Synthesis and Structure of Copper(I), Silver(I) and Zinc(II) Amides $[Cu_2(mpsa)_2]$, $[Cu_6X_2(mpsa)_4]$ (X = Cl or Br), $[Ag_4(mpsa)_4]$ and $[(ZnEt)_2(mpsa)_2]$ [mpsa = 2-N$(SiMe_3)$-C_5H_3N-6-Me]†

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The copper(I) amide $[Cu_2(mpsa)_2]$ **1** and its 1:1 adduct with CuX, $[Cu_6(mpsa)_4X_2]$ (X = Cl, **2a** or Br, **2b**) {mpsa = [2-(6-methyl)pyridyl]trimethylsilylamido, 2-N$(SiMe_3)C_5H_3N$-6-Me}, the silver(I) amide $[Ag_4(mpsa)_4]$ **3** and the zinc(II) amides $[(ZnEt)_2(mpsa)_2]$ **4**, [ZnCl(mpsa)] **5**, and $[Zn(mpsa)_2]$ **6**, have been prepared from lithium reagents and the appropriate metal halide, and Hmpsa and $ZnEt_2$ (**4** and **6**). The amides **1**–**4** have been characterized crystallographically. In **1** the ligands span the two metal centres with Cu–N_{amido} 1.875(4), 1.887(4), Å, Cu–$N_{pyridyl}$ 1.902(4), 1.903(4) Å, N–Cu–N 174.6(2), 173.4(2)°, and Cu ··· Cu 2.420(1) Å. Complexes **2a** and **2b** are isomorphous diethyl etherates; mpsa ligands span three metal centres with each N_{amido} bridging (i) a two-co-ordinate copper, the other co-ordination site being another N_{amido}, Cu–N 1.893(6)–1.927(7) Å, **2a**, 1.884(9)–1.919(8) Å, **2b**, and (ii) a three-co-ordinate copper bound by the amido centre, Cu–N, 2.100(6)–2.133(6) Å, **2a**, 2.100(8)–2.152(9) Å, **2b**, a pyridyl N-centre, 1.993(7)–2.006(7) Å, **2a**, 1.983(9)–2.013(8) Å, **2b**, and a halide, Cu–X 2.270(3)–2.303(3) Å, **2a**, 2.409(3)–2.410(2) Å, **2b**. Complex **3** is a hexane solvate; mpsa ligands link four silver atoms in a plane; two silver atoms lie on a C_2 axis and are two-co-ordinate, bound by pairs of $N_{pyridyl}$ groups; Ag–N, 2.140(3), 2.169(6) Å with N–Ag–N, 169.3(2), 171.2(2)°; the other (symmetry-related) pair are two-co-ordinate, bound by pairs of N_{amido} groups: Ag–N, 2.099(3), 2.097(4), with N–Ag–N, 168.6(2)°. In complex **4** the N_{amido} groups bridge the metal centres with $N_{pyridyl}$ forming chelate rings on the same side of a Zn_2N_2 plane; Zn–$N_{pyridyl}$ 2.125(5), 2.108(5) Å, Zn–N_{amido} 2.061(5), 2.072(5) Å (chelate ring), 2.245(5), 2.225(5) Å, Zn ··· Zn 2.958(2) Å. Compound **1** forms an adduct with trimethylphosphine, $[Cu(mpsa)(PMe_3)_2]$ **7**.

Copper(I) complexes of N-centred anionic ligands form aggregates.[1–9] For bidentate ligands binuclear complexes with short metal–metal contacts prevail.[7–9] These are of interest in relation to whether there is any metal–metal interaction, particularly with theoretical studies being at odds with each other.[7,10] In the present study we report the synthesis and structure of some copper(I) amide complexes, including a binuclear complex, $[Cu_2(mpsa)_2]$ {mpsa = [2-(6-methyl)-pyridyl]trimethylsilylamido, 2-N$(SiMe_3)C_5H_3N$-6-Me}, in which the ligands span two metal centres by acting as formally two electron-pair donors through the amido group and N-pyridyl functionalities. In so doing, the amido groups are still electron rich and can in principle act as Lewis bases to other metal centres. In this regard we have gained access to 1:1 adducts of $[Cu_2(mpsa)_2]$ with CuX, *viz.* $[Cu_6(mpsa)_4X_2]$ (X = Cl or Br), which have been structurally authenticated. In addition, the metal centres in the binuclear species are co-ordinatively unsaturated and the complexes can therefore act as Lewis acids at the metal centres with the integrity of the binuclear structure being maintained. It is also possible for mononuclear species to form by competitive complexation between the N-pyridyl from an adjacent Cu(mpsa) entity and added Lewis base. We also note that $[Cu_2(mpsa)_2]$ readily forms a trimethylphosphine derivative.

Silver(I) complex aggregates are also of interest in relation to any metal–metal interaction.[10] Accordingly we have prepared and structurally characterised the homoleptic silver(I) complex with mpsa and find that it is tetranuclear rather than binuclear with a head to head/tail to tail metal ligand arrangement.

We also report the synthesis of some zinc amides based on mpsa, including the binuclear compound $[(ZnEt)_2(mpsa)_2]$ (structurally authenticated) in which the amido ligands span both metal centres by utilizing all three available pairs of electrons, as in the binuclear lithium compound $[Li_2(mpsa)_2(OEt_2)_2]$.[11] Like the binuclear copper(I) compound the zinc compound has a formally d^{10} configuration and therefore poses similar interest about the prospect of metal–metal interaction. It is noteworthy that alkylzinc derivatives of amides form dimers or higher aggregates, with dimers dominating if the amido group is bulky[12] or bidentate,[1] as in the present case. This paper is an extension of our recent studies dealing with lithium and boron chemistry of the same amido ligand, mpsa.[11,13]

Experimental

Syntheses were carried out using standard Schlenk techniques under an atmosphere of high purity argon. Solvents were dried then freeze degassed prior to use. 6-Methyl-2-trimethylsilylaminopyridine was prepared according to a published procedure.[11] Hydrogen-1 and carbon-13 NMR spectra were

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

obtained on Bruker WP-80 and WM-300 spectrometers, and mass spectra were recorded on a Varian CH7 spectrometer operating at 70 eV.

Preparations.—[Cu_2(mpsa)$_2$] **1**. A solution of Li(mpsa) (2.03 g, 10.90 mmol) in diethyl ether (30 cm^3) was added slowly to a slurry of CuCl (1.04 g, 10.51 mmol) in diethyl ether (10 cm^3) and stirred at room temperature for 1 h. The resulting yellow solution was filtered, concentrated *in vacuo* (30 cm^3) and stored at −30 °C for 3 h, yielding a yellow precipitate which was collected, washed with pentane (2 × 10 cm^3) and dried *in vacuo* (1.43 g, 56.0%). M.p. (decomp.) 122–128 °C (Found: C, 44.60; H, 6.05; N, 11.60: Calc. for $C_{18}H_{30}Cu_2N_4Si_2$: C, 44.50; H, 6.20; N, 11.5%). ^{1}H NMR (80 MHz, C_6D_6), δ 0.42 (s, 9 H, $SiMe_3$), 2.11 (s, 3 H, CH_3), 5.9–7.0 (m, 3 H, aromatic); ^{13}C NMR (20.1 MHz, C_6D_6), δ 2.2 (q, $SiMe_3$), 26.0 (q, CH_3), 108.4, 113.8, 126.8, 155.0, 170.7 (aromatic); ^{29}Si NMR (59.63 MHz, C_6D_6), δ −1.52 (s).

[Cu_6(mpsa)$_4Cl_2$] **2a**. A solution of Li(mpsa) (0.44 g, 2.38 mmol) in diethyl ether (20 cm^3) was added slowly to a slurry of CuCl (0.71 g, 7.15 mmol) in diethyl ether (15 cm^3) at room temperature. After stirring for 2 h, the orange solution was filtered off from the LiCl, and the filtrate allowed to stand for 15 min whereupon orange crystals began to form. After 1 h, the crystals were collected and washed briefly with cold hexane (15 cm^3), then dried *in vacuo* as the monoetherate of **2a** (0.12 g, 17.1%). M.p. (decomp.) 106–110 °C (Found: C, 38.10; H, 5.55; N, 9.15. Calc. for $C_{40}H_{70}Cl_2Cu_6N_8OSi_4$: C, 38.65; H, 5.65; N, 9.00%). ^{1}H NMR (300 MHz, C_6D_6), δ 0.69 (s, 9 H, $SiMe_3$), 1.11 (t, 3 H, OCH_2CH_3), 2.49 (s, 3 H, CH_3), 3.25 (q, 2 H, OCH_2CH_3), 5.8–6.7 (m, 3 H, aromatic); ^{13}C NMR (20.1 MHz, C_6D_6), δ 3.4 (q, $SiMe_3$), 15.6 (q, OCH_2CH_3), 25.0 (q, CH_3), 65.9 (t, OCH_2CH_3), 115, 112.4, 137.0, 156.0, 165.5 (aromatic); ^{29}Si NMR (59.63 MHz, C_6D_6), δ 5.42 (s).

[Cu_6(mpsa)$_4Br_2$] **2b**. A diethyl ether (20 cm^3) solution of Li(mpsa) (1.31 g, 7.04 mmol) was added slowly to a slurry of CuBr (2.02 g, 14.08 mmol) in diethyl ether (20 cm^3), and stirred at room temperature for 30 min. The orange solution was filtered off from the LiCl and excess CuBr, and the volume reduced to 15 cm^3. After standing for 5 h, the resulting orange crystals were collected and dried *in vacuo* as the monoetherate of **2b** (1.44 g, 65.0%). M.p. (decomp.) 84–102 °C (Found: C, 36.00; H, 5.05; Br, 12.90; N, 8.35. Calc. for $C_{40}H_{70}Br_2Cu_6N_8OSi_4$: C, 36.05; H, 5.30; Br, 12.00; N, 8.40%).

