New Confacial Bioctahedral Diplatinum(IV) Complexes with 3-Aminoalkanethiolate Bridges†

William Clegg,[*,a] **Núria Duran,**[b] **Kelly Anne Fraser,**[a] **Pilar González-Duarte,**[*,b] **Joan Sola**[b] **and Ian C. Taylor**[a]
[a] *Department of Chemistry, University of Newcastle, Newcastle upon Tyne NE1 7RU, UK*
[b] *Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain*

Reaction of $[(PtIMe_3)_4]$ with the cyclic 3-aminoalkanethiol $HSCH(CH_2CH_2)_2NMe$, with the acyclic 3-aminoalkanethiol $HS(CH_2)_3NMe_2$, or with the sodium salt of each of these thiols, under various stoichiometries in organic solvents gave the complexes $Na[(PtMe_3)_2\{\mu\text{-}SCH(CH_2CH_2)_2NMe\}_3]$, $[(PtMe_3)_2\{\mu\text{-}SCH(CH_2CH_2)_2NHMe\}_3]I_2$ and $[(PtMe_3)_2\{\mu\text{-}S(CH_2)_3NHMe_2\}_3]X_2$ (X = I or BPh_4). The complexes have been characterized by spectroscopic methods and the structures of two established by single-crystal X-ray diffraction. They consist of face-shared bioctahedral diplatinum(IV) complexes, in which the 3-aminothiolates function as bridging ligands through their sulfur atoms, to give a distorted-octahedral co-ordination of Pt with a *fac*-PtC_3S_3 configuration. In $Na[(PtMe_3)_2\{\mu\text{-}SCH(CH_2CH_2)_2NMe\}_3]\cdot MeCN$ the nitrogen atoms of the ligands co-ordinate to the sodium cations to give a highly flattened trigonal-pyramidal geometry. In $[(PtMe_3)_2\{\mu\text{-}S(CH_2)_3NHMe_2\}_3][BPh_4]_2\cdot MeCN$ the nitrogen atoms are protonated and take no part in co-ordination.

The substantial number of metal thiolate complexes which have been structurally characterized to date includes very few examples of platinum(IV) complexes. The cubane clusters $[(PtMe_3)_4(\mu_3\text{-}SR)_4]$, with R = Me[1] or Ph,[2] and the incomplete cubane cluster $[(PtMe_3)_3(\mu\text{-}I)_2(\mu\text{-}SR)(\mu_3\text{-}SR)]I\cdot MeCN$ with $R = CH_2CH_2NHEt_2$[3] are the only platinum(IV) thiolate complexes which have been crystallographically characterized, apart from the mixed platinum(II)–platinum(IV) species $[(dppe)Pt(\mu\text{-}SMe)_2PtClMe_3]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), which is representative of a family of complexes with general formula $[(dppe)M(\mu\text{-}SMe)_2PtXMe_3]$ (M = Pd or Pt; X = Cl, Br or I).[4]

As part of a continuing research programme involving metal complexes of aminoalkanethiolate ligands, which can behave as simple thiols with a solubilizing amine function or as chelating ligands, we are engaged in a study the first results of which have revealed some new types of structure for platinum(IV) thiolate complexes. We report here the synthesis, NMR (^1H, ^{13}C and ^{195}Pt) spectroscopic data and crystal structures of the complexes $Na[Me_3Pt\{\mu\text{-}SCH(CH_2CH_2)_2NMe\}_3PtMe_3]\cdot MeCN$ and $[Me_3Pt\{\mu\text{-}S(CH_2)_3NHMe_2\}_3PtMe_3][BPh_4]_2\cdot MeCN$, each of which contains two octahedrally co-ordinated platinum(IV) ions bridged by three thiolate ligands.

Experimental

3-Dimethylaminopropane-1-thiol[5] and 4-mercapto-1-methylpiperidine[6] were prepared according to known procedures. They were both purified by vacuum distillation until their purity, checked by iodometric determination of the SH group, was >99%. The compound $[(PtIMe_3)_4]$ was procured commercially (Johnson Matthey).

Preparation of Complexes.—$Na[Me_3Pt\{\mu\text{-}SCH(CH_2CH_2)_2NMe\}_3PtMe_3]\cdot MeCN$ **1**. A solution of the sodium salt of 4-mercapto-1-methylpiperidine (1.3 mmol) in dry methanol (10 cm^3) was added with stirring under nitrogen to a solution of $[(PtIMe_3)_4]$ (0.5 g, 0.34 mmol) in dried and degassed chloroform (15 cm^3). Stirring was continued for 5 d. The reaction mixture was evaporated to dryness and the solid residue dissolved in acetonitrile containing a few drops of water. Slow evaporation of the filtered yellowish solution afforded colourless crystals, which were filtered off, washed with heptane, and dried in the air. Yield 0.24 g, 40% (Found: C, 32.20; N, 6.00; S, 9.70. $C_{24}H_{54}N_3NaPt_2S_3\cdot CH_3CN$ requires C, 33.35; N, 6.00; S, 10.25%).

