Mechanism of Formation of $[Ag_2L_2I_2]$ and Crystal Structure of the Intermediate $[Ag_3L_2I_3]$ Cluster (L= 1,8-diisocyano-*p*-menthane)†

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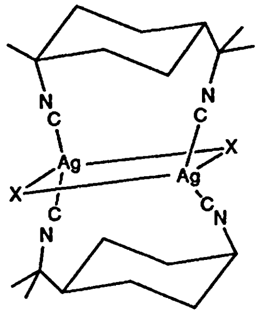
The complexes $[Ag_nL_2I_n]$ (n = 2–4, L = 1,8-diisocyano-*p*-menthane) have been prepared from the direct reaction of AgI with L in the appropriate stoichiometric amount and have been identified either by chemical analysis and fast atom bombardment mass spectroscopy (n = 2 or 4), or by X-ray crystallography (n = 2 or 3). Addition of excess of L to benzene solutions of AgI, $[Ag_4L_2I_4]$ or $[Ag_3L_2I_3]$ always led to $[Ag_2L_2I_2]$, indicating that the synthesis of the Ag_2 complexes from AgI must proceed *via* the formation of the Ag_4 and Ag_3 species. The single-crystal X-ray analysis of $[Ag_3L_2I_3]$ reveals the formation of a quasi-isosceles triangular Ag_3 structure [apex angle 44.55(7)°] with the following r(Ag$\cdots$Ag) values: 3.633(4), 3.760(4) and a relatively short one of 2.805(4) Å. The triangular structure is bicapped by two iodine atoms [r(Ag–I) ranging from 2.789(3) to 3.085(5) Å], while the third iodine atom bridges the two least separated Ag atoms. The Raman-active $\nu(Ag_2)$ mode associated with this short binding is observed at 122 cm^{-1} (with a force constant, F extracted from the diatomic approximation, of 0.47 mdyn Å^{-1}). These non-bonding Ag$\cdots$Ag interactions correspond approximately to an Ag–Ag bond order of ≈0.5.

The use of bridging ligands such as diisocyanides and diphosphines in the synthesis of polynuclear silver and gold complexes leads to the formation of dimeric,[1,2] trimeric,[3] polymeric[4] and quasi-unidimensional structures in the solid state.[5] We have recently prepared and characterized by X-ray crystallography and Raman spectroscopy a series of complexes $[Ag_2L_2X_2]$ [L = 1,8-diisocyano-*p*-menthane; X = Cl, Br or I (Scheme 1)][6a] which exhibit interesting luminescence properties.[6b] During the course of our studies we have observed that it was possible to synthesise the trimeric and tetrameric forms of $[Ag_nL_2I_n]$ complexes (n = 3 or 4) and that these two forms could easily be converted into the dimeric form. We now report the preparation of such complexes, and in particular the crystal structure of the $[Ag_3L_2L_3]$ complex, in which a relatively short non-bonded Ag$\cdots$Ag distance *via* a $(\mu\text{-}I)_3$ bridge is observed.



Scheme 1 X = Cl, Br or I

Experimental

Materials.—Diisocyanide L,[7] $[Ag_2L_2I_2]$,[6] $[Ag_3(dppm)_3Br_2]Br$[3] [dppm = bis(diphenylphosphino)methane] and $[Pd_3(dppm)_3(CO)][CF_3CO_2]_2$[8] were prepared according to known procedures. Silver iodide was prepared from the direct reaction of $AgNO_3$ with NaI in water and dried *in vacuo* for several days. The purity of the materials was checked by elemental analysis.

Preparations.—$[Ag_4L_2I_4]$. Silver iodide (0.47 g, 2 mmol) was suspended in benzene (20 cm^3) containing L in stoichiometric amount (0.35 g, 1 mmol), and stirred for 12 h at 40 °C. The crude white product was filtered and washed with benzene. Purification was performed by dissolving the white solid in a minimal amount of slightly warm acetonitrile, and precipitating it with diethyl ether. The bright white solid was washed with ether. Yield ≈70% (Found: C, 22.30; H, 2.85; Ag, 33.30; I, 39.15; N, 2.20. $C_{24}H_{36}Ag_4I_4N_4$ requires C, 22.30; H, 2.80; Ag, 33.40; I, 39.30; N, 2.15%). Fast atom bombardment (FAB) mass spectrum: m/z 1165, $Ag_4L_2I_3^{\cdot +}$ and 1038, $Ag_4L_2I_2^{\cdot +}$. IR (CsI): 2176 cm^{-1} [ν(N≡C)]. All attempts to obtain crystals suitable for X-ray diffraction analysis uniformly failed.

