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**Supporting Information for:**

# Structure and photoluminescence of silver(I) trinuclear halopyrazolato complexes

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**Table S1**

X-ray crystallographic data for **L1** and **L5** complexes.

| | **[Ag(L1Cl)]$_2$**·0.5$C_6H_{14}$·3×0.25$H_2O$ | **[Ag(L1I)]** | **[Ag(L1I)]$_2$**·$C_6H_{14}$ | **[Ag(L5Cl)]**·2$CH_2Cl_2$ |
|---|---|---|---|---|
| Formula | $C_{57}H_{92.5}Ag_6Cl_6N_{12}O_{0.75}$ | $C_{27}H_{42}Ag_3I_3N_6$ | $C_{60}H_{98}Ag_6I_6N_{12}$ | $C_{47}H_{34}Ag_3Cl_7N_6$ |
| Formula weight | 1817.86 | 1154.99 | 2396.15 | 1254.60 |
| Crystal system | Monoclinic | Orthorhombic | Monoclinic | Orthorhombic |
| Space group | $P2_1/c$ (No. 14) | $Pna2_1$ (No. 33) | $P2_1/c$ (No. 14) | $Pna2_1$ (No. 33) |
| $a$ /Å | 10.2520(11) | 11.5188(10) | 14.823(2) | 9.544(2) |
| $b$ /Å | 29.412(2) | 23.8743(13) | 12.7462(11) | 20.286(4) |
| $c$ /Å | 27.446(3) | 14.0966(7) | 20.735(3) | 24.142(4) |
| $\beta$ /° | 99.3800(11) | --- | 90.874(2) | --- |
| $V$ /Å$^3$ | 8165.2(12) | 3876.6(5) | 3917.1(8) | 4674(2) |
| $Z$ | 4 | 4 | 2 | 4 |
| $D$calc /gcm$^{-3}$ | 1.479 | 1.979 | 2.031 | 1.783 |
| $R$ (int) | 0.0512 | 0.0281 | 0.0456 | 0.0780 |
| $\mu$(Mo $K\alpha$) /cm$^{-1}$ | 16.417 | 39.099 | 38.734 | 16.821 |
| Reflections collected | 63254 | 30308 | 28371 | 37740 |
| Unique reflections | 18485 | 4590 | 8762 | 8670 |
| No. of observations | 7487 ( $I > 3\sigma(I)$) | 4145 ( $I > 3\sigma(I)$) | 6953 ( $I > 3\sigma(I)$) | 5024( $I > 2\sigma(I)$) |
| No. of variables | 823 | 395 | 428 | 603 |
| Reflections/para. ratio | 9.10 | 10.49 | 16.25 | 8.33 |
| $R$ ( $I > 3\sigma(I)$) | 0.0603 | 0.0306 | 0.0517 | 0.0390( $I > 2\sigma(I)$) |
| $R_w$ ( $I > 3\sigma(I)$) | 0.1335 | 0.0755 | 0.1282 | 0.0530 ( $I > 2\sigma(I)$) |
| Good. of fit indicator | 1.854 | 1.628 | 2.546 | 0.567 |
| Flack parameter | --- | 0.25(8) | | 0.06(3) |
| | | (Friedel pairs = 3956) | | (Friedel pairs = 3170) |
| Max/min peak, /e Å$^3$ | 1.68 / –0.69 | 0.89 / –0.59 | 2.51 / –1.73 | 1.29 / –1.12 |

$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo|$; $R_w = [(\Sigma \, w( \, (Fo^2 - Fc^2)^2 \, ) / \, \Sigma \, w( \, Fo^2)^2]^{1/2}$

