Displacement of Ligands in [$PtBr_2$(en)] (en = ethylenediamine) by β- and γ-Mercaptoamines†

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The reactions of [$PtBr_2$(en)] (en = ethylenediamine) with 2-(dimethylamino)ethanethiol, 3-dimethylaminopropane-1-thiol and 4-mercapto-1-methylpiperidine in alkaline aqueous solution give different types of complexes depending on the nature of the mercaptoamine. With the *N*-substituted β-mercaptoamine the product is *cyclo*-[{Pt(μ-$SCH_2CH_2NMe_2$-*N*,μ-*S*)Br}$_3$], consisting of discrete trimeric molecules with a central Pt_3S_3 ring. Each platinum atom is square-planar co-ordinated by a S_2NBr donor set; the aminothiolate ligands are simultaneously chelating, through S and N, and bridging, through S, while bromine is terminally bonded. With the two γ-mercaptoamines, three crystalline products have been obtained, of formulae [(en)Pt(μ-SR)$_2$Pt(en)]$^{n+}$$Br_n$·$xH_2O$ [R = $(CH_2)_3NMe_2$, $n = 2$, $x = 0$; R = C_5H_9NMe, $n = 2$, $x = 6$; R = C_5H_9NHMe, $n = 4$, $x = 2$]. The three cations differ chemically only in the nature of the thiolate substituent group R, and their core geometries are essentially identical, consisting of a central exactly planar Pt_2S_2 ring linked to two five-membered chelate Pt(en) rings. There is extensive hydrogen bonding in the hydrated complexes. The different chelating ability of the β- and γ-mercaptoamines results in total displacement of ethylenediamine from the starting material by the β-mercaptoamine, but substitution of only bromine by the γ-mercaptoamines.

While extensive work has been carried out on the interaction of cisplatin, *cis*-[$PtCl_2(NH_3)_2$], and related compounds with DNA,[1] much less attention has been devoted to that of platinum antitumour drugs with proteins.[2] However, it is thought that their inactivation and negative effects are probably due to the binding of platinum with sulfur-containing biomolecules.[3] On the other hand it has been reported that, after administration of cisplatin, about 25% of the cytosolic Pt in kidney tissue is bound to metallothionein (MT),[4] the main characteristic of this low-molecular-weight protein being its high content of cysteine residues. Also, very recent studies show that platinum(II) displaces metal atoms in Cd_7MT and native (Cd,Zn)MT despite their different co-ordination preferences.[5]

Our current interest in aliphatic mercaptoamine complexes, which can also be taken as models for simple thiolates when they co-ordinate only through the sulfur atom, together with the above reports, stimulated us to study the behaviour of these ligands towards platinum compounds containing ethylenediamine (en). Studies of several homo- and hetero-bimetallic complexes of Ni^{II}, Pd^{II} and Pt^{II} with mixed mercaptoamine and phosphine ligands are also in progress.[6]

Herein we report the preparation and structural characterization of *cyclo*-[{Pt(μ-$SCH_2CH_2NMe_2$-*N*,μ-*S*)Br}$_3$] **1**, [{Pt-[μ-$S(CH_2)_3NMe_2$](en)}$_2$]Br_2 **2**, [{Pt(μ-SC_5H_9NMe)(en)}$_2$]-Br_2·$6H_2O$ **3** and [{Pt(μ-SC_5H_9NHMe)(en)}$_2$]Br_4·$2H_2O$ **4**, which contribute to the structural diversity already established for Pd^{II} (refs. 7 and 8) and Pt^{II}.[9] Reference to the already reported [$Pt_6(SCH_2CH_2NH_2)_8$]Br_4·$6H_2O$[10] also allows us to compare the different ability of mercaptoamines to displace ethylenediamine and/or halide ligands in the platinum-containing starting material.

Experimental

Synthesis.—The complex [$PtBr_2$(en)][10] was prepared from $K_2[PtCl_4]$ *via* [PtI_2(en)].[11] 2-(Dimethylamino)ethanethiol hydrochloride was obtained commercially and used without further purification. 3-Dimethylaminopropane-1-thiol[12] and 4-mercapto-1-methylpiperidine[13] were synthesised according to known procedures. They were both purified by vacuum distillation until their purity, checked by iodometric determination of the SH group, was >99%.

Preparation of Complexes.—*Complex* **1**. A solution of 2-(dimethylamino)ethanethiol (0.19 g, 1.20 mmol) in water (10 cm^3) was prepared and the pH adjusted to 10.5 with 0.5 mol dm^{-3} aqueous sodium hydroxide. The solution was heated to 60 °C on a steam-bath and then [$PtBr_2$(en)] (0.5 g, 1.20 mmol) was added with stirring. After approximately 12 min all the solid had dissolved, but stirring was continued for *ca.* 15 min. The solution was cooled in an ice–water mixture for 1 h and was then filtered. Slow evaporation of this light yellow solution afforded after 2 d a yellow powder, which was filtered off, washed with ethanol and dried in the air (Found: C, 13.10; H, 2.75; N, 4.05; S, 8.50. Calc. for $C_{12}H_{30}Br_3N_3Pt_3S_3$: C, 12.65; H, 2.65; N, 3.70; S, 8.45%). Yellow crystals suitable for X-ray diffraction were grown from an aqueous solution of the complex containing several drops of dimethylformamide (dmf) and kept at 45 °C. The crystals were filtered off, washed with ethanol and air dried.

Complex **2**. By the same procedure as that indicated for complex **1**, [$PtBr_2$(en)] (0.5 g, 1.20 mmol) was added to a warm (60 °C) basic (pH 10.5) solution of 3-dimethylaminopropane-1-thiol (0.16 cm^3, 1.20 mmol). Complete dissolution of [$PtBr_2$(en)] required 30 min of stirring. Then the reaction mixture was cooled to 0 °C for 1 h. Slow evaporation of the filtered yellow solution containing some drops of dimethyl sulfoxide (dmso) and dmf afforded colourless single crystals after 2 weeks. They were filtered off, washed with cold ethanol and dried in the air (Found: C, 18.75; H, 4.50; N, 8.95; S, 7.10. Calc. for $C_{14}H_{40}Br_2N_6Pt_2S_2$: C, 18.55; H, 4.40; N, 9.25; S, 7.05%).