$[Ag_3L_2I_3]$. Silver iodide (0.47 g, 2 mmol) was suspended in benzene (20 cm^3) containing L (0.528 g, 1.5 mmol), and stirred for 12 h at 40 °C. The crude white product was filtered off and washed with benzene. Purification was as for $[Ag_4L_2L_4]$. Yield ≈80% (Found: C, 27.35; H, 3.40; Ag, 31.00; I, 36.85; N, 2.70. $C_{24}H_{36}Ag_3I_3N_4$ requires C, 27.25; H, 3.45; Ag, 30.60; I, 36.00; N, 2.65%). IR (CsI): 2175 cm^{-1} [ν(N≡C)]. Crystals suitable for X-ray crystallography were obtained by slowly cooling a saturated solution of the product in ethanol, in a refrigerator maintained at −5 °C. The X-ray analysis revealed that the crystals obtained were of $[Ag_3L_2I_3]\cdot$EtOH.

$[AgL_2I_2]$. *Method* (*a*). Silver iodide (0.47 g, 2 mmol) was suspended in benzene (20 cm^3) containing L in excess of the required stoichiometry (1.41 g, 4 mmol), and stirred for 12 h at 40 °C. Purification was performed as for $[Ag_4L_2I_4]$. Yield 70–

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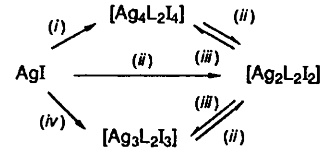
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: dyn = 1 × 10^{-5} N.

Table 1 Data collection and processing parameters

Molecular formula	$C_{24}H_{36}Ag_3I_3N_4 \cdot C_2H_6O$
M	112.95
Colour and habit	Colourless stick
Crystal symmetry	Orthorhombic
Space group	*Pcab* (no. 61)
a/Å	15.7290(8)
b/Å	16.8566(11)
c/Å	30.1498(16)
U/Å^3	7993.8(8)
Z	8
$F(000)$	4272
D_c/g cm^{-3}	1.850
μ/cm^{-1}	37.6
Crystal size/mm	0.08 × 0.08 × 0.20
Transmission factors	0.4316, 0.4347
Scan type	ω–2θ
Scan speed/° min^{-1}	2.7
Scan range/°	$2 \leqslant 2\theta \leqslant 40$
Collection range (h,k,l)	0–15, 0–16, 0–29
Unique data measured (n)	3727
Observed data [$I \geqslant 2.5\sigma(I_{net})$]	2192
Number of variables p	328
$R(=\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|)$	0.067
$R'\{=[\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|]^{\frac{1}{2}}\}$	0.064
Weighting scheme	$1/\sigma^2(F)$
$S\{=[\Sigma w(\|F_o\| - F_c\|^2/(n - p)]^{\frac{1}{2}}\}$	2.7
Residual extrema in final difference map/e Å^{-3}	−1.20, +1.35
Secondary extinction coefficient	0.09(1)



Scheme 2 (*i*) 0.5 L, (*ii*) excess of L, (*iii*) AgI, (*iv*) 0.67 L

80% (Found: C, 35.10; H, 4.45; Ag, 25.90; I, 29.90; N, 3.30. $C_{24}H_{36}Ag_2I_2N_4$ requires C, 35.05; H, 4.40; Ag, 26.25; I, 30.85; N, 3.40%). IR (CsI): 2176 cm^{-1} [ν(N≡C)]. Crystals suitable for X-ray crystallography were obtained in the same way as for [$Ag_3L_2I_3$]. Analysis reveals that the crystals are of [$Ag_2L_2I_2$]·EtOH. The structure will be published elsewhere.

Method (*b*). The complex [$Ag_4L_2I_4$] (1.29 g, 1 mmol) was suspended in benzene (20 cm^3) with a large excess of (0.70 g, 2 mmol) and stirred for 12 h at 40 °C. Purification was as for [$Ag_4L_2I_4$]. Yield >90%. The compound was identified by comparison of its chemical analysis and the UV/VIS spectrum with the product obtained by method (*a*) above.

Method (*c*). The complex [$Ag_3L_2I_3$] (0.26 g, 0.25 mmol) was suspended in benzene (10 cm^3) with a large excess of L (0.18 g, 0.5 mmol) and stirred for 12 h at 40 °C. Purification was as for [$Ag_4L_2I_4$]. Yield ≈60%. The compound was identified by comparison of its chemical analysis and the UV/VIS spectrum (as above).