[Ag_4(mpsa)$_4$] **3**. In the absence of light, a solution of Li(mpsa) (0.83 g, 4.47 mmol) in tetrahydrofuran (thf) (15 cm^3) was added slowly to a solution of $AgNO_3$ (0.76 g, 4.47 mmol) in thf (15 cm^3), and the mixture stirred at −78 °C for 30 min. The solvent was then removed *in vacuo*, hexane added (30 cm^3) and the mixture stored at −30 °C overnight. A pale yellow solution and a brown solid resulted. The solution was filtered, and the volume reduced *in vacuo* (10 cm^3). After storing at −30 °C for 10 h, a pale yellow solid deposited which was collected and dried *in vacuo* (0.33 g, 25.7%) (Found: C, 38.55; H, 5.45; N, 9.90. Calc. for $C_{36}H_{60}Ag_4N_8Si_4$: C, 37.65; H, 5.25; N, 9.75%). ^{1}H NMR (300 MHz, [$^2H_8$]toluene), δ 0.29 (s, 9 H, $SiMe_3$), 2.39 (s, 3 H, CH_3), 5.7–6.8 (m, 3 H, aromatic); ^{13}C NMR (20.1 MHz, C_6D_6), δ 2.8 (q, $SiMe_3$), 27.3 (q, CH_3), 109.5, 114.2, 137.5, 155.3, 165.9 (aromatic); ^{29}Si NMR (59.63 MHz, C_6D_6), δ −1.83 (s).

[(ZnEt)$_2$(mpsa)$_2$] **4**. Diethyl zinc (0.7 cm^3, 5.7 mmol) was added slowly to a stirred solution of Hmpsa (1.03 g, 5.71 mmol) in hexane (10 cm^3) at 0 °C. The solution was stirred at 0 °C for a further 5 min, then at room temperature for 2 h. Solvent was removed *in vacuo* and the residue dissolved in pentane (10 cm^3) and cooled to −30 °C for 24 h, during which time colourless crystals formed. They were isolated at −30 °C, washed with cold pentane (10 cm^3) and dried *in vacuo* (0.60 g, 60.5%). M.p. (decomp.) 178–184 °C (Found: C, 47.85; H, 7.20; N, 10.25. Calc. for $C_{22}H_{40}N_4Si_2Zn_2$: C, 48.25; H, 7.35; N, 10.25%). ^{1}H NMR (300 MHz, C_6D_6), δ 0.40 (s, 9 H, $SiMe_3$), 0.76 (q, 2 H, CH_2CH_3), 1.58 (t, 3 H, CH_2CH_3), 1.57 (s 3 H, CH_3), 5.8–6.8 (m, 3 H, aromatic); ^{13}C NMR (20.1 MHz, C_6D_6), δ 1.6 (t, CH_2), 1.7 (q, $SiMe_3$), 13.9 (q, CH_2CH_3), 22.2 (q, CH_3), 113.5, 139.3, 154.4, 167.6 (aromatic); *m/e* 180 (M^+, 23), 165 (100%).

[ZnCl(mpsa)] **5**. A solution of Li(mpsa) (1.71 g, 9.20 mmol) in thf (10 cm^3) was added slowly to a stirred solution of $ZnCl_2$ (1.25 g, 9.20 mmol) in thf at 0 °C. After stirring at room temperature for 10 h, the solvent was removed *in vacuo*, hexane (20 cm^3) added, and the yellow solution filtered. The hexane was removed *in vacuo* and the resulting solid dissolved in pentane (10 cm^3), from which the product crystallized at −30 °C over 2 d (1.03 g, 40%). M.p. (decomp.) 192–220 °C (Found: C, 37.45; H, 5.35; Cl, 12.50; N, 9.70. Calc. for $C_9H_{15}ClN_2SiZn$: C, 38.60; H, 5.40; Cl, 12.65; N, 10.00%). ^{1}H NMR (300 MHz, C_6D_6), δ 0.30 (s, 9 H, $SiMe_3$), 1.94 (s, 3 H, CH_3), 5.9–7.1 (m, 3 H, aromatic); ^{13}C NMR (20.1 MHz, C_6D_6), δ 1.0 (q, $SiMe_3$), 22.2 (q, CH_3), 107.3, 109.2, 128.3, 140.2, 155.1 (aromatic); *m/e* 180 (M^+, 65), 165 (100%).

[Zn(mpsa)$_2$] **6**. Diethyl zinc (1.79 g, 14.49 mmol) was added slowly to an ice-cooled stirred solution of Hmpsa (5.25 g, 29.11 mmol) in hexane (15 cm^3), and the mixture stirred at room temperature for 4 h. The solvent was then removed *in vacuo*, the white precipitate washed with pentane (2 × 25 cm^3), and dried *in vacuo* (2.76 g, 51.8%). M.p. 96–98 °C (Found: C, 51.20; H, 7.55; N, 12.00: Calc. for $C_{18}H_{30}N_4Si_2Zn$: C, 51.00; H, 7.15; N, 13.20%). ^{1}H NMR (300 MHz, C_6D_6), δ 0.29 (s, 9 H, $SiMe_3$), 1.94 (s, 3 H, CH_3), 5.9–7.0 (m, 3 H, aromatic); ^{13}C NMR (20.1 MHz, C_6D_6), δ 1.0 (q, $SiMe_3$), 22.7 (q, CH_3), 107.3, 109.2, 140.2, 155.1, 168.2 (aromatic); ^{29}Si NMR (59.63 MHz, C_6D_6), δ −2.98 (s); *m/e* 280 (M^+, 3), 165 (100%).

[Cu(mpsa)(PMe_3)$_2$] **7**. To a stirred solution of **1** (0.85 g, 3.50 mmol) in hexane (35 cm^3) at room temperature was added slowly an excess of PMe_3 (1.5 cm^3, 14.7 mmol). The mixture was stirred until the yellow colour of **1** discharged (*ca.* 1 h). After standing at −30 °C for 2 h, a white precipitate formed which was collected, washed with cold hexane (10 cm^3)–PMe_3 (0.2 cm^3) and dried *in vacuo* (0.84 g, 60.7%). (Found: C, 45.35; H, 8.25; N, 7.25. Calc. for $C_{15}H_{33}CuN_2P_2Si$: C, 45.60; H, 8.40; N, 7.10%). ^{1}H NMR (60 MHz, C_6D_6), δ 0.40 (s, 9 H, $SiMe_3$), 0.82 (m, 18 H, PMe_3), 2.13 (s, 3 H, CH_3), 5.7–7.5 (m, 3 H, aromatic).

Structure Determinations.—Crystals were mounted in capillaries; unique diffractometer data sets were measured carefully at 295 K to the specified $2\theta_{max}$ limit in conventional 2θ–θ scan mode with monochromatic Mo-Kα radiation (λ = 0.7106_9 Å). *N* Reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the large block least-squares refinement, minimizing $\Sigma w\Delta^2$ after solution of the structures by the heavy-atom method, **1**, **3** and **4**, or direct methods, **2**, and absorption correction (Gaussian), **4** excepted. Anisotropic thermal parameters were refined for non-hydrogen atoms; $(x,y,z,U_{iso})_H$ were constrained at estimated values. Conventional residuals on $|F|$ at convergence are quoted, R,R'; statistical weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0005\sigma^4(I_{diff})$ were used. No extensive, significant extinction effects were found. Neutral-atom complex scattering factors were employed;[14] computation used XTAL 2.2 program system[15] implemented by S. R. Hall. Crystal data, atomic coordinates and molecular core geometries are given in Tables 1–6. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

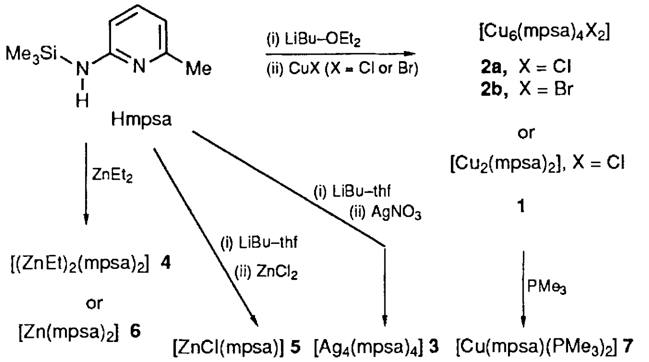
Discussion

Synthesis of Complexes.—A summary of the reactions is presented in Scheme 1. All new compounds were characterized using spectroscopic techniques, mass spectrometry, and elemental analysis and by X-ray structure determinations where suitable crystals were accessible. Reaction between Li(OEt_2)(mpsa) and one equivalent of CuCl in diethyl ether resulted in the formation of a bright orange yellow solution from which yellow crystals of **1** were obtained. In the presence of an excess of

Table 1 Summary of crystal data for compounds $[Cu_2(mpsa)_2]$ **1**, $[Cu_6(mpsa)_4X_2]\cdot OEt_2$ (X = Cl, **2a** or Br, **2b**), $[Ag_4(mpsa)_4]$ **3** and $[(ZnEt)_2(mpsa)_2]$ **4**

