

Polymeric silver(I) complexes of the multinucleating ligand 4,7-dihydro-5-methyl-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine. Analogous hydrogen-bonded structures in the crystal and vapour phases of the ligand

Jorge A. R. Navarro,^a M. Angustias Romero,^a Juan M. Salas,^{*†,a} René Faure^b and Xavier Solans^c

^a Departamento de Química Inorgánica, Universidad de Granada, Av. de Fuentenueva S/N, 18071 Granada, Spain

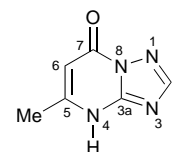
^b Laboratoire de Chimie Analytique II, LICAS, Université Claude Bernard, Lyon-1, 69622 Villeurbanne, France

^c Departamento de Cristalografía, Mineralogía y Depositos Minerales, Universidad de Barcelona, Barcelona, Spain

X-Ray crystallography showed that the crystal structure of Hmtpo (4,7-dihydro-5-methyl-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine) is built up of hydrogen-bonded polymeric chains, whereas mass spectroscopy and solution ¹⁵N NMR spectroscopy suggested the existence of a dimeric structure comprising eight-membered $\cdots\text{H-N-C-N}\cdots\text{H-N-C-N}\cdots$ rings in less condensed phases. On the other hand, the reaction between the silver(I) salts AgX (X = NO₃, ClO₄ or $\frac{1}{2}\text{SO}_4$) and Hmtpo yielded polymeric complexes. The compounds have been structurally characterised by IR spectroscopy and X-ray crystallography. The X-ray results show that the compounds containing the Hmtpo derivative in its neutral form comprise infinite one-dimensional chains, in which the ligand bridges the metal centres through N(1) and N(3) donor atoms. The presence of an additional soft and bulky ligand such as triphenylphosphine in $[\{\text{AgX}(\mu\text{-Hmtpo-}\kappa^2\text{N}^1, \text{N}^3)(\text{PPh}_3)\}_n]$ (X = NO₃ or ClO₄) partially changes the tendency to form polymeric complexes, lengthening the Ag–N(1) bond distance by 0.35 Å. Finally, deprotonation of Hmtpo results in an additional available coordination position at N(4), the ligand bridging three metal centres in $[\{\text{Ag}_3(\mu_3\text{-mtpo-}\kappa^4\text{N}^1, \text{N}^3, \text{N}^4, \text{O}^7)(\text{HSO}_4)(\text{H}_2\text{O})_2\cdot\text{H}_2\text{O}\}_n]$. The new co-ordination mode results in the formation of eight-membered Ag–N–C–N–Ag–N–C–N rings, which give rise to short intermetallic contacts of 3.078(1) Å. The structures of free Hmtpo in the solid state and the postulated vapour-phase structure are compared to those of linear co-ordinated silver(I) complexes.

Hydrogen bonding plays a fundamental role in several chemical and biochemical processes. Its highly selective and directional nature makes it ideal for the construction and stabilisation of large non-covalently linked molecular and supramolecular architectures.¹ Indeed, the biological world is replete with examples of such systems: nucleic acids and protein tertiary structures.² Some authors have extensively studied the replacement of hydrogen bonds by metal entities of appropriate geometry [e.g. Ag^I, *trans*-(H₃N)₂Pt^{II}, Au^I, etc.] in models of biological interest, such as nucleobase Watson–Crick and Hoogsteen pairs,^{3,4} triplets⁵ and quartets,⁶ or materials of technological interest,⁷ concluding that the basic structures are preserved, but the strength of interaction is changed. At the same time, the tendency of Ag^I to build polymeric complexes with the help of ligands containing multiple donor positions makes this ion suitable for building supramolecular co-ordination compounds.^{8,9}

We are currently involved in a detailed study of the co-ordination chemistry of the polydentate 4,7-dihydro-5-methyl-7-oxo[1,2,4]triazolo[1,5-*a*]pyrimidine (Hmtpo), which has a great versatility as a ligand forming either mono-¹⁰ or polynuclear metal complexes.^{11,12} At the same time, this derivative is well known as a stabilising agent for photographic silver halide emulsions.^{13,14} Its behaviour has been related to the stability and high insolubility of the compounds formed in its reactions with silver salts as a result of its multidentate co-ordination to the metal centres,¹⁵ e.g. $\text{p}K_{\text{sp}} = 9.7$ for $[\{\text{Ag}(\mu_3\text{-mtpo-}\text{N}^1, \text{N}^3, \text{N}^4, \text{O}^7)\}_2]^{16}$.



In this paper we present results concerning the preparation and structural characterisation by IR spectroscopy and X-ray crystallography of a series of silver(I) complexes formed upon reaction of Ag^I and Hmtpo in acidic aqueous or ethanolic media. The hydrogen-bonded polymeric crystal structure of free Hmtpo, as well as its postulated vapour-phase dimer structure, from mass spectroscopy, comprising eight-membered $\text{H-N-C-N}\cdots\text{H-N-C-N}\cdots$ rings, are also reported and compared to the similar structures found in linearly co-ordinated silver(I) complexes.

Experimental

Reactants and methods

The compound Hmtpo was obtained from Aldrich Chem. Co. and used as received. Crystals suitable for X-ray analysis were obtained by recrystallisation from MeOH. The other chemical reagents and solvents were supplied by commercial sources. All experiments were performed in air.

Preparations

$[\{\text{Ag}(\text{NO}_3)(\mu\text{-Hmtpo-}\kappa^2\text{N}^1, \text{N}^3)\}_n]$ **1**. The addition of an acidic solution of Hmtpo (1 mmol in ca. 20 cm³ of HNO₃, 4.5 mol

† E-Mail: jsalas@goliat.ugr.es

dm⁻³) to another one of AgNO₃ (1 mmol in ca. 20 cm³ of HNO₃, 4.5 mol dm⁻³) gave a colourless solution that yielded, after 1 week, a precipitate of colourless crystals of **1**. The crystals were rinsed with water and air dried. Yield 18% [Found (Calc. for C₆H₆AgN₅O₄): C, 22.7 (22.5); H, 1.9 (1.9); Ag, 31.7 (32.9); N, 21.8 (21.9)%]. IR data (selected bands, cm⁻¹): 650m, 820m, 1250s, 1380vs, 1570vs, 1625s, 1700vs, 2890s and 3000s.