$[Me_3Pt\{\mu\text{-}S(CH_2)_3NHMe_2\}_3PtMe_3]X_2\cdot MeCN$, X = I **2** *or* BPh_4 **3**. To a solution of 3-dimethylaminopropane-1-thiol (0.3 cm^3, 2.01 mmol) in acetonitrile (15 cm^3) was added $[(PtIMe_3)_4]$ (0.5 g, 0.34 mmol) under nitrogen and the mixture was stirred until the solid was completely dissolved (2 d). Reduction of the volume of the filtered colourless solution afforded a white solid **2**, which was filtered off, washed with cold acetonitrile and dried in the air. Yield 0.32 g, 42.4% (Found: C, 57.05; N, 3.80; S, 6.70. $C_{21}H_{54}I_2N_3Pt_2S_3\cdot CH_3CN$ requires C, 56.20; N, 3.70; S, 6.30%). Complex **2** is soluble in acetonitrile and dimethyl sulfoxide (dmso), but insoluble in dichloromethane and chloroform. Slow evaporation from a solution of **2** in acetonitrile afforded colourless crystals which suffered degradation of quality as soon as they were removed from the mother-liquor. Single crystals of complex **3** were grown from a solution of **2** in acetonitrile, to which the stoichiometric amount of sodium tetraphenylborate in the same solvent had been added.

$[Me_3Pt\{\mu\text{-}SCH(CH_2CH_2)_2NHMe\}_3PtMe_3]I_2$ **4**. To a solution of 4-mercapto-1-methylpiperidine (0.27 cm^3, 1.75 mmol) in acetonitrile (15 cm^3) was added $[(PtMe_3I)_4]$ (0.3 g, 0.2 mmol) under nitrogen. Stirring was continued for 3 d until a white solid was formed. This was filtered off, washed with diethyl ether, and dried under nitrogen. Yield 0.39 g, 85.5% (Found: C, 25.05; N, 3.55; S, 8.35. $C_{24}H_{57}I_2N_3Pt_2S_3$ requires C, 25.55; N, 3.70; S, 8.50%).

Instrumentation.—Microanalyses were performed with a Carlo-Erba NA-1500 analyser. Infrared spectra in the range 4000–400 cm^{-1} were recorded from KBr discs on a Perkin Elmer 1710 spectrophotometer, proton, ^{13}C and ^{195}Pt NMR spectra on a Bruker AM-400 or AC-400 spectrometer from samples in $(CD_3)_2SO$ solution with $SiMe_4$ or H_2PtCl_6 as reference.

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

X-Ray Crystallography.—Colourless crystals of complexes **1** and **3** were examined on a Stoe-Siemens diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) and a Cryostream cooler.[7] Crystallographic data are given in Table 2. Cell parameters were refined from 2θ values (22–25°) of 36 (**1**) or 32 (**3**) reflections measured at $\pm\omega$. Intensities were measured from ω–θ scans with an on-line profile-fitting procedure.[8] Each data set comprised a unique set of reflections together with a partial set of equivalent reflections; for **1** a complete set of Friedel opposites was collected. Corrections were made for absorption (semiempirically[9]) and for a decay of *ca.* 8% in the intensities of five standard reflections in the case of **3**.

The structures were solved by heavy-atom methods[9] and refined[10] by full-matrix least-squares techniques on all measured F^2 values, with a weighting scheme $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (2F_c^2 + F_o^2)/3$. Large apparent thermal vibration of the atoms of one of the anions in complex **3** indicated probable disorder, which was not resolved. These atoms were refined isotropically, with geometrical constraints (ideal hexagons with C–C 1.395 Å for phenyl groups) and restraints (of similarity on B–C bonds and on C–B–C and B–C–C angles), but anisotropic displacement parameters were refined for all other non-hydrogen atoms. Constrained hydrogen atoms were included for all the thiolate ligands, for the anions of **3**, and for the acetonitrile solvent in **1** (most of these hydrogen atoms were revealed in difference syntheses) [C–H and N–H in the range 0.90–1.00 Å depending on the data-collection temperature and on the type of hydrogen atom, H–C–H 109.5°, aromatic H on ring-angle external bisectors, U(H) set at 1.2 or 1.5 times the U_{eq} value of the corresponding C or N atom]. Extinction effects were negligible. The absolute structure for **1** was confirmed by refinement of the enantiopole parameter x to a value of $-0.08(3)$.[11] Residuals are defined by $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ for all measured data, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for 'observed' data having $F_o^2 > 2\sigma(F_o^2)$ (for comparison with conventional refinements on F); the goodness of fit is based on all F^2 values. Final difference syntheses showed no features of chemical significance for **1** and indications of possible disordered acetonitrile for **3**, but no sensible assignment and refinement of atoms to these peaks could be made: refinement of two anisotropic carbon atoms accounted for the residual electron density, after which no other significant features were found.

Refined atomic coordinates are given in Tables 3 and 4, and selected bond lengths and angles are in Table 5 and 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Synthesis.—The reaction of [(PtIMe$_3$)$_4$] with 4-mercapto-1-methylpiperidine at several metal to ligand mole ratios (1:2, 2:3 and 4:3) has always led to complex **4** as the only identified product. The same complex has been obtained from the reaction of [(PtIMe$_3$)$_4$] with the sodium salt of the thiol in 1:2 mole ratio in the presence of tetrafluoroboric acid. Complex **1** was the only species obtained from the reaction of the platinum starting material with the sodium salt of the thiol at either 1:1 or 2:3 mole ratio. By following analogous synthetic procedures with 3-dimethylaminopropane-1-thiol as ligand, the complexes **2** and **3** have been obtained from either a 1:1 or a 2:3 mole ratio, but no complex analogous to **1** (without protonation of the ligand nitrogen atom) has been obtained. The fact that different metal:thiol ratios and different reaction conditions have always led to complexes of general formula [Me$_3$Pt(μ-SR)$_3$-PtMe$_3$]^z indicates that under these experimental conditions such dinuclear species are preferred to the cubane structures already known for simple thiolate ligands.[1,2] This preference does not depend on whether the ligand is anionic (as in complex **1**) or zwitterionic (as in complexes **2**–**4**). Accordingly, complete substitution of iodide by 3-aminothiolate ligands leads to fragmentation of the cubane structure of the starting material. We have already found that partial substitution of iodide by a 2-aminothiolate ligand causes loss of the cubane core, leading to an incomplete cubane structure with only three trimethylplatinum vertices and a mixture of bridging iodide and aminothiolate ligands.[3]

