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Silver(I) and mercury(II) complexes of $\text{Me}_3\text{N}(+)\text{--N}(-)\text{X}$ ylides: synthesis and structure

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Abstract

The ligating properties of $\text{Me}_3\text{N}(+)\text{--N}(-)\text{X}$ trimethylammonio-stabilised nitrogen ylides have been investigated. The electron-rich nitrogen atom of the ylide can be attached to silver(I) and mercury(II), giving rise to new solids with unusual architectures. The mono-ylide complex LAgNO_3 [$\text{L} = \text{Me}_3\text{N}(+)\text{--N}(-)\text{C}(\text{O})\text{C}_6\text{H}_4\text{Cl-}p$] contains chains in which LAg units are μ_2 -bridged through nitrate oxygen atoms, whereas the di-ylide species L_2AgNO_3 [$\text{L} = \text{Me}_3\text{N}(+)\text{--N}(-)\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3\text{-}p$] contains L_2Ag units with nearly linear coordination (N--Ag--N 158°); if account is taken of weaker $\text{Ag}\cdots\text{O}$ interactions the crystal is built from discrete L_2AgNO_3 molecules containing chiral tris(chelate)silver(I) ions which have spontaneously resolved during crystallisation. The ylide $\text{L} = \text{Me}_3\text{N}(+)\text{--N}(-)\text{CO}_2\text{Me}$ forms *catena*- $[\text{LHgCl}_2]$ in which the planar LHgCl_2 sub-units are weakly linked into chains through $\text{Hg}\cdots\text{Cl}$ contacts of 3.12 Å. Treatment of $\text{L} = \text{Me}_3\text{N}(+)\text{--N}(-)\text{C}(\text{O})\text{C}_6\text{H}_4\text{Cl-}p$ with HgCl_2 leads to hydrolysis and formation of $[\text{LH}][\text{Hg}_2\text{Cl}_5]$ which contains a novel $[\text{Hg}_2\text{Cl}_5]^-_\infty$ sheet structure formed by 2:1 association of linear HgCl_2 molecules with dinuclear $\text{Hg}_2\text{Cl}_6^{2-}$ anions.

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Keywords: Ylide complexes; Crystal structures; Mercury(II); Silver(I)

1. Introduction

Nitrogen ylides of the type $\text{R}_3\text{N}(+)\text{--N}(-)\text{X}$ ($\text{R} = \text{alkyl}$) contain a dipolar $\text{R}_3\text{N}(+)\text{--N}(-)$ group which is highly effective in releasing electrons to the stabilising substituent X [1,2]. For example, the presence of such a dipolar group greatly enhances both the basicity of the cyano group in $^t\text{Bu}_3\text{N}(+)\text{--N}(-)\text{CN}$ [3] and the capacity of the phosphinyl group in $\text{Me}_3\text{N}(+)\text{--N}(-)\text{P}(\text{O})\text{Ph}_2$ to act as an acceptor of hydrogen bonds [4]. Since $\text{R}_3\text{N}(+)\text{--N}(-)\text{X}$ ylides contain an electron-rich nitrogen atom, these molecules might also be expected to behave as N-donor ligands to metal atoms. Despite this, their ligating properties do not appear to have been previously investigated. In contrast, the coordination chemistry of ylides of the phosphorus-carbon and sulfur-carbon type is well developed and that of sulfur-nitrogen ylides has also received some attention [5].

Accordingly, we describe here attempts to attach ylides of the type $\text{L} = \text{Me}_3\text{N}(+)\text{--N}(-)\text{X}$ **1** (Scheme 1) to cations of various metals belonging to groups 10, 11 and 12. These attempts have been successful in the case of Ag(I) and Hg(II) and have led to the structural characterisation of ylide complexes of different stoichiometries for each metal.

2. Experimental

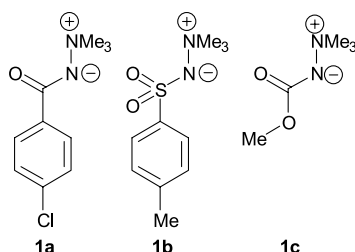
Ylides **1a–1c** (Scheme 1) were prepared by standard procedures [6–8]. Distilled water was used in all experiments.

2.1. Trimethylammonio-4-chlorobenzimidate (**1a**) $p\text{-ClC}_6\text{H}_4\text{C}(\text{O})\text{N}(-)\text{--N}(+)\text{Me}_3$

A solution consisting of 8.24 g (0.040 mol) of *N,N'*-dicyclohexylcarbodiimide and 2.43 g (0.041 mol) of *N,N*-dimethylhydrazine in 50 ml of dichloromethane was treated with 6.30 g (0.040 mol) of *p*-chlorobenzoic

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Scheme 1.

acid in an ice-water bath and stirred overnight. Precipitated *N,N'*-dicyclohexylurea was then removed by filtration. Hydrazide was recovered from the filtrate by evaporation of the solvent and any remaining dimethylhydrazine under reduced pressure. The solid hydrazide was dissolved in dichloromethane or chloroform, and to this solution was added an excess, ca. 20 ml, of iodomethane. Crystals started to separate within an hour; after standing overnight the hydrazinium iodide was obtained by filtration. This was treated with an equimolar amount of sodium hydroxide in concentrated aqueous solution. It is advisable to have this solution as concentrated as possible since the product ylide is itself water soluble. Its isolation by extraction into dichloromethane in a separating funnel is more efficient if the aqueous solution is concentrated. The yield of crude ylide was 1.2 g (53%). Crystallisation from ethyl acetate gave white crystals of **1a**, m.p. 120–124 °C.