**Experimental section**

**Preparation of Complexes**

**{[Ag(μ-4-Br-3,5-*i*Pr$_2$pz)]$_3$}$_2$ ([Ag(L1Br)]$_2$)**[1]

This complex was prepared by a procedure analogous to that used for [**Ag(L1Cl)]**$_2$, substituting Na**L1Br** (742 mg, 2.93 mmol). Colorless crystals (753 mg, 0.371 mmol, yield 76%) were isolated from hexane at –15 °C. Far-IR (CsI, cm$^{-1}$): 670w, 658w, 646w, 585m, 555m, 545w (C–Br), 505m (Ag–N), 405s, 366s, 344w, 242vs, 211s. Raman (solid, cm$^{-1}$): 2970vs (C-H, aliphatic), 2910vs (C–H, aliphatic), 2868vs (C–H, aliphatic), 2754w, 2713w, 1499m (C=N), 1486m, 1443s, 1431m, 1367vs, 1303m, 1280m, 1181m, 1145m, 1109m, 1091m, 1045m, 957m, 881s, 708w, 647m, 586w, 533s (C–Br), 506m (Ag–N), 401w, 331w, 239m, 186w (Ag···Ag). UV–Vis (solution, cyclohexane, $\lambda_{max}$/nm ($\varepsilon$/cm$^{-1}$mol$^{-1}$dm$^3$)): 227 (38100). UV–Vis (solid, nujol, nm): 227.5. Emission (solid, 299 K, $\lambda_{max}$/nm): 312, 379, 620 (ex. 280 nm).

**{[Ag(μ-3,5-Ph$_2$pz)]$_3$}$_2$ ([Ag(L5H)]$_2$)**[2–3]

A solution of Na**L5H** (688 mg, 2.84 mmol) in tetrahydrofuran (20 cm$^3$) was added dropwise to a suspension of silver(I) nitrate (484 mg, 2.85 mmol) in tetrahydrofuran (10 cm$^3$) over 15 min. The reaction was protected from light and after stirring for a few days, the solvent was evaporated under vacuum. The resulting solid was extracted with dichloromethane (40 cm$^3$) to remove sodium nitrate. The filtrate was concentrated under vacuum to provide a white powder that was recrystallized from dichloromethane at –15 °C. These colorless crystals (615 mg, 0.313 mmol, yield 66%) were filtered and dried under vacuum. IR (KBr, cm$^{-1}$): 3061m (C–H, aliphatic), 3028m(C–H, aliphatic), 1943w, 1870w, 1799w, 1748w, 1603m, 1573m, 1538w, 1512w, 1496w, 1470vs (C=N), 1425m, 1400s, 1335m, 1322m, 1306m, 1275m, 1220w, 1156m, 1103s, 1071s, 1028m, 1002m, 992m, 978w, 908m, 801m, 752vs, 693vs, 553m, 507w, 437w. Far-IR (CsI, cm$^{-1}$): 618m, 553vs, 533m, 526w, 508vs (Ag–N), 479m, 450m, 439s, 415m, 405m, 359m, 288m, 233m, 194s, 178ws, 159w, 152w. Raman (solid, cm$^{-1}$): 3124m (C-H, aromatic), 3061m (C-H, aromatic), 1606vs, 1574w, 1537w, 1516m, 1464w (C=N), 1451w, 1428s, 1413m, 1404m, 1322w, 1296w, 1223w, 1182w, 1158w, 1102w, 1046w, 1030w, 1002s, 963m, 843w, 768w, 697w, 669w, 619w, 510w (Ag–N), 407w, 350w, 276w, 244w (Ag···Ag). ). $^1$H-NMR ($CDCl_3$, 500 MHz): δ 6.77 (s, 6H, pz-*H*), 7.15 (t, *J* = 7 Hz, 24H, *m*-Ph), 7.26 (t, *J* = 7 Hz, 12H,

*p*-Ph), 7.65 (d, *J* = 3.5 Hz, 24H, *o*-Ph). $^{13}$C-NMR ($CDCl_3$, 125 MHz): δ 101.7 (pz-*C*$_4$), 126.7 (*o*-Ph), 128.2 (*p*-Ph), 129.2 (*m*-Ph), 133.8 (Ph-*C*$_1$), 155.5 (pz-*C*$_{3,5}$). UV–Vis (solution, $CH_2Cl_2$, $\lambda_{max}$/nm (ε/$cm^{-1}mol^{-1}dm^3$)): 253.5 (103000). UV–Vis (solid, nujol, nm): 257. Emission (solid, 299 K, $\lambda_{max}$/nm): 329, 649 (ex. 280 nm).