Infrared Spectra.—The IR spectra of complexes **1**, **2** and **4** compare very well. A common feature is the appearance of the same bands as those present for [(PtIMe$_3$)$_4$] in the regions 3000–2800 and 1300–1200 cm^{-1}. The most significant features of the region 3000–2500 cm^{-1} which indicate how aminoalkanethiols co-ordinate metal atoms have already been reported.[12] In the case of **2** and **4** an intense band at *ca.* 2700 cm^{-1} indicates that the amine group of the ligand is protonated, so that the ligand is in zwitterionic form. For **1** the absence of this band shows that the ligand here is in anionic form and behaves as a simple thiolate without protonation of the amine group. Bands in the region 1500–400 cm^{-1} are also characteristic of the ligands in these complexes. The spectrum of **3** shows the bands appearing for **2**, together with those due to the aromatic rings of the BPh$_4$ anion.

NMR Spectra.—Peaks observed in ^{1}H, ^{13}C-{^{1}H}, ^{195}Pt-{^{1}H} and non-decoupled ^{195}Pt NMR spectra of (CD$_3$)$_2$SO solutions of complexes **1**, **2** and **4** are given in Table 1, together with the corresponding assignments. Complex **3**, which differs from **2** only in the anion, has not been studied because of its lower solubility in most usual solvents. Comparison of the proton spectra of **2** and **4** with that of **1** shows that the singlet corresponding to the NMe groups is shifted 0.66 ppm to lower field, consistent with protonation of the nitrogen atom in **2** and **4** and the lone pair of electrons on nitrogen in **1**.[12] The methyl groups bonded to platinum give rise to a 1:4:1 triplet centred at *ca.* δ 0.72 with very similar ^2J(Pt–H) coupling constants for all three complexes; this triplet occurs at δ1.84 for [(PtIMe$_3$)$_4$] in C$_6$D$_6$ solution. Presumably this shift is due to the replacement of iodide by thiolate bridging ligands. Proton-homodecoupling techniques have been used to make the assignments given in Table 1. For complex **2** the fortuitous fact that ^3J(Pt–H) is twice the value of ^3J(H–H) for the Pt$_2$SCH_2CH$_2$ methylene protons causes the expected quintet of triplets to appear as five lines, which are the observed inner components of a 1:10:35:52:35:10:1 septet pattern.

As expected for the platinum-bonded methyl groups, the proton-decoupled ^{13}C NMR spectra show a 1:4:1 triplet. Both the chemical shifts and the ^1J(Pt–C) coupling constants compare well with reported values for the cubane structures of [{PtMe$_3$(μ_3-SR)}$_4$] [R = Me, δ = 2.5, ^1J(Pt–C) = 628.2; R = Ph, δ = 5.9, ^1J(Pt–C) = 639.5 Hz], considering that these have a different core structure and the spectra were recorded from a different solvent.[13] The other ^{13}C peaks corresponding to carbon atoms of the aminoalkanethiolate ligands have been assigned according to literature data.[14]

The ^{195}Pt NMR spectra have only one signal each, showing the chemical equivalence of the two platinum atoms in the dinuclear complexes. The chemical shifts are very different from those of the thiolate-bridged cubane complexes in CDCl$_3$ solution (R = Me, δ -2015; R = Ph, δ -1976).[13,*] In the case of the dinuclear complexes reported here the nature of the thiolate substituent does not greatly affect the ^{195}Pt chemical shift. The proton-coupled spectra would be expected to show a ten-line multiplet due to coupling of the nine methyl protons to the platinum nucleus, and each line should be further split by additional coupling with protons of the thiolate ligands. However, only the more intense six inner lines have been

---

[*] Literature values have been referenced to H$_2$PtCl$_6$.[15]

Table 1 Proton, ^{13}C and ^{195}Pt NMR data[a] for complexes $\mathrm{Na[(PtMe_3)_2(\mu\text{-}SC_5H_9NMe)_3]}$ **1**, $\mathrm{[(PtMe_3)_2(\mu\text{-}SC_3H_6NHMe_2)_3]I_2}$ **2** and $\mathrm{[(PtMe_3)_2(\mu\text{-}SC_5H_9NHMe)_3]I_2}$ **4** in dmso