[Ag(ClO₄)(μ-Hmtpo-κ²N¹,N³)]_n 2. A similar procedure to the previous one resulted in the immediate formation of a white microcrystalline precipitate of complex **2**. Yield 70% [Found (Calc. for C₆H₆AgClN₅O₅): C, 20.2 (20.1); H, 1.7 (1.7); N, 16.1 (15.7)%]. IR data (selected bands, cm⁻¹): 625s, 920m, 1110vs, 1190s, 1570s, 1635vs, 1700vs and 3080m.

[Ag(NO₃)(μ-Hmtpo-κ²N¹,N³)(PPh₃)]_n 3. An ethanol solution of Hmtpo (2 mmol in ca. 50 cm³) was added to another one containing PPh₃ (2 mmol) and AgNO₃ (2 mmol) in ethanol (80 cm³), forming a turbid solution. The subsequent careful addition of concentrated HNO₃ (2 cm³) resulted in the formation of a clear solution; after some hours plate-like crystals of complex **3** were formed. Yield 81% [Found (Calc. for C₂₄H₂₁AgN₅O₄P): C, 49.1 (49.5); H, 3.6 (3.6); Ag, 19.1 (18.5); N, 12.5 (12.0)%]. IR data (selected bands, cm⁻¹): 830w, 1270s, 1420s, 1570vs, 1640s, 1710vs and 3080m.

[Ag(ClO₄)(μ-Hmtpo-κ²N¹,N³)(PPh₃)]_n 4. Following the same procedure as for compound **3**, but using AgClO₄ instead of AgNO₃ and without addition of acid, crystals suitable for X-ray diffraction were obtained. Yield 71% [Found (Calc. for C₂₄H₂₁AgClN₅O₅P): C, 46.1 (46.5); H, 3.4 (3.4); N, 9.0 (9.0)%]. IR data (selected bands, cm⁻¹): 620s, 925m, 1040s, 1100vs, 1130s, 1570vs, 1640s, 1710vs and 3080m.

[[H₂mtpo][Ag(SO₄)(μ-Hmtpo-κ²N¹,N³)]·H₂O]_n 5. This compound was obtained by diffusion, through a sintered-glass membrane, of an acidic solution of Ag₂SO₄ (1 mmol in ca. 120 cm³ H₂SO₄, 6 mol dm⁻³) into another one containing Hmtpo (2 mmol in ca. 120 cm³ H₂SO₄, 6 mol dm⁻³). After some days, plate crystals of **5** were obtained. Yield 18% [Found (Calc. for C₁₂H₁₅AgN₈O₇S): C, 27.3 (27.5); H, 2.8 (2.9); Ag, 20.5 (20.6); N, 21.4 (21.4)%]. IR data (selected bands, cm⁻¹): 420w, 450w, 600s, 900m, 1190vs, 1410s, 1575vs, 1620vs, 1665vs, 1700vs, 1725vs, 2890s, 3160s and 3480m.

[[Ag₃(μ₃-mtpo-κ⁴N¹,N³,N⁴,O⁷)₂(HSO₄)(H₂O)₂]·H₂O]_n 6. The addition with stirring of an acidic solution of Hmtpo (1 mmol in ca. 40 cm³ of H₂SO₄, 6 mol dm⁻³) to another one of Ag₂SO₄ (1 mmol in ca. 50 cm³ H₂SO₄, 6 mol dm⁻³) gives a clear solution from which crystals of complex **6** suitable for X-ray analysis separated after some days. Yield 63% [Found (Calc. for C₁₂H₁₇Ag₃N₈O₉S): C, 18.8 (18.6); H, 2.1 (2.2); Ag, 41.8 (41.9); N, 14.5 (14.7)%]. IR data (selected bands, cm⁻¹): 435w, 595w, 620s, 960m, 1110vs, 1140 (sh), 1195m, 1515s, 1570s, 1630s, 1695vs, 2800m and 3440s.

[H₂mtpo]Cl·H₂O 7. This compound was prepared by dissolving Hmtpo (2 mmol) in concentrated HCl (ca. 5 cm³). From the resulting clear solution it was possible to collect, after 1 week, chunky colourless crystals of **7** [Found (Calc. for C₆H₉ClN₄O₂): C, 35.1 (35.2); H, 4.4 (4.4); N, 27.2 (27.4)%]. IR data (selected bands, cm⁻¹): 1410s, 1600m, 1665vs, 1725vs, 3165s and 3480m.

Instrumentation

Microanalyses of C, H and N were performed with a Fisons-Instruments EA-1008 microanalyser at the Instrumentation Centre of the University of Granada, whereas the silver content was determined thermogravimetrically by means of Mettler TA-3000 equipment provided with a Mettler TG-50 thermo-

balance, at a heating rate of 20 K min⁻¹ and using an atmosphere of pure air (100 cm³ min⁻¹). Infrared spectra were recorded in the range 4000–180 cm⁻¹ on a Perkin-Elmer 983G spectrophotometer, using KBr and polyethylene pellets. Mass spectra by chemical ionisation were performed with Fisons Platform-II equipment, using direct sample injection and a potential of 36 eV (ca. 5.76 × 10⁻¹⁸ J) and methane as reactant gas.

