Synthesis and X-ray molecular structures of the silver(I) amides $[\{Ag[\mu\text{-}N(SiMe_3)_2]\}_4]$ and $[\{Ag[\mu\text{-}\overline{NCMe_2(CH_2)_3CMe_2}]\}_4]$†

Peter B. Hitchcock, Michael F. Lappert and Luc J.-M. Pierssens

School of Chemistry and Molecular Sciences, University of Sussex, Brighton, UK BN1 9QJ

The thermally stable silver(I) amides $[\{Ag(\mu\text{-}NR_2)\}_4]$ (R = $SiMe_3$) 1 and $[\{Ag(\mu\text{-}NR'_2)\}_4]$ [NR'_2 = $\overline{NCMe_2(CH_2)_3CMe_2}$] 2, prepared from AgNCO and $Sn(NR_2)_2$ or $Sn(NR'_2)_2$, or for 1 also from $M(NR_2)_2$ (M = Pb or Yb) or $[\{Sn(\mu\text{-}F)NR_2\}_2]$, are centrosymmetric, tetranuclear clusters comprising a square of Ag atoms [mean Ag···Ag 3.001(2) Å for 1 and 2.995(2) Å for 2] linked by singly bridging amido groups [mean Ag–N 2.148(5) Å for 1 and ranging from 2.126(7) to 2.184(7) Å for 2], the $(AgN)_4$ macrocycle being planar for 1 but puckered for 2, and the N–Ag–N′ and Ag–N–Ag′ arrangements being essentially linear and rectangular, respectively.

The bis(trimethylsilyl)amido ligand $\bar{N}R_2$ (R = $SiMe_3$) has occupied a central role in the characterisation of thermally stable low-coordination-number metal and metalloid complexes of the majority of the elements in the Periodic table, due to its steric bulk and freedom of β-hydrogen,[1] although examples of noble- or heavier coinage-metal amides are scant: *cf.*,[2] $[Rh(NR_2)(PPh_3)_2]$ and *trans*-$[Ru(NR_2)(H)(PPh_3)_2]$. The silver(I) amide $Ag(NR_2)$ {obtained from $[Ag(NH_3)_2]Cl$ and $K(NR_2)$ in liquid ammonia} was briefly mentioned in a conference report, without any data other than its description as being explosive.[3] No other silver complex derived from an unfunctionalised amide has been reported; the sole example of a functionalised analogue, by Veith and Woll, is of the crystallographically characterised amide $[\{Ag_2(LL)\}_2]$ {$[LL]^{2-}$ = $o\text{-}C_6H_4[OSiMe_2\bar{N}Bu^t]_2$}, deemed to owe its thermal stability to having coordinatively saturated silver atoms, each with 2 N and 2 O nearest neighbours.[4]

We now describe (*i*) the convenient synthesis under ambient conditions of the colourless, crystalline, *thermally robust* silver(I) amides $[\{Ag(\mu\text{-}NR_2)\}_4]$ 1 and $[\{Ag(\mu\text{-}NR'_2)\}_4]$ 2 [NR'_2 = $\overline{NCMe_2(CH_2)_3CMe_2}$]; (*ii*) their NMR spectroscopic‡ and EI mass spectrometric characterisation and (*iii*) the single-crystal X-ray structures§ of 1 and 2.

The amides 1 and 2 were obtained by the metathetical exchange reaction between the readily available $Sn(NR_2)_2$[5] or $Sn(NR'_2)_2$[6] and silver cyanate (Scheme 1). For 1, alternative metal precursors $Pb(NR_2)_2$,[5] $[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2]$[7] or $[\{Sn(\mu\text{-}F)(NR_2)\}_2]$[8] proved to be equally effective. The reactions were carried out in vessels shielded from direct light, owing to the photosensitivity of both AgNCO and 1 or 2; the yield of crystalline 1 or 2 was *ca.* 50%.