	^{1}H NMR			^{13}C-{^{1}H} NMR			^{195}Pt-{^{1}H} NMR
Complex	δ(SiMe$_4$)[b]	Assignment[c]	J/Hz	δ(SiMe$_4$)	Assignment	J/Hz	δ(H$_2$PtCl$_6$)
1	2.62 (d)	$-\mathrm{CH_a}\mathit{H}_\mathrm{e})_2\mathrm{NMe}$	^gJ(H–H) 11	55.47	$\mathit{C}\mathrm{H_2)_2NMe}$		−2740 (s)
	2.41 (vbr)	$\mathrm{SC}\mathit{H}\mathrm{(CH_2}-$		35.88	$\mathrm{S}\mathit{C}\mathrm{H(CH_2}-$		
	2.06 (s)	NMe		46.17	NMe		
	1.79 (m)	$-\mathrm{C}\mathit{H}_\mathrm{a}\mathrm{H_e)_2NMe}$[d] $\mathrm{SCH(CH_a}\mathit{H}_\mathrm{e}-$[d]		34.55	$\mathrm{SCH(}\mathit{C}\mathrm{H_2}-$		
	1.33 (q)	$\mathrm{SCH(C}\mathit{H}_\mathrm{a}\mathrm{H_e}-$	^gJ(H–H) 11				
	0.73 (t)[e]	PtMe$_3$	^2J(Pt–H) 70	−1.34 (t)[e]	PtMe$_3$	^1J(Pt–C) 645	
2	3.03 (t)	$\mathrm{C}\mathit{CH}_2\mathrm{NHMe_2}$	^3J(H–H) 7	54.95	$\mathit{C}\mathrm{H_2NHMe_2}$		−2827 (s)
	2.72 (s)	$\mathrm{CNH}\mathit{Me}_2$		42.34	NHMe$_2$		
	2.32 (hpt)[f]	PtSCH$_2$	^3J(Pt–H) 14 ^3J(H–H) ≈7	27.96	PtSCH$_2$		
	1.72 (qnt)[g]	CCH$_2$C	^3J(H–H) 7	19.61	$\mathrm{C}\mathit{C}\mathrm{H_2C}$		
	0.66 (t)[e]	PtMe$_3$	^2J(Pt–H) 70	−0.52 (t)[e]	PtMe$_3$	^1J(Pt–C) 650	
4	3.31 (d)	$-\mathrm{CH_a}\mathit{H}_\mathrm{e})_2\mathrm{NHMe}$	^gJ(H–H) 11.5	53.15	$-\mathit{C}\mathrm{H_2)_2NHMe}$		−2749 (s)
	3.02 (vbr)	$-\mathrm{C}\mathit{H}_\mathrm{a}\mathrm{H}_e)_2\mathrm{NHMe}$					
	2.70 (s)	$\mathrm{SC}\mathit{H}\mathrm{(CH_2}-$[d] $\mathrm{NH}\mathit{Me}$[d]		33.00 42.42	$\mathrm{S}\mathit{C}\mathrm{H(CH_2}-$ NHMe		
	1.93 (d)	$\mathrm{SCH(CH_a}\mathit{H}_\mathrm{e}-$	^gJ(H–H) 12.5	31.43	$\mathrm{SCH(}\mathit{C}\mathrm{H_2}-$		
	1.56 (q)	$\mathrm{SCH(C}\mathit{H}_\mathrm{a}\mathrm{H_e}-$	^gJ(H–H) 11				
	0.76 (t)[e]	PtMe$_3$	^2J(Pt–H) 72	0.32 (t)[e]	PtMe$_3$	^1J(Pt–C) 643	

[a] s = Singlet, d = doublet, t = triplet, q = quartet, qnt = quintet and hpt = heptet; m and vbr stand for partially resolved and very broad unresolved signals, respectively. [b] In dimethylformamide: δ 3 (d) $\mathrm{CH_a}\mathit{H}_\mathrm{e})_2\mathrm{NMe}$; 2.67 (vbr) $\mathrm{SC}\mathit{H}\mathrm{(CH_2}$; 2.4 (s) NMe; 2.31 (t) $\mathrm{C}\mathit{H}_\mathrm{a}\mathrm{H_e)_2NMe}$; 2 (d) $\mathrm{SCH(CH_a}\mathit{H}_\mathrm{e}$; 1.61 (q) $\mathrm{SCH(C}\mathit{H}_\mathrm{a}\mathrm{H_e}$; 0.85 (t) PtMe$_3$. [c] a = Axial, e = equatorial and g = geminal. [d] Overlapping signals. [e] 1:4:1 Triplet due to the 33.3% natural abundance of ^{195}Pt. [f] See text. [g] Owing to the similarity between the coupling constants with the protons of the two neighbouring methylene groups, the 3 × 3 multiplet becomes a quintet.

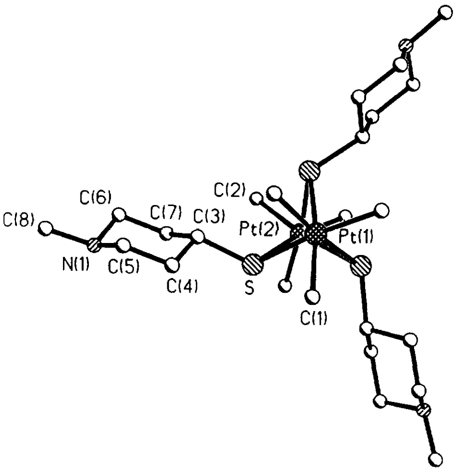

Fig. 1 Structure of the complex anion of **1**. Crystallographically unique atoms are labelled and H atoms are omitted