Crystallography

Relevant crystallographic data and details of the refinement are presented in Table 1. A crystal of compound **1** was mounted on a Philips PW-1100, **4** on a Nonius CAD-4 and **6** and Hmtpo on a Stoe-Siemens AED-2 diffractometer. The intensity data were corrected for Lorentz-polarisation effects and empirically (ψ scans) for absorption (with the exception of Hmtpo). The structures were solved by direct methods in the case of Hmtpo, and by heavy-atom and Fourier methods in the other cases, applying the SHELXTL PLUS¹⁷ (compounds **1**, **6** and Hmtpo) and SDP¹⁸ programs (**4**). Full-matrix least-squares refinements were performed with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms of the organic ligands were idealised and those of water and hydrogensulfate groups refined with fixed O–H distances (0.85 Å). In the case of compounds **6** and Hmtpo, the last sets of refinements were made on F^2 applying the SHELXL 93 program package.¹⁹

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/507.

Results

Crystal and vapour-phase structures of Hmtpo

A view of the crystal structure of Hmtpo is presented in Fig. 1 and the most relevant interatomic parameters are summarised in Table 2. The structure is built of one-dimensional infinite polymers, supported by strong hydrogen bonds formed between N(4)–H and O(7) groups from adjacent Hmtpo moieties, such that the H(4)···O(7) separation is 1.80 Å [N(4)···O(7) is 2.630(2) Å and the N(4)–H···O(7) angle is 163°]. The geometry of the Hmtpo rings, which are planar to ±0.01 Å, does not differ significantly from that of the unco-ordinated Hmtpo in [Pd(tu)₄]Cl₂·2Hmtpo·2H₂O²¹ (tu = thiourea). An examination of the derived interatomic parameters reveals that each of the N(1)–C(2), N(3)–C(3A), C(5)–C(6) and C(7)–O(7) bonds has significant double-bond character, which is in accord with the presence of the N(4)–H tautomer in the solid state.

The chemical ionisation mass spectrum of free Hmtpo presents a high-intensity peak with m/z 301 corresponding to $2M + 1$. This result points to the existence of a dimeric structure in the vapour phase of Hmtpo. A feasible structure may be such that it contains H–N–C–N···H–N–C–N··· rings (see Fig. 2). Analogous structures are also found for similar compounds such as 8-azaxanthine²² in the solid state. The formation of dimeric structures in the vapour phase is reasonable, since the less-condensed matter may favour interactions of lower multiplicity²³ than those of the polymer found in the solid state (see Fig. 2). On the other hand, ¹⁵N NMR studies for Hmtpo, reported by Kleinpeter *et al.*,²⁴ show the N(3) and N(4) signals broadened by proton exchange. A dimeric structure in solution similar to that postulated in the vapour phase may facilitate such N(3), N(4) proton transfer.

Silver complexes

The reaction of AgX (X = NO₃ or ClO₄) with Hmtpo in 1:1 molar ratio in strongly acidic aqueous media yields polymeric

Table 1 Crystal data and details of refinement for compounds **1**, **4**, **6** and Hmpto studied by X-ray crystallography*

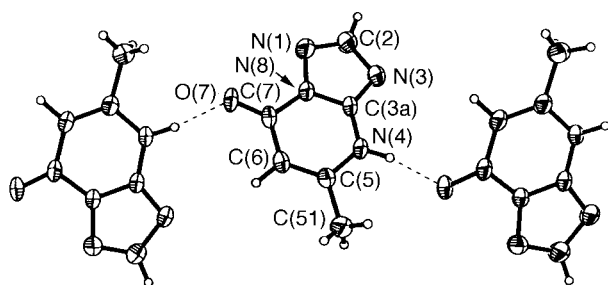
	1	4	6	Hmpto
Formula	C ₆ H ₆ AgN ₅ O ₄	C ₂₄ H ₂₁ AgClN ₄ O ₅ P	C ₁₂ H ₁₇ Ag ₃ N ₈ O ₉ S	C ₆ H ₆ N ₄ O
<i>M</i>	320.0	619.7	773.0	150.15
Space group	<i>P2</i> ₁ / <i>c</i>	<i>P2</i> ₁ / <i>c</i>	<i>P2</i> ₁ / <i>c</i>	<i>P2</i> ₁ / <i>n</i>
<i>a</i> /Å	12.205(3)	16.489(3)	11.972(2)	3.9119(8)
<i>b</i> /Å	8.269(3)	8.064(2)	13.455(3)	14.711(2)
<i>c</i> /Å	9.858(3)	25.462(8)	13.672(3)	11.711(3)
β/°	109.03(3)	132.92(2)	112.30(3)	85.670(8)
<i>U</i> /Å ³	940.5(9)	2479(2)	2037.6(7)	672.0(2)
Crystal dimensions	0.3 × 0.08 × 0.08	0.5 × 0.5 × 0.35	0.8 × 0.5 × 0.5	1 × 0.5 × 0.1
<i>D</i> _m /g cm ⁻³	2.33	—	2.52	—
<i>D</i> _x /g cm ⁻³	2.26	1.661	2.517	1.484
<i>F</i> (000)	624	1248	1496	312
μ(Mo-Kα)/mm ⁻¹	2.1	1.0	3.0	0.11
<i>h</i>	-15 to 15	-1 to 16	-8 to 8	-5 to 5
<i>k</i>	0-7	-1 to 18	-10 to 10	-17 to 17
<i>l</i>	0-13	-18 to 17	0-13	0-21
2θ _{max} /°	62	60	60	65
Maximum, minimum transmission	83, 62	100, 98	87, 52	—
Maximum feature in Δ <i>F</i> map/e Å ⁻³	0.4	0.69	1.56	0.246
No. parameters refined	175	389	322	101
No. reflections measured	3156 (0.05)	7377 (0.05)	6866 (0.07)	9525 (0.04)
No. reflections independent	3060	7222	6613	2890
No. reflections observed	965 [<i>I</i> > 2.5σ(<i>I</i>)]	5685 [<i>I</i> > 3σ(<i>I</i>)]	6613	2890
<i>R</i>	0.054	0.031	0.058	0.062
<i>R</i> '	0.054	0.031	—	—
<i>wR</i> ₂ (<i>F</i> ² , all)	—	—	0.193	0.178
Weighting scheme	1/[σ ² (<i>F</i> _o) + 0.005 <i>F</i> _o ²]	1/[σ ² (<i>F</i> _o)]	1/[σ ² (<i>F</i> _o) + (0.1 <i>P</i>) ²]	1/[σ ² (<i>F</i> _o) + (0.1 <i>P</i>) ²]
Goodness of fit	1.18	1.10	1.26	1.05

