

Synthesis and Full Characterisation of the First Discrete Binuclear Complex Featuring a Two-Electron (σ) μ_2 - $\kappa\text{C}:\kappa\text{C}$ Bridging Cyanide

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Abstract: Small ring macrocycles incorporating nitrile-functionalised arms can support binuclear Ag^{I} complexes bearing bridging CN^- ligands. The X-ray crystal structure, IR and CP MAS ^{13}C NMR spectra are reported for $[\text{Ag}_2(\text{L}^1)_2(\mu\text{-CN})][\text{BF}_4] \cdot \text{MeCN}$ (**1**), which represents the first complex incorporating a discrete μ_2 - $\kappa\text{C}:\kappa\text{C}$ symmetrically

bridged two-electron-donating CN^- ligand. The complexes $[\text{Ag}_2(\text{L}^2)_2(\mu\text{-CN})][\text{BF}_4]$ (**3**), and $[\text{Ag}_2(\text{L}^3)_2(\mu\text{-CN})][\text{BF}_4]$ (**4**), have also been synthesised, and

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have been characterised both structurally and spectroscopically. In contrast to **1**, **3** and **4** feature linear bridging μ_2 - $\kappa\text{C}:\kappa\text{N}$, four-electron-donating CN^- ligands. Therefore, the length of the aliphatic chain in the functionalised macrocycles plays a crucial role in determining the observed co-ordination mode of the bridging CN^- ligand.

Introduction

Transition metal carbonyls^[1] and cyanides^[2a] are among the best known classes of organometallic compounds and their spectroscopic and structural characterisation has allowed a deeper understanding of the nature of the chemical bond in co-ordination compounds. Even though CO and CN^- are isoelectronic, they can show rather different bonding modes. The most common co-ordination modes of CN^- to transition metal ions (M) are either terminal (M–CN) or double-bridging (μ_2 - $\kappa\text{C}:\kappa\text{N}$) to give linear M–CN–M(M') links within binuclear or multinuclear polymeric complexes.^[2] Complexes containing triply bridged CN^- groups are rare and feature the tridentate CN^- ligand either C-bonded^[3–6] or N-bonded^[7, 8] to two metal centres with the remaining N or C atom co-ordinated to a third metal atom. In contrast to metal carbonyls,^[1] only a few compounds are known in which CN^- asymmetrically bridges or semibrings two metal centres to give a μ_2 - $\kappa\text{C}:\eta^2\text{-C,N}$ co-ordination mode.^[9–13] For example, in $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-CN})][\text{Et}_4\text{N}]$,^[12] the CN^- ion is seen as a four-

electron donor; two electrons are donated to one Mo centre in a σ fashion within a linear Mo–CN moiety, and two electrons are donated from the CN^- π system to give a η^2 -CN interaction to the other Mo atom. Interestingly, co-ordination modes such as μ_2 - $\kappa\text{C}:\kappa\text{C}$ and μ_3 - $\kappa\text{C}:\kappa\text{C}:\kappa\text{C}$, featuring a two-electron σ donation from the carbon atom to two or three metal centres, are unknown for CN^- but are rather common for the isoelectronic carbonyl group, especially in polynuclear clusters and in conjunction with metal–metal bonds.^[1, 14]

