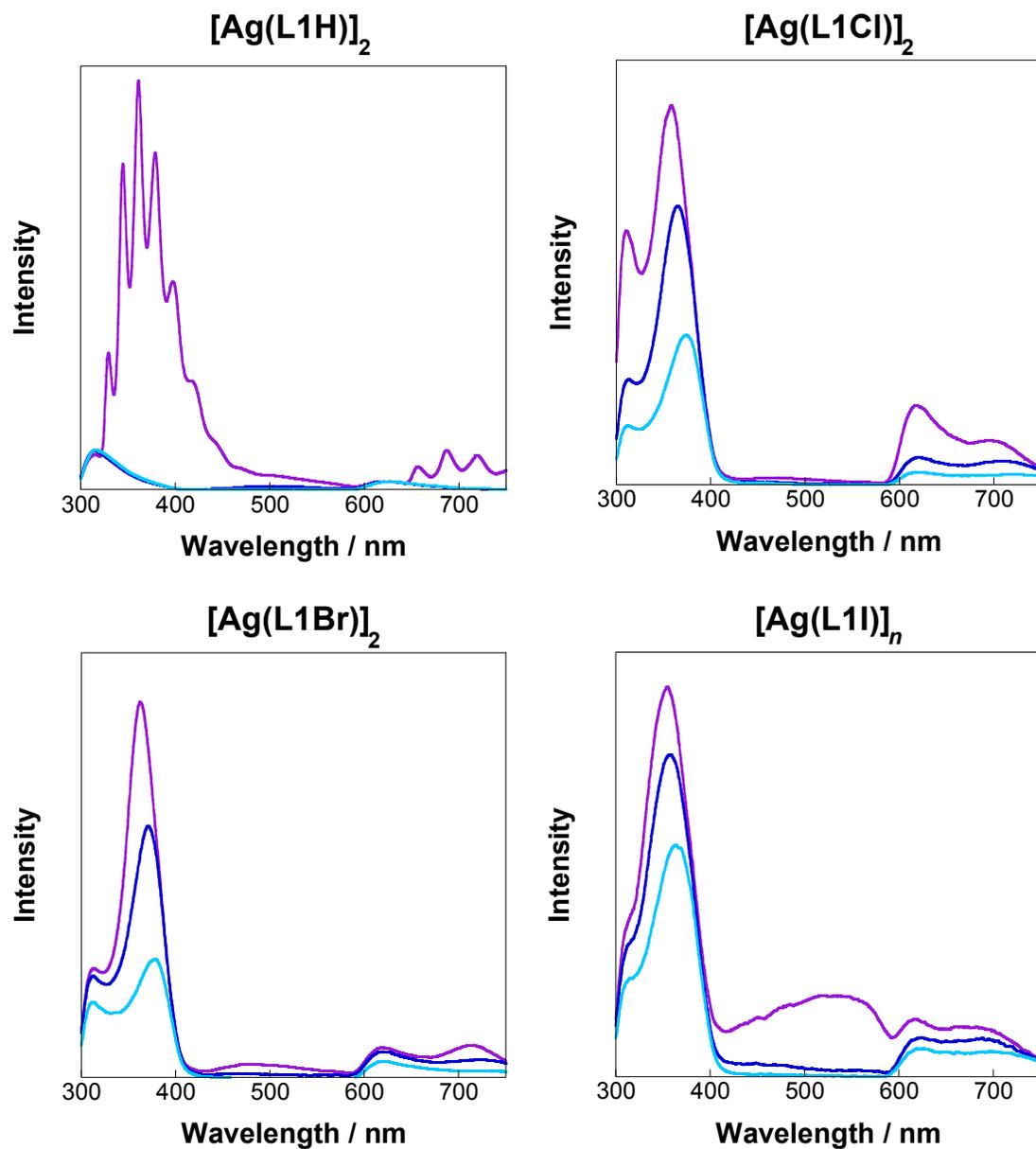


Fig. 8. Emission spectra of L1 complexes at variable temperatures at 280 nm irradiation (aqua: 299 K, blue: 173 K, purple: 83 K).