* Details in common: monoclinic; *Z* = 4, colourless, 293 K, λ(Mo-Kα) 0.710 73 Å, *R* = ||*F*_o| - |*F*_c||/Σ|*F*_o|; *R*' = (||*F*_o| - |*F*_c|| *w*)^{1/2}/Σ|*F*_o| *w*^{1/2}; *wR*₂ = [Σ *w*(*F*_o² - *F*_c²)²]/Σ(*wF*_o⁴)^{1/2}; *P* = (*F*_o² + 2*F*_c²)/3.

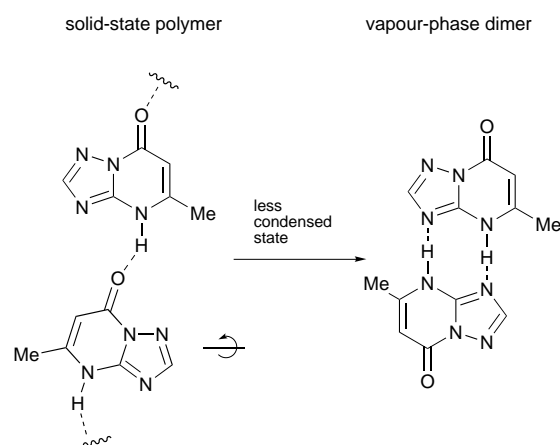
Table 2 Bond distances (Å) and angles (°) for Hmpto

N(1)-C(2)	1.243(3)	N(1)-N(8)	1.406(2)
C(2)-N(3)	1.382(3)	N(3)-C(3A)	1.283(2)
C(3A)-N(8)	1.320(2)	C(3A)-N(4)	1.381(3)
N(4)-C(5)	1.230(2)	C(5)-C(6)	1.323(3)
C(5)-C(5)	1.524(3)	C(6)-C(7)	1.456(3)
C(7)-O(7)	1.200(2)	C(7)-N(8)	1.349(2)
N(4)⋯O(7 ^b)	2.630(2)		
C(2)-N(1)-N(8)	100.2(2)	N(1)-C(2)-N(3)	115.6(2)
C(3A)-N(3)-C(2)	105.3(2)	N(3)-C(3A)-N(8)	107.0(2)
N(3)-C(3A)-N(4)	131.2(2)	N(8)-C(3A)-N(4)	121.8(2)
C(5)-N(4)-C(3A)	121.8(2)	N(4)-C(5)-C(6)	116.4(2)
N(4)-C(5)-C(51)	117.8(2)	C(6)-C(5)-C(51)	125.7(2)
C(5)-C(6)-C(7)	124.8(2)	O(7)-C(7)-N(8)	115.7(2)
O(7)-C(7)-C(6)	130.0(2)	N(8)-C(7)-C(6)	114.3(2)
C(3A)-N(8)-C(7)	120.9(2)	C(3A)-N(8)-N(1)	112.0(2)
C(7)-N(8)-N(1)	127.1(2)		

Symmetry relation: *I* *x* - 1, *y*, *z* + 1.

**Fig. 1** An ORTEP²⁰ view of the one-dimensional chain in the crystal structure of Hmpto

complexes of formula [$\{\text{AgX}(\mu\text{-Hmpto-}\kappa^2\text{N}^1, \text{N}^3)\}_n$] (*X* = NO₃ **1** or ClO₄ **2**) in which the Hmpto ligand shows a bidentate bridging mode *via* N(1), N(3). The additional presence of PPh₃ gives also rise to the formation of [$\{\text{AgX}(\mu\text{-Hmpto-}\kappa^2\text{N}^1, \text{N}^3)(\text{PPh}_3)\}_n$] with Hmpto coordinated in the same way but with weaker Ag-N(1) bonds.

**Fig. 2** Structure conversion from solid-state hydrogen-bonded polymers to vapour-phase dimers

Structure of [$\{\text{Ag}(\text{NO}_3)(\mu\text{-Hmpto-}\kappa^2\text{N}^1, \text{N}^3)\}_n$] **1.** A view of the polymeric structure of compound **1** is presented in Fig. 3 and the most relevant interatomic parameters are summarised in Table 3. The structure of the complex comprises infinite chains, as a result of the nearly linear co-ordination shown by the Ag atom and the Hmpto ligand in a N(1), N(3) bidentate bridging mode. The weaker interactions with the oxygen atoms O(1) [2.412(9) Å] and O(7) [2.691(9) Å] from the nitrate group and Hmpto, respectively, make the effective co-ordination number 2+2. The Ag-N and Ag-O bond distances are comparable to those found in other complexes with similar environments.^{3,25} The geometry of Hmpto appears almost unaltered after co-ordination, compared to that of free Hmpto (see above). With respect to the geometry of the nitrate group, O(1) co-ordination to Ag results in a lengthening of the N-O(1) bond by ≈0.04(1) Å.