Instrumentation.—The Fourier-transform IR (4000–200 cm^{-1}) spectra were obtained on a Bomem (MB-102) spectrometer. Mass spectra were acquired using a Kratos MS-50 TCTA spectrometer and a FAB 11 NF model Iontech saddle field source operating at 70 kV with 2 mA current. The samples were in thiolglycerol matrices. Elemental analyses (C,H,N) were performed by Guelph Chemical Laboratories, Ltd. (Guelph, Ontario), and in our department using a KEVEX-700 X-ray emission spectrofluorometer operating at 60 kV (Ag, I).

The Raman spectra were measured on two different spectrometers. For the solid silver complexes, an Instruments SA Raman spectrometer equipped with a U-1000 Jobin-Yvon 1.0 m double monochromator was employed using either the 647.1 nm red line or the 514.5 nm green line of Spectra-Physics argon ion lasers, for excitation. A BOMEM FT-Raman model spectrometer was used for the solid [$Pd_3(dppm)_3(CO)$][CF_3CO_2]$_2$ sample (due to laser sensitivity of the compound). 300 Scans were acquired with 100 mW laser power at the sample with a 4 cm^{-1} resolution (no smoothing). A Notch filter was employed with a cut-off at ≈90–100 cm^{-1}. The UV/VIS spectra were measured using a Hewlett-Packard (HP8452 A) diode array spectrophotometer.

Crystallography.—*Crystal data*. A colourless stick shape crystal was mounted in a capillary tube for X-ray crystallographic analysis in the presence of mother-liquor to avoid efflorescence. Diffraction intensities were measured at 293 K on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) running the NRCCAD[9a] control program. An ω–2θ scan was used at a speed of 2.7° min^{-1}. The unit-cell parameters were obtained by least-squares refinement using the coordinates of 24 reflections, centred using the TRUANG option of NRCCAD, thereby minimizing the effects of instrumental and crystal-alignment errors. Lorentz and polarization factors were applied and absorption corrections were made using interpolation methods from the ABSORP program of NRCVAX.[9b] The structure was solved by direct-method techniques and subsequent difference syntheses. The H atoms were generated geometrically and included in structure-factor calculations but not refined. A Δ*F* map revealed the presence of a disordered ethanol molecule. Crystal data are summarized in Table 1. Refinement was by full-matrix least squares with weights based on counter statistics. All non-H atoms were refined with anisotropic thermal parameters except for the disordered ethanol molecule which was assigned isotropic thermal parameters. Computations were performed using the NRCVAX suite of crystal structure programs. Scattering factors were taken from ref. 9(*c*). The final residual densities were located in the vicinity of the Ag atoms. No H-bond distances were found between the oxygen atom of the ethanol molecule and the other atoms [O(1)···I(3) 5.01, O(1)···Ag(2) 5.39, O(1)···N(1) 5.29 Å]. The poor quality of the crystal and data prevented better refinement. Furthermore, this poor quality and the small size of the crystal did not allow us to observe any reflections at θ > 40°.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

With the appropriate stoichiometric amounts of L and AgI, the [$Ag_nL_2I_n$] complexes (n = 2–4) are easily prepared in good yields. Furthermore, [$Ag_2L_2I_2$] can also be prepared from [$Ag_4L_2I_4$] or [$Ag_3L_2I_3$] using an excess of L. Scheme 2 summarizes these syntheses. Since the polynuclear products appear to be practically identical according to IR and ^{1}H NMR spectroscopy, identification can only be made reliably by chemical analysis. On the other hand, the UV/VIS spectra exhibit relatively sharp features at different wavelengths (Fig. 1) and are convenient for the identification of the products. Appropriate stoichiometric additions of AgI to a solution of [$Ag_2L_2I_2$] in acetonitrile at 298 K produces the [$Ag_3L_2I_3$] and [$Ag_4L_2I_4$] clusters which were identified by UV/VIS spectroscopy (Fig. 1). These results indicate that the diisocyanide L is labile (see Scheme 2).

The above results show that the mechanism for the formation of the [$Ag_2L_2I_2$] dimer from AgI must proceed *via* the initial preparation of higher nuclearity complexes, in particular [$Ag_4L_2I_4$]. The conversion of [$Ag_4L_2I_4$] into [$Ag_3L_2I_3$] was not studied in this work, but it appears that such a conversion should occur. Nardin and co-workers[10] have reported the preparation and X-ray structures of [$Cu_3(dppm)_3Cl_2$]$^+$, [Cu$_3$(dppm)$_2$I$_3$] and [Cu$_4$(dppm)$_2$X$_4$] (X = Cl, Br or I), and have proposed a mechanism for the formation of some of the complexes. No proposed interpretation of the possible conversion of Cu$_4$ into Cu$_3$ species was however provided.

