Platinum(II) and Palladium(II) Complexes with 2-Amino-4-methylsulfanylbutanol and 2-(Ethylsulfanyl)ethylamine†

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The reaction of $K_2[PtX_4]$ (X = Cl or Br) with 2-(ethylsulfanyl)ethylamine (esea) (molar ratio 1:1) in aqueous solution yielded ionic $[Pt(esea)_2][PtX_4]$ complexes which undergo thermal rearrangement to $[PtX_2(esea)]$. By treating $[PtCl_2(esea)]$ or $[PtX_2(ambo)]$ (ambo = L-2-amino-4-methylsulfanylbutanol; X = Cl or Br) with an excess of the corresponding $[PtX_4]^{2-}$ in water the binuclear complexes $K[Pt_2Cl_5(esea)]$ and $K[Pt_2X_5(ambo)]$ have been obtained. The crystal structure of $K[Pt_2Cl_5(ambo)]$ was determined by X-ray crystallography and refined to $R = 0.034$, based on 1685 observed reflections. This binuclear complex, in which the ambo ligand is chelated to Pt(1) through the N and S donor atoms and also co-ordinated to Pt(2) through the S atom, is the first example of a chelated methionine derivative with S acting as bridging donor. The Pt atoms are four-co-ordinate in a slightly distorted square-planar geometry. Selected bond distances are Pt–Cl 2.30 (mean of five values), Pt–S 2.26 (mean), and Pt–N 2.05(1) Å; the Pt(1)–S–Pt(2) angle is 116.8(2)°. Proton NMR spectra support rupture of the sulfur bridge of the binuclear complexes in dimethyl sulfoxide to form the corresponding $[PtX_2L]$ species. The presence of equilibria between ionic and neutral species in the same solvent is also discussed.

As a part of the study on methionine and analogues we recently reported on palladium and platinum dihalide complexes with L-methioninol (L-2-amino-4-methylsulfanylbutanol, ambo).[1] By reaction of MX_2(M = Pd or Pt, X = halide) with ambo in organic media either $[MX_2(ambo)]$, in which the ligand is S,N-chelated, or $[MX_2(ambo)_2]$ complexes, in which the ligand is S-monodentate, have been obtained. In aqueous solution the behaviour of the $[PdX_4]^{2-}$–ambo system differs from that of $[PtX_4]^{2-}$–ambo. In the first case the neutral $[PdX_2(ambo)]$ species were obtained, whereas addition of ambo to aqueous $[PtX_4]^{2-}$ in 1:1 molar ratio resulted in the immediate precipitation of ionic $[Pt(ambo)_2][PtX_4]$ complexes, which transformed into the corresponding $[PtX_2(ambo)]$ adducts either in solution or by thermal rearrangement in the solid phase. Under analogous conditions methionine (Met) reacts with both $[PdCl_4]^{2-}$ and $[PtCl_4]^{2-}$ yielding neutral 1:1 complexes,[2–7] whereas $[PtL_2][PtX_4]$ species were obtained when the ligands were bis(thioethers) or aminoethers, their thermal behaviour resembling that of the ambo analogues.[8–11] Moreover, by treating $[PtX_4]^{2-}$ with methionine at 1:2 molar ratio in aqueous solution, soluble 1:2 complexes were formed in which either S,N-chelated or S-monodentate ligand was present.[12,13] The interest in those systems concerns the interaction of platinum-based drugs with the methionine residues of proteins, leading to formation of various metabolites, such as $[Pt(MetO)_2]$ (MetO = methioninate).[13–25]

This paper reports a study on the interaction of $[PtX_4]^{2-}$ (X = Cl or Br) with ambo and 2-(ethylsulfanyl)ethylamine (esea) in aqueous solution at various molar ratios.