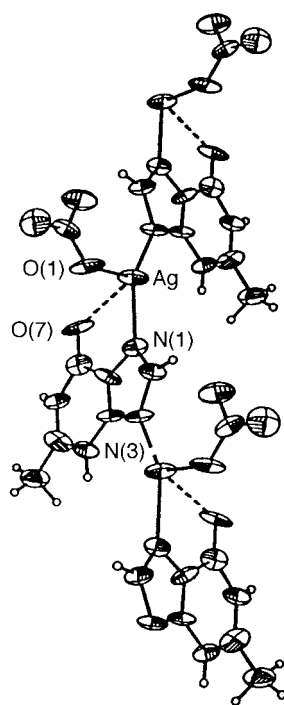
Structure of [$\{\text{Ag}(\text{ClO}_4)(\mu\text{-Hmpto-}\kappa^2\text{N}^1, \text{N}^3)(\text{PPh}_3)\}_n$] **4.** This compound is also built of infinite Hmpto N(1), N(3)-bridged

Table 3 Selected bond distances (Å) and angles (°) for compound **1**

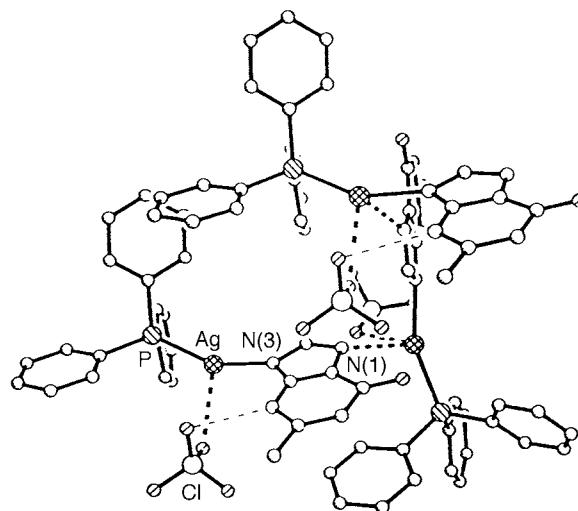
Ag–N(1)	2.253(8)	Ag–O(7)	2.691(9)
Ag–N(3 ^l)	2.154(8)	Ag–O(1)	2.412(9)
N–O(1)	1.28(1)	N–O(2)	1.23(1)
N–O(3)	1.25(1)		
N(4)⋯O(1 ^{ll})	2.760		
N(3 ^l)–Ag–N(1)	150.8(3)	O(1)–Ag–N(1)	82.3(3)
O(7)–Ag–N(1)	70.1(3)	O(1)–Ag–N(3 ^l)	126.6(3)
O(7)–Ag–N(3 ^l)	105.3(3)	O(1)–Ag–O(7)	98.9(3)

Symmetry relations: I $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; II $-x + 1, -y, -z + 1$.**Table 4** Selected bond distances (Å) and angles (°) for compound **4**

Ag–P	2.3603(7)	Ag–N(1 ^l)	2.597(2)
Ag–N(3)	2.217(2)	Ag–O(4)	2.728(3)
Cl–O(1)	1.451(3)	Cl–O(2)	1.419(3)
Cl–O(3)	1.395(3)	Cl–O(4)	1.380(2)
N(4)⋯O(1)	2.864		
P–Ag–N(3)	154.81(6)	N(3)–Ag–N(1 ^l)	82.7(1)
P–Ag–N(1 ^l)	108.22(6)	N(3)–Ag–O(4)	96.8(1)
P–Ag–O(4)	107.82(7)	O(4)–Ag–N(1 ^l)	75.9(1)

Symmetry relation: I $-x, y - \frac{1}{2}, -z + \frac{1}{2}$.**Fig. 3** View of the polymeric $[\{\text{Ag}(\text{NO}_3)(\mu\text{-Hmtpo-}N^1, N^3)\}_n]$ chains in compound **1**

chains (see Fig. 4) but the addition of the bulky and soft ligand PPh_3 nearly displaces N(1) from the co-ordination environment of Ag, lengthening the Ag–N(1) bond distance by 0.35 Å, compared to the previous structure (see Tables 3 and 4). This displacement is a consequence of the preference of the soft acid Ag^I for a ligand such as PPh_3 which is softer than Hmtpo. The silver atoms are placed in a distorted-tetrahedral N_2PO environment. Nitrogen N(3) from Hmtpo and P from PPh_3 appear strongly bonded to Ag, whereas N(1) and O(4) interact weakly. The Ag–P separation is normal.²⁶ Regarding the geometry of the perchlorate group, the lengthening of the Cl–O(1) bond, as a consequence of its involvement in a hydrogen bond $[\text{N}(4)\cdots\text{O}(1), 2.864 \text{ Å}]$, is noteworthy, whereas the weak $\text{O}(4)\cdots\text{Ag}$ interaction does not result in an appreciable modification of the Cl–O(4) distance.

**Fig. 4** Perspective of loosely polymeric $[\{\text{Ag}(\text{ClO}_4)(\mu\text{-Hmtpo-}N^1, N^3)(\text{PPh}_3)\}_n]$ chains in compound **4**

IR spectroscopy and thermal studies for compounds $[\{\text{AgX}(\mu\text{-Hmtpo-}\kappa^2 N^1, N^3)\}_n]$ and $[\{\text{AgX}(\mu\text{-Hmtpo-}\kappa^2 N^1, N^3)(\text{PPh}_3)\}_n]$ (X = $\text{NO}_3, \text{ClO}_4$)

Thermogravimetry has been shown to be of poor structural value. The compounds are thermally stable up to 150–300 °C, when pyrolysis commences. This process is very violent in the complexes containing the ClO_4^- anion.

The IR spectra of compounds **1–4** present only small changes when compared to free Hmtpo, the only appreciable change above 600 cm^{-1} being due to the concurrence of PPh_3 , NO_3^- and ClO_4^- characteristic bands. The absorption bands assigned to vibrations of the nitrate group, ν_3 ($1380, 1250$), ν_2 (820), ν_4 (650 cm^{-1}) for compound **1**, ν_3 ($1420, 1270$), ν_2 (830 cm^{-1}) for **3**, can be related to the presence of monoco-ordinated nitrate groups in both complexes. In **2** the original T_d symmetry of the perchlorate group is preserved with ν_3 , ν_1 and ν_4 appearing at $1120, 920$ and 625 cm^{-1} , respectively. In the case of compound **4** the clear splitting of the perchlorate vibration mode ν_3 ($1130, 1100, 1040 \text{ cm}^{-1}$) and ν_1 and ν_4 appearing at 925 and 620 cm^{-1} , respectively, are in accord with the loosening of the original T_d geometry (see Table 4).