The ^1H NMR spectra of **1a** initially showed the presence of traces of water which were routinely removed by evacuation of the sample at 0.05 mm Hg and 50 °C for 8 h. The structure of **1a** was then established by ^1H NMR (CDCl_3) spectroscopy at 400 MHz: δ/ppm 3.50 (singlet, 9 methyl-H), 7.28–7.92 (dd, 4 aromatic-H) and confirmed by a mass spectrum which showed parent ion peaks at 212.15 and 214.15 m/z in the ratio expected for the $^{35}\text{Cl}/^{37}\text{Cl}$ isotopes.

2.2. Trimethylammonio-*p*-toluenesulfonamidate (**1b**) $p=\text{MeC}_6\text{H}_4\text{SO}_2\text{N}(-)\text{-N}(+)\text{Me}_3$

The ligand **1b** was made by an established route and was characterised by ^1H NMR and mass spectroscopy [7].

2.3. Trimethylammonio-carbonamidate (**1c**) $\text{MeO}_2\text{CN}(-)\text{-N}(+)\text{Me}_3$

The ligand **1c** was also made by an established route and was characterised by ^1H NMR, which again showed that traces of water were present, and mass spectroscopy [8]. ^1H NMR (CDCl_3) at 400 MHz; chemical shifts are relative to 7.28 ppm for (CHCl_3). δ/ppm : 2.55 (broad singlet, water-H), 3.38 (singlet, 9 methyl-H), 3.56 (singlet, 3 methyl-H). The mass spectrum showed the parent ion peak at 132.13 m/z expected for **1c**.

2.4. $L\text{AgNO}_3$ **2** ($L=\mathbf{1a}$)

Separate solutions containing 0.213 g (1.0 mmol) of the ylide **1a** and 0.170 g (1.0 mmol) of AgNO_3 , each dissolved in the minimum amount of water, were mixed and set aside in the dark at room temperature. After 3 days white crystals appeared. They were filtered off, washed with water and dried. They had m.p. 171–172 °C, and were further characterised by X-ray crystallography.

2.5. $L_2\text{AgNO}_3$ **3** ($L=\mathbf{1b}$)

In a similar fashion aqueous solutions of 0.228 g (1.0 mmol) of the ylide **1b** and 0.170 g (1.0 mmol) of AgNO_3 were mixed and left in darkness for 3 days after which crystals had separated. Filtration, washing and drying gave white crystals, m.p. 187–188 °C, which were characterised by X-ray crystallography.

2.6. $L\text{HgCl}_2$ **4** ($L=\mathbf{1c}$)

0.172 g of **1c** (1.3 mmol) was added to 0.271 g (1.0 mmol) of mercuric chloride dissolved in the minimum amount of water. Thin colourless needle-like crystals were obtained. A small quantity of black material, thought to be metallic Hg, was also observed on the sides of the flask. The crystals were characterised by X-ray crystallography.

2.7. $[\text{LH}][\text{Hg}_2\text{Cl}_5]$ **5** from $L=\mathbf{1a}$ and HgCl_2

0.425g (2.0 mmol) of **1a** was dissolved in the minimum amount of water. 0.271 g (1.0 mmol) of HgCl_2 was dissolved in a mixture of ethanol and water. The two solutions were mixed and left to stand in the dark for 3 days. Small amounts of a fine red precipitate were observed. This precipitate has not been positively identified but is thought to arise from hydrolysis of HgCl_2 . After removal of this solid by filtration white crystals separated from the filtrate after several days. They were washed with water and dried in vacuo. They had m.p. 158–159 °C and were further characterised by X-ray crystallography.

2.8. Crystal structure analyses of **1a**, **2**, **3**, **4**, **5**

All experimental measurements were made on a Bruker–Nonius Kappa CCD diffractometer using Mo $\text{K}\alpha$ X-rays, $\lambda = 0.71073$ Å. Integrated intensities were obtained from the program DENZO and the final sorted and averaged data sets were derived using either SCALEPACK (**1a**, **2**, **3**) or (**4**, **5**) the DENZOX, analytical absorption correction and SORTAV options of WINGX. WINGX was also used for all structure solution and refinement calculations [9]. Details of individual experi-