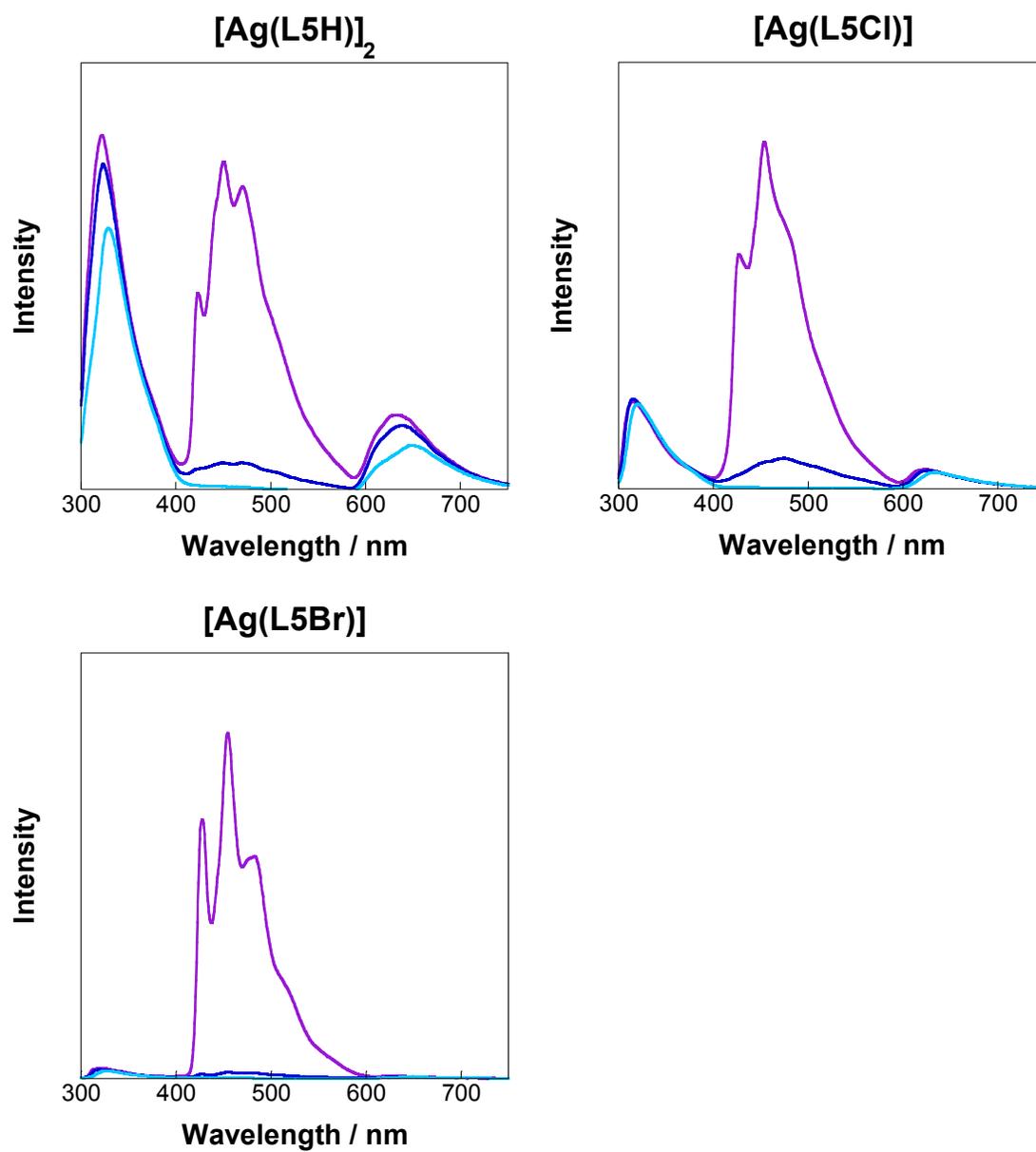


Fig. 9. Emission spectra of **L5** complexes at variable temperatures at 280 nm irradiation (aqua: 299 K, blue: 173 K, purple: 83 K).