In general the ligand $\bar{N}R_2$ (R = $SiMe_3$) confers lipophilicity upon its metal or metalloid complexes. It is surprising, therefore that $[\{Ag(\mu\text{-}NR_2)\}_4]$ 1 proved to be insoluble in hydrocarbons or diethyl ether, while attempts to dissolve 1 in hot tetrahydrofuran or pyridine resulted in deposition of silver; this may be due to the thermal instability of the mononuclear complexes $[Ag(NR_2)L]$ (L = thf or py). NMR spectroscopic analysis in solution was hampered by its insolubility or decomposition. However CP-MAS NMR spectroscopic data for 1 were obtained.‡ By contrast the 2,6-tetramethylpiperidinatosilver(I) compound $[\{Ag(\mu\text{-}NR'_2)\}_4]$ 2 showed good solubility in hydrocarbons; the $^{13}C\{^1H\}$ NMR spectrum‡ in toluene at 323 K showed sharp singlets for each of the four chemically distinct types of carbon atom. The complexes 1 and 2 gave satisfactory elemental microanalytical data. The EI mass spectra revealed the parent tetranuclear ion; *e.g.* for 1 at *m*/*z* = 1072 (6% of the intensity of the most abundant fragment), with the expected isotopic fine structure, also for fragment ions.

$$Sn(NR''_2)_2 + 2\,AgCNO \xrightarrow{\text{i}} 1/4[\{Ag(\mu\text{-}NR''_2)\}_4]$$

1 R″ = $SiMe_3$, mp 275–280 °C

2 NR''_2 = $\overline{NCMe_2(CH_2)_3CMe_2}$, mp 240–244 °C (decomp.)

Scheme 1 Synthesis of the silver(I) amides 1 and 2. *Reagents and conditions*: i, Et_2O, 25 °C, 16 h, absence of light.

The molecular structures of the crystalline amides 1 and 2 are illustrated in Figs. 1 and 2, respectively and show that each is tetranuclear, based on a square of two-coordinate silver atoms. Each Ag atom is linked to its neighbour by a singly bridging amido ligand, the nitrogen donor sites thus being four-coordinate and the N–Ag–N′ arrangements being essentially linear.

In 1, the macrocyclic $(AgN)_4$ skeleton is coplanar, the four N atoms comprising an outer square. The two silicon atoms on each nitrogen are on opposite sides of the $(AgN)_4$ plane. The numerical data cited below refer to crystals belonging to the

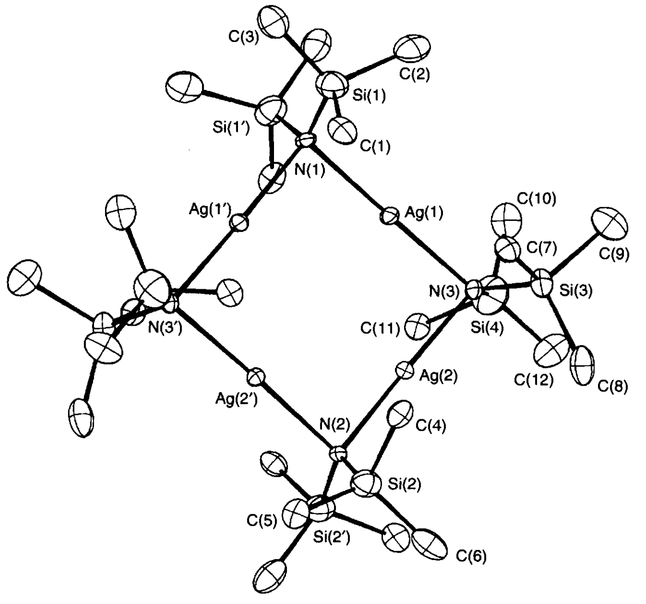

Fig. 1 The X-ray structure and atom labelling scheme for $[\{Ag(\mu\text{-}NR_2)\}_4]$ (R = $SiMe_3$) 1. Selected bond lengths (Å) and angles (°): Ag(1)–N(3) 2.142(5), Ag(1)–N(1) 2.147(5), Ag(2)–N(2) 2.149(5), Ag(2)–N(3) 2.155(5), Ag(1)···Ag(2) 2.973(2), Ag(1)···Ag(1′) 3.024(2), Ag(2)···Ag(2′) 3.002(2); N(3)–Ag(1)–N(1) 178.6(2), N(2)–Ag(2)–N(3) 178.1(2), Ag(1)–N(1)–Ag(1′) 89.5(2), Ag(2′)–N(2)–Ag(2) 88.6(2), Ag(1)–N(3)–Ag(2) 87.6(2).