Table 1
Crystallographic data

Compound	1a	2	3	4 ^b	5
Empirical formula	C ₁₀ H ₁₃ ClN ₂ O	C ₁₀ H ₁₃ AgClN ₃ O ₄	C ₂₀ H ₃₂ AgN ₅ O ₇ S ₂	C ₅ H ₁₂ Cl ₂ HgN ₂ O ₂	C ₁₀ H ₁₄ Cl ₆ Hg ₂ N ₂ O
Crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> <i>m</i> <i>n</i> <i>b</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	7.1126(2)	9.9793(1)	11.2230(2)	6.1334(1)	23.0602(7)
<i>b</i> (Å)	10.8102(3)	7.4823(1)	5.8838(1)	10.0109(2)	7.8555(3)
<i>c</i> (Å)	13.6271(5)	17.8234(2)	39.4321(9)	18.3138(4)	21.0096(6)
β (°)		102.096(1)			102.765(1)
<i>Z</i>	4	4	4	4	8
Reflections, θ max (°)	16475, 33	27459, 34	11428, 27.5	8290, 30	19142, 30
Independent reflections, R_{int}	3970, 0.045 (2267) ^a	5169, 0.026	5262, 0.071 (3286) ^a	1789, 0.041	5248, 0.086
Transmission factors		0.843–0.619		0.236–0.075	0.725–0.097
Data/parameters	3970/131	5169/175	5262/324	1789/72	5248/190
<i>R</i> 1, <i>wR</i> 2 (all data)	0.052, 0.074	0.028, 0.057	0.106, 0.106	0.039, 0.146	0.077, 0.172
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ^{−3})	0.31, −0.29 (e Å ^{−3})	0.56, −0.92	1.01, −0.90	0.63 and −0.87	4.78 and −2.81

For all structures refinement was by full matrix least squares on F^2 .

^a After merging Friedel pairs.

^b Extinction parameter 0.0039(12).

ments are summarised in Table 1. Data for **4**, which undergoes a phase change to an apparently disordered structure on cooling, were measured at room temperature (20 °C). All other measurements were made at 100 K. The Flack parameter for **1a** is of low precision: its value [0.43(5)] suggests that the specimen was a racemic twin. For **5** a crystal specimen of diffraction quality in the form of a very thin plate was obtained only with great difficulty and the absorption correction has been only partly successful. The quality of this analysis is in consequence somewhat poorer than that of the other four.

3. Results and discussion

Complexes obtained from reactions of ylides with silver nitrate and mercury(II) chloride are summarised in Scheme 2. Solutions containing **1a** and either PtCl₂ or NiCl₂ did not give complexes which could be isolated. We consider first the stereochemistry of the metal atoms in the new complexes and then comment briefly on how the structures of the ylides are affected by coordination to the metal.

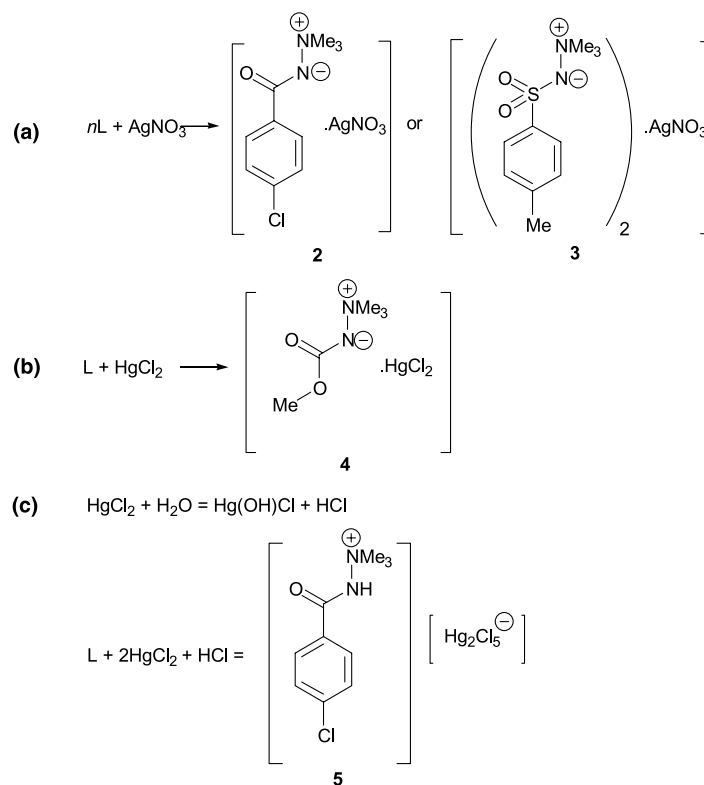
3.1. Ylide complexes of silver(I)

Silver(I) readily forms linear AgL⁺ and AgL₂⁺ complexes with nitrogen-donor ligands [10]. The formation of LAgNO₃ (**2** L = **1a**) and L₂AgNO₃ (**3** L = **1b**) indicates that nitrogen ylides resemble other nitrogen-donor ligands in their reactions with AgNO₃.

The structure of the ylide **1a** is shown in Fig. 1. This molecule reacts with silver nitrate to form the chain polymer **2**. The silver coordination in **2** (Table 2 and Fig. 2(a)) is probably best described as fourfold and irregular. Ag1 forms two strong bonds – to the ylide

nitrogen atom N1 [2.212(1) Å] and to the nitrate O2 oxygen atom [2.293(1) Å] – which define an angle of 143.5(1)° at Ag1. Ag1 also is more weakly coordinated by O2ⁱ and O3ⁱ [2.597(1) and 2.681(1) Å] and is 2.98 Å from O4. Ag1 is nearly coplanar with N1, O2 and O2ⁱ. The result is a chain polymer in which silver(I) and nitrate ions alternate, the basic AgNO₃ unit being replicated by the operations of a 2₁ screw axis (Fig. 2(b)). The ylide ligands help to stabilise this structure, both by donating lone pairs from N1 to complete the silver coordination and by shielding the polymer chains from one another. Although the Cambridge Structural Database contains many examples of catenated silver nitrate complexes, none is an exact match to the geometry of the AgNO₃ chain in **2**. Perhaps the closest resemblance is found in *catena*-(μ -pyrimidine-*N,N'*)bis(μ -nitrate)disilver(I) where an irregular fourfold coordination at each silver atom comprises an Ag–N(pyrimidine) bond of 2.23 Å and three rather similar Ag–O bonds of 2.41–2.53 Å to two different nitrate anions; however, there are also two weaker Ag···O interactions of 2.77 and 2.87 Å, each nitrate bonds strongly to three silver cations, and the pyrimidine also bridges between metal ions [11].