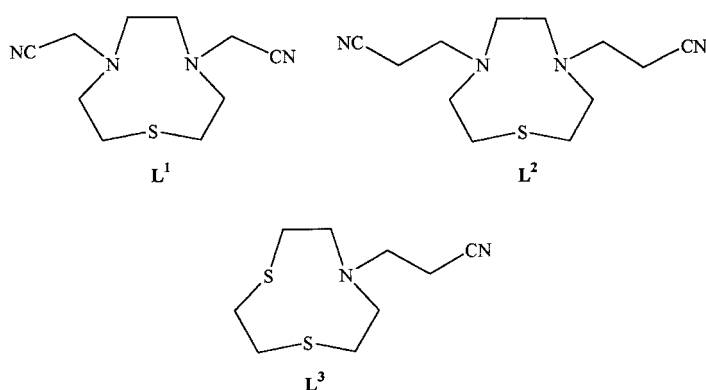
We have been studying the co-ordination chemistry of pendant arm derivatives of the nine-membered ring crowns 1,4,7-triazacyclononane ([9]aneN₃), 1-thia-4,7-diazacyclononane ([9]aneN₂S) and 1,4-dithia-7-azacyclononane ([9]aneNS₂)^[15, 16] with the aim of preparing transition metal complexes having co-ordinatively unsaturated metal centres. Such complexes are of particular interest since they can be used as building blocks for the synthesis of multinuclear systems,^[15, 16] or they can potentially bind and activate small molecules at the free co-ordination sites. We report herein the results of our investigation of the co-ordination chemistry of the ligands 4,7-bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane (**L**¹), 4,7-bis(2-cyanoethyl)-1-thia-4,7-diazacyclononane (**L**²) and 7-(2-cyanoethyl)-7-aza-1,4-dithiacyclononane (**L**³) towards Ag^{I} in the presence of CN^- ions (Scheme 1).

Results and Discussion

The reaction of **L**¹ and AgBF_4 (1:1 molar ratio) in MeCN followed by the addition of 0.5 molar equivalents of

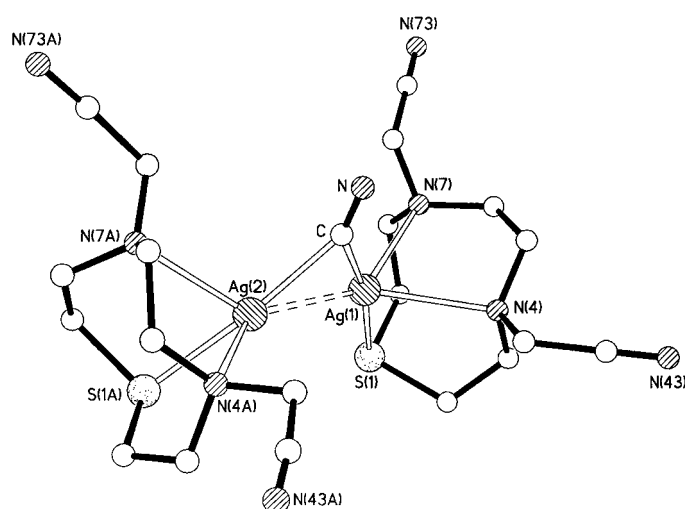
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Scheme 1. Ligands used in this study.

$n\text{Bu}_4\text{NCN}$ in MeCN gives colourless columnar crystals following partial removal of the solvent and diffusion of Et_2O vapour into the remaining solution. An X-ray crystal structure determination shows the compound to be the binuclear Ag^{I} complex $[\text{Ag}_2(\text{L}^1)_2(\mu\text{-CN})][\text{BF}_4] \cdot \text{MeCN}$ (**1**), which features a genuine and unprecedented $\mu_2\text{-}\kappa\text{C}:\kappa\text{C}$ bridging CN^- moiety between the two metal centres [$\text{Ag}(1)\text{-C}$ 2.153(8), $\text{Ag}(2)\text{-C}$ 2.155(8), C-N 1.076(11) Å] (Figure 1, Table 1). The C and N atoms of the CN^- were

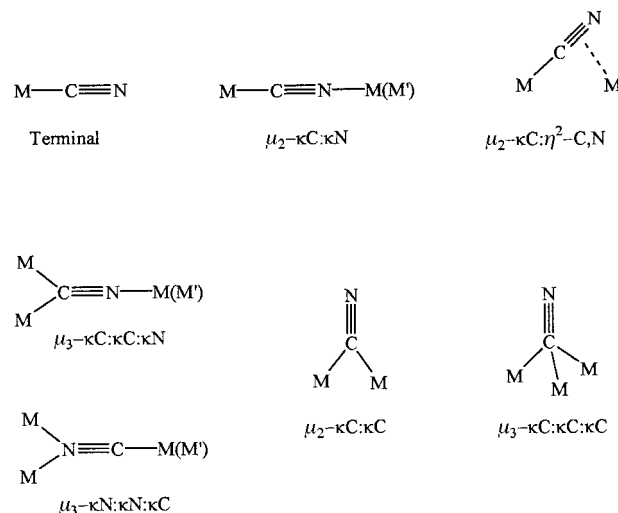
Figure 1. View of the $[\text{Ag}_2(\text{L}^1)_2\text{CN}]^+$ cation in **1** with the numbering scheme adopted. Hydrogen atoms are omitted for clarity.Table 1. Selected bond lengths [Å] and angles [°] for **1**.