Table 2 Crystallographic data

Compound	1	3
Formula	$\mathrm{C_{24}H_{54}N_3NaPt_2S_3\cdot C_2H_3N}$	$\mathrm{C_{69}H_{97}B_2N_3Pt_2S_3\cdot C_2H_3N}$
M	935.11	1517.53
Crystal system	Cubic	Triclinic
Space group	$P2_13$	$P\bar{1}$
a/Å	15.254(2)	9.701(4)
b/Å		14.872(5)
c/Å		25.050(8)
α/°		75.57(2)
β/°		83.45(2)
γ/°		83.81(2)
U/Å^3	3549.4(8)	3465(2)
Z	4	2
D_c/g cm^{-3}	1.750	1.454
μ/mm^{-1}	8.08	4.17
F(000)	1824	1536
T/K	240	160
Crystal size/mm	0.18 × 0.18 × 0.18	0.36 × 0.32 × 0.28
Maximum 2θ/°	45	45
Maximum indices hkl	16, 16, 16	10, 16, 26
Transmission	0.122–0.193	0.216–0.248
Reflections measured	2100	10 962
Unique reflections	1563	9035
R_int	0.043	0.041
Weighting parameters a, b	0.0330, 20.2353	0.0657, 48.1209
No. of refined parameters	111	557
R'(all data)	0.101	0.152
R (observed data)	0.039 (1304)	0.052 (7352)
Goodness of fit	1.135	1.053
Maximum shift/e.s.d.	< 0.0005	0.027
Maximum, minimum electron density/e Å^{-3}	0.52, −0.52	1.80, −1.42

observed for **2**, showing a ^2J(Pt–H) coupling of 70 Hz, which agrees with the coupling constants measured in the proton spectrum. The width of the signals in the proton-coupled platinum spectrum precludes the resolution of the fine structure due to ^3J(Pt–H) coupling.

Structures.—The complex anion of **1** is shown in Fig. 1, and the complex cation of **3** in Fig. 2. The difference in overall charge is entirely a consequence of the protonation of the nitrogen atoms of the ligands in **3** and has no significant effect on the essential geometry of the diplatinum complex. Both complex ions consist of confacial bioctahedral units in which two trimethylplatinum(IV) fragments are linked together by three 3-aminothiolate ligands bridging through their sulfur atoms. The nitrogen atoms of the ligands play no part in the co-ordination to platinum, so the ligands act as simple thiolate bridges in this respect. Although these complexes contrast strongly with the cubane structures adopted with methane- and benzene-thiolate ligands,[1,2] both types of structure have the same primary co-ordination of platinum, a *fac*-$\mathrm{Me_3Pt(SR)_3}$ distorted-octahedral geometry. Undistorted octahedral angles at platinum would give a Pt–S–Pt bridging angle of only 70.5°;

the larger angles found in the present complexes (85.7 in **1**, mean of 82.8° in **3**) enable a larger Pt • • • Pt non-bonded separation (3.368 in **1**, 3.275 Å in **3**). These geometrical parameters of the central core of the structures, together with the Pt–S and Pt–C bond lengths, are comparable with the values found in the complete cubane structures of $[\{PtMe_3SR\}_4]$ and the incomplete cubane structure of $[(Me_3Pt)_3I_2(SCH_2CH_2NHEt_2)_2]^+$, which are the most closely related platinum(IV) complexes for which structural information is available. The only reported structures of simple species consisting of two face-shared octahedra with bridging sulfur atoms and little or no direct metal–metal bonding are for the isoelectronic series of complexes $[Fe_2(CO)_6(\mu\text{-SMe})_3]^+$,[16] $[FeMn(CO)_6(\mu\text{-SPh})_3]$[17] and $[Mn_2(CO)_6(\mu\text{-SPh})_3]^-$,[18] together with the closely related phosphine derivative $[Fe_2(CO)_4(PMe_2Ph)_2(\mu\text{-SMe})_3]^+$.[19] A

Table 3 Atomic coordinates * (× 10⁴) for complex **1**

Atom	*x*	*y*	*z*
Pt(1)	4224.6(4)		
Pt(2)	2950.0(4)		
C(1)	5605(10)	4139(11)	4371(13)
C(2)	1901(11)	2177(12)	3333(11)
S	4069(3)	2615(2)	4078(3)
C(3)	3741(10)	2164(11)	5138(10)
C(4)	4581(10)	2025(11)	5687(10)
C(5)	4393(11)	1633(11)	6551(10)
C(6)	3079(11)	939(11)	6007(10)
C(7)	3237(10)	1329(10)	5092(10)
C(8)	3799(13)	393(14)	7332(11)
N(1)	3934(8)	792(9)	6466(8)
Na	380(8)		
N(2)	7765(13)		
C(9)	8196(12)		
C(10)	8734(13)		

* Atoms for which only *x* is given lie on a three-fold rotation axis, with *x* = *y* = *z* by symmetry.