Experimental

Chemicals.—The reagents L-2-amino-4-methylsulfanylbutanol (Janssen) and 2-(ethylsulfanyl)ethylamine hydrochloride (Aldrich) were used as supplied. Platinum and palladium salts were Johnson Matthey products. The complexes $[MX_2(ambo)]$ and $[MX_2(L\text{-}Met)]$ (M = Pd or Pt, X = Cl or Br) were prepared as reported in refs. 1–4 and 26.

Preparation of the Complexes.—The complex $K[Pt_2Cl_5(ambo)]$ was prepared by adding solid $[PtCl_2(ambo)]$ (0.2 mmol) to an aqueous solution of $K_2[PtCl_4]$ (0.6 mmol in 7 cm^3) with vigorous stirring. The pale yellow 1:1 complex dissolved slowly (1 h) at room temperature leaving a small residue which was discarded. By slow evaporation in the air (1 week) the deep orange solution yielded well formed orange crystals which were filtered off, washed with water, MeOH and Et_2O and dried under reduced pressure (yield 55%). The same product was obtained in a lower yield by adding a methanolic solution of ambo (0.5 mmol in 1 cm^3) to aqueous $K_2[PtCl_4]$ (1 mmol in 5 cm^3). A yellow powder precipitated within a few minutes, which was filtered off. By slow evaporation the orange solution gave a few $K[Pt_2Cl_5(ambo)]$ crystals, which were used for structural work. The amount of the yellow product obtained as a first precipitate changed in different preparations (yield 10–25%), related samples showing identical infrared spectra [3430s (br), 3180w (br), 3110 (sh, br), 1575 (br); ν(Pt–Cl) 330 cm^{-1}]. Elemental analyses were not reproducible owing to the presence of variable water contents {Found: C, 13.2; H, 3.8; N, 3.0. Calc. for $[PtCl_2(ambo)]$: C, 15.0; H, 3.3; N, 3.5%}. When the solid was left in the mother-liquor overnight with stirring it turned into $[PtCl_2(ambo)]$ [3441s, 3247m, 3118m, 3135 (sh), 1589m, 1567m; ν(Pt–Cl) 330 and 324 cm^{-1}].

The complex $K[Pt_2Br_5(ambo)]$ was prepared by reaction of $[PtBr_2(ambo)]$ with $K_2[PtBr_4]$ (molar ratio 1:3) following the above procedure.

The $[PdX_2(ambo)]$ (X = Cl or Br) complexes did not show any tendency to dissolve in aqueous solutions containing an excess of the corresponding $[PdX_4]^{2-}$ ion, also on heating up to *ca.* 70 °C, the initial product being unchanged within a few days. Conversely they dissolve slowly at room temperature in aqueous $[PtX_4]^{2-}$ (molar ratio 1:3), yielding on evaporation the corresponding $K[Pt_2X_5(ambo)]$ complexes.

The complex $K[Pt_2Cl_5(esea)]$ was prepared by dissolving

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical data for the complexes

		Analysis (%)			
Compound	Colour	C	H	N	S
[$PtCl_2$(esea)]	Yellow	13.10	2.75	3.55	8.65
		(12.95)	(2.95)	(3.80)	(8.65)
[$PtBr_2$(esea)]	Yellow	10.70	2.25	2.85	7.10
		(10.45)	(2.40)	(3.05)	(6.95)
[$PdCl_2$(esea)]	Orange	17.35	3.85	5.10	11.65
		(17.10)	(3.90)	(4.95)	(11.35)
[Pt(esea)$_2$][$PtCl_4$]	Pink	13.00	2.80	3.45	9.60
		(12.95)	(2.95)	(3.80)	(8.65)
[Pt(esea)$_2$][$PtBr_4$]	Beige	10.35	2.05	2.80	6.85
		(10.45)	(2.40)	(3.05)	(6.95)
K[Pt_2Cl_5(esea)]	Pale pink	7.35	1.45	1.90	5.20
		(6.75)	(1.55)	(1.95)	(4.50)
K[Pt_2Cl_5(ambo)]	Orange	8.05	1.65	1.80	4.30
		(8.10)	(1.75)	(1.90)	(4.30)
K[Pt_2Br_5(ambo)]	Orange	5.95	1.10	1.35	3.15
		(6.25)	(1.35)	(1.45)	(3.35)