$\text{Ag}(1)\text{-C}$	2.153(8)	$\text{Ag}(2)\text{-S}(1\text{A})$	2.476(2)
$\text{Ag}(2)\text{-C}$	2.155(8)	$\text{Ag}(2)\text{-N}(4\text{A})$	2.546(6)
$\text{Ag}(1)\text{-S}(1)$	2.476(2)	$\text{Ag}(2)\text{-N}(7\text{A})$	2.575(6)
$\text{Ag}(1)\text{-N}(4)$	2.531(6)	$\text{Ag}(1)\text{-Ag}(2)$	2.7557(10)
$\text{Ag}(1)\text{-N}(7)$	2.525(6)	C-N	1.076(11)
$\text{Ag}(1)\text{-C-N}$	140.0(8)	$\text{Ag}(1)\text{-C-Ag}(2)$	79.5(3)
$\text{Ag}(2)\text{-C-N}$	140.4(8)	$\text{C-Ag}(2)\text{-Ag}(1)$	50.3(2)
$\text{C-Ag}(1)\text{-S}(1)$	170.3(2)	$\text{C-Ag}(2)\text{-S}(1\text{A})$	165.7(2)

distinguished clearly by refinement of an alternative model in which these atoms are interchanged and by comparison with the model adopted. The latter was clearly superior and there is no evidence for disorder of the bridging CN^- . Because of the small bite angle imposed by the bridging CN^- [$\text{Ag}(1)\text{-C-Ag}(2)$ 79.5(3)°], the two metal centres are forced together at a

distance of 2.7557(10) Å, indicative of a strong $d^{10}\text{-}d^{10}$ interaction,^[17] with the CN^- acting as an overall two-electron donor. The $[\text{Ag}_2(\mu\text{-CN})]^+$ core is planar and each metal centre is capped by a molecule of **L**¹ whose S-donor ligand centre is capped *trans* to the CN^- ligand [$\text{S}(1)\text{-Ag}(1)\text{-C}$ 170.3(2), $\text{S}(1\text{A})\text{-Ag}(2)\text{-C}$ 165.7(2)°] (Figure 1).

Curtis et al. have proposed a criterion for distinguishing between two-electron (σ) and four-electron ($\sigma + \pi$) donor behaviour of bridging carbonyl ligands.^[18] In the two-electron donation mode, the M-C-O angle θ decreases monotonically with decreasing asymmetric parameter α ($\alpha = d_2 - d_1/d_1$ where d_1 and d_2 are the short and long M-C distances respectively); in contrast four-electron donation is characterised by essential invariance of θ with respect to α . Curtis et al. used this approach to classify the donor behaviour of the bridging CN^- in $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-CN})][\text{Et}_4\text{N}]$ as a semibridging four-electron interaction.^[12] In the case of **1**, the values for θ [$\text{Ag}(1)\text{-C-N}$] and α are 140.0(8)° and 0.001, respectively, and, according to the published curves of θ versus α ,^[18] these classify the CN^- in **1** as a pure two-electron $\mu_2\text{-}\kappa\text{C}:\kappa\text{C}$ bridging ligand (Scheme 2). An overall three-centre two-electron description can, therefore, be adopted for the chemical bonding in the $[\text{Ag}_2(\mu\text{-CN})]^+$ core of **1**.

Scheme 2. Possible binding modes of CN^- to metal centres.

The IR spectrum of single crystals of **1** shows two bands at 2238 and 2098 cm^{-1} , which can be assigned to the $\nu(\text{CN})$ stretching vibration of the nitrile groups in **L**¹ and the bridging CN^- unit, respectively. These assignments were confirmed by ^{13}C -enrichment at CN^- in **1** which leads to a shift of the peak at 2098 cm^{-1} to 2053 cm^{-1} , in excellent agreement with the expected isotopic shift to lower energy of the $\nu(\text{CN})$ stretching mode.