Reactivity of Ag_2SO_4 towards Hmtpo

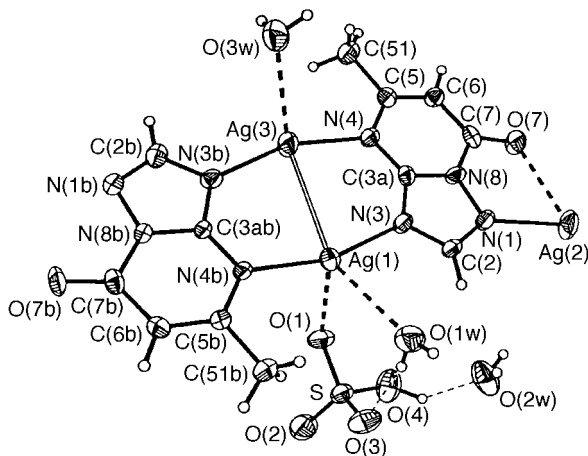
The Hmtpo compound behaves very variably towards Ag_2SO_4 . Thus, its reaction in neutral or basic media yields $[\{\text{Ag}(\mu_3\text{-mtpo-}\kappa^4 N^1, N^3, N^4, O^7)\}_2]^{2+}$ as reported by Smith and Luss.¹⁶ In strongly acidic aqueous media and depending on the silver to Hmtpo ratio, the reaction gives alternatively $[\{\text{H}_2\text{mtpo}\}[\text{Ag}(\text{SO}_4)(\mu\text{-Hmtpo-}\kappa^2 N^1, N^3)]\cdot\text{H}_2\text{O}]_n$ **5** and $[\{\text{Ag}_3(\mu_3\text{-mtpo-}\kappa^4 N^1, N^3, N^4, O^7)_2(\text{HSO}_4)(\text{H}_2\text{O})_2\}\cdot\text{H}_2\text{O}]_n$ **6**. The structure of **5** will be discussed on the basis of the IR data, whereas in the case of **6** it was possible to solve its structure by crystallography.

Structure of compound 6. A perspective view of the asymmetric unit of the complex is shown in Fig. 5 and the most relevant interatomic parameters are summarised in Table 5. The crystal structure comprises infinite cationic $[\{\text{Ag}_3(\mu_3\text{-mtpo-}\kappa^4 N^1, N^3, N^4, O^7)\}_2]^{2+}$ chains and hydrogensulfate anions and water molecules weakly interacting with the silver atoms. The cationic chains contain dimeric $[\text{Ag}(\text{mtpo})_2]$ units, displaying $\text{Ag}_2\text{N}_4\text{C}_2$ rings, which give rise to short $\text{Ag}\cdots\text{Ag}$ contacts of $3.078(1) \text{ Å}$. The polymeric structure is generated by a third silver nucleus linearly bridging the N(1) atoms of adjacent dimeric $[\text{Ag}(\text{mtpo})_2]$ units. The co-ordination geometry about the metal centres is nearly linear (N_2) with weak $\text{Ag}\cdots\text{O}$ interactions from mtpo, HSO_4^- and water molecules also being present.

Table 5 Selected bond distances (Å) and angles (°) for compound **6**

Ag(2)–Ag(1 ^I)	3.268(1)	Ag(2)–O(7b ^{II})	2.628(5)
Ag(1)–Ag(3)	3.078(1)	Ag(2)–N(1)	2.178(5)
Ag(1)–N(3)	2.176(5)	Ag(2)–N(1b ^{III})	2.202(5)
Ag(1)–N(4b)	2.159(5)	Ag(3)–N(4)	2.186(6)
Ag(1)–O(1)	2.689(5)	Ag(3)–N(3b)	2.154(5)
Ag(1)–O(1w)	2.718(6)	Ag(3)–O(3w)	2.882(6)
Ag(2)–O(7)	2.698(5)	Ag(3)–O(1 ^{III})	2.746(5)
S–O(1)	1.444(6)	S–O(3)	1.446(5)
S–O(2)	1.455(8)	S–O(4)	1.555(7)
O(1w)⋯O(3)	2.831	O(4)⋯O(2w)	2.528
O(1w)⋯O(4 ^{IV})	2.976	O(3w)⋯O(2 ^{III})	2.858
O(2w)⋯O(7 ^I)	2.755	O(3w)⋯O(7b ^V)	2.725
O(2w)⋯O(3w ^V)	2.837		
Ag(1)–Ag(3)–Ag(2 ^I)	76.8(1)	Ag(1)–N(4b)–C(3ab)	119.0(4)
N(3)–Ag(1)–N(4b)	162.8(2)	Ag(3)–N(4)–C(3a)	118.5(4)
N(1)–Ag(2)–N(1b ^{II})	175.7(2)	Ag(3)–N(3b)–C(3ab)	129.8(4)
N(4)–Ag(3)–N(3b)	161.6(2)	N(4)–C(3a)–N(3)	129.2(6)
Ag(1)–N(3)–C(3a)	129.3(4)	N(4b)–C(3ab)–N(3b)	128.3(5)

Symmetry relations: I $-x, 1-y, -z$; II $x, 1+y, z$; III $-x, -y, -z$; IV $x, \frac{1}{2}-y, \frac{1}{2}+z$; V $-x, \frac{1}{2}+y, \frac{1}{2}-z$.

**Fig. 5** An ORTEP view of the asymmetric unit of compound **6**. The thermal ellipsoids are drawn at the 25% probability level

In the crystal, the chains associate in pairs supported by π – π interactions between the planar mtpo rings (mean separation 3.22 Å). Also, an intercatena Ag⋯Ag contact of 3.268(1) Å is noted. Finally, the double chains are associated by means of weaker stacking interactions, with an interplanar separation of 3.20 Å but with lower overlap between the π rings than in the previous association.