Complex **3**. By an analogous procedure a reaction mixture of [$PtBr_2$(en)] with a basic (pH 10.5) solution of 4-mercapto-1-methylpiperidine (0.17 cm^3, 1.20 mmol) was heated to 60 °C

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Crystallographic data

Complex	**1**	**2**	**3**	**4**
Formula	$C_{12}H_{30}Br_3N_3Pt_3S_3$	$C_{14}H_{40}Br_2N_6Pt_2S_2$	$C_{16}H_{52}Br_2N_6O_6Pt_2S_2$	$C_{16}H_{46}Br_4N_6O_2Pt_2S_2$
M	1137.6	906.6	1038.7	1128.5
Crystal system	Orthorhombic	Tetragonal	Monoclinic	Orthorhombic
Space group	*Pbca*	$P4_2/m$	$P2_1/c$	*Pccn*
a/Å	36.384(7)	12.241(1)	12.370(1)	15.012(4)
b/Å	11.938(2)		14.091(1)	18.509(4)
c/Å	10.933(2)	9.006(1)	9.446(1)	11.547(3)
β/°			97.12(1)	
U/Å^3	4748.8	1349.5	1633.8	3208.4
Z	8	2	2	4
D_c/g cm^{-3}	3.182	2.231	2.111	2.336
μ/mm^{-1}	23.08	13.56	11.23	13.89
F(000)	4080	848	992	2112
Crystal size/mm	0.40 × 0.36 × 0.12	0.15 × 0.04 × 0.04	0.24 × 0.20 × 0.10	0.28 × 0.22 × 0.20
Transmission factors	0.016–0.053	0.255–0.301	0.062–0.132	0.017–0.042
Reflections measured	7032	8445	3657	7798
Unique reflections	4161	1275	2876	2839
Observed reflections	3067	1118	2395	2303
R_{int}	0.026	0.031	0.017	0.033
Weighting parameters A_n	767, 703, 15 681, −2221, 1792, −4694	14, −137, 261, 21, −3, −76	64, 47, 1005, −199, 180, −501	104, −361, 707, −231, 156, 114
No. of parameters	212	103	155	148
R	0.0537	0.0300	0.0348	0.0306
$R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$	0.0466	0.0162	0.0336	0.0268
Goodness of fit	1.39	0.97	1.29	1.09
Mean, maximum shift/e.s.d.	0.001, 0.008	0.001, 0.007	0.013, 0.122	0.003, 0.019
Maximum, minimum electron density/e Å^{-3}	2.58, −2.52	1.13, −1.10	1.83, −1.82	1.20, −0.84

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters (Å^2 × 10^3) for complex **1**

Atom	x	y	z	U_{eq}
Pt(1)	4 372.6(1)	9 572.4(4)	1 346.1(5)	34.9(2)
Pt(2)	3 347.3(1)	9 719.3(4)	823.7(6)	39.9(2)
Pt(3)	3 722.6(1)	9 932.5(4)	3 894.6(5)	36.4(1)
Br(1)	4 897.1(5)	9 343.3(16)	2 759.1(19)	63.4(6)
Br(2)	3 127.6(6)	10 791.1(25)	−954.4(26)	87.2(8)
Br(3)	3 391.0(7)	8 968.8(20)	5 523.3(22)	77.0(7)
S(1)	3 916(1)	9 861(3)	−12(4)	40(1)
C(11)	3 960(6)	8 571(15)	−907(19)	57(6)
C(12)	4 368(4)	8 379(16)	−1 046(17)	50(5)
N(1)	4 566(4)	8 302(10)	127(13)	41(4)
C(13)	4 953(4)	8 408(16)	−188(20)	55(6)
C(14)	4 492(6)	7 167(13)	729(19)	58(6)
S(2)	3 560(1)	8 665(3)	2 399(4)	38(1)
C(21)	3 135(5)	8 071(14)	2 851(18)	55(6)
C(22)	2 830(4)	8 975(20)	2 770(21)	64(7)
N(2)	2 811(3)	9 543(13)	1 604(15)	55(4)
C(23)	2 635(5)	10 651(25)	1 689(37)	100(12)
C(24)	2 606(6)	8 787(23)	698(25)	80(8)
S(3)	4 071(1)	10 877(3)	2 500(4)	42(1)
C(31)	4 356(6)	11 582(19)	3 604(20)	63(6)
C(32)	4 102(7)	12 078(15)	4 559(21)	66(7)
N(3)	3 893(4)	11 163(11)	5 186(13)	49(4)
C(33)	4 135(7)	10 685(18)	6 103(22)	69(7)
C(34)	3 571(8)	11 697(16)	5 786(20)	71(7)

Table 3 Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters (Å^2 × 10^3) for complex **2**

Atom	x	y	z	U_{eq}
Pt	6341.3(3)	398.2(2)	0.0	28.1(1)
Br	1248.3(8)	2305.6(8)	0.0	59.6(4)
S	4826(2)	574(2)	1476(3)	36(1)
C(1)	5157(19)	−237(22)	3097(11)	53(9)
C(2)	5672(10)	−1371(10)	2806(12)	50(4)
C(3)	5734(9)	−2015(11)	4258(15)	69(5)
N(1)	6428(17)	−2955(13)	4198(19)	60(5)
C(4)	6157(14)	−3735(13)	2950(22)	121(9)
C(5)	6457(22)	−3475(17)	5651(30)	140(17)
N(21)	7437(6)	1249(7)	1392(9)	35(3)
N(22)	7708(6)	203(7)	−1320(10)	34(3)
C(6)	8566(4)	949(5)	852(5)	44(2)

Table 4 Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters (Å^2 × 10^3) for complex **3**

Atom	x	y	z	U_{eq}
Pt	4 595.1(2)	5 680.0(2)	6 359.6(2)	27.6(1)
Br	−3 256.0(7)	6 529.6(6)	856.6(7)	52.6(2)
S	5 949(1)	5 668(1)	4 898(1)	31(1)
C(1)	7 201(5)	5 479(5)	6 125(7)	37(2)
C(2)	8 191(5)	5 462(6)	5 328(8)	45(2)
C(3)	9 221(6)	5 419(7)	6 415(9)	51(3)
N(1)	9 219(5)	4 573(6)	7 268(6)	53(2)
C(4)	8 288(6)	4 556(7)	8 065(7)	53(3)
C(5)	7 233(6)	4 600(6)	7 046(7)	42(2)
C(6)	10 247(8)	4 523(11)	8 233(11)	82(4)
N(2)	3 373(5)	5 705(4)	7 679(5)	38(2)
N(3)	5 175(4)	6 823(4)	7 597(6)	40(2)
C(7)	3 713(6)	6 343(7)	8 942(7)	51(3)
C(8)	4 279(6)	7 194(6)	8 377(8)	47(2)
O(1)	−1 610(5)	7 645(5)	3 526(7)	66(2)
O(2)	627(5)	7 219(5)	3 955(6)	65(2)
O(3)	1 664(5)	6 943(5)	6 723(6)	74(2)

until all the solid dissolved (approximately 3 min). Stirring was continued for *ca.* 10 min and then the solution was allowed to cool and stand at 0 °C for 1 h. Slow evaporation of the light yellow filtered solution afforded colourless single crystals after 1 week. They were filtered off, washed with cold water and dried in the air (Found: C, 18.70; H, 5.00; N, 8.00; S, 6.15. Calc. for $C_{16}H_{52}Br_2N_6O_6Pt_2S_2$: C, 18.50; H, 5.00; N, 8.10; S, 6.15%).

Complex **4**.—After 3 or 4 weeks of slow evaporation of the solution which gave complex **3**, colourless single crystals different from **3** separated out. By this time the pH of the solution had dropped to 9. The crystals were filtered off, washed with very cold ethanol and dried in the air; they lost crystallinity if washed with cold water. The IR and ^1H NMR spectra confirmed that this was a new product (Found: C, 17.20; H, 4.15; N, 7.55; S, 5.65. Calc. for $C_{16}H_{46}Br_4N_6O_2Pt_2S_2$: C, 17.00; H, 4.05; N, 7.45; S, 5.65%).