The CP MAS ^{13}C NMR spectrum of **1** in the range $\delta = 110\text{-}140$ shows two broad peaks at $\delta = 117.70$ and 119.16 and a broad triplet at $\delta = 128.02$ (Figure 2a). The first two signals can be attributed to the carbon atoms of the nitrile groups in **L**¹ and the MeCN molecule present in the crystal lattice of **1**. The broad triplet at $\delta = 128.02$ is assigned to the carbon atom of the bridging $\mu_2\text{-}\kappa\text{C}:\kappa\text{C}$ CN^- unit; the splitting pattern results from the coupling to ^{107}Ag and ^{109}Ag nuclei of similar gyromagnetic ratios ($J_{\text{Ag,C}} = 121.4$ Hz). CP MAS ^{13}C NMR

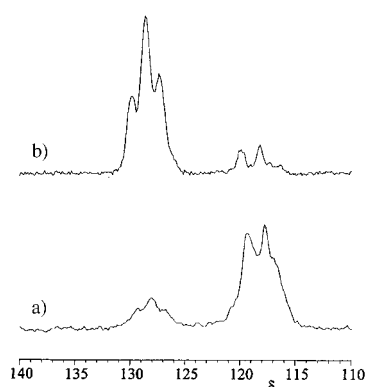


Figure 2. a) Solid-state CP MAS ^{13}C NMR spectrum of **1** in the range $\delta = 110\text{--}140$; b) solid-state CP MAS ^{13}C NMR spectrum of a sample of **1** with ^{13}C -enriched CN^- .

spectroscopy of **1** ^{13}C -enriched at CN^- confirms this assignment, since the triplet at $\delta = 128.02$ is observed with increased intensity (Figure 2b). This represents one of the very few cases reported in the literature in which a $J_{\text{Ag,C}}$ coupling constant has been observed by NMR spectroscopy either in solution or in the solid state.^[19]

Interestingly, the binuclear complex $[\text{Ag}_2(\text{L}^1)_2(\mu\text{-CN})][\text{BF}_4] \cdot \text{MeNO}_2$ (**2**) shows structural features very similar to those of **1**. Compound **2** has been unexpectedly obtained in very low yields from the direct reaction of L^1 with AgBF_4 in MeCN after removal of the solvent and crystallisation of the residue from $\text{MeNO}_2/\text{Et}_2\text{O}$ but without addition of external CN^- . The formation of free CN^- in this reaction may be tentatively attributed to in situ decomposition of MeCN or L^1 .

In order to study the influence of the pendant arms of the macrocyclic ligand on the co-ordination mode of the CN^- group, we treated L^2 and L^3 with AgBF_4 in the presence of $n\text{Bu}_4\text{NCN}$ under the same experimental conditions used for the preparation of **1**. Single-crystal X-ray structure determinations confirm the products obtained to be the binuclear Ag^I complexes $[\text{Ag}_2(\text{L}^2)_2(\mu\text{-CN})][\text{BF}_4]$ (**3**) and $[\text{Ag}_2(\text{L}^3)_2(\mu\text{-CN})][\text{BF}_4]$ (**4**). Both **3** and **4** exhibit a CN^- ligand bridging the two metal centres in a linear $\mu_2\text{-}\kappa\text{C}:\kappa\text{N}$ manner (Figures 3 and 4, Table 2); the C and N atoms of the CN^- unit are fully

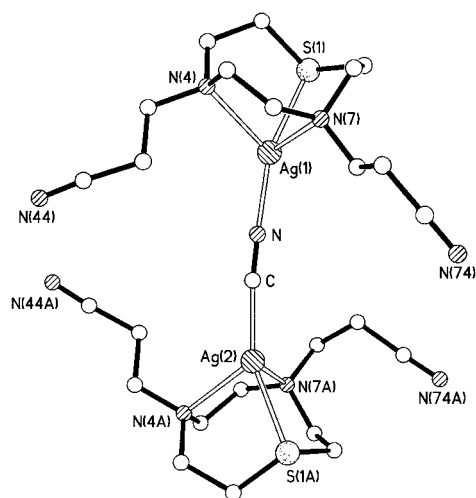


Figure 3. View of the $[\text{Ag}_2(\text{L}^2)_2\text{CN}]^+$ cation in **3** with the numbering scheme adopted. Only one component of the disordered bridging cyanide is shown and hydrogen atoms are omitted for clarity.