The coexistence of two kinds of short Ag⋯Ag contacts in this structure is of note. The shorter one, with separation 3.078(1) Å, is supported by two bridging mtpo, acting in a N(3), N(4) bidentate mode. The unsupported one shows an intermetallic separation of 3.268(1) Å. The existence of direct Ag⋯Ag bonding interactions, in compounds displaying intermetallic distances in the range 2.655–3.377 Å, is a matter of current controversy.²⁷ However, our *ab initio* molecular orbital studies^{27a} on the dimer $[\{\text{Ag}(\text{NO}_3)_2\text{L}\}]_2$ (L = 5,7-dimethyl[1,2,4]triazolo [1,5a]pyrimidine), which displays an intermetallic separation of 3.058(1) Å, show the stabilising nature of these interactions. The fact that compound **6** displays also a short Ag⋯Ag contact without bridging ligands points to the existence of a direct intermetallic interaction. A similar conclusion has been made in the case of other unsupported silver polynuclear compounds.⁹ However, it should be noted that even if there is not a bridging ligand, other interactions contribute to the stabilisation of these associations such as hydrogen bonding in $[\{\text{Ag}(\text{NH}_3)_2(\text{SO}_4)\}]_n$,²⁸ stacking inter-

actions between aromatic rings in our case, *etc.* The final result may be the sum of the whole set of interactions.

Another interesting feature of compound **6** is that it represents one of the few examples of X-ray characterised hydrogensulfate groups.^{27b,29} The location of the acidic proton at oxygen O(4) is responsible for the lengthening of the S–O bond by 0.1 Å, which results in a C_{3v} geometry for the anion (see Table 5). Hydrogen bonding appears to be especially important in the stabilisation of the hydrogensulfate group. Thus, a very strong hydrogen-bond interaction between the hydrogensulfate group and solvation water O(2w) is noted, such that H⋯O(2w) is 1.71 Å [O(4)⋯O(2w) 2.528 Å and O(4)–H⋯O(2w) is 143°].

Thermal studies and IR spectroscopy. Thermogravimetric curves reveal that the dehydration processes take place in the temperature ranges 110–140 and 45–130 °C for compounds **5** and **6**, respectively. A thermal stability zone follows up to 200 and 300 °C, respectively, temperatures at which a pyrolytic process starts which is finished at 700 °C, leaving metallic silver as final residue.

In order to establish the nature of the Hmtpo ligands in compound **5** the chlorohydrate of Hmtpo was prepared, giving $[\text{H}_2\text{mtpo}]\text{Cl}\cdot\text{H}_2\text{O}$ **7**. The IR spectrum **5**, apart from the anions bands, can be considered the sum of those of **1** + **7**. From this result a similar polymeric structure to that found in **1** is proposed for **5** in which the ligand acts in bidentate N(1), N(3) bridging mode. The SO_4^{2-} bands (assigned T_d symmetry) are as follows: ν_3 at 1190, ν_1 900, ν_4 600 cm^{-1} and ν_2 450, 420 cm^{-1} . The splitting of the ν_2 band suggests a C_{2v} geometry for the sulfate group, consistent with a possible bidentate behaviour,³⁰ although such a geometry would require a splitting of ν_3 and ν_4 .

The IR spectrum of compound **6** shows a broad band in the 2900–2000 cm^{-1} range, corresponding to the presence of the acidic hydrogensulfate proton, this region being similar to that of KHSO_4 . With respect to the characteristic bands of the Hmtpo ligand, they differ considerably from those found for $[\{\text{Ag}(\mu_3\text{-mtpo-}\kappa^4\text{N}^1, \text{N}^3, \text{N}^4, \text{O}^7)\}]_{2n}]^{16}$ and other complexes containing Hmtpo in its monoanionic form,¹¹ these are very similar, however, to those containing the ligand in its neutral form.¹⁰ It appears that the higher strength of the silver–ligand interactions in **6**, compared to the similarly co-ordinated $[\{\text{Ag}(\mu_3\text{-mtpo-}\kappa^4\text{N}^1, \text{N}^3, \text{N}^4, \text{O}^7)\}]_{2n}]^{16}$ is responsible for a major charge localisation in the molecule, resulting in a shift of the bands to higher frequency, similar to the protonation effect. The sulfate bands are consistent with the C_{3v} symmetry found in the solid state. The activation of the ν_1 vibration mode centred at 960 cm^{-1} , together with the splitting of ν_4 into two bands at 620 and 595 cm^{-1} and ν_3 , ν_2 appearing, respectively, at 1110 and 435 cm^{-1} , is in accord with the X-ray results.

Discussion

The hydrogen-bonded structures, found in the solid and vapour phases of free Hmtpo are similar to those of the nearly linear co-ordinated silver(i) complexes. However, there are some significant differences: in the case of the silver polymeric systems, the involvement of the exocyclic O(7) donor atom in the co-ordination is minimal, in agreement with the soft nature of the Ag^{I} ion. On the other hand, the tendency of the ligand to display eight-membered A–N–C–N–A–N–C–N rings (A = H or Ag) is shown to occur both in the vapour phase of free Hmtpo and in the silver complexes containing Hmtpo in its monoanionic form, namely **6** and $[\{\text{Ag}(\mu_3\text{-mtpo-}\kappa^4\text{N}^1, \text{N}^3, \text{N}^4, \text{O}^7)\}]_{2n}]^{16}$. These kind of structures may be considered the result of a formal replacement of the hydrogen atom of a hydrogen bond by a metal atom with a linear co-ordination geometry. This replacement appears to have a marked effect on the strength of the association but not on the geometry of the

system.⁶ The formation of eight-membered Ag–N–C–N–Ag–N–C–N rings is also interesting from a theoretical point of view, since they give rise to short intermetallic contacts of 3.078(1) Å for **6** and 3.187 Å for $[\{Ag(\mu_3\text{-mtpo-}\kappa^4N^1, N^6, N^4, O^7)\}_2]^{16}$ which suggest the possibility of direct M–M bonding interactions.⁶ Similar eight-membered rings are also found in the binuclear compound $[Pt_2(\mu\text{-mtpo-}\kappa^2N^3, N^4)]^{11a}$ which displays a very short M–M separation of 2.744(2) Å, the M–M interaction being suggested, from *ab initio* molecular orbital calculations, to be of bonding nature.