Table 5 Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for complex **4**

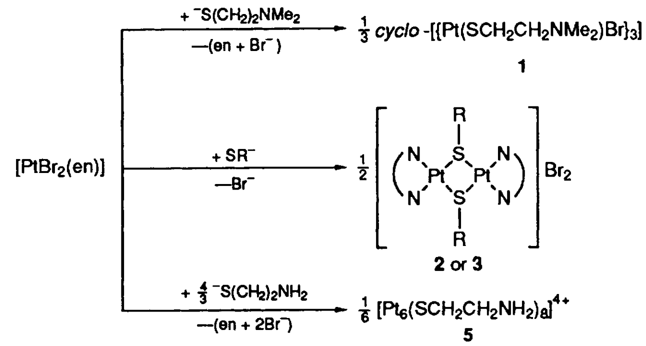
Atom	x	y	z	U_{eq}
Pt	5322.7(2)	5890.8(1)	5115.7(2)	29.8(1)
Br(1)	7513.2(6)	6287.4(4)	7429.2(6)	57.4(2)
Br(2)	3900.5(5)	7359.2(3)	8187.5(5)	42.5(2)
S	4746(1)	4999(1)	6279(1)	35(1)
C(1)	5644(4)	4776(3)	7311(5)	34(2)
C(2)	5299(5)	4244(4)	8215(5)	44(2)
C(3)	6021(5)	4044(4)	9064(5)	46(2)
N(1)	6825(4)	3733(3)	8449(4)	39(2)
C(4)	7181(5)	4267(3)	7573(6)	41(2)
C(5)	6468(4)	4472(4)	6722(5)	38(2)
C(6)	7527(7)	3514(5)	9284(6)	58(3)
N(2)	5786(4)	6729(3)	4088(4)	35(2)
N(3)	5496(4)	6650(3)	6414(4)	39(2)
C(7)	6250(5)	7269(3)	4835(6)	47(2)
C(8)	5665(5)	7381(3)	5901(6)	47(2)
O	6703(8)	9364(5)	4939(6)	129(4)

Table 6 Bond lengths (Å) and angles (°) for complex **1**

Pt(1)–Br(1)	2.470(2)	Pt(1)–S(1)	2.255(4)
Pt(1)–N(1)	2.138(13)	Pt(1)–S(3)	2.285(4)
Pt(2)–Br(2)	2.461(3)	Pt(2)–S(1)	2.268(4)
Pt(2)–S(2)	2.269(4)	Pt(2)–N(2)	2.141(14)
Pt(3)–Br(3)	2.439(3)	Pt(3)–S(2)	2.305(4)
Pt(3)–S(3)	2.281(4)	Pt(3)–N(3)	2.130(14)
S(1)–C(11)	1.832(19)	C(11)–C(12)	1.510(26)
C(12)–N(1)	1.474(23)	N(1)–C(13)	1.453(20)
N(1)–C(14)	1.530(21)	S(2)–C(21)	1.772(19)
C(21)–C(22)	1.551(27)	C(22)–N(2)	1.445(29)
N(2)–C(23)	1.472(32)	N(2)–C(24)	1.533(31)
S(3)–C(31)	1.801(22)	C(31)–C(32)	1.515(32)
C(32)–N(3)	1.497(25)	N(3)–C(33)	1.451(28)
N(3)–C(34)	1.488(29)		
Br(1)–Pt(1)–S(1)	176.3(1)	Br(1)–Pt(1)–N(1)	93.3(4)
S(1)–Pt(1)–N(1)	86.6(4)	Br(1)–Pt(1)–S(3)	95.8(1)
S(1)–Pt(1)–S(3)	84.6(1)	N(1)–Pt(1)–S(3)	170.3(4)
Br(2)–Pt(2)–S(1)	86.5(1)	Br(2)–Pt(2)–S(2)	177.2(1)
S(1)–Pt(2)–S(2)	92.1(1)	Br(2)–Pt(2)–N(2)	94.0(4)
S(1)–Pt(2)–N(2)	178.6(5)	S(2)–Pt(2)–N(2)	87.3(4)
Br(3)–Pt(3)–S(2)	94.7(1)	Br(3)–Pt(3)–S(3)	174.9(1)
S(2)–Pt(3)–S(3)	89.6(1)	Br(3)–Pt(3)–N(3)	89.2(4)
S(2)–Pt(3)–N(3)	176.2(4)	S(3)–Pt(3)–N(3)	86.6(4)
Pt(1)–S(1)–Pt(2)	113.3(2)	Pt(1)–S(1)–C(11)	99.1(7)
Pt(2)–S(1)–C(11)	103.4(7)	S(1)–C(11)–C(12)	105.5(13)
C(11)–C(12)–N(1)	113.7(15)	Pt(1)–N(1)–C(12)	109.7(10)
Pt(1)–N(1)–C(13)	113.9(11)	C(12)–N(1)–C(13)	105.1(14)
Pt(1)–N(1)–C(14)	107.6(11)	C(12)–N(1)–C(14)	110.1(13)
C(13)–N(1)–C(14)	110.4(13)	Pt(2)–S(2)–Pt(3)	105.2(1)
Pt(2)–S(2)–C(21)	97.8(6)	Pt(3)–S(2)–C(21)	106.8(6)
S(2)–C(21)–C(22)	109.3(12)	C(21)–C(22)–N(2)	114.3(16)
Pt(2)–N(2)–C(22)	110.8(10)	Pt(2)–N(2)–C(23)	109.4(13)
C(22)–N(2)–C(23)	112.7(21)	Pt(2)–N(2)–C(24)	104.0(12)
C(22)–N(2)–C(24)	108.5(17)	C(23)–N(2)–C(24)	111.1(18)
Pt(1)–S(3)–Pt(3)	107.4(1)	Pt(1)–S(3)–C(31)	114.3(7)
Pt(3)–S(3)–C(31)	95.9(7)	S(3)–C(31)–C(32)	107.1(15)
C(31)–C(32)–N(3)	109.9(15)	Pt(3)–N(3)–C(32)	110.4(11)
Pt(3)–N(3)–C(33)	111.3(11)	C(32)–N(3)–C(33)	107.2(16)
Pt(3)–N(3)–C(34)	111.0(12)	C(32)–N(3)–C(34)	106.8(14)
C(33)–N(3)–C(34)	110.0(16)		

Complexes **1**–**4** are highly insoluble in most common organic solvents. They are partially soluble in dmf and dmso.

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, and proton NMR spectra on a Bruker AM-400 from samples in $(CD_3)_2SO$ solution with $SiMe_4$ as reference.



Scheme 1 SR$^-$ denotes $^-S(CH_2)_3NMe_2$ in **2** and $^-SC_5H_9NMe$ in **3**

X-Ray Crystallography.—Crystal data are given in Table 1, with other information on the data collection and structure determination. All measurements were made on a Stoe–Siemens diffractometer, with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Unit-cell parameters were refined in each case from 2θ values (20–25°) of 32 reflections measured at $\pm\omega$. Data were collected at room temperature for complexes **1**–**3** and at 240 K for **4**, with the aid of an Oxford Cryostream cooler.[14] On-line profile analysis of ω–θ scans was performed.[15]

Each data set consisted of a complete unique set of reflections to $2\theta_{max} = 50°$, together with some equivalent reflections: for **2**, over six equivalent sets were collected, and an intensity decay of *ca.* 5%, monitored by three periodically measured standard reflections, was corrected; no decay was observed for the other crystals. Semiempirical absorption corrections were applied.