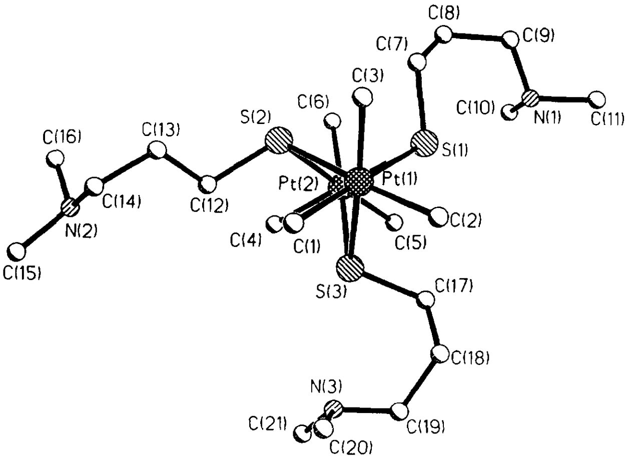

Fig. 2 Structure of the complex cation of **3** with atom labelling and without H atoms

Table 4 Atomic coordinates (× 10⁴) for complex **3**

Atom	*x*	*y*	*z*
Pt(1)	4 014.5(4)	4 593.3(3)	1 791.4(2)
Pt(2)	733.2(4)	4 280.1(3)	1 769.5(2)
C(1)	4 783(12)	5 215(9)	2 333(6)
C(2)	5 694(13)	3 584(10)	1 916(6)
C(3)	5 280(12)	5 381(10)	1 152(6)
C(4)	−906(12)	4 692(9)	2 288(6)
C(5)	−167(13)	3 022(8)	1 897(5)
C(6)	−496(12)	4 833(8)	1 125(6)
S(1)	2 865(3)	3 821(2)	1 204.6(11)
N(1)	2 369(9)	2 563(6)	386(4)
C(7)	2 946(13)	4 602(8)	515(5)
C(8)	2 154(13)	4 342(8)	106(5)
C(9)	2 711(13)	3 431(8)	−44(5)
C(10)	842(13)	2 447(9)	479(5)
C(11)	3 146(13)	1 730(9)	228(5)
S(2)	1 952(3)	5 705(2)	1 599.0(14)
N(2)	236(11)	7 738(7)	2 764(5)
C(12)	1 462(13)	6 240(8)	2 185(6)
C(13)	1 965(14)	7 212(9)	2 053(7)
C(14)	1 714(15)	7 676(10)	2 534(8)
C(15)	40(21)	8 054(12)	3 288(7)
C(16)	−676(15)	8 321(10)	2 367(6)
S(3)	2 327(3)	3 736(2)	2 504.3(12)
N(3)	2 669(21)	2 874(16)	3 771(9)
C(17)	2 761(15)	2 488(8)	2 575(5)
C(18)	3 765(20)	2 075(11)	3 006(7)
C(19)	3 048(21)	2 018(13)	3 614(8)
C(20)	4 178(32)	3 178(23)	3 914(13)
C(21)	1 071(53)	2 793(28)	4 124(20)
B(1)	−3 834(13)	10 088(8)	1 376(5)
C(22)	−3 356(11)	10 166(7)	1 979(4)
C(23)	−2 257(11)	10 695(7)	2 015(5)
C(24)	−1 816(13)	10 696(8)	2 523(5)
C(25)	−2 461(13)	10 173(9)	3 003(5)
C(26)	−3 527(13)	9 646(9)	2 982(5)
C(27)	−3 951(12)	9 654(8)	2 477(5)
C(28)	−3 532(10)	11 032(7)	874(4)
C(29)	−3 698(13)	11 924(8)	973(5)
C(30)	−3 527(14)	12 715(8)	566(5)
C(31)	−3 199(13)	12 672(8)	20(5)
C(32)	−3 071(12)	11 823(8)	−103(5)
C(33)	−3 226(11)	11 016(8)	316(5)
C(34)	−5 530(11)	10 032(7)	1 428(4)
C(35)	−6 197(11)	9 534(8)	1 150(5)
C(36)	−7 636(12)	9 555(8)	1 170(6)
C(37)	−8 482(12)	10 096(8)	1 478(5)
C(38)	−7 852(12)	10 606(8)	1 751(5)
C(39)	−6 407(12)	10 579(8)	1 731(5)
C(40)	−2 928(11)	9 141(7)	1 256(5)
C(41)	−1 601(11)	9 155(8)	957(5)
C(42)	−785(13)	8 357(9)	907(6)
C(43)	−1 266(14)	7 495(8)	1 146(6)
C(44)	−2 578(13)	7 438(8)	1 448(6)
C(45)	−3 373(13)	8 257(7)	1 486(5)
B(2)	−3 020(15)	2 374(9)	5 347(5)
C(46)	−2 602(15)	3 212(10)	5 603(6)
C(47)	−3 405(17)	3 460(14)	6 048(8)
C(48)	−2 928(25)	4 070(16)	6 312(8)
C(49)	−1 649(26)	4 433(13)	6 130(9)
C(50)	−846(19)	4 185(14)	5 685(10)
C(51)	−1 323(15)	3 575(12)	5 421(7)
C(52)	−2 508(17)	2 541(11)	4 689(6)
C(53)	−2 267(25)	3 435(11)	4 381(8)
C(54)	−1 986(29)	3 606(15)	3 809(8)
C(55)	−1 948(25)	2 883(20)	3 546(6)
C(56)	−2 189(23)	1 989(17)	3 854(8)
C(57)	−2 470(20)	1 818(11)	4 425(8)
C(58)	−2 328(10)	1 400(6)	5 721(4)
C(59)	−2 967(9)	1 112(7)	6 253(4)
C(60)	−2 382(10)	348(7)	6 624(3)
C(61)	−1 157(10)	−129(6)	6 461(4)
C(62)	−518(9)	158(6)	5 928(4)
C(63)	−1 104(10)	923(7)	5 558(3)
C(64)	−4 723(17)	2 428(13)	5 393(8)
C(65)	−5 430(25)	3 306(13)	5 340(12)
C(66)	−6 877(25)	3 399(22)	5 383(14)
C(67)	−7 617(17)	2 616(29)	5 479(13)
C(68)	−6 910(24)	1 738(24)	5 532(12)
C(69)	−5 463(24)	1 645(14)	5 489(10)
X(1)	−1 629(29)	6 277(14)	3 182(10)
X(2)	−2 973(79)	6 218(50)	3 303(20)