The X-ray analysis of [Ag$_3$L$_2$I$_3$] reveals a butterfly-type structure (Fig. 2, Tables 1–3) which exhibits a triangular geometry for the silver atoms with two long Ag $\cdots$ Ag distances [3.633(4) and 3.760(4) Å], and one relatively short [2.805(4) Å] [apex angle 44.55(7)°]. The long Ag $\cdots$ Ag separations [Ag(1) $\cdots$ Ag(2) and Ag(1) $\cdots$ Ag(3)] are induced by the presence of the bridging L ligands, which normally exhibit a bite distance of ≈4.4 Å.[12] The orientation of these ligands is head-to-head, and does not exhibit the disordered structure (head-to-tail and head-to-head) commonly encountered[12] for complexes of L. Two of the iodine atoms triply bridge each face of the triangular structure with Ag–I distances ranging from 2.789(3) to 3.085(5) Å [average 2.98(10) Å]. These values appear to be somewhat longer (on average) than those found in [Ag$_2$L$_2$I$_2$] [2.9050(13) and 2.9335(12) Å],[6] in AgI (2.87 Å),[13] the closely related silver iodide polymeric [Ag$_3$I$_4$]$^-$ ion r[(AgI) 2.89(9) Å] and the linear [Ag$_4$I$_8$]$^{4-}$ cluster [*r*(AgI) 2.83(16) Å],[14] indicating that the Ag–I bonding possesses some ionic character (for a covalent bond, $r_{Ag} + r_I = 1.44 + 1.33 = 2.77$ Å; *cf.* an ionic interaction, $r_{Ag} + r_I = 1.08 + 2.06 = 3.14$ Å).[15] Iodine atom I(3) bridges the shortly separated silver atoms [Ag(2), Ag(3)] with Ag–I bond distances of 2.830(4) and 2.789(4) Å indicating that these Ag–I bonds are essentially covalent in nature. The Ag–C bond distances [2.09(8) Å] are somewhat smaller than those found in the dinuclear silver diylide complex [Ag$_2${μ-[{CH(CO$_2$R)}$_2$PPh$_2$]}$_2$] [*r*(Ag–C) 2.183(2) and 2.169(2) Å].[16]

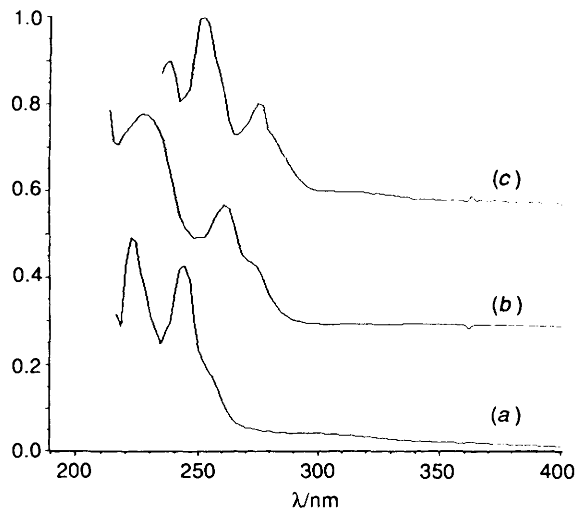


Fig. 1 UV/VIS spectra of the [Ag$_n$L$_2$I$_n$] complexes [*n* = 2(*a*), 4(*b*) or 3(*c*)] in ethanol at 77 K