Table 2 Crystal and intensity data for K[Pt_2Cl_5(ambo)]

Formula	$C_5H_{13}Cl_5KNOPt_2S$
M	741.55
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	7.621(3)
b/Å	8.419(3)
c/Å	12.194(4)
β/°	91.42(4)
U/Å^3	782
D_c/g cm^{-3}	3.15
Z	2
F(000)	668
μ(Mo-Kα)/cm^{-1}	191
Scan method	θ–2θ
Scan speed/° min^{-1}	2
θ_{max}/°	28
hkl ranges	−10 to 10, 0–11, 0–16
Recorded reflections	1793
Unique reflections	1717
Observed reflections	1685 [$I > 3\sigma(I)$]
Corrections	Lorentz polarization, absorption[27b]
Final R	0.034

Table 3 Fractional coordinates

Atom	x	y	z
Pt(1)	0.273 32(7)	0.799 900	0.158 58(4)
Cl(1)	0.221 6(6)	0.617 1(7)	0.020 2(4)
Cl(2)	0.367 8(7)	0.600 7(7)	0.274 7(4)
O	0.245(2)	1.063(2)	−0.171(1)
N	0.192(2)	0.969(2)	0.047(1)
C(1)	0.258(2)	1.175(2)	−0.084(1)
C(2)	0.325(2)	1.093(2)	0.020(1)
C(3)	0.341(2)	1.211(2)	0.115(1)
C(4)	0.435(2)	1.147(2)	0.217(1)
S	0.312 5(5)	0.994 0(5)	0.283 7(3)
C(5)	0.461(2)	0.941(3)	0.394(1)
Pt(2)	0.067 61(7)	1.109 0(1)	0.348 57(4)
Cl(5)	0.235 8(6)	1.280 4(6)	0.453 6(3)
K	−0.020 1(6)	1.582 8(5)	0.359 9(3)
Cl(3)	−0.109 7(5)	0.938 0(5)	0.251 0(3)
Cl(4)	−0.177 9(6)	1.234 7(6)	0.413 5(4)

[$PtCl_2$(esea)] in aqueous $K_2[PtCl_4]$ (molar ratio 1:4) with gentle heating (60 °C). The saturated solution was filtered at room temperature from the residual 1:1 complex. On evaporation nice crystals of the binuclear complex were obtained, which were separated mechanically from the coprecipitated powdered [Pt(esea)$_2$][$PtCl_4$]. The analogous [$PtBr_2$(esea)]–[$PtBr_4$]$^{2-}$ system behaves similarly, the binuclear complex being probably present in solution, whereas the evaporation residue is essentially a mixture of the neutral and ionic 1:1 species.

The [Pt(esea)$_2$][PtX_4] (X = Cl or Br) complexes were obtained by adding aqueous esea·HCl (0.4 mmol) to an aqueous solution of $K_2[PtX_4]$ (0.35 mmol in 5 cm^3). The product, which precipitated immediately, was filtered off, washed with water and dried under reduced pressure. The complexes [PtX_2(esea)] were obtained by heating the corresponding [Pt(esea)$_2$][PtX_4] species in oil-bath to 160 °C. Attempts to synthesize the 1:1 neutral adducts by treating PtX_2 with esea in methanol yielded mixtures of ionic and neutral species.

The [$PdCl_2$(esea)] complex precipitated immediately by addition of esea·HCl to an aqueous solution of $K_2[PdCl_4]$ (molar ratio 1:1). The orange product was washed with water and MeOH and dried *in vacuo*.

Analytical data for the complexes are given in Table 1.