The structures were solved[16] from Patterson and difference syntheses and refined by blocked-cascade least squares on F, with data having $F > 4\sigma_c(F)$ (σ_c from counting statistics only). The weighting function[17] was $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + A_1 + A_2G + A_3G^2 + A_4H + A_5H^2 + A_6GH$ (where $G = F_o/F_{max}$ and $H = \sin\theta/\sin\theta_{max}$); atomic scattering factors were taken from ref. 18. The refinement included anisotropic thermal parameters for all non-H atoms, and constrained H atoms [C–H and N–H 0.96 Å, H–C–H and H–N–H 109.5°, U(H) = $1.2U_{eq}$(C) or $1.2U_{eq}$(N)]; H atoms of water molecules were not located. Extinction effects were insignificant. Two-fold disorder of orientation of the cations of **2** was successfully resolved, with equal site occupancies: only the Pt atoms and the C atoms of the ethylenediamine ligands coincide in the two disorder components.

Atomic coordinates and equivalent isotropic thermal parameters (defined as one-third of the trace of the orthogonalised U_{ij} matrix) are given in Tables 2–5, bond lengths and angles in Tables 6–9. The structures are shown in the Figures.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Synthesis.—The reaction of [PtBr$_2$(en)] with either β or γ aliphatic mercaptoamine ligands in a basic medium has led to different complexes. Since the reaction conditions were essentially the same in each case the nature of the ligand dictates the form of the product. Thus, in the case of the β-mercaptoamine 2-(dimethylamino)ethanethiol, the cyclic trinuclear molecule **1** is obtained, while the γ-mercaptoamines 3-dimethylaminopropane-1-thiol and 4-mercapto-1-methylpiperidine give the dinuclear cationic species of **2**–**4**, all three of which have the same basic composition and structure, differing radically from that of **1**.

We may contrast the different pathways followed by these reactions, as indicated in Scheme 1. In the synthesis of complex **1**, chelating ethylenediamine in the starting material [PtBr$_2$(en)] has been totally displaced by an equimolecular amount of the

Table 7 Bond lengths (Å) and angles (°) for complex **2**

Pt–S	2.292(3)	Pt–N(21)	2.111(8)
Pt–N(22)	2.066(8)	Pt–S(a)	2.286(3)
S–C(1)	1.811(18)	C(1)–C(2)	1.547(28)
C(2)–C(3)	1.529(18)	C(3)–N(1)	1.431(22)
N(1)–C(4)	1.512(25)	N(1)–C(5)	1.455(31)
N(21)–C(6)	1.511(9)	N(22)–C(6b)	1.453(10)
C(6)–C(6b)	1.534(9)		

S–Pt–N(21)	97.1(2)	S–Pt–N(22)	178.8(3)
N(21)–Pt–N(22)	83.3(3)	S–Pt–S(a)	83.1(1)
N(21)–Pt–S(a)	178.2(2)	N(22)–Pt–S(a)	96.4(2)
Pt–S–C(1)	103.6(7)	Pt–S–Pt(a)	96.9(1)
C(1)–S–Pt(a)	108.9(8)	S–C(1)–C(2)	116.5(8)
C(1)–C(2)–C(3)	109.8(9)	C(2)–C(3)–N(1)	114.3(12)
C(3)–N(1)–C(4)	113.9(15)	C(3)–N(1)–C(5)	109.4(16)
C(4)–N(1)–C(5)	113.4(15)	Pt–N(21)–C(6)	105.6(5)
Pt–N(22)–C(6b)	110.2(5)	N(21)–C(6)–C(6b)	108.8(4)
N(22)–C(6b)–C(6)	106.9(4)		

Symmetry operators: (a) $1 - x, -y, -z$; (b) $x, y, -z$.

Table 8 Bond lengths (Å) and angles (°) for complex **3**

Pt–S	2.299(2)	Pt–N(2)	2.075(6)
Pt–N(3)	2.066(6)	Pt–S(a)	2.297(2)
S–C(1)	1.835(6)	C(1)–C(2)	1.515(10)
C(1)–C(5)	1.511(11)	C(2)–C(3)	1.535(10)
C(3)–N(1)	1.440(12)	N(1)–C(4)	1.452(10)
N(1)–C(6)	1.472(11)	C(4)–C(5)	1.524(10)
N(2)–C(7)	1.511(9)	N(3)–C(8)	1.499(10)
C(7)–C(8)	1.518(12)		

S–Pt–N(2)	179.4(2)	S–Pt–N(3)	96.7(2)
N(2)–Pt–N(3)	82.8(2)	S–Pt–S(a)	82.7(1)
N(2)–Pt–S(a)	97.8(2)	N(3)–Pt–S(a)	175.2(2)
Pt–S–C(1)	104.0(2)	Pt–S–Pt(a)	97.3(1)
C(1)–S–Pt(a)	112.1(2)	S–C(1)–C(2)	111.0(5)
S–C(1)–C(5)	116.3(5)	C(2)–C(1)–C(5)	107.9(6)
C(1)–C(2)–C(3)	108.8(6)	C(2)–C(3)–N(1)	110.3(7)
C(3)–N(1)–C(4)	111.1(7)	C(3)–N(1)–C(6)	108.9(8)
C(4)–N(1)–C(6)	111.0(6)	N(1)–C(4)–C(5)	110.1(6)
C(1)–C(5)–C(4)	110.9(6)	Pt–N(2)–C(7)	109.4(4)
Pt–N(3)–C(8)	108.9(4)	N(2)–C(7)–C(8)	106.7(6)
N(3)–C(8)–C(7)	107.4(6)		

Symmetry operator: (a) $1 - x, 1 - y, 1 - z$.

Table 9 Bond lengths (Å) and angles (°) for complex **4**

Pt–S	2.296(2)	Pt–N(2)	2.074(5)
Pt–N(3)	2.071(5)	Pt–S(a)	2.306(2)
S–C(1)	1.846(6)	C(1)–C(2)	1.526(9)
C(1)–C(5)	1.520(9)	C(2)–C(3)	1.507(10)
C(3)–N(1)	1.515(9)	N(1)–C(4)	1.513(8)
N(1)–C(6)	1.484(10)	C(4)–C(5)	1.501(9)
N(2)–C(7)	1.492(9)	N(3)–C(8)	1.498(8)
C(7)–C(8)	1.526(10)		

S–Pt–N(2)	177.0(2)	S–Pt–N(3)	96.4(1)
N(2)–Pt–N(3)	82.2(2)	S–Pt–S(a)	83.0(1)
N(2)–Pt–S(a)	98.6(1)	N(3)–Pt–S(a)	174.7(2)
Pt–S–C(1)	105.3(2)	Pt–S–Pt(a)	97.0(1)
C(1)–S–Pt(a)	108.9(2)	S–C(1)–C(2)	109.8(5)
S–C(1)–C(5)	112.9(4)	C(2)–C(1)–C(5)	110.1(5)
C(1)–C(2)–C(3)	111.1(6)	C(2)–C(3)–N(1)	111.2(5)
C(3)–N(1)–C(4)	110.2(5)	C(3)–N(1)–C(6)	111.4(5)
C(4)–N(1)–C(6)	111.2(6)	N(1)–C(4)–C(5)	110.6(6)
C(1)–C(5)–C(4)	112.4(5)	Pt–N(2)–C(7)	109.0(4)
Pt–N(3)–C(8)	110.4(4)	N(2)–C(7)–C(8)	106.8(6)
N(3)–C(8)–C(7)	107.1(5)		

Symmetry operator: (a) $1 - x, 1 - y, 1 - z$.