**[Ag(μ-4-Br-3,5-$Ph_2$pz)]$_3$** ([**Ag(L5Br)**])$^4$

This complex was prepared by a procedure analogous to that used for [**Ag(L5H)]**, substituting Na**L5Br** (198 mg, 0.617 mmol). Colorless crystals (102.8 mg, 0.0422 mmol, yield 41%) were isolated from dichloromethane at –15 °C. IR (KBr, $cm^{-1}$): 3063m (C–H, aromatic), 3023m (C–H, aromatic), 2963w, 1948w, 1876w, 1802w, 1750w, 1603m, 1577w, 1462s (C=N), 1435m, 1319w, 1294w, 1262m, 1179w, 1137s, 1072m, 1030m, 992m, 980m, 911m, 840w, 805w, 765vs, 733m, 695vs, 596m, 547w, 486w, 459m, 429w, 409w. Far-IR (CsI, $cm^{-1}$): 669w, 618m, 597vs, 549s (C–Br), 499w, 488s (Ag–N), 460s, 432m, 406w, 387w, 331w, 316w, 284w, 254s, 231w, 205s, 163w, 153w. Raman (solid, $cm^{-1}$): 3066m (C-H, aromatic), 2986w, 1605vs, 1577w, 1553w, 1518s, 1465w (C=N), 1437s, 1402m, 1322w, 1296w, 1274w, 1181w, 1158w, 1034w, 1003s, 982m, 843w, 767w, 703w, 670m, 619w, 546w (C–Br), 488w (Ag–N), 408w, 331w, 253m, 241w, 221w, 202w. $^{13}$C-NMR ($CDCl_3$, 125 MHz): δ128.2 (*o*-Ph), 128.9 (*m*-Ph). UV–Vis (solution, $CH_2Cl_2$, $\lambda_{max}$/nm (ε/$cm^{-1}mol^{-1}dm^3$)): 242 (86000). UV–Vis (solid, nujol, nm): 252.5. Emission (solid, 299 K, $\lambda_{max}$/nm): 326.5, 449, 647 (ex. 280 nm).