By contrast, crystals of **3** contain discrete molecules (Table 2 and Fig. 3) in which two Me₃N(+)-N(−)SO₂C₆H₄CH₃-*p* ylide ligands are linked to the Ag1 atom through strong Ag–N bonds [2.163(4) and 2.171(5) Å] which define a distorted linear coordination [N–Ag–N 158.0(2)°]. The Ag1 atom also interacts weakly with one oxygen atom of each ylide [Ag1–O11 2.820(5), Ag1–O12 2.826(4) Å] and with two nitrate oxygen atoms [Ag1–O1 2.826(4), Ag1–O3 2.925(5) Å]. The result can be viewed as a formally chiral pseudo-octahedral tris(chelate) complex of silver with approximate twofold symmetry. Remarkably, since the kinetic stability of the complex in solution cannot be great, the silver atoms in crystals of **3** are homochiral. The structure of **3** shows



Scheme 2.

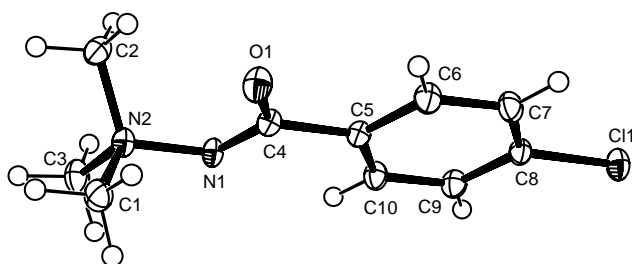


Fig. 1. A view of the $Me_3N(+)–N(–)C(O)C_6H_4Cl$ ylide molecule **1a**. 50% probability ellipsoids are shown here and in Figs. 2(a), 3, 4(a) and 5(a).

similarities with that of $Ag(NH_3)_2NO_3$ [12] which contains two independent linear diamminesilver(I) cations with Ag–N distances of 2.12(1) Å – rather shorter than those in **3**. The nitrate interacts weakly with only one of the $Ag(NH_3)_2^+$ cations through $Ag \cdots O$ contacts of 2.90(1) Å which are roughly comparable in length with those in **3**.

3.2. Ylide complexes of mercury(II)

The ability of mercury(II) chloride to react with nitrogen donors is well-known, as is the structural versatility displayed by $Hg(II)_xCl_y^{n-}$ anions [13]. Thus, the ylide **1c** readily forms the adduct **4** with $HgCl_2$. In the solid (Fig. 4) the ylide ligand lies on a crystallographic

mirror plane which also contains the atoms Hg1, Cl1 and Cl2. The ylide forms a normal Hg–N bond of 2.154(5) Å. The terminal Hg–Cl1 bond length [2.371(2) Å] is also normal, and the N1–Hg1–Cl1 angle is 141.3(2)°. The Cl2 atom completes the in-plane three-fold coordination of Hg1, the Hg1–Cl2 distance of 2.596(1) Å indicating a weaker interaction. These ylide- $HgCl_2$ units are finally linked into infinite chains by weaker contacts of 3.124(1) Å from Hg1 to Cl2ⁱ and Cl2ⁱⁱ (Fig. 4(b)). It has recently been argued that Hg–Cl distances of less than 3.35 Å are structurally significant [13]. When these weaker interactions are taken into account, the mercury coordination polyhedron is an axially elongated, distorted trigonal bipyramid, unusual though not unknown for mercury(II), and Cl2 bonds to three metal atoms arranged in a T shape.

The ylide ligand in **4** remains planar on coordination, so that O2 is brought close to Hg1 [2.85 Å]. This distance is ca. 0.7 Å longer than is observed for Hg–O single bonds [14] and is therefore probably only of minor significance. It can be argued that the C3–O1 and –O2 bonds show no sign of perturbation by the metal atom since their lengths [1.199(7) and 1.347(8) Å] are virtually identical to the average values found in alkyl esters [1.196 and 1.336 Å: [15]]. However, the C3–O1 distance in **4** is markedly shorter than the corresponding bonds in **1a**, **2**, and **5** (see Table 3) suggesting that the A:B ratio (Scheme 3) is larger for **1c** than it is for **1a**.