N-disubstituted β-mercaptoamine. This displacement can be attributed to the stronger affinity of platinum for sulfur than for nitrogen, since this is the only significant difference between the chelate rings of the starting material and the product. However, the negative charge of the entering aminothiolate ligand makes half the initially co-ordinated bromide anions unnecessary, the remaining half being responsible for completing square-planar co-ordination around platinum and for the electrical neutrality of complex **1**. The empirical formula of this complex would, in fact, also be compatible with a dinuclear molecule, $[\{Pt[\mu\text{-}S(CH_2)_2NMe_2]Br\}_2]$, in which both aminothiolate ligands simultaneously bridge and chelate metal atoms and halogen atoms are terminal ligands; such an arrangement has already been found in $[\{Pd[\mu\text{-}S(CH_2)_3NMe_2]Cl\}_2]$[7] and $[\{Pt(\mu\text{-}SC_5H_9NMe)Br\}_2]$.[9]

The greater chelating ability of β-[10,19,20] compared to γ-mercaptoamines[7–9,21] is well known; the latter often co-ordinate through the sulfur atom exclusively.[22] The observed formation of complexes **1**–**3** allows us to rank the chelating ability of ethylenediamine for platinum(II) relative to these mercaptoamines as: $^{-}S(CH_2)_2NMe_2$ > en > $^{-}S(CH_2)_3NMe_2 \approx {}^{-}SC_5H_9NMe$. The position of the γ-mercaptoamines in this series is based on the fact that the reactions leading to complexes **2** and **3** can be explained in terms of an initial displacement of half of the bromide ions in $[PtBr_2(en)]$ molecules by unidentate aminothiolate ligands. This substitution does not proceed further because the strong tendency of the thiolate sulfur to behave as a bridging ligand leads to the formation of dinuclear cationic species instead of the mononuclear $[PtBr(SR)(en)]$ or $[Pt(SR)_2(en)]$ molecules; the initially unsubstituted halogen atoms ultimately act as counter ions in complexes **2** and **3**.

These results are in very good agreement with those reported for reactions of *cis*-$[Pt(NH_3)_2(H_2O)_2]^{2+}$ with glutathione [*N*-(*N*-L-γ-glutamyl-L-cysteinyl)glycine] and amino acids containing a thiol group, where dinuclear complexes containing a Pt_2S_2 four-membered ring are formed,[23] and with those of the reaction of [PtCl(dien)]Cl (dien = diethylenetriamine) with glutathione.[24] In this case, first a 1:1 complex with the ligand bound through sulfur is formed and then a subsequent reaction leads to a complex in which sulfur bridges two Pt(dien) units.

The synthetic procedures followed in this work are analogous to that reported for the hexanuclear complex $[Pt_6(SCH_2CH_2NH_2)_8]Br_4\cdot 6H_2O$ **5**,[10] which is also included in Scheme 1. However, two significant features should be noted. First, complex **5** with a 3:4 metal to ligand ratio is obtained from a 1:1 reaction mixture but both 1:1 and 3:4 ratios of reactants give complexes **1**–**3**, and no product analogous to **5** is formed. It seems then that the relative stability and/or insolubility of the possible platinum complexes, rather than the metal to ligand ratio in the reaction mixture, determines the stoichiometry of the products actually isolated. Secondly, all the platinum atoms of **5** are co-ordinated only by sulfur and nitrogen of aminothiolate ligands, $^{-}SCH_2CH_2NH_2$, and thus ethylenediamine and bromide ligands of the starting material have all been displaced. Consequently, the different compositions and structures of complexes **1** and **5** are very likely due to the steric constraints imposed by the methyl groups on the nitrogen atom. As a simple test of this suggestion, we have taken the reported crystal structure of complex **5** and replaced the hydrogen atoms on the amino nitrogens by methyl groups, maintaining approximate tetrahedral geometry with C–N bond lengths of 1.488 Å (the mean of those found in **1**). The resulting structure shows some impossibly short Me···S and Me···Pt intramolecular distances across the central core of the structure; these steric problems are so severe that they would probably not be avoided by only minor adjustments to the structure, and it is unlikely that the extra methyl groups can be accommodated, but we have not actually attempted any potential-energy minimization calculations to prove this conclusively.

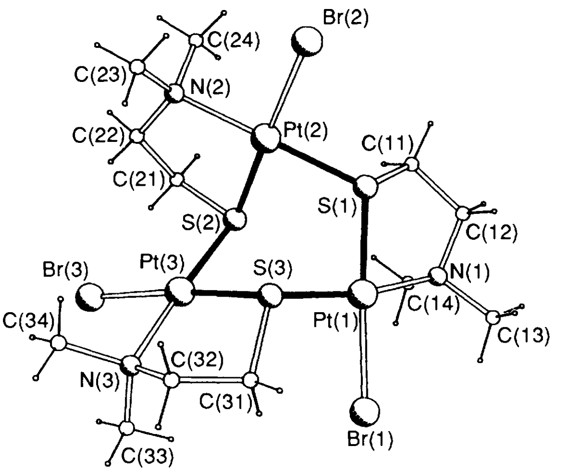


Fig. 1 Molecular structure of complex **1**, with the labelling of the atoms

It also appears likely that the methyl groups hinder the formation of *cis*-Pt$\{S(CH_2)_2NMe_2\}_2$ units; equivalent *cis*-M$\{S(CH_2)_nNH_2\}_2$ units are building blocks in the structures of **5** and of $[M_3\{S(CH_2)_nNH_2\}_4]^{2+}$ (M = Ni or Pd, n = 2 or 3) and related trinuclear complexes,[7,10,25] in which two such units are linked together by a central M^{2+} ion. For aminothiolate ligands SR^- containing a methyl-substituted amino group, no *cis*-$M(SR)_2$ units have been found in any structure; instead, metal ions are complexed by only one chelating SR^- ligand, with the co-ordination completed by additional ligands and by ring formation through sulfur bridges.[7,9,26] We note that the *cis*-$M(SR)_2$ unit is known only as part of larger assemblies, and not as a discrete mononuclear entity; although such a *cis* structure was originally proposed[27] for $[Ni(SCH_2CH_2NH_2)_2]$, the complex was subsequently found to have a *trans* arrangement of ligands.[28,*]

The fact that half of the bromine atoms of the starting material remain co-ordinated to platinum in complex **1** indicates that the base-promoted substitution of bromide by a thiolate ligand is not necessarily the initial step in the reaction mechanism forming **5**, as has been postulated.[10] In fact recent results[23] show that ammine loss may be competitive with halide displacement in cisplatin substitution with thiolate ligands.

Complex **3** is formed from solution at pH 10.5 and **4** is formed when the pH drops to about 9 after the solution has been standing in the open atmosphere for several weeks. In view of solution equilibria studies with 4-mercapto-1-methylpiperidine, which have only been reported for Zn^{II},[30] Cd^{II}[31] and Ag^{I},[32] protonation of the amine group at pH 9 to give **4** is reasonable. Because of the rather low yields of these reactions other complex species must be present in solution, and so it is not difficult to accept that two more bromide ions can be supplied to balance the electrical charge of the new cationic species.