The Ag(2) $\cdots$ Ag(3) distance [*r*(Ag$_2$)] of 2.805(4) Å where formally non-bonding Ag $\cdots$ Ag interactions occur is shorter than that found in most Ag$_2$ species in which no formal Ag–Ag bond is present.[6] The only known exception is [Ag$_2$(PhNNNPh)$_2$] for which Ag $\cdots$ Ag 2.669 Å.[17] Other relatively short Ag$^+$ $\cdots$ Ag$^+$ contacts (2.564–2.796 Å) have been observed in the solid state for polymeric silver d^{10} materials.[18] In order to quantify the strength of the Ag $\cdots$ Ag interactions, v(Ag$_2$) was measured from Raman spectroscopy. Since [Ag$_3$L$_2$I$_3$] is laser sensitive, no polarization study could be performed and therefore assignment of this mode was based upon comparisons with related species. Fig. 3 shows the Raman spectrum of [Ag$_3$L$_2$I$_3$] and of two related cyclic trinuclear complexes [Ag$_3$(dppm)$_2$Br$_2$]$^+$(D_{3h}) and [Pd$_3$(dppm)$_3$(CO)]$^{2+}$(C_{3v}) for which the average *r*(Ag$_2$) and *r*(Pd$_2$) values are 3.30[3] and 2.60 Å,[8] respectively. The two v(Pd$_2$) modes (a$_1$ + e) are easily assigned (from spectral comparison of the two latter clusters) at 205 and 143 cm^{-1}. The observed frequency ratio [205(a$_1$)/143(e) = 1.43] is consistent with the theoretically predicted value for an equilateral structure [v(a$_1$)/v(e) = $2^{\frac{1}{2}}$]. Bearing in mind that v(Ag$_2$) is observed at 80 cm^{-1} for Ag$_2$(O$_2$CCF$_3$)$_2$ [*r*(Ag$_2$) 2.967(3) Å],[19] and that the v(Pd$_2$) e mode in [Pd$_3$(dppm)$_3$(CO)]$^{2+}$ is located at 143 cm^{-1}, v(Ag$_2$) for the Ag(μ-I)$_3$Ag moiety is then expected to lie between these

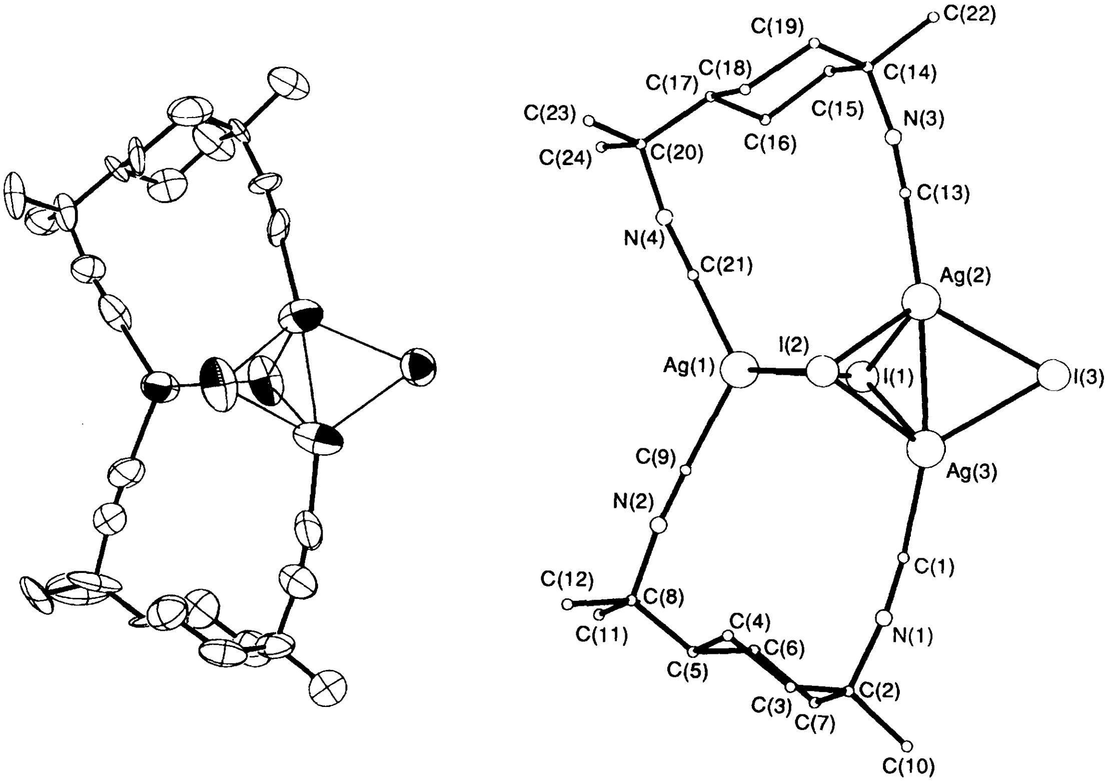


Fig. 2 Molecular structure of [Ag$_3$L$_2$I$_3$], and ORTEP representation[11] showing 50% probability ellipsoids. The H atoms are not shown for clarity