Table 2

Selected bond lengths (Å) and angles (°) in silver(I) and mercury(II) complexes

(a) Complex 2

Ag(1)–N(1)	2.212(1)	Ag(1)···O(4)	2.981(1)
Ag(1)–O(2)	2.293(1)	O(2)–N(3)	1.282(2)
Ag(1)–O(2) ⁱ	2.597(1)	O(3)–N(3)	1.243(2)
Ag(1)–O(3) ⁱ	2.681(1)	O(4)–N(3)	1.244(2)
N(1)–Ag(1)–O(2)	143.5(1)	Ag(1)–O(2)–Ag(1) ⁱⁱ	148.7(1)
N(1)–Ag(1)–O(2) ⁱ	106.9(1)	C(4)–N(1)–Ag(1)	118.4(1)
O(2)–Ag(1)–O(2) ⁱ	108.0(1)	N(1)–N(1)–Ag(1)	118.6(1)
N(1)–Ag(1)–O(3) ⁱ	138.1(1)	C(3)–N(2)–N(1)–Ag(1)	34.6(1)
O(2)–Ag(1)–O(3) ⁱ	75.6(1)	O(2) ⁱ –Ag(1)–O(2)–Ag(1) ⁱⁱ	–30.9(1)
O(2) ⁱ –Ag(1)–O(3) ⁱ	48.4(1)	Ag(1) ⁱⁱ –O(2)–N(3)–O(3)	–9.1(1)
N(3)–O(2)–Ag(1)	113.1(1)	Ag(1)–O(2)–N(3)–O(4)	–4.4(2)
N(3)–O(2)–Ag(1) ⁱⁱ	97.8(1)		

Symmetry transformations used to generate equivalent atoms:

(i) $-x + 1, y + 1/2, -z + 1/2$; (ii) $-x + 1, y - 1/2, -z + 1/2$ *(b) Complex 3*

Ag(1)–N(11)	2.163(4)	Ag(1)–N(12)	2.171(5)
S(11)–O(11)	1.436(4)	S(12)–O(22)	1.446(4)
S(11)–O(21)	1.448(4)	S(12)–O(12)	1.446(4)
S(11)–N(11)	1.616(5)	S(12)–N(12)	1.603(5)
S(11)–C(11)	1.761(7)	S(12)–C(12)	1.779(6)
N(11)–N(21)	1.467(7)	N(12)–N(22)	1.481(6)
O(1)–N(1)	1.251(7)	O(3)–N(1)	1.222(7)
O(2)–N(1)	1.233(6)		
O(11)–S(11)–O(21)	118.8(3)	O(22)–S(12)–O(12)	117.5(2)
N(11)–S(11)–C(11)	107.8(3)	N(12)–S(12)–C(12)	109.0(3)
N(21)–N(11)–S(21)	118.5(3)	N(22)–N(12)–S(12)	118.1(3)
N(21)–N(11)–Ag(1)	129.0(4)	N(22)–N(12)–Ag(1)	124.9(3)
S(21)–N(11)–Ag(1)	111.8(2)	S(12)–N(12)–Ag(1)	111.9(2)
N(11)–Ag(1)–N(12)	158.0(2)		

(c) Complex 4

Hg(1)–N(1)	2.154(5)	Hg(1)–Cl(2) ⁱ	3.124(1)
Hg(1)–Cl(1)	2.371(2)	Hg(1)–Cl(2) ⁱⁱ	3.124(1)
Hg(1)–Cl(2)	2.596(1)	Hg(1)···O(2)	2.847(4)
N(1)–Hg(1)–Cl(1)	141.3(2)	Cl(2)–Hg(1)–Cl(2) ⁱⁱ	84.5(1)
N(1)–Hg(1)–Cl(2)	119.6(2)	Cl(2) ⁱ –Hg(1)–Cl(2) ⁱⁱ	158.1(1)
Cl(1)–Hg(1)–Cl(2)	99.1(1)	Hg(1)–Cl(2)–Hg(1) ⁱ	95.5(1)
N(1)–Hg(1)–Cl(2) ⁱ	84.6(1)	Hg(1)–Cl(2)–Hg(1) ⁱⁱ	95.5(1)
Cl(1)–Hg(1)–Cl(2) ⁱ	100.2(1)	Hg(1) ⁱ –Cl(2)–Hg(1) ⁱⁱ	158.1(1)
Cl(2)–Hg(1)–Cl(2) ⁱ	84.5(1)	C(3)–N(1)–Hg(1)	117.5(4)
N(1)–Hg(1)–Cl(2) ⁱⁱ	84.6(1)	N(2)–N(1)–Hg(1)	126.2(4)
Cl(1)–Hg(1)–Cl(2) ⁱⁱ	100.2(1)		

Symmetry transformations used to generate equivalent atoms:

(i) $-x, -y, -z + 1$; (ii) $-x + 1, -y, -z + 1$; (iii) $-x + 1/2, y, z$ *(d) Complex 5*

Hg(1)–Cl(4)	2.392(2)	Hg(2)–Cl(5) ⁱⁱⁱ	2.330(2)
Hg(1)–Cl(3)	2.393(2)	Hg(2)–Cl(3)	2.912(2)
Hg(1)–Cl(2) ⁱ	2.612(2)	Hg(2)–Cl(5)	3.054(2)
Hg(1)–Cl(2)	2.633(2)	Hg(2)–Cl(6)	3.067(2)
Hg(2)–Cl(6) ⁱⁱ	2.326(2)	Hg(2)–Cl(4) ⁱⁱ	3.136(2)
Cl(4)–Hg(1)–Cl(3)	137.50(9)	Cl(3)–Hg(1)–Cl(2)	103.78(8)
Cl(4)–Hg(1)–Cl(2) ⁱ	110.48(8)	Cl(2) ⁱ –Hg(1)–Cl(2)	86.78(7)
Cl(3)–Hg(1)–Cl(2) ⁱ	104.36(8)	Cl(6) ⁱⁱ –Hg(2)–Cl(5) ⁱⁱⁱ	172.43(8)
Cl(4)–Hg(1)–Cl(2)	101.77(7)		