	1	**2a**	**2b**	**3**[a]	**4**
Formula	$C_{18}H_{30}Cu_2N_4Si_2$	$C_{40}H_{70}Cl_2Cu_6N_8OSi_4$	$C_{40}H_{70}Br_2Cu_6N_8OSi_4$	$C_{42}H_{74}Ag_4N_8Si_4$	$C_{22}H_{40}N_4Si_2Zn_2$
M	485.5	1243.7	1332.6	1234.9	547.5
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1$ (no. 4)	$P2_1$ (no. 4)	$C2/c$ (no. 15)	$P2/c$ (no. 14)
a/Å	12.351(4)	18.883(2)	19.157(8)	28.67(1)	10.384(8)
b/Å	10.157(3)	11.928(3)	11.848(6)	11.493(3)	14.957(10)
c/Å	9.755(3)	12.151(3)	12.214(5)	20.565(8)	19.281(12)
α/°	90.30(3)				
β/°	108.39(2)	90.36(2)	90.71(4)[b]	126.25(2)	100.56(6)
γ/°	104.08(2)				
U/Å^3	1121.9	2737	2772	5465	2944
D_c/g cm^{-3}	1.44	1.51	1.60	1.50	1.24
Specimen(mm)	0.3 × 0.3 × 0.3	0.22 × 0.22 × 0.3	0.2 × 0.2 × 0.2	0.40 × 0.45 × 0.20	0.35 × 0.15 × 0.35
μ_{Mo}/cm^{-1}	20.8	24.2	37.2	13.3	17.7
Z	2	2	2	4	4
2θ	50	50	50	50	45
F(000)	504	1276	1348	2504	1152
A*(min.–max.)	1.54–1.56	1.39–2.26	1.84–2.43	1.30–1.41	No correction
N	3893	5059	5129	4761	3243
N_o	2682	3861	3861	2920	1858
R	0.035	0.035[c]	0.039[c]	0.029	0.038
R'	0.040	0.034	0.040	0.031	0.032

[a] Hexane solvate; meaningful refinement supported for isotropic thermal parameters only for this moiety. [b] Note that the coordinate settings for **2a** and **2b** are (x,y,z) and ($\bar{x},y,z$), *i.e.* in the same setting, one β angle would be obtuse and the other acute. [c] Preferred chirality.



Scheme 1

CuCl at room temperature the solution turns orange and a 2:1 ratio for CuCl to $Li(OEt_2)(mpsa)$ yielded analytically pure, dark orange crystals of **2a** as an etherate at room temperature. Attempts to recrystallise the complex led to decomposition to **1** and CuCl, and benzene solutions contained a mixture of **1**, **2a** and CuCl (^1H, ^{13}C NMR), equation (1). Similar results were

$$\begin{array}{ll}[Cu_6X_2(mpsa)_4] \rightleftharpoons 2[Cu_2(mpsa)_2] + 2CuX & (1) \\ X = Cl, \mathbf{2a} \qquad\qquad\quad \mathbf{1} & \\ X = Br, \mathbf{2b} & \end{array}$$

obtained for the reaction of an excess of CuBr with $Li(OEt_2)(mpsa)$, yielding **2b**, whereas CuI gave a red, then black solution from which only a few crystals of **1** were obtained. Both **2a** and **2b** decompose slowly in air overnight whereas the parent compound **1** decomposes in *ca.* 15 min.

Addition of an excess of PMe_3 to a solution of **1** in diethyl ether yielded a colourless solution from which a trimethylphosphine adduct of Cu(mpsa) was obtained at −30 °C, as evidenced by a colour change and by the presence of characteristic IR bands for PMe_3 at 1302, 1288 and 940 cm^{-1}.[16] Microanalysis and ^1H NMR spectroscopy were consistent with the formula $Cu(mpsa)(PMe_3)_2$ **7**. It slowly decomposed to a brown oil in the absence of an excess of the phosphine. Reaction of a solution of **1** with CO gave black solutions and black solids devoid of metal carbonyl species (IR).

The tetranuclear silver(I) amide, **3**, was formed by the reaction of silver nitrate with a stoichiometric amount of Li(mpsa) in thf. Reaction of $Li(OEt_2)(mpsa)$ with AgCl in thf also gave compound **3**, as did the use of an excess of AgCl in an attempt to prepare a silver chloride adduct of **3**, analogous to the copper halide adduct of **1**.

Addition of diethylzinc to a solution of Hmpsa in hexane (ratio 1:1), resulted in the formation of the heteroleptic zinc ethyl amide, $[(ZnEt)_2(mpsa)_2]$ **4**, as a hexane solvate. It slowly decomposed in hexane yielding a black solid over 3 h. Attempts to sublime **4** (134 °C, 0.10 mmHg) resulted in redistribution affording $ZnEt_2$ and the homoleptic amide $[Zn(mpsa)_2]$ **6**, equation (2), which could also be prepared from Hmpsa and

$$\underset{\mathbf{4}}{[(ZnEt)_2(mpsa)_2]} \rightleftharpoons \underset{\mathbf{6}}{[Zn(mpsa)_2]} + ZnEt_2 \qquad (2)$$

the appropriate amount of diethylzinc. Compound **6** is likely to be a bis(chelate) species as in the related compound, $[Zn(qsa)_2]$ [qsa = (8-quinolyltrimethylsilylamido].[17] The mixed amide–chloride complex, **5**, is accessible from $ZnCl_2$ and Li(mpsa) in thf. It is most likely dimeric in solution and in the solid state with amide bridging (as in **4**, see below) and/or chloro-bridging to achieve four-fold co-ordination, and is possibly monomeric in the gas phase with mass spectrometry yielding a mononuclear ion peak. Compound **4** has characteristic IR bands for Zn–CH_2 {620 and 518 cm^{-1}, as in $[(ZnEt)_2(NPh_2)_2]$} [18] and NMR data are consistent with one diastereoisomer, presumably that found in the solid, with both ligands on the same side of the Zn_2N_2 plane (see below). Compounds **4**–**6** rapidly decompose in air.

The mild conditions for the formation of **6** using diethylzinc (0 °C) are noteworthy. It is in contrast with more forcing conditions required for the formation of $[(ZnMe)_2(NPh_2)_2]$[12,18] from dimethylzinc and diphenylamine (70 °C). The presence of the pyridine N-centre may facilitate the metallation of Hmpsa by initial complexation of the pyridyl N-centre to zinc. This type of activation is well known in lithium and magnesium[19] metallation reactions.

X-Ray Crystal Structures of Compounds **1**, **2a**, **2b**, **3** *and* **4**.—Complex **1** consists of discrete binuclear species as the asymmetric unit in a triclinic $P\bar{1}$ cell. Bond distances and angles,

Table 2 Selected bond distances (Å) and angles (°) for compounds **1**–**4***

Compound **1**			
Cu(A)–N(1A,2B)	1.875(4), 1.902(4)	N(1A)–Cu(A)–N(2B)	174.6(2)
Cu(B)–N(1B,2A)	1.887(4), 1.903(4)	N(1B)–Cu(B)–N(2A)	173.4(2)
Cu(A) ··· Cu(B)	2.420(1)		
Compounds **2a**, **2b**			
Cu(1)–N(1A)	1.893(6), 1.884(9)	N(1A)–Cu(1)–N(1C)	161.7(3), 159.9(3)
Cu(1)–N(1C)	1.927(7), 1.919(9)	N(1B)–Cu(2)–N(1D)	162.2(3), 161.7(3)
Cu(2)–N(1B)	1.912(6), 1.897(8)	Cl(1)–Cu(A)–N(2A)	127.5(2), 125.2(3)
Cu(2)–N(1D)	1.916(6), 1.914(8)	Cl(1)–Cu(A)–N(1B)	109.6(2), 109.8(2)
Cl(1)–Cu(A)	2.303(3), 2.409(3)	N(2A)–Cu(A)–N(1B)	114.5(3), 115.0(4)
Cl(1)–Cu(D)	2.288(3), 2.412(2)	Cl(2)–Cu(B)–N(1A)	111.5(2), 111.7(2)
Cl(2)–Cu(B)	2.270(3), 2.410(2)	Cl(2)–Cu(B)–N(2B)	125.6(2), 123.7(3)
Cl(2)–Cu(C)	2.274(3), 2.443(3)	N(1A)–Cu(B)–N(2B)	115.8(3), 116.1(3)
Cu(A)–N(2A)	1.993(7), 2.013(8)	Cl(2)–Cu(C)–N(2C)	128.8(2), 126.9(3)
Cu(A)–N(1B)	2.111(6), 2.100(8)	Cl(2)–Cu(C)–N(1D)	111.5(2), 113.0(3)
N(1A)–Cu(B)	2.125(6), 2.152(9)	N(2C)–Cu(C)–N(1D)	111.7(3), 111.7(3)
Cu(B)–N(2B)	1.998(6), 1.983(9)	Cl(1)–Cu(D)–N(1C)	111.7(2), 112.8(2)
Cu(C)–N(2C)	1.994(6), 2.011(9)	Cl(1)–Cu(D)–N(2D)	128.2(2), 126.7(3)
Cu(C)–N(1D)	2.133(6), 2.141(8)	N(1C)–Cu(D)–N(2D)	111.1(2), 110.7(3)
N(1C)–Cu(D)	2.100(6), 2.116(8)	Cu(2) ··· Cu(B)	2.688(2), 2.690(2)
Cu(D)–N(2D)	2.006(7), 2.011(9)	Cu(2) ··· Cu(C)	2.603(2), 2.600(2)
Cu(1) ··· Cu(A)	2.667(2), 2.678(2)	Cu(2) ··· Cu(D)	2.666(2), 2.684(3)
Cu(1) ··· Cu(B)	2.624(2), 2.621(2)	Cu(A) ··· Cu(B)	2.940(2), 2.930(3)
Cu(1) ··· Cu(C)	2.660(1), 2.672(2)	Cu(A) ··· Cu(D)	2.684(2), 2.689(2)
Cu(1) ··· Cu(D)	2.622(2), 2.608(2)	Cu(B) ··· Cu(C)	2.682(2), 2.694(2)
Cu(2) ··· Cu(A)	2.631(2), 2.620(2)	Cu(C) ··· Cu(D)	3.029(2), 3.026(3)
Compound **3**			
Ag(1)–N(1A)	2.099(5)	N(1A)–Ag(1)–N(1B)	168.6(2)
Ag(1)–N(1B)	2.097(4)	N(2B)–Ag(2)–N(2B′)	169.3(2)
Ag(2)–N(2B)	2.140(3)	N(2A)–Ag(3)–N(2A′)	171.2(2)
Ag(3)–N(2A)	2.169(6)	Ag(2) ··· Ag(1) ··· Ag(3)	62.84(3)
Ag(1) ··· Ag(2)	3.0622(9)	Ag(1) ··· Ag(2) ··· Ag(1′)	115.42(4)
Ag(1) ··· Ag(2)	3.0059(9)	Ag(1) ··· Ag(3) ··· Ag(1′)	118.90(4)
Ag(2) ··· Ag(3)	3.164(1)		
Compound **4** [entries for Zn(A), Zn(B) respectively]			
Zn–C(01)	1.937(7), 1.957(6)	C(01)–Zn–N(1)	127.6(3), 128.2(3)
Zn–N(1)	2.245(5), 2.225(5)	C(01)–Zn–N(1′)	128.5(3), 129.8(3)
Zn–N(1′)	2.061(5), 2.072(5)	C(01)–Zn–N(2)	124.0(3), 120.9(3)
Zn–N(2)	2.125(5), 2.108(5)	N(1)–Zn–N(1′)	92.8(2), 93.1(2)
Zn ··· Zn	2.958(2)	N(1)–Zn–N(2)	63.2(2), 63.5(2)
		N(1′)–Zn–N(2)	100.9(2), 101.5(2)
		Zn–N(1,1′)–Zn	86.4(2), 87.2(2)