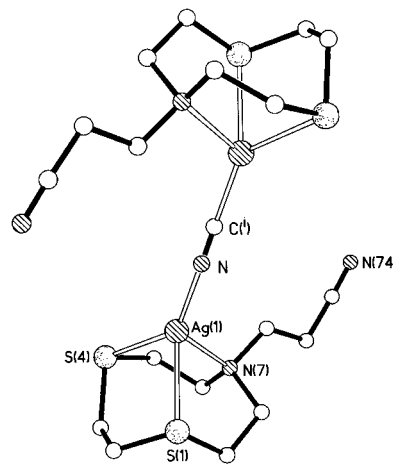


Figure 4. View of the $[\text{Ag}_2(\text{L}^3)_2\text{CN}]^+$ cation in **4** with the numbering scheme adopted. The bridging cyanide and the macrocyclic ligand are both affected by disorder, and only one component of each disorder model is shown. H atoms are omitted for clarity. Symmetry operation $i = -x + 2, -y, -z + 1$.

Table 2. Selected bond lengths [\AA] and angles [$^\circ$] for **3** and **4**.

3			
Ag(1)–N	2.083(2)	Ag(2)–S(1A)	2.506(6)
Ag(2)–C	2.083(2)	Ag(2)–N(4A)	2.462(2)
Ag(1)–S(1)	2.481(6)	Ag(2)–N(7A)	2.489(2)
Ag(1)–N(4)	2.474(2)	C–N	1.16(2)
Ag(1)–N(7)	2.522(2)		
Ag(1)–N–C	177.5(2)	Ag(2)–C–N	170.7(2)
4			
Ag(1)–N	2.103(4)	Ag(1)–N(7)	2.475(4)
Ag(1)–S(1)	2.5835(13)	C(1)–N	1.129(8)
Ag(1)–S(4)	2.5586(14)	Ag(1)–N–C(1)	177.4(5)

$$i = -x + 2, -y, -z + 1$$

disordered between the two possible symmetrically bridging orientations. The geometry around each Ag^I centre is a distorted tetrahedron with three co-ordination sites occupied by the donor atoms from the ring of the macrocycle and the fourth position taken up by the CN^- ligand. In **3** and **4** it appears that the length of the nitrile functionalised pendant arms is the main factor controlling the co-ordination behaviour of the four-electron donor CN^- ligand.

The IR spectra of **3** and **4** each show two bands at 2246 and 2150 cm^{-1} for **3**, and at 2248 and 2148 cm^{-1} for **4**. The peaks at lower frequencies, 2150 cm^{-1} for **3**, and 2148 cm^{-1} for **4**, shift to lower energy on ^{13}C enrichment, to 2105 cm^{-1} for **3**, and 2103 cm^{-1} for **4**, and are therefore assigned to $\nu(\text{CN})$ stretching vibrations of the linear $\mu_2\text{-}\kappa\text{C}:\kappa\text{N}$ CN^- moiety. Linear M–CN–M complexes show $\nu(\text{CN})$ stretching vibrations at higher energies compared to terminal co-ordinated CN^- when the two M centres are non-coupling,^[2a, 20] as in the case of **3** and **4**. Likewise, the $\nu(\text{CN})$ stretching vibration for terminally bound CN^- complexes shifts to higher energy compared to the free CN^- (2080 cm^{-1} in water^[2a]) due to the strong σ donation of the weakly anti-bonding lone pair on CN^- to M. For **1**, the $\nu(\text{CN})$ stretching vibration at 2098 cm^{-1} is shifted to lower energy (by ca. 50 cm^{-1}) compared to **3** and **4**, but to higher energy compared to free CN^- , and is close to the recorded value for monomeric AgCN (2094 cm^{-1}).^[21]