Conclusion

Four new silver(I) complexes $\{[\text{Ag}(\mu\text{-}4\text{-X-}3,5\text{-R}_2\text{-pz})_3\}_n$ ($\text{R} = i\text{Pr}$, $\text{X} = \text{Cl}$, $n = 2$: $[\text{Ag}(\text{L1Cl})]_2$; $\text{R} = i\text{Pr}$, $\text{X} = \text{I}$, $n = 1$: $[\text{Ag}(\text{L1I})]$, $n = 2$: $[\text{Ag}(\text{L1I})]_2$; $\text{R} = \text{Ph}$, $\text{X} = \text{Cl}$, $n = 1$: $[\text{Ag}(\text{L5Cl})]$) have been synthesized and structurally characterized together with the previously reported $\{[\text{Ag}(\mu\text{-}4\text{-X-}3,5\text{-R}_2\text{pz})_3\}_n$ ($\text{R} = i\text{Pr}$, $\text{X} = \text{H}$, $n = 2$: $[\text{Ag}(\text{L1H})]_2$; $\text{R} = i\text{Pr}$, $\text{X} = \text{Br}$, $n = 2$: $[\text{Ag}(\text{L1Br})]_2$; $\text{R} = \text{Ph}$, $\text{X} = \text{H}$, $n = 2$: $[\text{Ag}(\text{L5H})]_2$; $\text{R} = \text{Ph}$, $\text{X} = \text{Br}$, $n = 1$: $[\text{Ag}(\text{L5Br})]$). In the diisopropyl (**L1**) analogues, two argentophilic interactions in $[\text{Ag}(\text{L1H})]_2$ and $[\text{Ag}(\text{L1I})]_2$ and three in $[\text{Ag}(\text{L1Cl})]_2$ and $[\text{Ag}(\text{L1Br})]_2$ were observed in the Raman spectra and X-ray structures and relative strengths correlated with the electronegativity of the halogens. Only silver(I) ion (soft acid) and Iodide ion (soft base) soft – soft interactions were observed in the X-ray structure of $[\text{Ag}(\text{L1I})]$. Fewer argentophilic interactions were observed in the corresponding diphenyl (**L5**) analogues. Only one $\text{Ag}\cdots\text{Ag}$ contact was observed for $\text{X} = \text{H}$, $[\text{Ag}(\text{L5H})]_2$, but only $\text{Ag}\cdots\text{X}$ contacts were observed for $\text{X} = \text{Cl}$ and Br ($[\text{Ag}(\text{L5Cl})]$ and $[\text{Ag}(\text{L5Br})]$), in contrast to their **L1** counterparts (Fig. 10).

All complexes exhibited solid-state photoluminescent at visible wavelengths at liquid nitrogen temperatures. The strength of the argentophilic interactions could be correlated with the electronegativity of the halogen substituents and a similar relationship was observed for the emission wavelength of the **L1** complexes, pointing to a $\text{Ag}\text{-Ag}$ excited state as previously proposed. Emission from the **L5** complexes was dominated by the extended π -system of this chromophore. Our ongoing study will focus on this correlation of the electronic influences of the substituent on structure and emission colour tuning with a view to chemosensing and display applications.

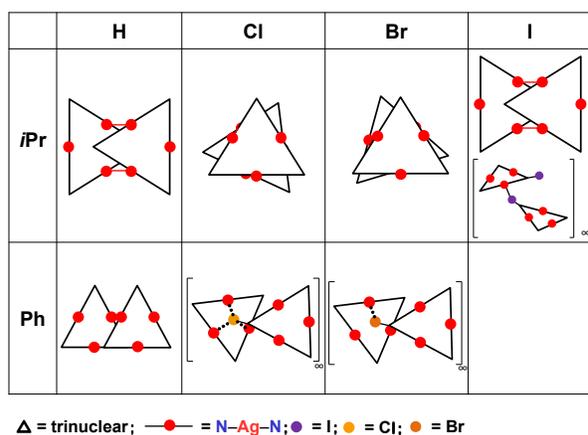


Fig. 10. Schematic diagram of synthesized complexes.

Acknowledgments

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