* For compounds **3** and **4** primed atoms are related to the unprimed atoms in the other half of the molecule.

Table 3 Non-hydrogen atom coordinates for compound **1**

	Ligand A			Ligand B		
Atom	x	y	z	x	y	z
Cu	−0.002 33(5)	0.265 78(7)	0.353 38(7)	0.021 92(5)	0.264 38(7)	0.116 79(7)
N(1)	−0.165 5(3)	0.213 4(4)	0.256 1(4)	0.176 5(3)	0.248 6(4)	0.211 7(4)
Si(1)	−0.252 0(1)	0.122 7(2)	0.351 2(2)	0.241 3(1)	0.180 3(2)	0.104 2(2)
C(100)	−0.317 8(5)	0.233 2(7)	0.438 2(7)	0.360 1(5)	0.308 6(6)	0.065 0(7)
C(101)	−0.372 9(5)	−0.021 3(6)	0.234 4(7)	0.125 9(5)	0.113 4(7)	−0.073 0(7)
C(102)	−0.151 9(5)	0.048 8(7)	0.497 6(7)	0.300 8(6)	0.036 2(7)	0.187 0(7)
C(1)	−0.206 9(4)	0.256 2(5)	0.122 8(5)	0.230 9(4)	0.294 7(5)	0.353 4(5)
N(2)	−0.133 1(3)	0.289 6(4)	0.041 8(4)	0.165 1(3)	0.322 1(4)	0.434 8(4)
C(3)	−0.170 3(4)	0.339 4(5)	−0.089 1(6)	0.217 1(4)	0.374 7(5)	0.574 3(5)
C(31)	−0.082 7(5)	0.373 1(6)	−0.170 4(6)	0.137 4(5)	0.406 3(6)	0.651 7(6)
C(4)	−0.283 7(5)	0.354 1(6)	−0.148 3(6)	0.337 5(5)	0.400 7(6)	0.643 4(6)
C(5)	−0.360 0(5)	0.319 0(6)	−0.069 4(6)	0.405 1(5)	0.369 4(6)	0.565 0(6)
C(6)	−0.323 7(4)	0.272 0(6)	0.062 4(6)	0.353 3(4)	0.315 7(6)	0.423 4(6)

and positional parameters are listed in Tables 2 and 3 with projections of a molecule and cell contents shown in Fig. 1. The small bite ligands span the two metal centres in a head to tail fashion forcing the metals into close proximity, Cu ··· Cu 2.420(1) Å; the co-ordination geometry is approximately linear, ignoring any metal–metal interaction, with N–Cu–N 174.6(2), 173.4(2)°. The bisector of each of these angles is directed towards the other metal centre with the 'N–Cu–N axes' skewed such that the potential symmetry of C_{2h} is reduced to C_2, seemingly in consequence of otherwise unfavourable non-

Table 4 Non-hydrogen atom coordinates for compounds **2a** and **2b**

	Chloride, **2a**			Bromide, **2b**		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Cu(1)*	0.814 70(5)	1	0.705 24(8)	−0.813 23(7)	1	0.698 9(1)
Cu(2)	0.696 19(5)	0.950 8(1)	0.914 49(7)	−0.696 08(7)	0.948 4(2)	0.910 0(1)
Cl, Br(1)	0.811 8(1)	1.207 8(2)	0.939 3(2)	−0.810 19(7)	1.218 7(2)	0.937 2(1)
Cl, Br(2)	0.702 1(1)	0.738 6(2)	0.691 6(2)	−0.703 06(7)	0.720 1(2)	0.683 1(1)
Cu(A)	0.828 97(6)	1.017 4(1)	0.923 12(8)	−0.825 79(7)	1.018 1(2)	0.916 3(1)
N(1A)	0.874 0(3)	0.872 9(6)	0.720 4(5)	−0.873 9(4)	0.875 8(7)	0.712 5(7)
Si(A)	0.890 3(2)	0.825 8(3)	0.585 2(2)	−0.891 6(2)	0.828 6(4)	0.578 4(3)
C(100A)	0.969 4(6)	0.903 4(9)	0.529 5(9)	−0.969 4(7)	0.905(1)	0.522(1)
C(101A)	0.903 2(6)	0.672 0(9)	0.574 0(9)	−0.904 3(9)	0.671(1)	0.566(1)
C(102A)	0.816 3(6)	0.862 1(9)	0.491 9(7)	−0.819 5(7)	0.865(1)	0.485(1)
C(1A)	0.928 5(4)	0.872 1(7)	0.798 1(7)	−0.925 8(5)	0.875(1)	0.789(1)
N(2A)	0.919 1(3)	0.937 7(6)	0.890 2(5)	−0.917 2(4)	0.940 8(8)	0.883 2(7)
C(3A)	0.969 8(4)	0.934 6(8)	0.971 8(7)	−0.965 0(6)	0.940(1)	0.961(1)
C(31A)	0.958 4(5)	1.010(1)	1.067 1(8)	−0.954 0(6)	1.016(1)	1.056(1)
C(4A)	1.029 2(5)	0.869 8(9)	0.963 4(9)	−1.025 2(6)	0.872(1)	0.954(1)
C(5A)	1.039 3(5)	0.809(1)	0.869(1)	−1.035 1(6)	0.810(1)	0.861(1)
C(6A)	0.989 3(5)	0.808 7(9)	0.789 3(8)	−0.985 9(6)	0.810(1)	0.780(1)
Cu(B)	0.784 53(6)	0.812 4(1)	0.807 48(8)	−0.785 18(7)	0.811 2(2)	0.802 2(1)
N(1B)	0.761 9(3)	0.932 2(6)	1.033 5(5)	−0.759 8(4)	0.932 1(7)	1.026 6(6)
Si(B)	0.724 2(1)	1.002 9(3)	1.147 1(2)	−0.722 0(2)	1.000 8(3)	1.142 1(2)
C(100B)	0.790 8(5)	1.082 5(9)	1.231 6(7)	−0.786 2(7)	1.082(1)	1.224 4(9)
C(101B)	0.659 5(5)	1.108 7(9)	1.099 5(7)	−0.657 5(6)	1.106(1)	1.095 5(9)
C(102B)	0.675 9(5)	0.900(1)	1.235 3(8)	−0.676 6(7)	0.895(1)	1.229(1)
C(1B)	0.796 7(4)	0.831 5(8)	1.047 8(6)	−0.796 8(5)	0.832(1)	1.041 5(9)
N(2B)	0.803 0(4)	0.762 5(6)	0.962 0(5)	−0.802 8(4)	0.762 2(7)	0.954 6(7)
C(3B)	0.834 7(5)	0.660 8(8)	0.975 1(7)	−0.837 3(6)	0.661(1)	0.970 6(9)
C(31B)	0.836 7(6)	0.588 2(9)	0.877 1(8)	−0.840 2(8)	0.584(1)	0.870(1)
C(4B)	0.865 4(5)	0.628 9(9)	1.074 4(8)	−0.866 5(7)	0.632(1)	1.070(1)
C(5B)	0.862 7(6)	0.702(1)	1.160 4(8)	−0.861 8(7)	0.703(1)	1.153(1)
C(6B)	0.828 2(5)	0.800 9(9)	1.149 0(7)	−0.827 3(6)	0.801(1)	1.141 8(9)
Cu(C)	0.681 80(6)	0.926 1(1)	0.702 70(8)	−0.682 19(7)	0.922 8(2)	0.700 0(1)
N(1C)	0.775 5(3)	1.139 5(6)	0.653 0(5)	−0.774 2(4)	1.137 8(8)	0.644 4(6)
Si(C)	0.848 0(1)	1.226 6(2)	0.622 9(2)	−0.844 9(2)	1.228 6(3)	0.612 8(3)
C(100C)	0.926 6(5)	1.183 6(9)	0.705 5(8)	−0.922 6(6)	1.185(1)	0.693(1)
C(101C)	0.870 5(5)	1.217(1)	0.474 4(7)	−0.867 9(7)	1.218(1)	0.463 4(9)
C(102C)	0.833 6(6)	1.377 1(9)	0.657 6(9)	−0.829 1(7)	1.381(1)	0.647(1)
C(1C)	0.718 0(5)	1.135 1(8)	0.581 4(6)	−0.717 5(6)	1.132(1)	0.577 6(9)
N(2C)	0.677 2(3)	1.038 9(6)	0.581 8(5)	−0.677 9(4)	1.036 0(8)	0.577 6(6)
C(3C)	0.621 0(4)	1.033 3(8)	0.510 2(6)	−0.621 8(6)	1.029(1)	0.509 6(8)
C(31C)	0.580 9(5)	0.925 2(9)	0.514 7(7)	−0.582 8(6)	0.920(1)	0.513(1)
C(4C)	0.602 3(5)	1.120(1)	0.441 5(8)	−0.603 1(6)	1.117(1)	0.439(1)
C(5C)	0.641 3(5)	1.216(1)	0.443 2(7)	−0.641 9(7)	1.215(1)	0.437 4(9)
C(6C)	0.698 8(5)	1.226 4(8)	0.513 1(7)	−0.697 5(6)	1.223(1)	0.507(1)
Cu(D)	0.732 92(5)	1.139 6(1)	0.812 22(8)	−0.731 58(7)	1.139 4(2)	0.805 0(1)
N(1D)	0.609 9(3)	0.965 2(7)	0.831 9(5)	−0.611 1(4)	0.964 2(8)	0.830 5(7)
Si(D)	0.553 8(1)	0.857 9(3)	0.876 7(2)	−0.555 4(2)	0.853 6(4)	0.877 0(3)
C(100D)	0.606 3(6)	0.748(1)	0.949 1(8)	−0.607 1(8)	0.749(1)	0.949(1)
C(101D)	0.504 3(5)	0.786(1)	0.764 2(9)	−0.505 7(7)	0.783(1)	0.766(1)
C(102D)	0.488 1(6)	0.918(1)	0.978 2(9)	−0.491 2(8)	0.915(2)	0.982(1)
C(1D)	0.584 7(5)	1.070(1)	0.803 2(7)	−0.585 0(6)	1.069(1)	0.801 7(9)
N(2D)	0.627 5(4)	1.159 8(7)	0.807 4(5)	−0.627 3(4)	1.158 4(8)	0.801 7(6)
C(3D)	0.603 6(5)	1.265 8(9)	0.785 7(7)	−0.601 0(6)	1.263(1)	0.779 2(9)
C(31D)	0.652 5(6)	1.358(1)	0.793 9(9)	−0.650 1(8)	1.359(1)	0.788(1)
C(4D)	0.534 1(6)	1.281(1)	0.751 9(8)	−0.533 6(8)	1.279(1)	0.750(1)
C(5D)	0.489 3(6)	1.190(1)	0.743 1(9)	−0.489 6(7)	1.186(2)	0.745(1)
C(6D)	0.513 1(5)	1.084(1)	0.767 3(7)	−0.514 6(6)	1.083(1)	0.768(1)
C(1′)	0.389(1)	1.043(2)	1.495(1)	−0.398(1)	1.036(2)	0.504(2)
C(2′)	0.327 7(9)	1.057(2)	1.566(2)	−0.336(1)	1.054(2)	0.570(2)
O(3′)	0.334 2(6)	0.994(1)	1.662(1)	−0.341 6(7)	0.993(1)	0.673(1)
C(4′)	0.281(1)	1.006(2)	1.731(2)	−0.283(1)	1.006(2)	0.739(3)
C(5′)	0.274(2)	0.927(2)	1.819(2)	−0.289(2)	0.940(3)	0.836(4)