Symmetry transformations used to generate equivalent atoms:

(i) $-x, y, -z + 1/2$; (ii) $-x, -y, -z + 1$; (iii) $-x, -y + 1, -z + 1$

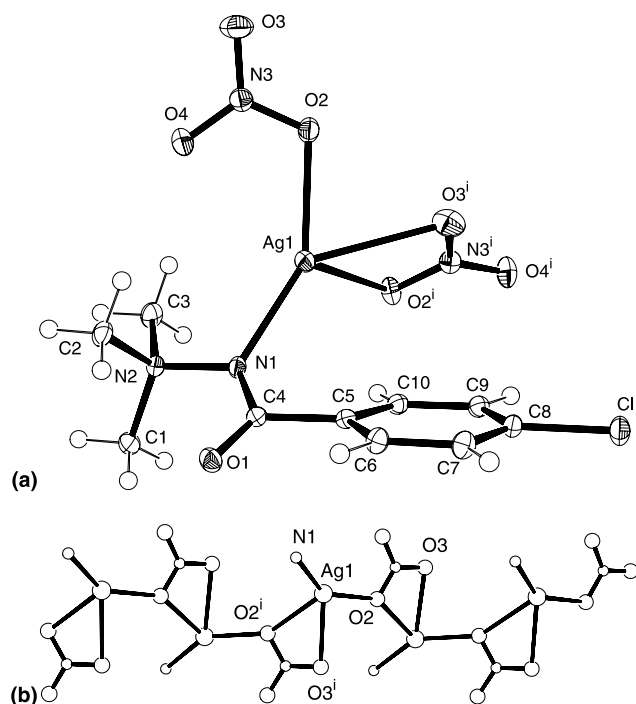


Fig. 2. (a) A view of the silver coordination in *catena*-LAgNO₃ **2** where L = **1a**. (b) The Ag(μ-NO₃) chain backbone in **2** built from successive operations of a 2₁ screw axis parallel to *b* (see Table 2(a)). Atoms are shown as spheres of arbitrary radius except for those of the **1a** ylide ligands which are omitted except for the N1 donor atoms.

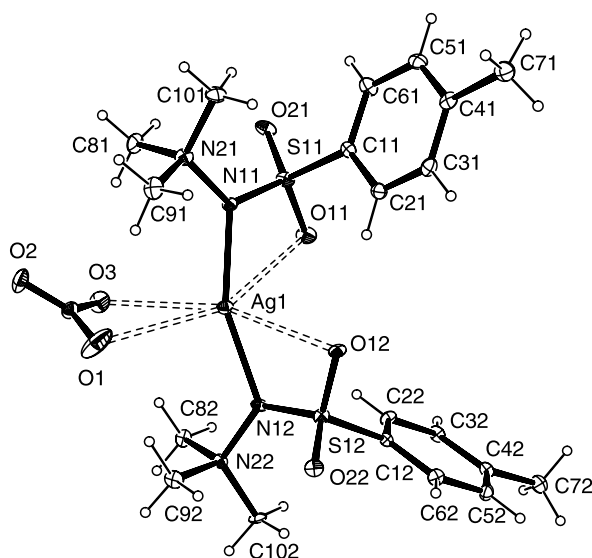


Fig. 3. A view of the complex L₂AgNO₃ **3** where L = **1c**.

The complex **5** (Table 2) was obtained when **1a** reacted with mercuric chloride. The crystal contains three distinct entities (Fig. 5(a)) which interact significantly with one another. (a) The ylide, which is protonated at the ylide nitrogen atom N2 to form a cation, (b) an [Hg₂Cl₆]²⁻ anion which straddles a crystallographic

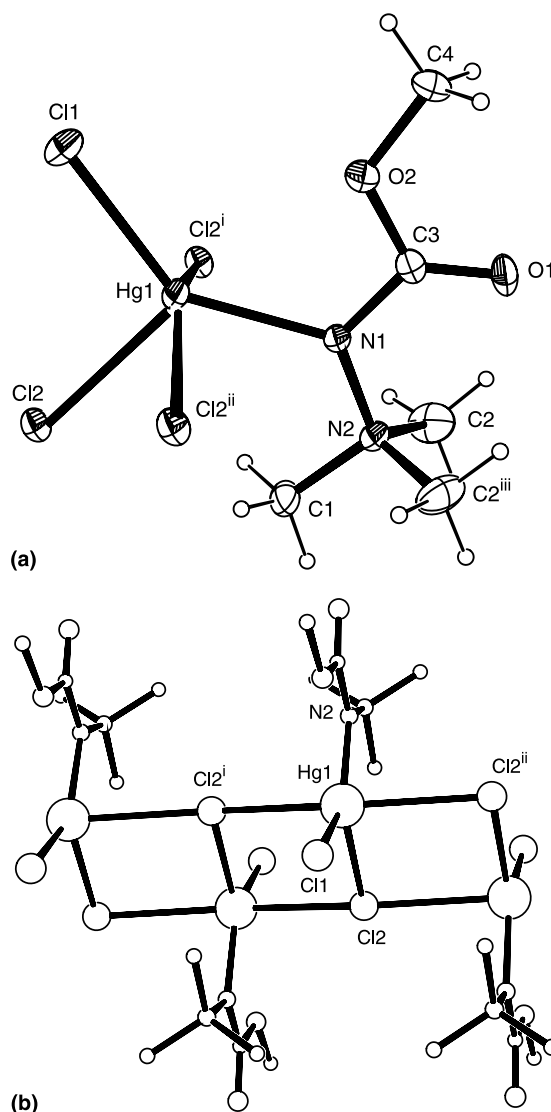


Fig. 4. (a) A view of the mercury coordination in LHgCl₂ **4** where L = **1c**. (b) Part of one of the polymer chains in **4**. Atoms are shown as spheres of arbitrary radius.