Despite the low yields (maximum 40%) all syntheses are reproducible. A side product has been isolated only in the synthesis of **2** and identified as $[Pt(en)_2]Br_2$. It is likely that oxidation of the ligand to the corresponding disulfide, which is clearly promoted in basic solution, accounts in part for the low yields.

Infrared Data.—Infrared spectra of the crystalline complexes **1**–**4** indicate unambiguously the behaviour of the aminothiolate ligand as well as the presence or absence of ethylenediamine. This latter ligand has two very strong absorptions in the region 3200–3000 cm^{-1}, assigned to ν(N–H), which are apparent in the spectra of **2**–**4** but not in that of **1**. The essential features of the region 3000–2500 cm^{-1} denoting whether aliphatic β-[19,33] or γ-mercaptoamines[9,34] behave as chelates or co-ordinate through the sulfur atom exclusively have already been reported. According to these data, the broad band centred at 2916 cm^{-1} of **1** indicates that 2-(dimethylamino)ethanethiolate co-ordinates to platinum through both sulfur and nitrogen. Also, the intense absorption at 2754 cm^{-1} of **4** gives evidence that the amine group of 4-mercapto-1-methylpiperidine is protonated, so that the complexed ligand is in zwitterionic form. A good indication that, in **2** and **3**, 3-dimethylaminopropane-1-thiol and 4-mercapto-1-methylpiperidine, respectively, behave as unidentate thiolato ligands is given by two groups of resolved bands of medium intensity in the range 2980–2780 cm^{-1}.

^1H *NMR Data.*—Information obtained from ^1H NMR data is in good agreement with that supplied by the infrared spectra in the case of complexes **2**–**4**. Unfortunately, the very low solubility of **1** even in dmso or dmf prevented us from recording the corresponding spectrum. Based on previous analyses of NMR data for *N*-methyl disubstituted β-[33] and γ-mercaptoamine[8,9,35] complexes, the position of the peak corresponding to hydrogen atoms of the CH_3N group, compared to those of the free ligand and corresponding hydrohalide, indicates clearly whether nitrogen participates or not in co-ordination. Thus, the singlets at δ 2.16 and 2.14 for **2** and **3**, respectively, are good evidence that the nitrogen atom does not co-ordinate platinum, as it keeps its free pair of electrons. However, the singlet appearing at δ 2.77 in the spectrum of **4**, together with another wide peak at δ 9.81, clearly indicate that a $MeNH^+$ group is present in the complex. Obviously, in this case the aminothiolate also behaves as a unidentate ligand, as in **2** and **3**, but now it is in zwitterionic form.

Peaks corresponding to NH_2 groups of the ethylenediamine ligand are also apparent in the spectra of **2** [δ 5.49(s)], **3** [5.42(s)] and **4** [5.63(s) and 5.77(s) in a 1:1 ratio; these coalesce at 35 °C].

The Structure of Complex **1**.—This consists of a cyclic trimer with a central Pt_3S_3 six-membered ring (Fig. 1). The ring is markedly non-planar, with a twist-boat conformation: an approximate C_2 axis lies along the Pt(3) $\cdots$ S(1) line when only the atoms of the ring are considered, but there is no approximate symmetry of any kind for the molecule as a whole. Each aminothiolate ligand chelates one Pt atom to give a $PtSC_2N$ ring with an envelope conformation; the α-carbon atom in each ligand lies out of the mean plane of the four other atoms of the chelate ring [deviations 0.669, 0.636 and 0.749 Å from planes with root-mean-square (r.m.s) deviations of 0.071, 0.037 and 0.048 Å respectively]. The sulfur atoms also act as bridges between Pt atoms to give the central Pt_3S_3 ring. Each Pt atom is co-ordinated by two S, one N and one terminally bonded Br atom in a square-planar geometry with the two sulfurs mutually *cis*. Deviations of the constituent atoms from each PtS_2NBr mean plane are all less than 0.09 Å; dihedral angles between pairs of mean planes are 117.6, 102.3 and 95.2°. The smallest angle at each Pt atom is the intrachelate N–Pt–S angle (mean 86.8°), but there is no regular pattern in the deviations of other co-ordination angles from the ideal square-planar values of 90 and 180°, nor in the Pt–S bond lengths around the central ring. The distances between Pt atoms are all greater than 3.6 Å and indicate no direct metal–metal bonding. The Pt–S–Pt angles, like the other angles at the sulfur atoms, are fairly close to the ideal tetrahedral value of 109.5°; the smallest angle at each S atom is the intrachelate Pt–S–C angle, somewhat below 100° in each case.

We have already commented above on the major differences between this trinuclear structure and the hexanuclear structure of the $[Pt_6\{S(CH_2)_2NH_2\}_8]^{4+}$ cation **5**;[10] the methyl groups bonded to nitrogen in **1** probably prevent the formation of a hexanuclear species. We note, however, that the centrosymmetric hexanuclear structure of **5** contains two symmetry-

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[*] *Note added at proof.* A mononuclear nickel complex with a *cis* disposition of two D-penicillamine ligands has been reported recently, $[Ni\{SC(CH_3)_2CH(NH_2)COO\}_2]^{2-}$.[29]

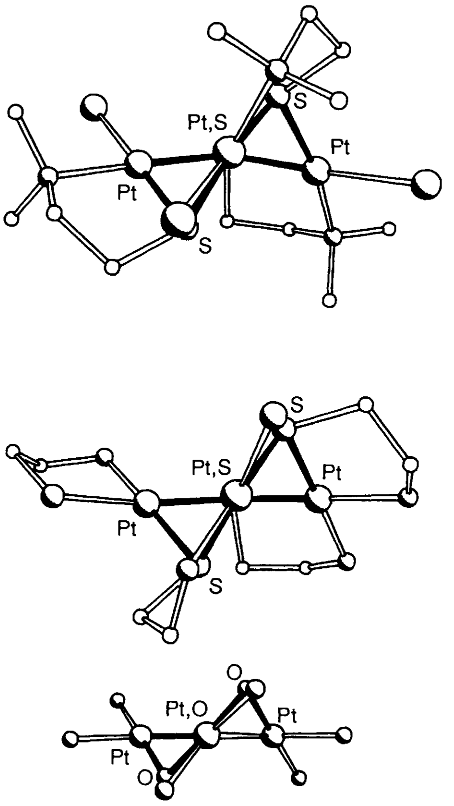

Fig. 2 Comparison of the structure of complex **1** (top) with half the molecule of **5** (middle) and with one form of $[\{Pt(\mu\text{-}OH)(NH_3)_2\}_3]^{3+}$ (bottom)

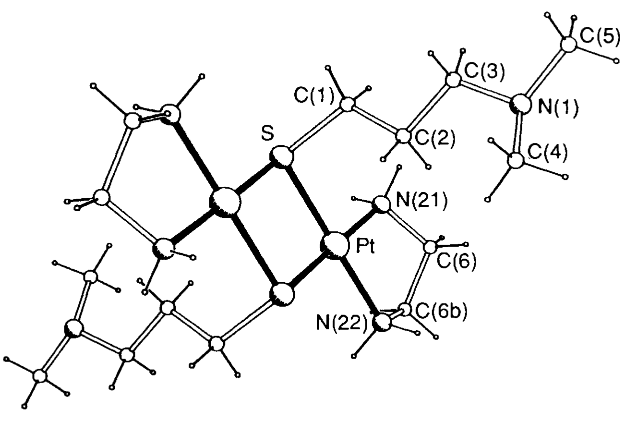

Fig. 3 The structure of the cation of complex **2**, with the labelling of the independent atoms