The CP MAS ^{13}C NMR spectra of **3** and **4** ^{13}C -enriched at CN^- show very strong doublets at $\delta = 152.22$ and 152.47 , respectively, assigned to the $\mu_2\text{-}\kappa\text{C}:\kappa\text{N}$ CN^- ligands, with $J_{\text{Ag-C}}$ coupling constants of 189.7 and 228.9 Hz, respectively. A larger upfield shift of this resonances is observed in **1** ($\delta = 128.02$, $J_{\text{Ag-C}} = 121.4$ Hz) consistent with the C centre interacting with two Ag^I nuclei. All the complexes **1**, **3** and **4** show upfield shifts for the C centre in the bridging $\mu\text{-CN}$ moiety with respect free CN^- in solution ($\delta = 166.2$).^[2a]

In conclusion, we have been able to synthesise the first complex containing a discrete $\mu_2\text{-}\kappa\text{C}:\kappa\text{C}$ symmetrical bridging CN^- using nitrile-functionalised pendant-arm macrocycles as supporting ligands. Studies are in progress to control the CN^- co-ordination mode and the polynuclearity of AgCN clusters by tuning the pendant-arms on these and related macrocyclic ligands.

Experimental Section

Melting points are uncorrected. The IR spectra as KBr disks were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer, whereas IR spectra on single crystals were recorded on a Perkin-Elmer System 2000 FT-IR spectrometer fitted with an i-Series FT-IR microscope. Microanalyses were performed by the University of Nottingham, School of Chemistry Micro-analytical service. NMR spectra (^1H and ^{13}C) were recorded on a Bruker DPX300 instrument. FAB mass spectra were measured at the EPSRC National Mass Spectrometry Service at Swansea (UK). CP MAS ^{13}C NMR spectra were recorded on a Varian Unity-400 spectrometer at 100.56 MHz; the samples were packed in a 7 mm zirconium oxide rotor and spun at a speed of 4–7 KHz at the magic angle; the ^{13}C chemical shifts were calibrated indirectly through the adamantane peaks ($\delta = 38.3, 29.2$) relative to SiMe_4 .

Ligand synthesis: **L**¹, **L**² and **L**³ were synthesised according to adapted procedures reported in the literature.^[22] Although **L**¹ and **L**² have been already described,^[22a, 23] there are no reports on their co-ordination properties. **L**³ was prepared for the first time during this study and characterisation data are given here. $\text{C}_9\text{H}_{16}\text{N}_2\text{S}_2$ (216.36): calcd C 50.0, H 7.45, N 12.95; found C 49.3, H 7.10, N 12.44; ^1H NMR (300 MHz, CDCl_3 , 25 °C): $\delta = 2.49$ (t, $^3J(\text{H}, \text{H}) = 6.68$ Hz, 2H, CH_2CN), 2.75–3.00 (m, 10H), 3.14 (s, 4H; $\text{SCH}_2\text{CH}_2\text{S}$); ^{13}C NMR (75.47 MHz, CDCl_3 , 25 °C): $\delta = 16.51$ ($\text{CH}_2\text{CH}_2\text{CN}$), 32.84, 34.86 (CH_2SCH_2), 52.98, 57.94 ($\text{NCCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{S}$) 119.8 (CN); IR (KBr pellet): $\tilde{\nu} = 2907\text{s}$, 2816s, 2244m, 1461m, 1419m, 1358m, 1300m, 1111m, 1043w, 1014w, 950w, 912w, 830w, 731w, 670w cm^{-1} ; MS (EI): m/z : 216 [M^+].

Complex synthesis: In a typical preparation a mixture of the macrocyclic ligand (0.10 mmol) and AgBF_4 (0.18 mmol) in MeCN (3 cm^3) was stirred in the dark at room temperature for 30 minutes. A solution of $n\text{Bu}_4\text{NCN}$ (0.09 mmol) was added and the resulting mixture stirred for a further 30 minutes. After partial removal of the solvent under reduced pressure, crystals were formed upon diffusion of Et_2O vapour into the remaining solution.