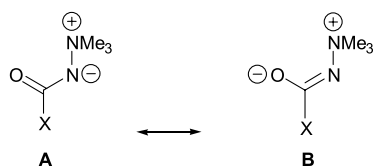
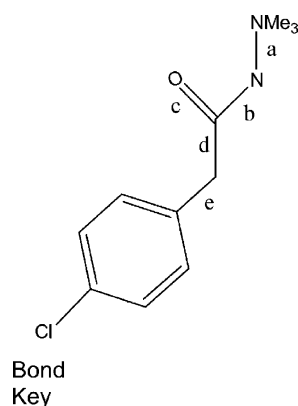
twofold symmetry axis, and (c) nearly linear HgCl₂ molecules. The structure of the [Hg₂Cl₆]²⁻ anion seems quite typical of those observed in other complexes (see [13] for average dimensions): the Hg1 mercury atoms display distorted tetrahedral coordination and the terminal Hg1–Cl3 and Hg1–Cl4 distances [2.392(2) and 2.393(2) Å] are ca. 0.2 Å shorter than the bridging Hg1–Cl2 distances [2.612(2) and 2.633(2) Å]. The chloro ligands Cl5 and Cl6 are even more strongly bound to Hg2 [Hg2–Cl5ⁱⁱⁱ 2.330(2) and Hg2–Cl6ⁱⁱ 2.326(2) Å].

Weaker interactions between these three entities build up an unusual and elegant layer structure (Fig. 5(b)). Thus, the Hg2 atom interacts weakly with four additional chlorine atoms [Hg2...Cl 2.9–3.2 Å] so that it achieves a compressed [2 + 4] octahedral coordination defined by six chlorine atoms. These weaker interactions

Table 3

Selected bond lengths (Å), bond angles and torsion angles (°) in free, complexed and protonated forms of Me₃NNCO-C₆H₅-Cl-*p* (**1a**)

		1a	2 (L = 1a)	5 (LH ⁺ , L = 1a)	H1a·Cl·H ₂ O
<i>a</i>	N–N	1.474(1)	1.470(2)	1.45(1)	1.447(2)
<i>b</i>	N–C	1.338(1)	1.355(2)	1.38(1)	1.374(2)
<i>c</i>	C=O	1.258(1)	1.240(2)	1.22(1)	1.221(2)
<i>d</i>	C–C/O	1.515(2)	1.511(2)	1.50(1)	1.496(2)
$\angle ab$		113.5(1)	114.7(1)	120(1)	119.7(1)
$\angle abd$		179.7(1)	177.0(1)	–176(1)	–176.7(1)
$\angle bde$		174.8(1)	153.4(1)	–155(1)	159.5(1)



Scheme 3.

involve both Cl5 and Cl6, which form asymmetric bridges between equivalent Hg2 atoms, and also Cl3 and Cl4 which thereby bridge asymmetrically between Hg1 and Hg2. The result (Fig. 5(b)) is a two-dimensional sheet of composition $[\text{Hg}_2\text{Cl}_5]_\infty$ containing equal numbers of octahedrally and tetrahedrally coordinated mercury(II) cations. The protonated ylides are attached to this sheet structure through N2–H···Cl4 hydrogen bonds [N2···Cl4 3.43(1), H···Cl4 2.67 Å, N–H···Cl 147°].

The structure of the $[\text{Hg}_2\text{Cl}_5]_\infty$ sheets in **5** appears to be new. The only other example we can find of octahedral $\{\text{HgCl}_6\}$ and tetrahedral $\{\text{HgCl}_4\}$ units linked via a common chloro ligand occurs in the discrete $[\text{Hg}_3\text{Cl}_{12}]^{6-}$ anion [16]. In $[\text{C}(\text{NH}_2)_3]^+[\text{Hg}_2\text{Cl}_5]^-$ the cations are hydrogen-bonded to a $[\text{Hg}_2\text{Cl}_5]^-$ sheet polyanion but the topology of the sheet is quite different to that found here: all the Hg atoms have identical $[2+2+2]$ octahedral coordination and the structure involves association of two HgCl_2 molecules with a chloride anion which is surrounded by a square plane of mercury atoms [17]. Similar arrangements have been found in other $\text{M}^+[\text{Hg}_2\text{Cl}_5]^-$ salts [18]. The occurrence