* Defines origin.

bonding contacts between ring methyl protons of one ligand with silyl methyl protons of the other. Such skewing has been noted in a related binuclear complex, $[Cu_2\{CPh(NSiMe_3)_2\}_2]$,[8] which has similar metal environments; Cu $\cdots$ Cu 2.425(2) Å, N–Cu–N 175.9°. That the skewing arises from ligand buttressing in these complexes is consistent with the essentially planar ligand/metal arrangement in the complex $[Cu_2\{CH(NC_6H_4Me\text{-}4)_2\}_2]$, where the substituents are able to avoid each other by rotation along the N–C_{phenyl} vectors.[7] Even so the metal environments are still similar to those in **1**; Cu $\cdots$ Cu 2.497(2) Å, N–Cu–N 174.5(3)°. A planar ligand/metal arrangement also occurs in the structure of the complex $[Cu_2(PhNNNPh)_2]$, albeit relatively inaccurately determined; Cu $\cdots$ Cu 2.45(2) Å.[9] In a bunuclear {(oxazolinyl)aryl}-

copper(I) species, again with a similar metal environment to **1** [Cu ··· Cu 2.4708(9) Å, C–Cu–N 177.8(2)°], skewing is evident but is in consequence of the orientation of the lone pair on each N-centre.[20]

Binuclear structures in the present and foregoing complexes are noteworthy since copper(I) amides are generally higher aggregates in the absence of chelating substituents,[1,6] or with a less sterically demanding bridging ligand such as in [Cu_4(MeNNNMe)$_4$].[5] These higher aggregates have Cu ··· Cu distances close to 2.65 Å, typically 0.2 Å longer than in the binuclear complexes. The most recent theoretical study on binuclear complexes, by Cotton *et al.*,[7] supports the absence of clearly defined Cu ··· Cu bonding interactions, at least for a Cu ··· Cu distance of 2.497(2) Å, as found in [Cu_2{CH(NC_6H_4Me-4)$_2$}$_2$]. Moreover, Cotton *et al.*[7] suggest that there is still no M ··· M bonding in [Cu_2{2-C($SiMe_3$)$_2$$C_5H_4N$}$_2$], which has a shorter Cu ··· Cu distance [2.412(1) Å] than **1**.[21]

Table 5 Non-hydrogen atom coordinates for compound **3**

Atom	*x*	*y*	*z*
Ag(1)	0.099 42(2)	0.130 60(4)	0.274 07(2)
Ag(2)	0	0.988 26(5)	1/4
Ag(3)	0	0.263 54(5)	1/4
N(1A)	0.086 0(2)	0.289 1(4)	0.214 6(3)
Si(1A)	0.150 51(8)	0.353 6(2)	0.243 6(1)
C(100A)	0.198 8(3)	0.360 0(8)	0.355 1(4)
C(101A)	0.188 1(3)	0.268 7(7)	0.210 2(5)
C(102A)	0.141 0(4)	0.504 6(7)	0.205 4(5)
C(1A)	0.035 6(2)	0.298 0(5)	0.140 9(3)
N(2A)	−0.014 3(2)	0.278 1(4)	0.134 3(2)
C(3A)	−0.066 5(2)	0.283 3(5)	0.061 5(3)
C(31A)	−0.117 7(3)	0.262 8(6)	0.060 1(4)
C(4A)	−0.071 0(3)	0.305 2(6)	−0.008 0(4)
C(5A)	−0.022 1(3)	0.326 9(6)	−0.003 4(4)
C(6A)	0.030 6(3)	0.324 5(6)	0.070 2(4)
N(1B)	0.128 6(2)	−0.027 5(4)	0.337 0(2)
Si(1B)	0.184 46(7)	−0.085 8(2)	0.337 3(1)
C(100B)	0.160 1(3)	−0.086 2(7)	0.230 8(4)
C(101B)	0.199 8(3)	−0.236 9(7)	0.373 4(4)
C(102B)	0.253 2(3)	−0.002 2(8)	0.400 7(4)
C(1B)	0.121 9(2)	−0.041 8(4)	0.395 8(3)
N(2B)	0.067 5(2)	−0.029 1(4)	0.376 2(2)
C(3B)	0.058 0(2)	−0.041 6(5)	0.433 4(3)
C(31B)	−0.004 0(2)	−0.031 7(6)	0.404 5(3)
C(4B)	0.101 3(2)	−0.063 2(6)	0.512 0(3)
C(5B)	0.157 1(2)	−0.074 7(6)	0.533 9(3)
C(6B)	0.167 5(2)	−0.065 8(5)	0.478 0(3)
C(1)	0.915 4(5)	−0.384(1)	1.071 8(8)
C(2)	0.963 8(7)	−0.380(1)	1.158(1)
C(3)	0.969 2(8)	−0.380(1)	1.212(1)

The Cu–$N_{pyridyl}$ distances, 1.902(4), 1.903(4) Å, are similar to those in related compounds with neutral sp^2 N-centres, *e.g.* 1.902(4) Å in an {(oxazolinyl)aryl}copper(I) species[20] and 1.910(3) Å in [Cu_2{2-C($SiMe_3$)$_2$$C_5H_4N$}$_2$].[21] They are also typical for mononuclear two-co-ordinate species containing pyridine-type ligands.[22] The Cu–N_{amino} distances, 1.875(4), 1.887(4) Å, are similar to those in [Cu_2{CH(NC_6H_4Me-4)$_2$}$_2$], 1.886(7) and 1.859(7),[7] and [Cu_2{PhC($NSiMe_3$)$_2$}$_2$], mean 1.890 Å,[8] even though here the charge on the ligand is delocalized to both N-centres. All are significantly shorter than in [Cu_4(NEt_2)$_4$], 1.904(3) Å, where the amido centres bridge two metal atoms.[6]

Compounds **2a** and **2b** crystallize isomorphously in the monoclinic space group $P2_1$ with the asymmetric unit as the 'hexanuclear' species, which consists of a distorted octahedral array of copper atoms, four amido ligands and two halogens. The amido ligands straddle four faces and the halogens bridge *trans*-equatorial edges such that the molecules possesses approximately D_2 symmetry, the symmetry axis passing through the two halogens. It represents a new structural type for copper(I) amides although the same structural unit has been established for N-functionalized arylcopper(I) complexes, in [Cu_6(2-$Me_2NC_6H_4$)$_4$$Br_2$][23] and an 2-(oxazolidinyl)aryl analogue.[20] Selected metal core geometries, and positional parameters are listed in Tables 2 and 4 with molecular projections shown in Fig. 2.