Table 5 Selected bond lengths (Å) and angles (°) for complex **1**

Pt(1)–C(1)	2.12(2)	Pt(1)–S	2.477(4)
Pt(2)–C(2)	2.07(2)	Pt(2)–S	2.476(4)
S–C(3)	1.83(2)	Na–N(1a)	2.653(14)
C(1b)–Pt(1)–C(1)	87.9(7)	C(1c)–Pt(1)–S	100.8(5)
C(1b)–Pt(1)–S	171.3(5)	C(1)–Pt(1)–S	92.5(5)
S–Pt(1)–S(b)	78.84(14)	C(2b)–Pt(2)–C(2)	86.5(7)
C(2)–Pt(2)–S(b)	170.7(6)	C(2b)–Pt(2)–S	92.4(6)
C(2)–Pt(2)–S	102.6(5)	S(b)–Pt(2)–S	78.85(14)
C(3)–S–Pt(2)	120.3(5)	C(3)–S–Pt(1)	108.7(6)
Pt(2)–S–Pt(1)	85.67(12)	N(1a)–Na–N(1d)	116.1(4)

Symmetry transformations used to generate equivalent atoms: a $-x + \frac{1}{2}, -y, z - \frac{1}{2}$; b z, x, y; c y, z, x; d $z - \frac{1}{2}, -x + \frac{1}{2}, -y$.

Table 6 Selected bond lengths (Å) and angles (°) for complex **3**

Pt(1)–C(1)	2.063(12)	Pt(1)–C(2)	2.088(12)
Pt(1)–C(3)	2.091(12)	Pt(1)–S(2)	2.466(3)
Pt(1)–S(3)	2.478(3)	Pt(1)–S(1)	2.493(3)
Pt(2)–C(6)	2.067(13)	Pt(2)–C(4)	2.074(11)
Pt(2)–C(5)	2.087(11)	Pt(2)–S(2)	2.459(3)
Pt(2)–S(3)	2.464(3)	Pt(2)–S(1)	2.501(3)
S(1)–C(7)	1.824(12)	S(2)–C(12)	1.832(13)
S(3)–C(17)	1.828(12)		
C(1)–Pt(1)–C(2)	88.2(5)	C(1)–Pt(1)–C(3)	88.4(5)
C(2)–Pt(1)–C(3)	87.6(6)	C(1)–Pt(1)–S(2)	96.6(4)
C(2)–Pt(1)–S(2)	175.2(3)	C(3)–Pt(1)–S(2)	93.1(4)
C(1)–Pt(1)–S(3)	94.1(4)	C(2)–Pt(1)–S(3)	97.2(4)
C(3)–Pt(1)–S(3)	174.7(4)	S(2)–Pt(1)–S(3)	81.89(10)
C(1)–Pt(1)–S(1)	174.1(4)	C(2)–Pt(1)–S(1)	94.7(4)
C(3)–Pt(1)–S(1)	96.9(4)	S(2)–Pt(1)–S(1)	80.46(10)
S(3)–Pt(1)–S(1)	80.47(9)	C(6)–Pt(2)–C(4)	87.1(6)
C(6)–Pt(2)–C(5)	88.8(5)	C(4)–Pt(2)–C(5)	87.7(5)
C(6)–Pt(2)–S(2)	92.8(3)	C(4)–Pt(2)–S(2)	96.2(3)
C(5)–Pt(2)–S(2)	175.9(3)	C(6)–Pt(2)–S(3)	175.0(3)
C(4)–Pt(2)–S(3)	94.6(5)	C(5)–Pt(2)–S(3)	96.0(4)
S(2)–Pt(2)–S(3)	82.33(10)	C(6)–Pt(2)–S(1)	97.5(4)
C(4)–Pt(2)–S(1)	174.4(4)	C(5)–Pt(2)–S(1)	95.6(3)
S(2)–Pt(2)–S(1)	80.43(9)	S(3)–Pt(2)–S(1)	80.59(10)
C(7)–S(1)–Pt(1)	105.8(4)	C(7)–S(1)–Pt(2)	109.6(4)
Pt(1)–S(1)–Pt(2)	81.96(9)	C(12)–S(2)–Pt(2)	108.1(4)
C(12)–S(2)–Pt(1)	109.4(4)	Pt(2)–S(2)–Pt(1)	83.37(9)
C(17)–S(3)–Pt(2)	107.7(4)	C(17)–S(3)–Pt(1)	108.5(5)
Pt(2)–S(3)–Pt(1)	83.00(10)		

similar arrangement is found in the $S_3M(SR)_3MS_3$ core units present in the double-cubane species of type $[M_2Fe_6S_8(SR)_9]^{3-}$, with M = Mo or W.[20] In fact, confacial bioctahedral dimers containing triple thiolate or thioether bridges are confined largely to those of niobium, tantalum,[21] molybdenum, tungsten[22] and rhenium,[23] where the triple bridge is usually supported by a direct metal–metal bond. In the context of complexes of aminothiolates, we note also dicobalt and tricobalt complexes with amino- and diamino-thiolate ligands which function simultaneously as chelating (N,S co-ordination) and bridging (μ-S) ligands to give related bi- and tri-octahedral structures.[24]