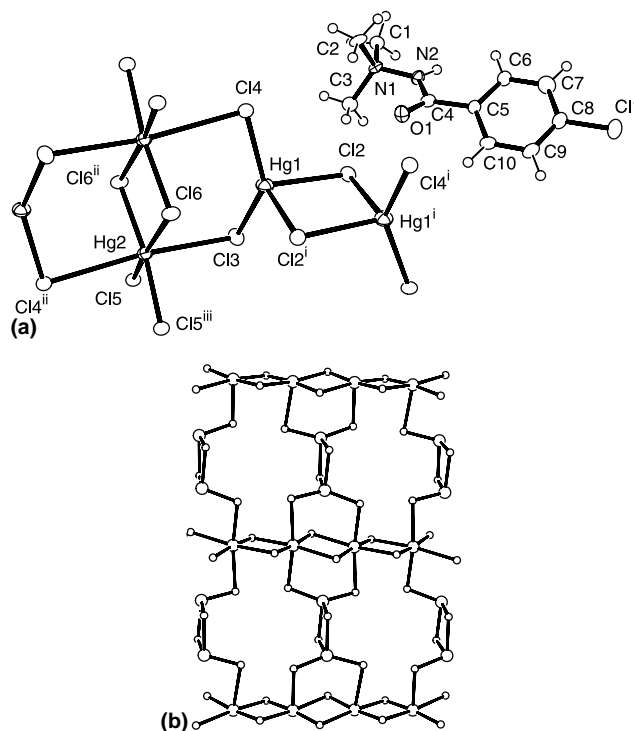


Fig. 5. (a) The LH⁺ cation (L = **1a**) and the coordination of the two independent mercury atoms in **5**. (b) One of the $[\text{Hg}_2\text{Cl}_5]_\infty$ sheets in **5**. Hg and Cl atoms are shown as spheres of arbitrary radius.

of different structures for the same $[\text{Hg}_x\text{Cl}_y]^{n-}$ stoichiometry is a well-established feature of mercury(II) coordination chemistry [13].

3.3. Structures of ylide ligands

The structures of the native ylide (**1a**), the same ylide complexed to silver(I) in **2** and the protonated form found in both in **5** and in (LH)Cl·H₂O (L = **1a**) are compared in Table 3. **1a** has a nearly planar heavy atom skeleton (Fig. 1) apart from methyl carbon atoms C1 and C2. The phenyl and ylide planes are slightly twisted relative to one another [C6–C5–C4–N1 = 174.8(2)°] and the lengths of the N(+)-N(-) and C4–C5 bonds (*a* and *d* in Table 3) are consistent with bond orders close to one. In contrast, the N1–C4 and C4–O1 bond lengths (*b* and *c* in Table 3) indicate substantial multiple character. The N1–C4 distance in **1a** [1.338(1) Å] is significantly shorter than the database mean [15] of 1.376 Å for C_{sp}²–N(2) bonds in imidazoles which also have some multiple character. The C4–O1 distance of 1.258(1) Å is a little longer than the value of 1.234 Å typical of amides of carboxylic acids and appreciably longer than the mean of 1.192 Å found for C=O bonds in ketones. Contributions from both canonical forms **A** and **B** (Scheme 3) are therefore significant.

The analyses of **1a** and **2** permit the small changes in the geometry of the ylide molecule brought about by coordination to silver to be realistically assessed. Donation of a lone pair from N to Ag in **2** increases the importance of canonical form **A**, so that the N–C bond is lengthened and the C–O bond shortened, in each case by ca. 0.02 Å, relative to **1a**. At the same time the dihedral angle between the ylide and phenyl planes changes to 153.4(1)° to accommodate the silver atom without introducing short Ag···H(phenyl) interactions. The single N–N and C_{sp}²–C_{phenyl} bond lengths are unaffected by coordination to the silver atom. The protonated forms of **1a** found in **5** and in (LH)Cl·H₂O (L = **1a**) are indistinguishable and display N–N–C angles of 120° which contrast with the values of 114°–116° found in the free and metal-complexed ylides of **1a** and **2**.

The structures of the two sulfonamidate ligands in **3** are nearly identical and they closely resemble that of the uncomplexed form of the same ylide **1b** [19].

4. Conclusions

We have shown that Me₃N(+)-N(-)X ylides are versatile monobasic nitrogen-donor ligands for silver(I) and mercury(II) ions and that their coordination to a metal cation involves only minor structural changes consistent with loss of charge from the stabilising group X. In the case of L₂AgNO₃ (**3**, L = Me₃N(+)-N(-)SO₂Tol-*p*) the sulfonyl oxygen atoms still retain sufficient basicity to interact weakly with the silver(I) cation. When they are complexed to ylides, both silver(I) and mercury(II) show a strong tendency to form coor-

dination polymers. In the reaction of **1a** with HgCl₂ infinite sheets of composition [Hg₂Cl₅]⁻ are formed by association of HgCl₂ molecules and [Hg₂Cl₆²⁻] anions. These results illustrate how difficult it is to predict the structural outcome of reacting a monobasic nitrogen-donor ligand, such as a nitrogen ylide, with silver nitrate or mercuric chloride. It is generally accepted that the stoichiometry of the complex and the size and coordinating power of the counter anions have a bearing on the resulting crystal architecture [20]. Structural prediction becomes even harder when polydentate nitrogen-donor ligands are involved, as they frequently are in attempts to crystal engineer [21] complexes containing silver(I) (e.g., see [22,23]).

5. Supporting information available

Crystallographic information files (CIF files) for each structure have been deposited with the Cambridge Structural Database. The deposition numbers are CCDC 208311–208315 for **1a**, **2**, **3**, **4** and **5**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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