1: M.p. 178 °C (decomp); $\text{C}_{23}\text{H}_{35}\text{Ag}_2\text{BF}_4\text{N}_{10}\text{S}_2$ (818.28): calcd C 33.76, H 4.31, N 17.12; found C 32.55, H 4.05, N 17.57; MS (FAB, 3-NOBA matrix): m/z : 690 [$^{107}\text{Ag}_2(\text{L}^1)_2\text{CN}^+$], 664

[$^{107}\text{Ag}_2(\text{L}^1)_2$]⁺; IR (single crystal): $\tilde{\nu} = 2990\text{m}$, 2959m, 2940m, 2840m, 2238m, 2098m, 1484w, 1456s, 1423s, 1379w, 1333s, 1305m, 1275m, 1251w, 1128m, 1051s, 991s, 978s, 953m, 932w, 916w, 879m cm^{-1} . The IR spectrum (single crystal) recorded on a sample of the complex ^{13}C -enriched at CN^- shows a band at 2053 cm^{-1} ; replacing that at 2098 cm^{-1} .

3: M.p. 158–160 °C (decomp); $\text{C}_{25}\text{H}_{40}\text{Ag}_2\text{BF}_4\text{N}_9\text{S}_2$ (833.33): calcd C 36.03, H 4.84, N 15.13; found C 35.55, H 4.41, N 14.76; MS (FAB, 3-NOBA matrix): m/z : 747 [$^{107}\text{Ag}_2(\text{L}^2)_2\text{CN}^+$], 494 [$^{107}\text{Ag}_2\text{L}^2\text{CN}^+$]; IR (single crystal): $\tilde{\nu} = 2978\text{m}$, 2931m, 2852m, 2246m, 2150m, 1470m, 1417m, 1367m, 1303m, 1220w, 1101s, 1052s, 922s, 953m, 885w cm^{-1} . The IR spectrum (single crystal) recorded on a sample of the complex ^{13}C -enriched at CN^- shows a band at 2105 cm^{-1} ; replacing that at 2150 cm^{-1} .

4: M.p. 200–202 °C (decomp), $\text{C}_{19}\text{H}_{32}\text{Ag}_2\text{BF}_4\text{N}_5\text{S}_4$ (761.29): calcd C 29.98, H 4.24, N 9.20; found C 29.15, H 3.95, N 8.78; MS (FAB, 3-NOBA matrix): m/z : 323 [$^{107}\text{AgL}^3$]⁺; IR (single crystal): $\tilde{\nu} = 2991\text{m}$, 2941m, 2859m, 2248s, 2148s, 1463m, 1449m, 1412s, 1406m, 1377s, 1370s, 1350m, 1304m, 1257m, 1125s, 1081s, 959m, 941w, 902w, 808w cm^{-1} . The IR spectrum (single crystal) recorded on a sample of the complex ^{13}C -enriched at CN^- shows a band at 2103 cm^{-1} ; replacing that at 2148 cm^{-1} .

Samples of **1**, **3** and **4** ^{13}C -enriched at CN^- were synthesised by using 50% ^{13}C -enriched $n\text{Bu}_4\text{NCN}$. This was prepared by extracting a solution of K^{13}CN and $n\text{Bu}_4\text{NCN}$ in a 1:1 molar ratio (3.84 mmol) in water with CH_2Cl_2 followed by removal of the organic solvent. The ^{13}C -enrichment was checked by ^{13}C NMR spectroscopy.

Synthesis of 2: A mixture of **L**¹ (20 mg, 0.089 mmol) and AgBF_4 (34.65 mg, 0.178 mmol) in MeCN (4 mL) was stirred in the dark at room temperature for 4 h. The solvent was removed under reduced pressure; the residue was taken up in MeNO_2 and filtered. A few colourless block crystals were grown by diffusion of Et_2O vapour into the MeNO_2 solution. M.p. 182–186 °C (decomp); $\text{C}_{22}\text{H}_{35}\text{Ag}_2\text{BF}_4\text{N}_{10}\text{O}_2\text{S}_2$ (838.27): calcd C 31.52, H 4.21, N 16.71; found C 30.95, H 3.85, N 16.34; MS (FAB, 3-NOBA matrix): m/z : 690 [$^{107}\text{Ag}_2(\text{L}^1)_2\text{CN}^+$]; IR (KBr disc): $\tilde{\nu} = 2900\text{w}$, 2846m, 2248m, 2119w, 1159w, 1483m, 1456m, 1424m, 1322m, 1074s, 986s, 949m, 873s, 729m cm^{-1} .