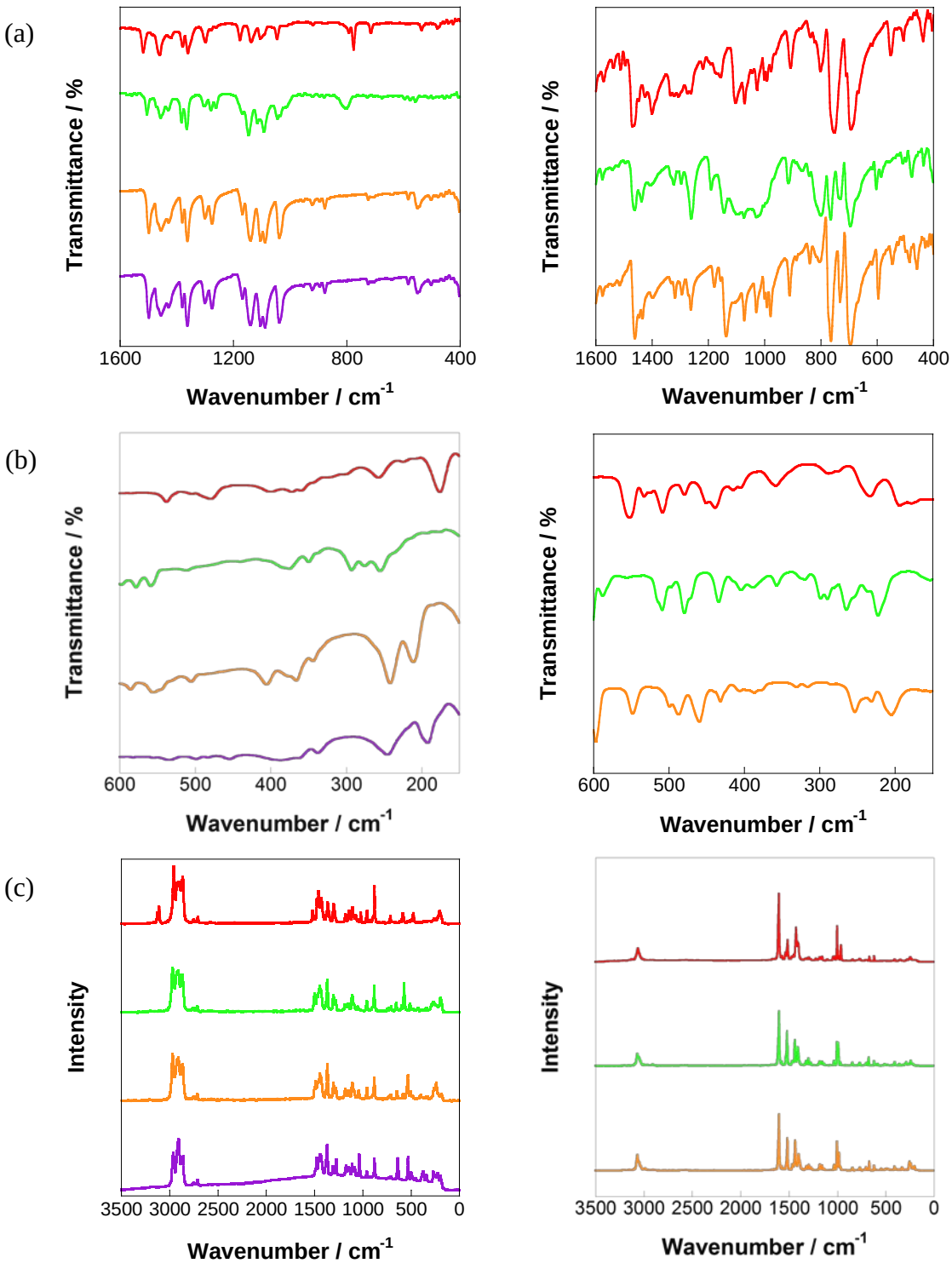


**Fig. S1** IR, far-IR, Raman spectra (left: **L1** complexes, right: **L5** complexes;
(a) IR, (b) far-IR, (c) Raman; red: H, green: Cl, orange: Br, purple: I).

**Table S2**
Emission wavelengths (nm) at variable temperatures and 280 nm irradiation.

| | | |
|---|---|---|
| **[Ag(L1H)]$_2$** | 299 K | 315.5, 493, 626.5 |
| | 173 K | 314.5, 507, 623 |
| | 83 K | 315, 329, 344.5, 361, 379, 397.5, 417, 620, 657, 687, 719.5 |
| **[Ag(L1Cl)]$_2$** | 299 K | 312, 373.5, 620, 721 |
| | 173 K | 313, 365, 620.5, 705 |
| | 83 K | 310.5, 358.5, 469.5, 618.5, 693.5 |
| **[Ag(L1Br)]$_2$** | 299 K | 312, 379, 620 |
| | 173 K | 313.5, 371, 469, 620.5, 723 |
| | 83 K | 313, 362.5, 479, 618.5, 712.5 |
| **[Ag(L1I)]$_n$** | 299 K | 314, 363.5, 621, 700 |
| | 173 K | 313.5, 358, 620, 688 |
| | 83 K | 313, 354, 481, 535, 616.5, 682 |
| **[Ag(L5H)]$_2$** | 299 K | 329, 649 |
| | 173 K | 323.5, 442, 449.5, 469.5, 639 |
| | 83 K | 322.5, 423.5, 450, 470.5, 633 |
| **[Ag(L5Cl)]** | 299 K | 320.5, 634.5 |
| | 173 K | 315, 455, 475, 626 |
| | 83 K | 315, 427.5, 454, 474, 623.5 |
| **[Ag(L5Br)]** | 299 K | 326.5, 449, 647 |
| | 173 K | 319, 427, 455, 478.5, 631.5 |
| | 83 K | 320, 427.5, 454.5, 483, 624 |

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