Acknowledgements

The authors thank Dirección General de Investigación Científica y Técnica for financial support (Grant No. PB94-0807-CO2-01), also Dr. M. Quirós for his helpful discussions and suggestions.

References

- 1 D. S. Lawrence, T. Jiang and M. Levett, *Chem. Rev.*, 1995, **95**, 2229; D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1154.
- 2 W. Saenger, *Principles of Nucleic Acid Structure*, Springer, New York, 1984; D. Voet and J. G. Voet, *Biochemistry*, Wiley, New York, 1990.
- 3 S. Menzer, M. Sabat and B. Lippert, *J. Am. Chem. Soc.*, 1992, **114**, 4644.
- 4 O. Krizanovic, M. Sabat, R. Beyerle-Pfnür and B. Lippert, *J. Am. Chem. Soc.*, 1993, **115**, 5538.
- 5 I. Dieter-Wurm, M. Sabat and B. Lippert, *J. Am. Chem. Soc.*, 1992, **114**, 357.
- 6 A. Schreiber, M. S. Lüth, A. Erxleben, E. C. Fusch and B. Lippert, *J. Am. Chem. Soc.*, 1996, **118**, 4124.
- 7 J. Barberá, A. Elduque, R. Giménez, L. A. Oro and J. L. Serrano, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2832.
- 8 G. Smith, D. E. Lynch and C. H. L. Kennard, *Inorg. Chem.*, 1996, **35**, 2711; C. M. Hartshorn and P. J. Steel, *Inorg. Chem.*, 1996, **35**, 6902; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1994, 2755; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1895.
- 9 M. Quirós, *Acta Crystallogr., Sect. C*, 1994, **50**, 1236.
- 10 E. J. Dirks, J. G. Haasnoot, A. J. Kinneging and J. Reedijk, *Inorg. Chem.*, 1987, **26**, 1902; J. A. R. Navarro, M. A. Romero, J. M. Salas, J. Molina and E. R. T. Tiekink, *Inorg. Chim. Acta*, submitted for publication; J. Salas, J. A. R. Navarro, M. A. Romero, J. M. Salas and M. Quirós, *An. Quim. Int. Ed.*, 1997, **93**, 55.
- 11 (a) J. A. R. Navarro, M. A. Romero, J. M. Salas, M. Quirós, J. El Bahraoui and J. Molina, *Inorg. Chem.*, 1996, **35**, 7829; (b) J. A. R. Navarro, M. A. Romero and J. M. Salas, *J. Chem. Soc., Dalton Trans.*, 1997, 1001.
- 12 J. A. R. Navarro, M. A. Romero, J. M. Salas and M. Quirós, *Inorg. Chem.*, in the press.
- 13 G. Fischer, *J. Inf. Rec. Mater.*, 1992, **20**, 43.
- 14 G. Fischer, *Adv. Heterocycl. Chem.*, 1995, **57**, 81.
- 15 G. Fischer, *J. Inf. Rec. Mater.*, 1992, **16**, 91.
- 16 D. L. Smith and H. R. Luss, *Photogr. Sci. Eng.*, 1976, **20**, 184.
- 17 G. M. Sheldrick, SHELXTL PLUS, Program package for the solution of crystal structures. Release 34, Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1989.
- 18 SDP, Structure Determination Package; B. A. Frenz & Associates Inc., College Station, TX, 1982.
- 19 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.
- 20 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
- 21 J. M. Salas, M. A. Romero, J. A. Rodríguez and R. Faure, *J. Chem. Crystallogr.*, 1996, **26**, 847.
- 22 H. C. Mez and J. Donahue, *Z. Kristallogr.*, 1969, **130**, 376.
- 23 J. A. Dobado and J. Molina Molina, *J. Phys. Chem.*, 1993, **97**, 7499; 1994, **98**, 1819.
- 24 E. Kleinpeter, St. Thomas and G. Fischer, *J. Mol. Struct.*, 1995, **355**, 273.
- 25 J. M. Salas, M. P. Sánchez, E. Colacio and R. Faure, *J. Crystallogr. Spectrosc. Res.*, 1990, **20**, 133.
- 26 T. S. A. Hor, S. P. Neo, C. S. Tan, T. C. W. Mak, K. W. P. Lesung and R.-J. Wang, *Inorg. Chem.*, 1992, **31**, 4510; S. P. Neo, Z.-Y. Zhou, T. C. W. Mak and T. S. A. Hor, *Inorg. Chem.*, 1995, **34**, 520.
- 27 (a) M. A. Romero, J. M. Salas, M. Quirós, M. P. Sánchez, J. Molina, J. El Bahraoui and R. Faure, *J. Mol. Struct.*, 1995, **354**, 189; (b) J. M. Salas, M. A. Romero, A. Rahmani and M. Quirós, *An. Quim. Int. Ed.*, 1996, **92**, 249 and refs. therein.
- 28 U. Zachwieja and H. Jacobs, *Z. Kristallogr.*, 1992, **201**, 207.
- 29 M. Y. Antipin, G. G. Aleksandrov, Y. T. Struckov, Y. A. Belousov, V. N. Babin and N. S. Kochetkova, *Inorg. Chim. Acta*, 1983, **68**, 228; J. M. Malin, E. O. Schlemper and R. K. Murmann, *Inorg. Chem.*, 1977, **16**, 615; R. D. Rogers, A. H. Bond, W. G. Ipplé, A. N. Rollins and R. F. Henry, *Inorg. Chem.*, 1991, **30**, 2671.
- 30 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 1977.

Received 7th February 1997; Paper 7/00888K