Crystallography: A summary of the crystal data for **1**, **3** and **4** is given in Table 3. Only special features of the analyses are noted here. For **2**, all the crystallographic data have been deposited as supplementary material. Data were collected on a Stoë Stadi-4 four-circle diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) and ω/θ scans to $2\theta_{\text{max}} = 50^\circ$ (for **1**, and **4**) and to $2\theta_{\text{max}} = 45^\circ$ (for **3**). All the structures were solved using direct methods^[24] and all non-hydrogen atoms were located by using subsequent ΔF methods, as were solvent methyl-H atoms.^[25] These H atoms were refined as part of rigid groups whereas other hydrogen atoms were placed geometrically and constrained to ride on their parent C atoms.^[25]

Table 3. Crystallographic data for the compounds **1**, **3** and **4**.

Compound	1	3	4
formula	$\text{C}_{23}\text{H}_{35}\text{Ag}_2\text{BF}_4\text{N}_{10}\text{S}_2$	$\text{C}_{25}\text{H}_{40}\text{Ag}_2\text{BF}_4\text{N}_9\text{S}_2$	$\text{C}_{19}\text{H}_{32}\text{Ag}_2\text{BF}_4\text{N}_5\text{S}_4$
<i>M</i>	818.28	833.33	761.29
crystal size	$0.50 \times 0.30 \times 0.20$	$0.30 \times 0.12 \times 0.04$	$0.55 \times 0.48 \times 0.47$
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
<i>a</i> [Å]	12.754(4)	12.721(6)	13.526(2)
<i>b</i> [Å]	13.951(2)	17.784(12)	8.391(2)
<i>c</i> [Å]	18.619(3)	14.780(9)	24.402(4)
β [°]	109.15(2)	97.89(5)	91.239(12)
<i>U</i> [Å ³]	3129.6(12)	3312(3)	2768.9(8)
ρ_{calcd} [g cm^{-3}]	1.737	1.671	1.826
<i>Z</i>	4	4	4
<i>T</i> [K]	150(2)	150(2)	200(2)
$\mu(\text{MoK}\alpha)$ [mm^{-1}]	1.442	1.363	1.762
absorption correction	numerical	numerical	ψ scans
$T_{\text{min}}, T_{\text{max}}$	0.648, 0.770	0.790, 0.952	0.450, 0.528
reflections collected	6173	5425	4218
unique reflections, R_{int}	5223, 0.074	4352, 0.200	2431, 0.022
reflections with $I \geq 2\sigma(I)$	4108	2547	2185
R_1	0.0540	0.1009	0.0374
wR_2 [all data], $S[F^2]$	0.1263, 1.27	0.2381, 1.22	0.0893, 1.05
refined parameters	380	378	176
$\Delta\rho_{\text{min,max}}$ [e Å^{-3}]	−0.77, 0.56	−1.30, 1.23	−0.87, 0.77

The structures were developed by alternating cycles of least-squares refinement on F^2 and ΔF synthesis.^[25] Competitive refinements for **1** followed by contoured difference electron density maps confirmed the atom assignments for the bridging cyanide ligand and showed no evidence for disordering of the cyanide. For **3** and **4**, during refinement, the C and N atoms in the bridging cyanide were found to be fully disordered with each other. The occupancy of the atoms of each disordered component were restrained to be 0.50 and positions and anisotropic displacement parameters of the respective C and N components at each site were constrained to be the same. Similarity restraints were applied for **3** to the N–C, C–C and C–S bond lengths within the macrocyclic ligand, and to the BF_4^- ion. Finally, for **4**, disorder was identified during refinement in the macrocyclic ligand; this was modelled by using partial occupancy model over two sites with the occupancy factor ranging from 0.55 to 0.67 for the major components. Appropriate restraints were applied to bond lengths and angles, and the anisotropic displacement parameters for all the atoms in the asymmetric unit were subject to rigid bond restraints during refinement. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-102951–CCDC-102954. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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