Measurements.—Elemental analyses were carried out on a Carlo Erba 1106 microanalyser at the Department of Inorganic Chemistry of the University of Padova. Infrared spectra were recorded on Nicolet 5SXC FT-IR and 20 far-IR spectrometers as either Nujol mulls between KBr and polyethylene discs or KBr pellets. The NMR (^1H and ^{13}C) spectra were measured in deuteriated dimethyl sulfoxide using a JEOL FX 90Q spectrometer (in ppm from $SiMe_4$ as internal standard; proton-decoupled ^{13}C).

Crystallography.—A crystal of K[Pt_2Cl_5(ambo)] of maximum dimension 0.2 mm was used for the analysis. Data collection was made with Mo-Kα radiation on a Philips PW 1100 (FEBO System) diffracrometer. Cell dimensions were determined by least-squares refinement of 15 medium-angle settings. Crystal and intensity data are reported in Table 2. The crystal was stable under irradiation. The structure was solved by standard methods, followed by full-matrix least-squares refinement of the atomic parameters. The H atoms were located on the electron-density maps, but were introduced in calculated positions with fixed C–H distances and thermal parameters (C–H 1.08 Å, U_{iso} = 0.08 Å^2). Anisotropy was introduced for the non-hydrogen atoms. Refinement of scale factor, positional and thermal parameters minimized the function $\Sigma w(\Delta F)^2$ with $w = 1$. Form factors for the atoms were supplied internally by the SHELX program system.[27a]

Final atomic parameters are listed in Table 3, bond distances and angles in Table 4.

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

Results and Discussion

The nature of the products obtained by treating [$PtCl_4$]$^{2-}$ with ambo in aqueous solution depends essentially on the reagent molar ratio. By operating at 1:2 a colourless solution of *trans*-[$PtCl_2$(ambo)$_2$] was formed which, on evaporating, yielded a colourless oil, owing to the high hygroscopicity of the product. At 1:1 molar ratio immediate precipitation of pink [Pt(ambo)$_2$][$PtCl_4$] takes place, the residual yellow solution giving on evaporation small fractions of [$PtCl_2$(ambo)]. When ambo was added to aqueous [$PtCl_4$]$^{2-}$ in molar ratio 0.5:1 a yellow powder separated in a short time, the solution turning from pink to deep orange. After filtration of the solid fraction, the solution gave, by slow evaporation in the air, orange crystals of the binuclear complex K[Pt_2Cl_5(ambo)]. The characteristics of the first yellow precipitate change with time. If the product is filtered within 1 h it seems to consist of a hydrated 1:1 adduct in which the ligand is bound to platinum by sulfur only. When

Table 4 Bond distances or contacts (Å) and angles (°) in K[Pt_2Cl_5(ambo)]

Pt(1)–Cl(1)	2.311(5)	Pt(2)–Cl(5)	2.299(5)
Pt(1)–Cl(2)	2.300(5)	Pt(2)–Cl(4)	2.307(5)
Pt(1)–S	2.251(4)	Pt(2)–Cl(3)	2.288(4)
Pt(1)–N	2.05(1)	Pt(2)–S	2.263(4)
N–C(2)	1.49(2)	O–C(1)	1.42(2)
C(1)–C(2)	1.54(2)	S–C(5)	1.79(2)
C(2)–C(3)	1.54(2)	C(4)–S	1.80(2)
C(3)–C(4)	1.52(2)		
K ··· Cl(5)	3.388(7)	K ··· Cl(4)	3.241(7)
K ··· Cl(2^I)	3.161(6)	K ··· Cl(3^{II})	3.335(6)
K ··· Cl(4^{II})	3.369(7)	K ··· Cl(5^{II})	3.291(7)
K ··· O(^{III})	2.837(7)		
N–Pt(1)–Cl(1)	86.2(4)	Cl(1)–Pt(1)–S	175.0(2)
Pt(1)–S–C(4)	106.1(5)	Pt(1)–S–C(5)	113.4(7)
N–Pt(1)–S	88.9(4)	Cl(2)–Pt(1)–S	94.4(2)
Cl(2)–Pt(1)–N	176.5(4)	Pt(1)–N–C(2)	116(1)
Cl(1)–Pt(1)–Cl(2)	90.5(2)	C(2)–C(3)–C(4)	115(1)
N–C(2)–C(3)	109(1)	C(4)–S–C(5)	101.3(8)
C(3)–C(4)–S	113(1)	Pt(1)–S–Pt(2)	116.8(2)
C(4)–S–Pt(2)	107.1(5)	C(2)–C(1)–O(1)	110(2)
N–C(2)–C(1)	107(1)	S–Pt(2)–Cl(4)	178.6(2)
C(1)–C(2)–C(3)	111(1)	S–Pt(2)–Cl(5)	90.6(2)
S–Pt(2)–Cl(3)	91.8(2)	Cl(5)–Pt(2)–Cl(4)	88.1(2)
Cl(3)–Pt(2)–Cl(4)	89.6(2)	Cl(5)–Pt(2)–Cl(3)	177.1(2)
C(5)–S–Pt(2)	110.7(7)		
Possible hydrogen bond			
Cl(3) ··· H(1)N	2.676	N–H ··· Cl(3)	127.3(3)
Cl(3) ··· N	3.439		