space group $P2/n$ (non-standard no. 13) **1a**; curiously, two other crops of crystals gave different crystal forms belonging to the space groups $P2_1/n$ (non-standard no. 14) **1b** and $C2/m$ (no. 12) **1c**, but provided virtually identical molecular geometric parameters.¶

In **2**, the molecule lies on a twofold rotation axis through the centre of the $(AgN)_4$ macrocycle and the nitrogen atoms are 0.57 to 0.58 Å out of the Ag_4 plane, alternating between being above or below the plane. Each piperidinato ligand is in a chair conformation, arranged in a staggered fashion with respect to its neighbour.

The Ag–N bond lengths range from 2.142(5) to 2.155(5) Å in **1** and 2.126(7) to 2.184(7) Å in **2**, these values being very similar to the 2.134(4) to 2.198(4) Å in the four-coordinate silver amide $[\{Ag_2(LL)\}_2]$ $\{[LL]^{2-} = o\text{-}C_6H_4\text{-}[OSiMe_2\bar{N}Bu^t]_2\}$.[4] In the latter the Ag···Ag separations of 2.990(2) and 3.018(2) Å are likewise very close to the 2.973(2), 3.024(2) and 3.002(2) Å in **1** and 2.973(2) and 3.016(2) Å in **2**. The Ag^I radius has been cited as 1.342 Å and the rather shorter Ag···Ag separation of 2.705(1) Å in the silver(I) amidinate $[\{Ag[\mu\text{-}\eta^3\text{-}N(C_6H_4Me\text{-}p)CHNC_6H_4Me\text{-}p]\}_2]$ was not taken (MO calculations) as implicating any Ag–Ag bonding;[9a] in that compound the mean Ag–N bond distance was 2.105 Å compared with 2.124 Å [Ag···Ag, 2.655(2) Å] in $[\{Ag[\mu\text{-}\eta^3\text{-}N(R)C(Ph)NR]\}_2]$.[9b] In related bi- or tetra-nuclear compounds having bonds between three-coordinate N and Ag, the mean Ag–N bond length was (*i*) 2.160 Å [Ag···Ag, 2.654(1) Å] in $[\{Ag[\mu\text{-}\eta^3\text{-}C(R)_2C_5H_4N\text{-}2]\}_2]$,[10] (*ii*) 2.150 Å [Ag···Ag, 2.669(1) Å] in $[\{Ag[\mu\text{-}\eta^3\text{-}N(Ph)NNPh]\}_2]$[11] and (*iii*) 2.13 Å [Ag···Ag, 2.82 Å] in $[\{Ag[\mu\text{-}\eta^3\text{-}N(C_6H_4F\text{-}p)NNC_6H_4F\text{-}p]\}_4]$.[12]

Planar, tetranuclear coinage metal(I) clusters singly bridged by monoanionic unfunctionalised ligands are well known for copper, including the X-ray characterised $[\{Cu(\mu\text{-}NR''_2)\}_4]$ ($R'' = R$[13a] or $SiMe_2Ph$[13b]), but for silver was previously limited to $[\{Ag(\mu\text{-}SCR_3)\}_4]$;[14] it is likely that this and complexes **1** and **2** will be the forerunners of a wider family.

We thank the European Commission for a category 20 fellowship for L. J.-M. P. and the EPSRC for other support. For the MS and CP-MAS spectral data, we are grateful to Dr A. Abdul-Sada (MS), Mr J. Keates and Dr G. A. Lawless.