Table 2 Atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Ag(1)	0.413 24(17)	0.334 70(13)	0.126 46(8)
Ag(2)	0.296 42(20)	0.517 82(17)	0.144 36(10)
Ag(3)	0.195 43(23)	0.409 99(18)	0.097 00(12)
I(1)	0.263 02(17)	0.352 77(13)	0.183 65(9)
I(2)	0.373 58(17)	0.457 86(13)	0.063 58(8)
I(3)	0.131 67(15)	0.560 84(12)	0.115 31(7)
N(1)	0.130 2(18)	0.267 0(15)	0.035 4(8)
N(2)	0.384 9(14)	0.161 8(13)	0.077 3(7)
N(3)	0.415 0(14)	0.596 6(12)	0.221 1(7)
N(4)	0.574 4(14)	0.384 5(12)	0.186 9(7)
C(1)	0.150 3(21)	0.322 7(19)	0.055 5(11)
C(2)	0.116 7(18)	0.191 6(17)	0.009 7(10)
C(3)	0.191 4(21)	0.188 4(17)	−0.021 6(9)
C(4)	0.277 7(18)	0.177 5(17)	−0.001 3(10)
C(5)	0.278 6(17)	0.103 8(16)	0.029 2(9)
C(6)	0.205 2(19)	0.112 3(17)	0.062 7(10)
C(7)	0.119 8(21)	0.122 5(19)	0.041 1(10)
C(8)	0.364 4(24)	0.092 7(15)	0.049 6(10)
C(9)	0.396 2(19)	0.221 1(17)	0.094 7(9)
C(10)	0.032 1(21)	0.197 0(21)	−0.012 0(13)
C(11)	0.363 2(3)	0.021 5(20)	0.081 7(13)
C(12)	0.438 1(21)	0.078 4(21)	0.016 5(11)
C(13)	0.373 7(17)	0.573 4(15)	0.193 4(9)
C(14)	0.476 4(16)	0.616 8(14)	0.255 5(10)
C(15)	0.488 2(23)	0.550 9(17)	0.288 8(10)
C(16)	0.518 3(19)	0.475 6(16)	0.267 5(9)
C(17)	0.601 5(17)	0.488 8(14)	0.242 6(9)
C(18)	0.595 5(17)	0.555 9(15)	0.209 0(9)
C(19)	0.559 4(20)	0.632 4(17)	0.230 1(10)
C(20)	0.638 0(17)	0.413 0(14)	0.219 9(9)
C(21)	0.514 0(20)	0.367 1(16)	0.163 2(8)
C(22)	0.446 5(22)	0.693 1(17)	0.278 3(12)
C(23)	0.717 7(19)	0.424 8(18)	0.197 7(11)
C(24)	0.651 8(19)	0.347 1(17)	0.253 6(10)
O(1)	0.757 0(21)	0.666 0(17)	0.125 7(10)
C(25)*	0.648(4)	0.638(4)	0.084 3(20)
C(26)*	0.684(4)	0.680(3)	0.112 6(20)
C(25′)*	0.888(5)	0.695(4)	0.150 3(24)
C(26′)*	0.822(5)	0.683(4)	0.164 3(23)

* Disordered carbon atoms of ethanol solvent were treated as C(25)–C(26) and C(25′)–C(26′) and each given half occupancy.

Table 3 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses

Ag(1) ··· Ag(2)	3.633(4)	I(1)–Ag(1)–I(2)	97.89(10)
Ag(1) ··· Ag(3)	3.760(4)	I(1)–Ag(2)–I(2)	94.58(10)
Ag(2) ··· Ag(3)	2.805(4)	I(1)–Ag(2)–I(3)	101.24(11)
Ag(1)–I(1)	2.941(4)	I(2)–Ag(2)–I(3)	102.26(11)
Ag(1)–I(2)	2.880(3)	I(1)–Ag(3)–I(2)	92.69(11)
Ag(2)–I(1)	3.069(4)	I(1)–Ag(3)–I(3)	104.47(12)
Ag(2)–I(2)	2.904(4)	I(2)–Ag(3)–I(3)	98.79(12)
Ag(2)–I(3)	2.830(4)	Ag(1)–I(1)–Ag(2)	74.34(9)
Ag(3)–I(1)	2.981(5)	Ag(1)–I(1)–Ag(3)	78.83(10)
Ag(3)–I(2)	3.085(5)	Ag(2)–I(1)–Ag(3)	55.22(9)
Ag(3)–I(3)	2.789(4)	Ag(1)–I(2)–Ag(2)	77.83(9)
Ag(1)–C(9)	2.16(3)	Ag(1)–I(2)–Ag(3)	78.06(10)
Ag(1)–C(21)	2.01(3)	Ag(2)–I(2)–Ag(3)	55.76(9)
Ag(2)–C(13)	2.13(3)	Ag(2)–I(3)–Ag(3)	59.88(10)
Ag(3)–C(1)	2.06(3)	Ag(2)–Ag(1)–Ag(3)	44.55(7)
		Ag(1)–Ag(2)–Ag(3)	70.13(10)
		Ag(1)–Ag(3)–Ag(2)	65.32(10)

limits. The observed signal at 122 cm^{-1} for [$Ag_3L_2I_3$] [Fig. 3(*a*)] may well be due to this stretching mode.