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

filtered after 1 d the solid has transformed into the normal [$PtCl_2$(ambo)] complex. Since binuclear species should result from the interaction of $[PtX_4]^{2-}$ with the neutral 1 : 1 adduct, the K[Pt_2X_5(ambo)] (X = Cl or Br) complexes were prepared by dissolving [PtX_2(ambo)], nearly insoluble in water, in aqueous solutions containing an excess of $[PtX_4]^{2-}$. No evidence for binuclear species was observed upon reaction of [PdX_2(ambo)] with an excess of $[PdX_4]^{2-}$, the neutral adduct being insoluble also on heating. The [PtX_2(L-Met)]–$[PtX_4]^{2-}$ system showed an analogously inert behaviour, whereas addition of L-Met to $[PtX_4]^{2-}$ (molar ratio 1:2) gave immediate precipitation of a yellow solid which, as in the case of ambo, should contain S-monodentate methionine in 1 : 1 stoichiometry. Subsequent evaporation of the residual yellow solution yielded [PtX_2(L-Met)] crystals. Attempts to obtain bimetallic complexes were unsuccessful. No reaction takes place in the [$PtCl_2$(ambo)]–$[PdCl_4]^{2-}$ system, whereas [$PdCl_2$(ambo)] has been found to undergo total ligand exchange in the presence of $[PtCl_4]^{2-}$ yielding K[Pt_2Cl_5(ambo)].

Owing to the fact that binuclear species were obtained only for the platinum–ambo system, which at the same time was the only system which formed ionic 1 : 1 species, our attention was turned to the S,N-chelating ligand esea, the behaviour of which is very similar to that of ambo. Accordingly (Table 1) the $[Pt(esea)_2][PtX_4]$ species have been prepared, which undergo phase transition on heating to form the corresponding [PtX_2(esea)] complexes. Formation of binuclear species is less easy than for ambo. By reaction of [$PtCl_2$(esea)] with an excess of aqueous $[PtCl_4]^{2-}$ a few crystals of K[Pt_2Cl_5(esea)] have been isolated, whereas no evidence of the bromo-analogue was found among the reaction products.

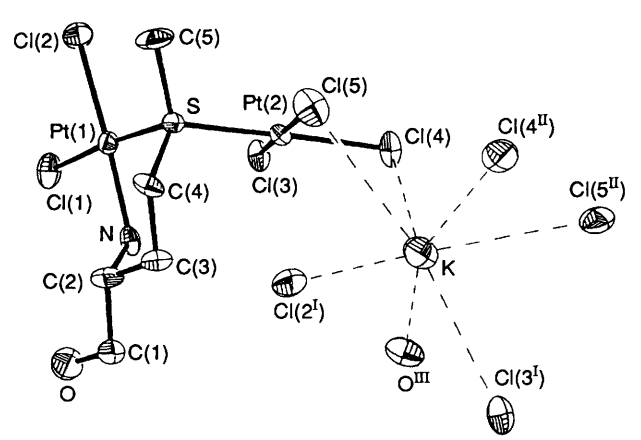


Fig. 1 Crystal structure of K[Pt_2Cl_5(ambo)] with the potassium environment. The symmetry codes are listed in Table 4