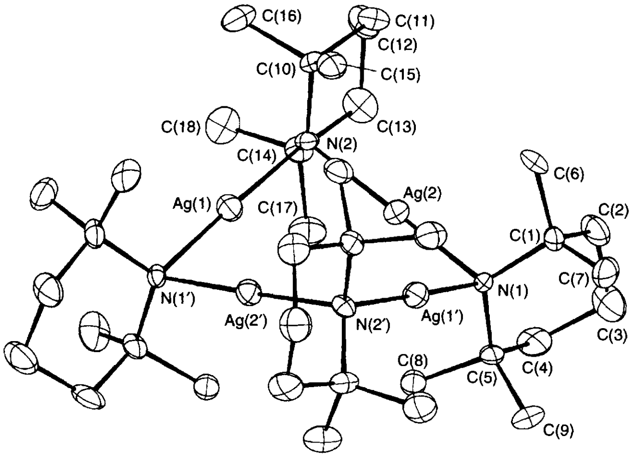

Fig. 2 The X-ray structure and atom labelling scheme for $[\{Ag(\mu\text{-}NR'_2)\}_4]$ $[NR'_2 = \overline{NCMe_2(CH_2)_3C}Me_2]$ **2**. Selected bond lengths (Å) and angles (°): Ag(1)–N(1') 2.126(7), Ag(1)–N(2) 2.133(7), Ag(2)–N(1) 2.164(7), Ag(2)–N(2) 2.184(7), Ag(1)···Ag(2') 2.973(2), Ag(1)···Ag(2) 3.016(2); N(1')–Ag(1)–N(2) 177.3(3), N(1)–Ag(2)–N(2) 177.9(3), Ag(1')–N(1)–Ag(2) 87.7(3), Ag(1)–N(2)–Ag(2) 88.6(3).

Footnotes

† No reprints available.

‡ *Selected spectroscopic data* (^1H NMR at 250 MHz and 298 K in C_6D_6 $^{13}C\{^1H\}$ NMR at 62.86 MHz and 323 K in PhMe with C_6D_6; ^{13}C CP-MAS NMR at 8 kHz and ^{29}Si CP-MAS NMR at 5 kHz). For **1**: ^{13}C CP-MAS NMR δ 6.1, 6.9 and 7.5; ^{29}Si CP-MAS NMR δ 1.6. For **2**: ^1H NMR δ 1.55–1.57 (CH_2, m), 1.63 (CH_3, s) and 1.74–1.76 (CH_2, m); $^{13}C\{^1H\}$ NMR δ 20.16 (s, CCH_2C), 38.83 (s, Me), 42.89 (s, $NCCH_2$) and 57.28 (s, CMe_2).

§ *Crystal data*: for **1a**, $C_{24}H_{72}Ag_4N_4Si_8$, $M = 1073.1$, monoclinic, space group $P2/n$ (non-standard no. 13), $a = 8.741(8)$, $b = 13.557(7)$, $c = 17.781(12)$ Å, $\beta = 91.66(6)°$, $U = 2106(3)$ Å^3, $F(000) = 1088$, $Z = 2$, $D_c = 1.69$ g cm^{-3}; μ(Mo-Kα) = 2.08 mm^{-1}, specimen 0.5 × 0.4 × 0.3 mm, 6142 unique reflections for $2 < \theta < 30°$, $R1 = 0.057$ for 3875 reflections with $|F^2| > 2\sigma(F^2)$, $wR2 = 0.189$ for all data, $S = 1.089$.

For **1b**, $C_{24}H_{72}Ag_4N_4Si_8$, $M = 1073.1$, monoclinic, space group $P2_1/n$ (non-standard no. 14), $a = 9.278(5)$, $b = 13.924(3)$, $c = 18.249(3)$ Å, $\beta = 91.13(3)°$, $U = 2357(1)$ Å^3, $F(000) = 1088$, $Z = 2$, $D_c = 1.51$ g cm^{-3}; μ(Mo-Kα) = 1.86 mm^{-1}, specimen 0.4 × 0.3 × 0.3 mm, 4128 unique reflections for $2 < \theta < 25°$, $R1 = 0.076$ for 2463 reflections with $|F^2| > 2\sigma(F^2)$, $wR2 = 0.201$ for all data, $S = 1.235$.