The structure can be viewed as arising from the condensation of two units of [Cu_2(mpsa)$_2$] and two units of CuX, although with cleavage of the copper–halogen bonds, elongation of the Cu ··· Cu vector in the binuclear units (see below), and folding of the ligands away from the metal core. The Cu(A) and Cu(B) atoms, of one unit, and Cu(C) and Cu(D) of the other are bridged by the halogens, one bridging Cu(A) and Cu(D), the other Cu(B) and Cu(C); the additional copper atoms, Cu(1) and Cu(2), span N(1A) and N(1C), and N(1B) and N(1D), being two-co-ordinate whereas the others are three-co-ordinate. The three symmetry axes pass through the two halogens, the two two-co-ordinate copper atoms and mid-points of the Cu(A) to Cu(B), and Cu(C) to Cu(D) vectors.

The mpsa ligands span three metal centres; the amido groups bridge two-co-ordinate coppers, Cu–N 1.893(6)–1.927(7) Å, **2a**, 1.884(9)–1.919(8) Å, **2b**, and three-co-ordinate copper atoms,

Table 6 Non-hydrogen atom coordinates for compound **4**

	Ligand A			Ligand B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Zn	0.629 84(8)	0.234 18(5)	0.081 68(4)	0.837 01(8)	0.271 58(6)	0.205 42(4)
Ethyl group						
C(01)	0.476 8(7)	0.166 3(5)	0.039 0(4)	0.934 9(6)	0.242 6(5)	0.299 4(3)
C(02)	0.379 3(9)	0.205 6(5)	−0.004 4(6)	1.076 0(9)	0.254 3(7)	0.309 6(4)
Amide ligand						
N(1)	0.650 8(5)	0.324 9(3)	0.175 9(2)	0.821 8(4)	0.192 2(3)	0.106 7(2)
Si	0.550 0(2)	0.323 1(2)	0.237 9(1)	0.848 3(2)	0.077 8(1)	0.103 9(1)
C(100)	0.615 1(9)	0.386 4(7)	0.319 7(4)	1.022 6(8)	0.053 8(5)	0.142 7(4)
C(101)	0.385 2(7)	0.368 6(6)	0.198 3(4)	0.808 6(9)	0.029 5(5)	0.013 6(4)
C(102)	0.534 8(8)	0.204 3(6)	0.261 7(4)	0.739 2(8)	0.027 1(5)	0.158 4(4)
C(1)	0.654 6(5)	0.397 0(4)	0.131 2(3)	0.904 5(5)	0.253 2(4)	0.082 8(3)
N(2)	0.655 9(4)	0.372 6(3)	0.063 4(2)	0.932 9(4)	0.324 2(3)	0.127 1(2)
C(3)	0.665 8(6)	0.439 6(4)	0.014 3(3)	1.004 4(6)	0.392 5(4)	0.109 5(3)
C(31)	0.671 3(7)	0.397 4(5)	−0.057 6(3)	1.026 8(7)	0.468 6(5)	0.160 3(4)
C(4)	0.670 6(6)	0.522 4(4)	0.030 2(4)	1.056 6(6)	0.391 5(5)	0.048 8(4)
C(5)	0.666 9(7)	0.548 7(4)	0.098 1(4)	1.031 9(7)	0.319 0(5)	0.005 4(4)
C(6)	0.659 8(7)	0.485 9(4)	0.149 7(3)	0.956 0(6)	0.249 0(5)	0.021 2(3)

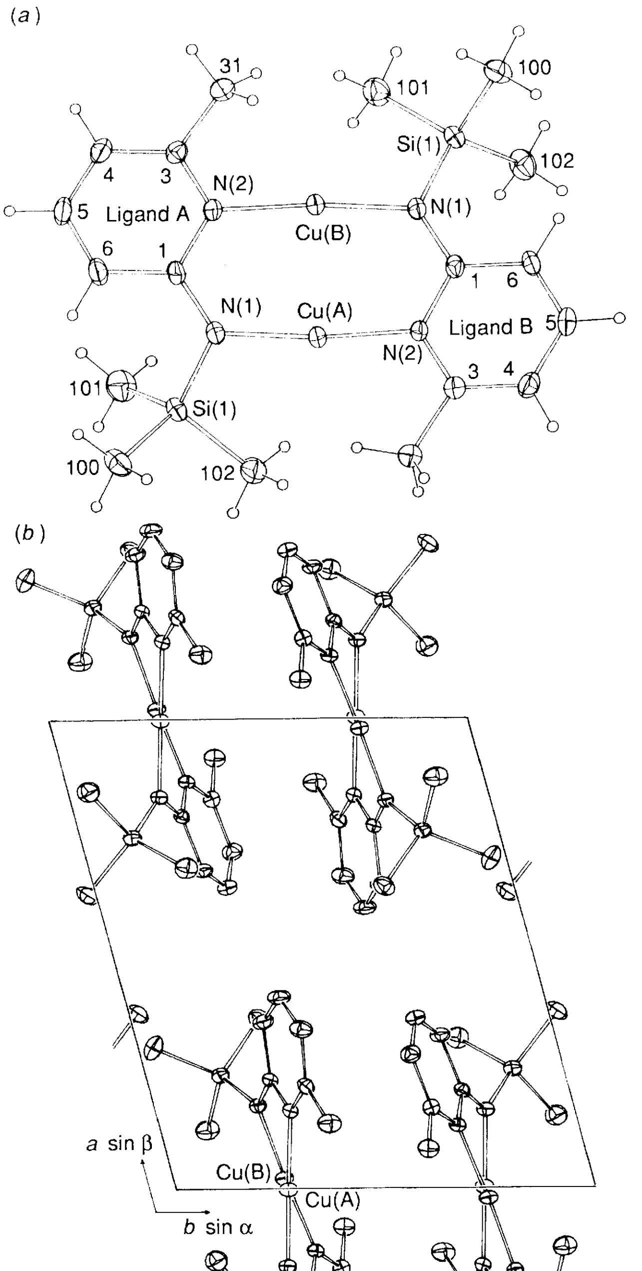
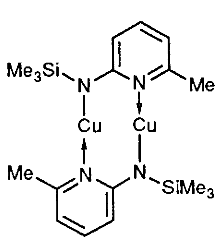


Fig. 1 Molecular structure (*a*) and unit-cell contents projected down *c* (*b*) of $[Cu_2(mpsa)_2]$ **1** showing labelling, together with 20% thermal envelopes for the non-hydrogen atoms. Hydrogen atoms have arbitrary radii of 0.1 Å



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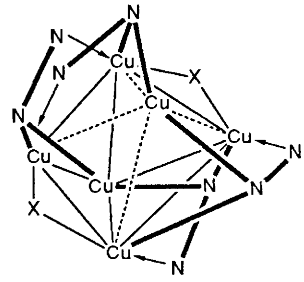
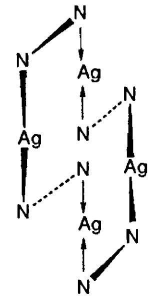


2a, X = Cl
2b, X = Br



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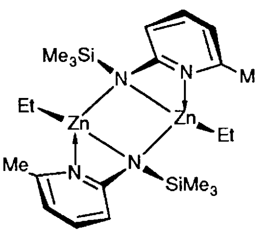

4

Cu–N 2.100(6)–2.133(6) Å, **2a**, 2.100(8)–2.152(9) Å, **2b**, and the pyridyl N-centre is bound to a three-co-ordinate copper, Cu(A),Cu(B), Cu–N 1.993(7)–2.006(7) Å, **2a**, 1.983(9)–2.013(8) Å, **2b**. All Cu–N distances are slightly longer than in **1** because the amido centres are now bridging, and also there is an increase in metal co-ordination number. The two-co-ordinate copper atoms, N–Cu–N 161.7(3), 162.2(3)°, **2a**, 159.9(3), 161.7(3)°, **2b**, have Cu–N distances that match those of the copper atoms in $[Cu_4(NEt_2)_4]$, 1.904(3) Å,[6] although there the angle at the metal is more obtuse, 175.4(1)°. Copper–halide distances, 2.270(3)–2.303(3) Å, **2a**, 2.409(3)–2.443(3) Å, **2b**, are unexceptional as are the angles subtended by the two copper atoms at the halogens, Cu(A)–X(1)–Cu(D), 71.55(1), X = Cl, 67.80(8), X = Br, Cu(B)–X(2)–Cu(C), 72.4(1), X = Cl, 67.45(8), X = Br.