The central $Pt_2C_6S_3$ core of complex **1** has exact crystallographic C_3 symmetry; the essential symmetry is D_{3h} for both complexes. Inclusion of the aminoalkanethiolate substituent groups reduces the essential symmetry to C_{3h} for **1** and to only C_s for **3**, because of the different orientations of the terminal groups. In both cases, however, the configuration at each sulfur atom is such as to produce a C_{3h} paddle-wheel arrangement for the central core together with the α-carbon atoms; the deviations of this unit from ideal C_{3h} symmetry are insignificant.

The aliphatic chains of the thiolate bridging ligands are of unremarkable geometry. The piperidine ring in complex **1** has a chair conformation with both the thiolate S atom and the methyl substituent on nitrogen placed equatorially. All three crystallographically independent carbon–nitrogen chains in **3** have a mixture of *trans* and *gauche* conformations. Protonation of the nitrogen atoms in **3** renders them effectively tetrahedral. The unprotonated nitrogen atoms in **1** co-ordinate to the sodium cations to give, once again, tetrahedral nitrogen and a highly flattened trigonal-pyramidal sodium co-ordination.

The acetonitrile solvent molecules (fully characterized crystallographically for complex **1**, but incompletely located for **3** and confirmed by elemental analysis) are not involved in any co-ordination of metal atoms, but merely occupy interstices in the crystal structures.

Acknowledgements

We thank the SERC and the Royal Society (UK) and the Ministerio de Educación y Ciencia (Spain, Grant PB90-0691) for financial support.

References

1 G. Smith, C. H. L. Kennard and T. C. W. Mak, *J. Organomet. Chem.*, 1985, **290**, C7.

2 D. C. Craig and I. G. Dance, *Polyhedron*, 1987, **5**, 1157.

3 W. Clegg, K. A. Fraser, N. Duran and P. González-Duarte, *Polyhedron*, in the press.

4 E. W. Abel, N. A. Cooley, K. Kite, K. G. Orrell, V. Sik, M. B. Hursthouse and H. M. Dawes, *Polyhedron*, 1987, **6**, 1261.

5 B. C. Cossar, J. O. Fournier, D. L. Fields and D. D. Reynolds, *J. Org. Chem.*, 1962, **27**, 93.

6 H. Barrera and R. R. Lyle, *J. Org. Chem.*, 1962, **27**, 641.

7 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.

8 W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

9 G. M. Sheldrick, *SHELXTL/PC manual*, Siemens X-Ray Analytical Instruments, Madison, WI, 1990.

10 G. M. Sheldrick, SHELXL 93, program for crystal structure refinement, beta-test version, University of Göttingen, 1992.

11 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.

12 M. Capdevila, W. Clegg, P. González-Duarte and I. Mira, *J. Chem. Soc., Dalton Trans.*, 1992, 173.

13 T. G. Appleton and J. R. Hall, *Aust. J. Chem.*, 1980, **33**, 2387.

14 *Tablas para la elucidación estructural de compuestos orgánicos por métodos espectroscópicos*, eds. E. Pretsch, T. Clerc, J. Seibl and W. Simon, Alhambra, Madrid, 1985.

15 R. K. Harris and B. E. Mann, *NMR and the Periodic Table*, Academic Press, London, 1978, ch. 8I.

16 A. J. Schulz and R. Eisenberg, *Inorg. Chem.*, 1973, **12**, 518.

17 M. A. Walters and J. C. Dewan, *Inorg. Chim. Acta*, 1991, **187**, 123.

18 D. Fenske, J. Meyer and K. Merzweiler, *Z. Naturforsch., Teil B*, 1987, **42**, 1207.

19 P. M. Treichel, K. A. Crane, R. Matthews, K. R. Bonnin and D. Powell, *J. Organomet. Chem.*, 1991, **402**, 233.

20 R. H. Holm, *Chem. Rev.*, 1981, **10**, 455.

21 F. A. Cotton, M. P. Diebold and W. J. Roth, *J. Am. Chem. Soc.*, 1987, **109**, 5506.

22 P. M. Boorman, X. Gao, G. K. W. Freeman and J. F. Fait, *J. Chem. Soc., Dalton Trans.*, 1991, 115.

23 P. J. Blower, J. R. Dilworth, J. P. Hutchinson, J. A. Zubieta and T. Nicholson, *J. Chem. Soc., Dalton Trans.*, 1985, 1533.

24 K.-I. Okamoto, S.-I. Aizawa, T. Kanno, H. Einaga and J. Hidaka, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 3859; R. E. Marsh, M. J. Heeg and E. Deutsch, *Inorg. Chem.*, 1986, **25**, 118; J. Suades, X. Solans, M. Font-Altaba and M. Aguilo, *Inorg. Chim. Acta*, 1985, **99**, 1; M. Mikuriya, S. Kida, S. Ueno and I. Murase, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 1857.

Received 2nd August 1993; *Paper* 3/04612E