For **1c**, $C_{24}H_{72}Ag_4N_4Si_8$, $M = 1073.1$, monoclinic, space group $C2/m$ (no. 12), $a = 20.347(5)$, $b = 13.943(3)$, $c = 9.283(2)$ Å, $\beta = 116.11(2)°$, $U = 2364.8(9)$ Å^3, $F(000) = 1088$, $Z = 2$, $D_c = 1.51$ g cm^{-3}; μ(Mo-Kα) = 1.85 mm^{-1}, specimen 0.3 × 0.3 × 0.2 mm, 2967 unique reflections for $2 < \theta < 28°$, $R1 = 0.039$ for 2528 reflections with $|F^2| > 2\sigma(F^2)$, $wR2 = 0.113$ for all data, $S = 0.934$.

For **2**, $C_{36}H_{72}Ag_4N_4$, $M = 992.5$, monoclinic, space group $C2/c$ (no. 15), $a = 22.58(2)$, $b = 8.312(5)$, $c = 23.217(12)$ Å, $\beta = 110.24(5)°$, $U = 4088(4)$ Å^3, $F(000) = 2016$, $Z = 4$, $D_c = 1.61$ g cm^{-3}; μ(Mo-Kα) = 1.92 mm^{-1}, specimen 0.20 × 0.20 × 0.10 mm, 3582 unique reflections for $2 < \theta\ 25°$, $R1 = 0.055$ for 2258 reflections with $|F^2| > 2\sigma(F^2)$, $wR2 = 0.152$ for all data, $S = 1.006$.

For both **1** and **2**, data at $T = 293$ K, Enraf-Nonius CAD-4 diffractometer, absorption correction, structural solution by heavy-atom methods, full-matrix least-squares refinement on F^2 using SHELXL-93 with non-hydrogen atoms anisotropic.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/52.

References

1 M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava, *Metal and Metalloid Amides*, Ellis Horwood–Wiley, Chichester, 1980.
2 B. Çetinkaya, M. F. Lappert and S. Torroni, *J. Chem. Soc., Chem. Commun.*, 1979, 843.
3 H. Bürger and H. Seyffert, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 646.
4 M. Veith and K. L. Woll, *Chem. Ber.*, 1993, **126**, 2383.
5 M. J. S. Gynane, D. H. Harris, M. F. Lappert, P. P. Power, P. Rivière and M. Rivière-Baudet, *J. Chem. Soc., Dalton Trans.*, 1977, 2004.
6 R. W. Chorley, P. B. Hitchcock, M. F. Lappert, W.-P. Leung, P. P. Power and M. M. Olmstead, *Inorg. Chim. Acta*, 1992, **198–200**, 203.
7 T. D. Tilley, R. A. Andersen and A. Zalkin, *Inorg. Chem.*, 1984, **23**, 2271.
8 R. W. Chorley, D. Ellis, P. B. Hitchcock and M. F. Lappert, *Bull. Soc. Chim. Fr.*, 1992, **129**, 599.
9 (*a*) F. A. Cotton, X. Feng, M. Matusz and R. Poli, *J. Am. Chem. Soc.*, 1988, **110** 7077; (*b*) D. Fenske, G. Baum, A. Zinn and K. Dehnicke, *Z. Naturforsch., Teil B*, 1990, **45**, 1273.
10 R. I. Papasergio, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1987, 3085.
11 J. Beck and J. Strähle, *Z. Naturforsch., Teil B*, 1986, **41**, 4.
12 E. Hartmann and J. Strähle, *Z. Anorg. Allg. Chem.*, 1990, **583**, 31.
13 (*a*) M. B. Hursthouse, cited in ref. 1 (p. 493); (*b*) H. Chen, M. M. Olmstead, S. C. Shoner and P. P. Power, *J. Chem. Soc., Dalton Trans.*, 1992, 451.
14 K. Tang, M. Aslam, E. Block, T. Nicholson and J. Zubieta, *Inorg. Chem.*, 1987, **26**, 1488.

Received, 16th February 1996; Com. 6/01159D