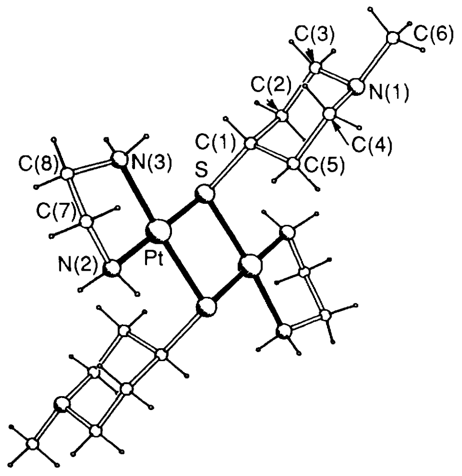

Fig. 4 The structure of the cation of complex **3**, with the labelling of the independent atoms

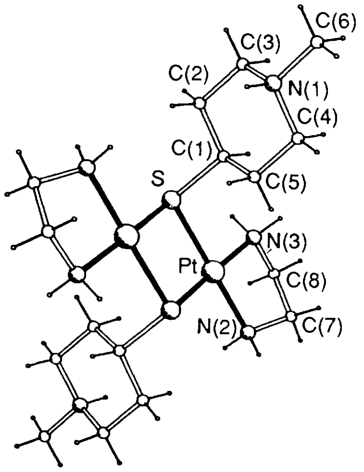

Fig. 5 The structure of the cation of complex **4**, with the labelling of the independent atoms

equivalent Pt_3S_3 rings, and the geometry and conformation of these is very similar to that reported here for **1**. A least-squares superposition of the rings of the two structures gives a r.m.s. deviation of only 0.13 Å, despite the quite different disposition of ligands around the Pt_3S_3 ring in each case.

A similar comparison can be made with one of the structures observed for the $[\{Pt(\mu\text{-}OH)(NH_3)_2\}_3]^{3+}$ cation. The hydrated sulfate[36] contains a cation of essentially C_{3v} symmetry, with a chair conformation (or crown shape) for the central Pt_3O_3 ring, the three O atoms all lying on one side of the Pt_3 plane. The nitrate,[37] however, contains a cation of lower, approximately C_2 symmetry, with a twist-boat conformation for the central Pt_3O_3 ring; one O atom lies essentially in the Pt_3 plane, the other two lie one on each side of it. This arrangement closely resembles the Pt_3S_3 ring in **1**. In spite of the obvious differences between the Pt–O bond lengths and Pt–O–Pt angles in this hydroxy-bridged complex and the Pt–S bond lengths and Pt–S–Pt angles in complex **1**, an r.m.s. deviation of 0.25 Å for a least-squares superposition of the observed Pt_3O_3 and Pt_3S_3 ring geometries indicates a remarkable degree of similarity.

The three structures which we have compared are shown together in Fig. 2, viewed in each case along the pseudo-C_2 axis of the central six-membered ring. The fact that **1** is found in this conformation, and not with approximate C_3 symmetry comparable to the $[\{Pt(\mu\text{-}OH)(NH_3)_2\}_3]^{3+}$ cation in its sulfate salt, must throw some doubt on the suggestion[36] that the C_2 form of the hydroxy-bridged trimer cation is intrinsically less stable than the C_{3v} form.

The Structures of Complexes **2**–**4**.—These complexes are all hydrated or anhydrous bromide salts of dinuclear $[(en)Pt(\mu\text{-}SR)_2Pt(en)]^{n+}$ cations, with $n = 2$ for **2** and **3** and $n = 4$ for **4**. The different overall charge for the cation of **4** is a consequence of protonation of the nitrogen atoms of the non-chelating aminothiolate ligands, and is of no significant consequence for the essential composition and geometry of the cation. Thus the three cations differ chemically only in the nature of the thiolate substituent group R, and their core geometries are all essentially identical (Figs. 3–5). They all have crystallographically imposed inversion symmetry. Consequently, the central Pt_2S_2 ring in each case is exactly planar, and the thiolate substituents lie on opposite sides of the ring, in

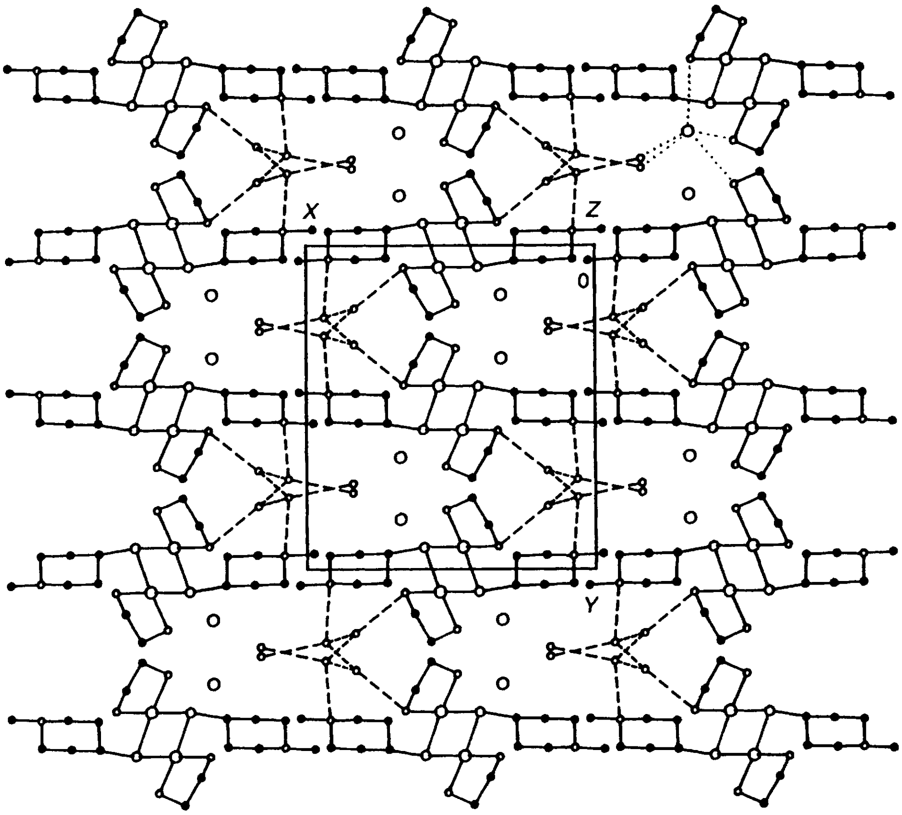

Fig. 6 The crystal packing of complex **3**, seen in projection along the *c* axis. Hydrogen bonding O ··· O and N ··· O is shown with dashed lines; H atoms are omitted. The five shortest Br ··· O and Br ··· N contacts are shown dotted for one Br^- anion, at the top right