The Cu ··· Cu distances vary according to the nature of the bridging moieties. Distances for amido bridged copper atoms are, Cu(1) ··· Cu(B,D), 2.624(2), 2.622(2); Cu(2) ··· Cu(A,C) 2.631(2), 2.603(2) Å, **2a**, corresponding values for **2b** are 2.621(2), 2.608(2), 2.620(2), 2.600(2) Å. Halogen bridged copper atoms are separated by 2.684(2) Å, **2a**, 2.689(2) Å, **2b**, Cu(A) ··· Cu(D), and 2.682(2) Å, **2a**, 2.694(2) Å, **2b**, Cu(B) ··· Cu(C). The remaining edges of the octahedron are spanned by the pyridyl N-centres and an amido centre, but can be subdivided further into (i) four edges involving the two-co-ordinate coppers, Cu(1) ··· Cu(A,C) 2.667(2), 2.660(1) Å, **2a**, 2.678(2), 2.672(2) Å, **2b**, Cu(2) ··· Cu(B,D) 2.688(2), 2.666(2) Å, **2a**, 2.690(2), 2.684(3) Å, **2b**, and (ii) two edges involving three-co-ordinate coppers only, Cu(A) ··· Cu(B) 2.940(2), **2a**, 2.930(3) Å, **2b**, Cu(C) ··· Cu(D) 3.029(2) Å, **2a**, 3.026(3) Å, **2b**. On the basis of longer Cu ··· Cu distances in **2** compared with **1** there is little prospect of significant metal–metal bonding.

Compound **3** crystallises in the monoclinic cell *C*2/*c* with half of the tetranuclear species as the asymmetric unit. Bond distances and angles, and positional parameters are listed in Tables 2 and 5 with a molecular projection shown in Fig. 3. Unlike in **1**, the ligands span the metal centres in a head to head and tail to tail arrangement, with the metal centres remote, Ag ··· Ag 3.006(1)–3.164(1) Å. Much shorter Ag ··· Ag distances are found in dimeric amide species, $[Ag_2(PhNNNPh)_2]$, 2.669(1) Å,[24] and $[Ag_2\{CH(NC_6H_4Me\text{-}4)_2\}_2]$, 2.705(1) Å,[7] and the dimeric alkyl $[Ag\{C(SiMe_3)_2C_5H_4N\}_2]$,[19] which has the shortest distance for silver complex aggregates, 2.654(1) Å. Indeed the Ag ··· Ag distance in **3** is more akin to that in the higher aggregate $[Ag_3(\mu\text{-}L)_3]$ (L = 3,5-diphenylpyrazolyl), 3.305(2)–3.496(2) Å.[25]

The difference in degree of association of M(mpsa) units in **1** and **3** is possibly a consequence of the small bite of mpsa which is unable to span two silver centres in a dimeric molecule without further departure from a linear co-ordination environment, coupled with the much larger size of silver relative to copper. In the tetranuclear **3** the N–Ag–N angles are 169.3(2) and 171.2(2)°, slightly less obtuse than in **1**, 173.4(2) and