This value compares particularly favourably with literature data for disilver compounds with similar *r*(Ag_2) values (Table 4). Furthermore, the Raman spectrum of [$Ag_2L_2I_2$][6] resembles that for [$Ag_3L_2I_3$] except that the 122 cm^{-1} feature is absent from the dimer spectrum, and hence confirms the assignment. The two ν(Ag_2) modes associated with the very weakly interacting Ag atoms [*r* ≈ 3.70(6) Å] are expected to appear below 48 cm^{-1} {see data for [$Ag_2(dmpm)_2Br_2$][dmpw = bis(dimethylphosphino)methane], *r*(Ag_2) 3.6 Å}.[4b] Due to the complexity of the spectra, particularly in the low wavenumber range, no further analysis has been made.

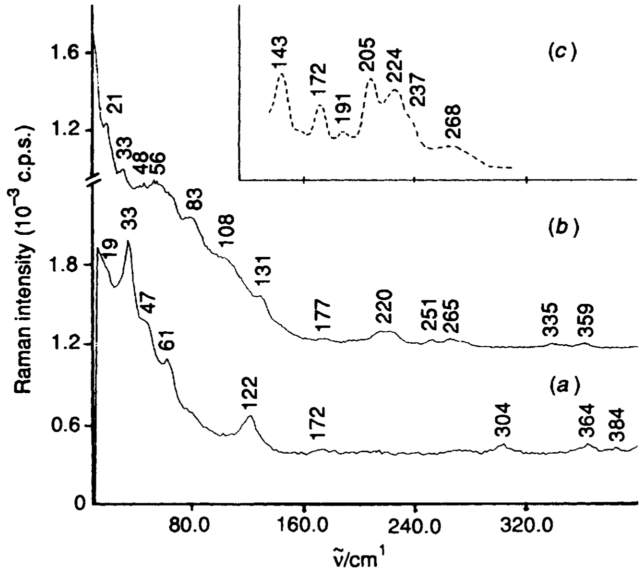


Fig. 3 Comparison of the Raman spectra of [$Ag_3L_2I_2$] (*a*), [$Ag_3(dppm)_3Br_2$]Br (*b*) and [$Pd_3(dppm)_3(CO)$][CF_3CO_2]$_2$ (*c*) in the solid state. Experimental conditions for the micro-Raman spectra (silver clusters only): laser power (at the sample) 5–10 mW, laser excitation 514.5 nm, 300 μm slits, 2s per point at every 1 cm^{-1}, 32 × objective, one scan, no smoothing. For [$Pd_3(dppm)_3$-(CO)][CF_3CO_2]$_2$, the laser excitation was 1064 nm, and laser power ≈ 100 mW

Table 4 Structural and structural data for selected Ag_n species

	ν(Ag_2)/cm^{-1}	*F*(Ag_2)[a]/mdyn Å^{-1}	*r*(Ag_2)/Å
[$Ag_3L_2I_3$]	122[b]	0.47	2.806[b]
Ag_3	120.5[c]	—	—
Ag_2^- ($^2\Sigma_u^+$)	118[d]	0.44	2.814[d]
[$Ag_2(PhNNNPh)_2$]	114[e]	0.41	2.669[f]

[a] Using the diatomic approximation, $F = \mu(2\pi c\nu)^2$. [b] This work. [c] Ref. 20. [d] Ref. 21. [e] Ref. 6. [f] Ref. 15.

The ν(Ag_2) mode (122 cm^{-1}) is obviously mixed with ν(AgI) and should be considered more accurately as a breathing mode. Nevertheless, using the diatomic oscillator model, an *approximated* force constant, *F*, of 0.47 mdyn Å^{-1} is obtained (Table 4). This vibrator possesses practically the same spectroscopic properties and *r*(Ag_2) values as for Ag_2^- (Table 4) which exhibits formally an Ag–Ag bond order of 0.5. These Ag ··· Ag interactions in [$Ag_3L_2I_3$] are therefore relatively strong.