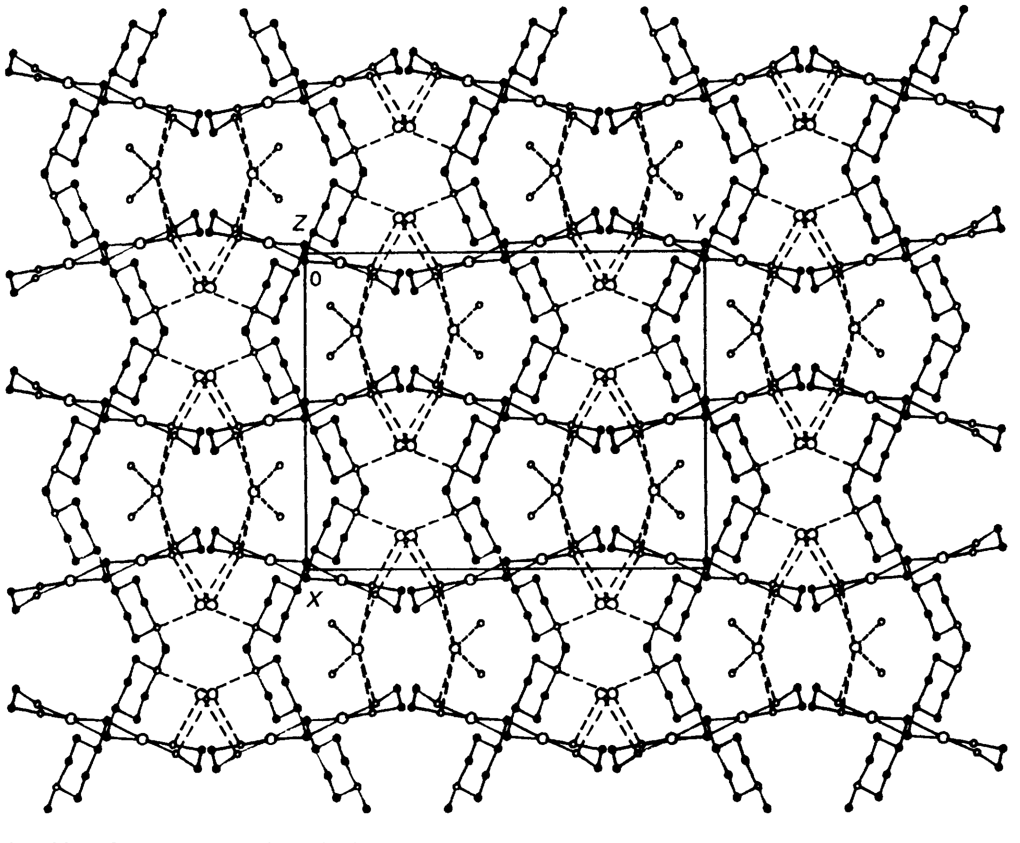

Fig. 7 The crystal packing of complex **4**, seen in projection along the *c* axis. Hydrogen bonding Br ··· O and Br ··· N is shown with dashed lines; H atoms are omitted

the ring plane normals are 25.1, 28.5 and 26.4° for **2**, **3** and an *anti* configuration; the angles between the S–C bonds and **4** respectively. The thiolate ligands function as symmetrical bridges. The central $Pt_2S_2N_4$ core of each cation has essentially D_{2h} symmetry.

The non-planar five-membered Pt(en) chelate rings have the usual twist conformation, with one carbon atom above and the other below the PtN_2 plane; this conformation best accommodates approximately tetrahedral geometry at the C and N atoms, square-planar co-ordination of Pt, and a staggered *gauche* arrangement for the N–C–C–N linkage. The intrachelate N–Pt–N angle, dictated by the N . . . N 'bite' of the bidentate ethylenediamine ligand, is significantly reduced from the ideal square-planar angle of 90°, as is the S–Pt–S angle within the central Pt_2S_2 ring in each of the cations. There is also a small twist distortion of the Pt square-planar co-ordination geometry, which is measured by the dihedral angle between PtS_2 and PtN_2 planes. This angle, which would be 0° for ideal square-planar co-ordination, is 2.1° in **2**, 4.8° in **3**, and 6.2° in **4**. The Pt–S bond lengths are similar to those in **1**.

The same basic shape for the tricyclic core is found in a number of aminothiolato-bridged dinuclear complexes of Ni, Pd and Pt with chelating diphosphine ligands (L–L), $[(L\text{–}L)M(\mu\text{-}SR)_2M(L\text{–}L)]^{2+}$, with a planar central M_2S_2 ring.[6] Such an arrangement is, however, by no means universal for complexes of the type $[(L)L'M(\mu\text{-}SR)_2ML(L')]$ (M = Ni, Pd or Pt) with a variety of thiolates SR and ligands L and L′. The central M_2S_2 ring may be planar or folded, with the dihedral angle between the two MS_2 planes (which measures the degree of folding about the S · · · S line) ranging from 180 down to 110°.[6,38] There is no obvious relationship between the degree of ring folding and the nature of the ligands in these complexes.

The aliphatic substituents of the thiolate bridging ligands are of unremarkable geometry. The carbon chain in complex **2** has an extended conformation, with an *anti* arrangement of substituents on each C–C bond. The piperidine rings of **3** and **4** have a chair conformation with both the thiolate S atom and the methyl substituent placed equatorially.

The hydrated complexes **3** and **4** have extensive networks of hydrogen bonding, involving ethylenediamine NH_2, piperidine N or NH^+, Br^- counter ions and H_2O molecules. In **3** the water molecules are grouped together in hydrogen-bonded clusters of $6H_2O$, which are then further linked to ethylenediamine (by N–H · · · O) and piperidine (pip) (by O–H · · · N) nitrogen atoms (Fig. 6). The shortest O · · · O distances are 2.793, 2.812 and 2.855 Å, shortest O · · · N(en) is 2.803 Å, and shortest O · · · N(pip) is 2.793 Å. Interactions with the bromide anions are weaker, with no Br · · · O or Br · · · N distances under 3.38 Å: shortest Br · · · O are 3.384 and 3.421 Å, shortest Br · · · N(en) 3.450, 3.454 and 3.556 Å. These contacts are shown for just one bromide anion in Fig. 6.

In complex **4** all the hydrogen bonds involve bromide ions (Fig. 7). One of the two crystallographically independent anions forms hydrogen bonds with two water molecules (Br · · · O 3.333 and 3.366 Å) and with two en NH_2 groups in different cations (Br · · · N 3.295 and 3.315 Å); the other forms hydrogen bonds with two en NH_2 groups in different cations (Br · · · N 3.414 and 3.455 Å) and with one piperidinium NH^+ (Br · · N 3.350 Å). All O–H and N–H bonds in both structures participate in hydrogen bonding.

Hydrogen bonding in the anhydrous complex **2** is restricted to (en)N–H · · · Br and (en)N–H · · · N(aminothiolate) interactions, with shortest N · · · Br distances of 3.264, 3.532 and 3.552 Å and N · · · N of 2.932 Å. This structure is somewhat complicated by disorder, which affects most of the atoms of the cations; only the anions, together with the Pt atoms and the C atoms of the en ligands, are ordered. The disorder, with 1:1 occupancies imposed by crystallographic symmetry, takes the form of two alternative orientations of the entire cation, the dihedral angle between the two possible positions of the central Pt_2S_2 ring being 57.9°.

Acknowledgements

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