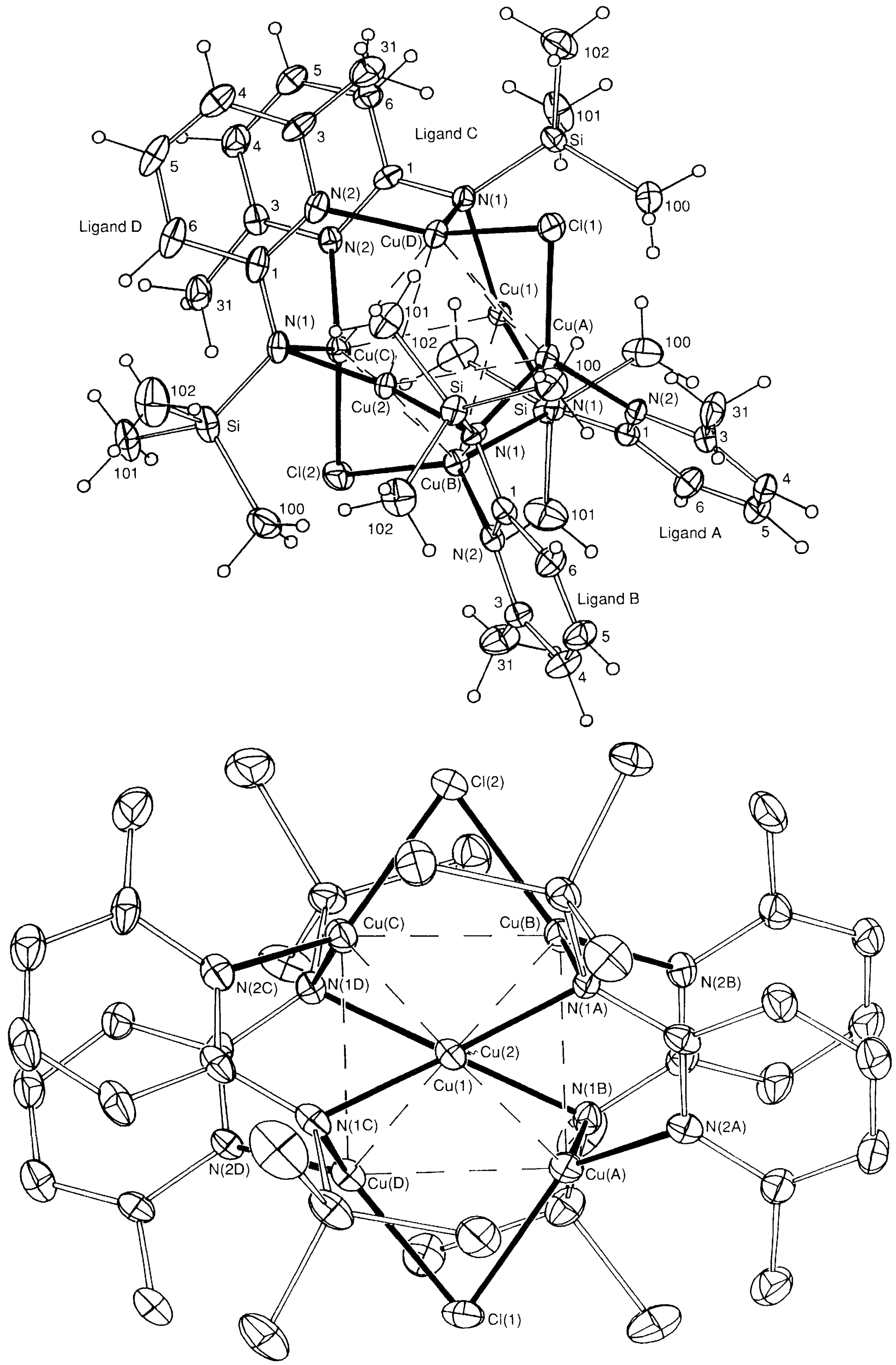

Fig. 2 Two views of a molecule of [Cu$_6$(mpsa)$_4$Cl$_2$] **2a**

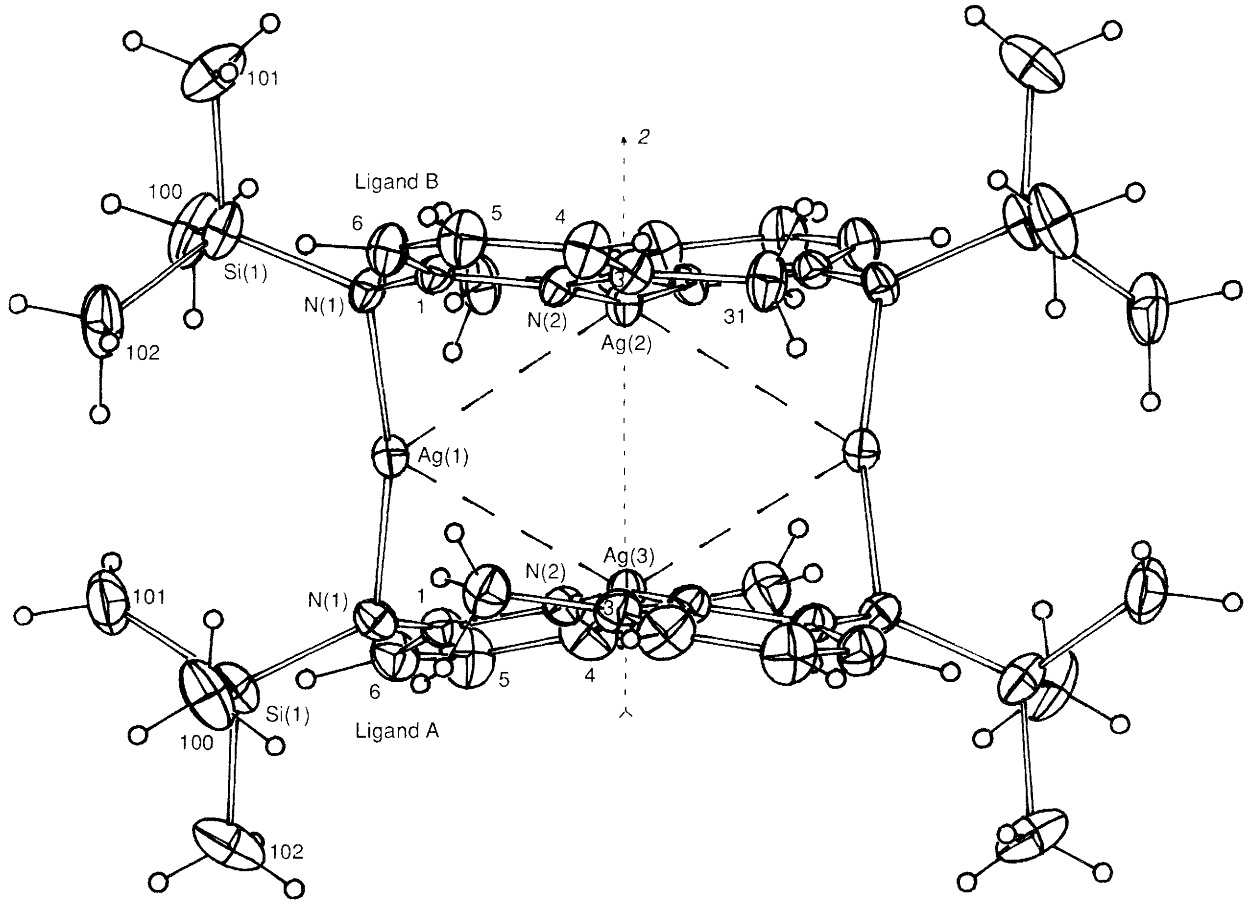

Fig. 3 Projection of the tetranuclear compound [Ag$_4$(mpsa)$_4$] **3**

174.6(2)°. It is noteworthy that theoretical studies on [Ag$_2$(HNCHNH)$_2$] are consistent with no significant amount of Ag · · · Ag bonding in [Ag$_2${CH(NC$_6$H$_4$Me-4)$_2$}$_2$].[7]

The Ag–N(amido) distances, 2.099(5) and 2.097(4) Å are comparable to those found in the trinuclear species [Ag$_3$(μ-L)$_3$],[25] 2.08(1)–2.09(1) Å, and to those in the binuclear species [Ag$_2${CH(NC$_6$H$_4$Me-4)$_2$}$_2$], 2.116(5) and 2.094(5) Å.[7] The Ag–N(pyridyl) bond lengths are longer, 2.140(3) and 2.169(6) Å, and are similar to that found for the Ag–N(pyridyl) distance in the alkyl metal species [Ag$_2${2-C(SiMe$_3$)$_2$C$_5$H$_4$N}$_2$], 2.160(5) Å.[17]

Complex **4** consists of discrete binuclear species as the asymmetric unit in the monoclinic cell $P2_1/c$. Bond distances and angles, and positional parameters are listed in Tables 2 and 6 with a molecular projection shown in Fig. 4. The binding mode of the amido ligands differs to that in the binuclear complex **1** in that the amido centres now bridge the two metal atoms. Thus the ligands bind in three directions but two of these are to the same metal forming a chelate ring. Binding is also in three directions in **2**, but all three are to different metal centres. Pairs of ligands are disposed on the same side of the Zn$_2$N$_2$ ring system (*cis*-) so that the molecules possess approximately C_2 symmetry; the alternative *trans*- or C_i arrangement would appear to have steric buttressing between the hydrogens of the ring methyl and silyl methyl groups. Similar structures, both *cis* and *trans*, have been noted for alkylzinc amides,[26] and also alkylzinc alkoxides.[27,28]

The Zn–N distances within the Zn$_2$N$_2$ ring are unsymmetrical, those in the chelate ring being significantly shorter, 2.061(5), 2.072(5) Å *versus* 2.245(5), 2.225(5) Å. The (weighted) Zn$_2$N$_2$ ring is substantially planar (χ^2 580), deviations (Å) Zn(A) 0.00, Zn(B) 0.00, N(1A) 0.11, N(1B) 0.09, [N(2A) 1.89, N(2B) 1.87, C(01A) −0.92, C(01B) −0.99]. The Zn–N–Zn angles, 86.4(2), 87.2(2)°, and N–Zn–N angles, 92.8(2), 93.1(2)°, depart from right angles in contrast to the corresponding angles in [(ZnMe)$_2$(NPh$_2$)$_2$][12] possibly due to asymmetry in the bridging ligands arising from the presence of chelate rings.

The Zn–N$_{\text{pyridyl}}$ distances, 2.125(5), 2.108(5) Å, compare with the analogous distances involving neutral sp^2 N-centres in [Zn(qsa)$_2$], mean 2.100 Å,[17] and in [(ZnEt)$_2${2-C(NBu^t)C$_5$H$_4$N}$_2$], mean 2.126 Å,[27] despite these centres being involved in five-membered chelate rings whereas in **4** less stereochemically favoured four-membered rings are present. The Zn–C distances, 1.937(3), 1.957(6) Å, are unexceptional for four-co-ordinate zinc attached to primary alkyls.[27,29] This aside there is only one example of a zinc alkyl amide with fewer co-ordinating groups, *viz*. three-co-ordinate [Zn{μ-H$_2$B(C$_3$H$_2$N$_2$-Bu^t-3}$_2$Bu^t], (C$_3$H$_2$N$_2$Bu^t-3 = 3-*tert*-butylpyrazol-1-yl) which has a Zn–C distance of 1.995(7) Å.[30]

Significant metal–metal interaction in **4** is unlikely with a Zn · · · Zn distance of 2.958(2) Å. This is much longer than in the metal, 2.6694 Å.[31] In contrast the metal–metal distance in **1**, 2.420(1) Å, is much shorter than in the metal, 2.56 Å, even though both **1** and **4** are formally d^{10} complexes. A higher co-ordination number in **4** (four) compared to **1** (two) arising from bridging of the amido groups, and the ethyl groups, might be at the expense of any metal–metal interaction; greater 'solvation' would tend to increase the charge on the metal centres resulting in a metal–metal repulsion component. Alternatively, the greater separation of metal centres could arise from the geometrical requirements of the now bridging N-amido groups. That ligand amido groups bridge in **4**, and also the related lithium complex [Li$_2$(mpsa)$_2$(OEt$_2$)$_2$],[11] but not **1**, reflects the preference for zinc, and lithium, to form four-co-ordinate species. In the case of copper(I) two-co-ordinate species are common and there is even one example of a co-ordination number of one.[32]

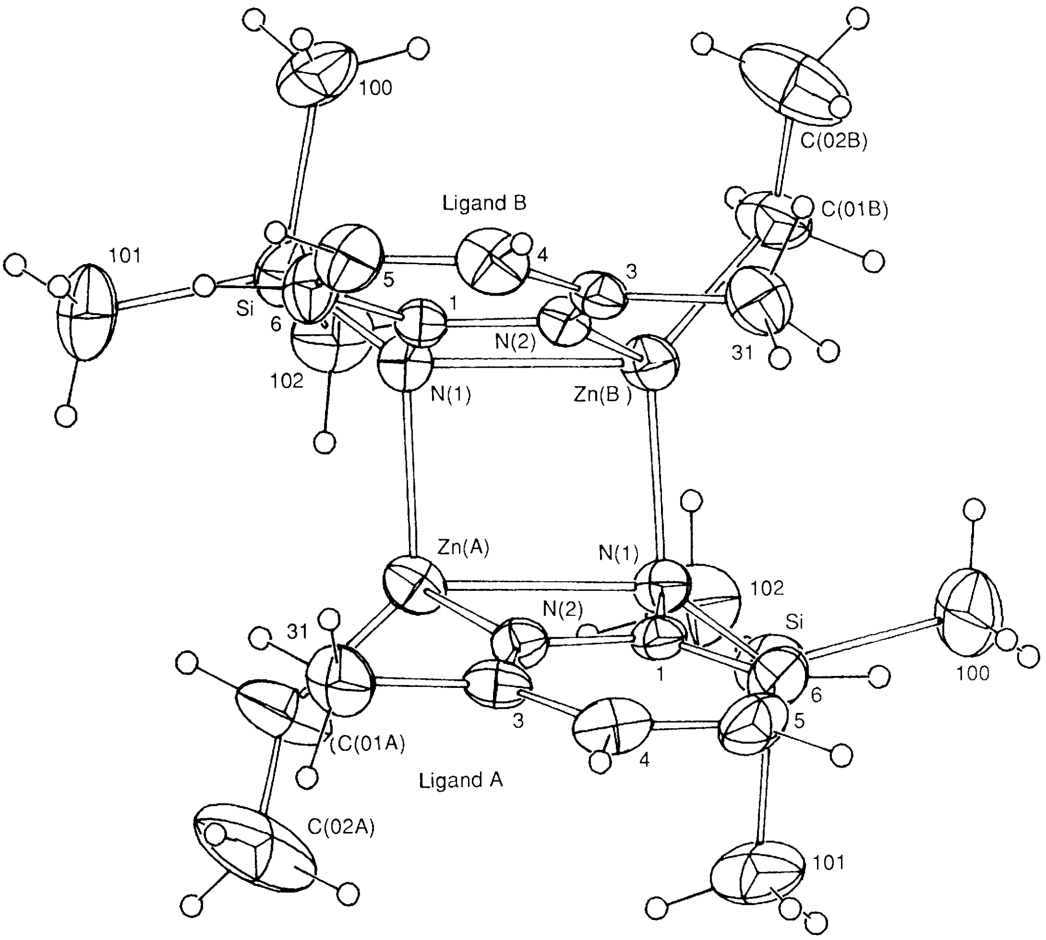

Fig. 4 Molecular projection of a molecule of $[(ZnEt)_2(mpsa)_2]$ **4**

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