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References

1 C.-M. Che, W.-T. Wong, T.-F. Lai and H.-L. Kwong, *J. Chem. Soc., Chem. Commun.*, 1989, 243; H. H. Karsh and V. Schubert, *Z. Naturforsch., Teil B*, 1982, 37, 186.

2 H. Schmidbaur, Th. Pollok, R. Herr, F. E. Wagner, R. Bau, J. Riede and G. Müller, *Organometallics*, 1986, **5**, 566.

3 A. M. Aly, D. Neugbauer, O. Orama, V. Schubert and H. Schmidbaur, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 125.

4 (*a*) D. M. Ho and R. Bau, *Inorg. Chem.*, 1983, **22**, 4073; (*b*) D. Perreault, M. Drouin, A. Michel, V. M. Miskowski, W. P. Schaefer and P. D. Harvey, *Inorg. Chem.*, 1992, **31**, 695; (*c*) M. Dartiguenave, Y. Dartiguenave, A. Mari, A. Guitard, M. J. Olivier and A. L. Beauchamp, *Can. J. Chem.*, 1988, **66**, 2386.

5 D. Perreault, M. Drouin, A. Michel and P. D. Harvey, *Inorg. Chem.*, 1991, **30**, 2; 1992, **31**, 3688.

6 (*a*) D. Perreault, M. Drouin, A. Michel and P. D. Harvey, *Inorg. Chem.*, 1993, in the press; (*b*) D. Piché and P. D. Harvey, unpublished work.

7 W. P. Weber, G. W. Gokel and I. K. Ugi, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 530.

8 L. Manojlovic-Muir, K. W. Muir, B. R. Lloyd and R. J. Puddephatt, *J. Chem. Soc., Chem. Commun.*, 1983, 1336.

9 (*a*) Y. LePage, P. S. White and E. J. Gabe, NRCCAD, An enhanced CAD-4 Control Program, Annual Meeting of American Crystallographic Association. Hamilton, Ontario, 1986; (*b*) E. J. Gabe, Y. Le Page, J.-P. Charland, F. L. Lee and P. S. White, *J. Appl. Crystallogr.*, 1989, **22**, 384; (*c*) D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, eds. J. A. Ibers and W. C. Hamilton, Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2B, pp. 99–101 (Present distributor, Kluwer Academic Press, Dordrecht); (*d*) A. C. Larson, *Acta Crystallogr.*, **23**, 664; (*e*) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139.

10 G. Nardin, L. Randaccio and E. Zangrando, *J. Chem. Soc., Dalton Trans.*, 1975, 2566; A. Camus, G. Nardin and L. Randaccio, *Inorg. Chim. Acta*, 1975, **12**, 23; G. Nardin and L. Randaccio, *Acta Crystallogr., Sect. B*, 1974, **30**, 1377; N. Bresciani, N. Marsich, G. Nardin and L. Randaccio, *Inorg. Chim. Acta*, 1974, **10**, L5; N. Marsich, G. Nardin and L. Randaccio, *J. Am. Chem. Soc.*, 1973, **95**, 4053.

11 C. K. Johnson, ORTEP, Technical Report ORNL-5138, Oak Ridge National Laboratory, TN, 1976.

12 D. Perreault, M. Drouin, A. Michel and P. D. Harvey, *Inorg. Chem.*, 1992, **31**, 2740 and refs. therein.

13 J. E. Huheey, *Inorganic Chemistry; Principles of Structure and Reactivity*, 3rd edn., Harper and Row, New York, 1983, p. 73.

14 G. Helgesson and S. Jagner, *J. Chem. Soc., Dalton Trans.*, 1990, 2413.

15 F. A. Cotton, G. Wilkinson and P. L. Gauss, *Basic Inorganic Chemistry*, 2nd edn., Wiley, Toronto, 1987, p. 60.

16 J. Vicente, M. T. Chicote and I. Saura-Llamas, *Organometallics*, 1989, **8**, 767.

17 J. Beck and J. Strahle, *Z. Naturforsch., Teil B*, 1986, **41**, 4.

18 M. Jansen, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1098 and refs. therein.

19 R. G. Griffin, J. D. Ellett, jun., M. Mehring, J. G. Mullitt and J. S. Waugh, *J. Chem. Phys.*, 1972, **57**, 2147.

20 W. Schulze, H. W. Becker, R. Minkwitz and K. Manzel, *Chem. Phys. Lett.*, 1978, **55**, 59.

21 C. S. Baushlicher, jun., S. R. Langhoff and H. Partridge, *J. Chem. Phys.*, 1989, **91**, 2412.

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