Crystal Structure.—The structure of K[Pt_2Cl_5(ambo)] (Fig. 1) reveals that the two metal ions of the binuclear anion are linked through a sulfur bridge. In this way the ligand is chelated to Pt(1) through the N and S donor atoms and co-ordinated to Pt(2) through the same S atom. The co-ordination geometry around each platinum is essentially square planar but small deviations with respect to the ideal model are observed in the Pt(1) angles because of the different steric hindrances of the co-ordinated atoms. Mean-plane calculations show that the donor atoms are coplanar within 0.02 Å around Pt(1) and within 0.03 Å around Pt(2). The dihedral angle between the $NSCl_2$ and SCl_3 planes is 80.8°. The Pt–Cl distances range between 2.288(4) and 2.311(5) Å (mean 2.30 Å) which compares well with the sum of the covalent radii (2.29 Å). Also the Pt–N distance of 2.05(1) Å corresponds to the covalent radii sum, whereas the Pt(1)–S [2.251(4) Å] and Pt(2)–S [2.263(4) Å] distances are significantly shorter. The angles at the sulfur atom are distorted with respect to the tetrahedral values, the evident asymmetry between the large Pt(1)–S–Pt(2) angle [116.8(2)°] and the small C(4)–S–C(5) angle [101.3(8)°] being clearly attributable to the different dimensions of the bonded atoms. The hexaatomic ring resulting from the chelation to Pt(1) shows a chair configuration, as was observed in [$PtCl_2$L] {L = L-Met or DL-ethionine [DL-$EtS(CH_2)_2CH(NH_2)CO_2H$]} complexes.[28,29] Bond distances in the present complex are very close to the values reported for those, whereas the N–Pt(1)–S angle [88.9(4)°] is smaller {99.0(2)° in [$PtCl_2$(L-Met)] and 97.3(2)° in [$PtCl_2$L] (L = ethionine)}. The hydrogen H(1) of the amine group makes a contact of 2.676 Å with Cl(3) which can be regarded as an intramolecular hydrogen bond. Each K^+ ion is surrounded by six Cl atoms of three different anions with similar K ··· Cl distances and by one oxygen atom (see Table 4) in an environment which cannot be described as a regular polyhedron. The packing is arranged in such a way that all Cl atoms of the anions, apart from Cl(1), are involved in significant Cl ··· K contacts. In particular, while Cl(2) and Cl(3) make contacts with one K^+ ion, Cl(4) and Cl(5) make comparable contacts with two other K^+ ions, which gives stability and compactness to the entire structure, as shown also by the relatively high value of the crystal density. The anion is particularly compact, a quite rare situation for the sulfur atom, which binds two carbon atoms and at the same time bridges through both lone pairs. A similar behaviour has been observed in dimeric [$\{PtX_2(R_2S)\}_2$] complexes, in which the dialkyl sulfide molecules form two nearly symmetric bridges between the platinum atoms.[30,31] Conversely, sulfur bridges are usual in aminothiolato complexes.[32–34] As an example, in the hexanuclear $[Pt_6(SCH_2CH_2NH_2)_8]Br_4$ complex all sulfur atoms of the S,N-chelated anions bind two nearby platinum atoms, leading to an extended network of bridges. Reference can be made also to the binuclear complex [$Pt_2Cl_3(PEt_3)_2(S_2CNMe_2)$], where the dithiocarbamato ion is bidentate in the $PtCl(PEt_3)(S_2CNMe_2)$ moiety and at the same time bonds, *via*

Table 5 Proton NMR data for the complexes in $(CD_3)_2SO$ (25 °C)

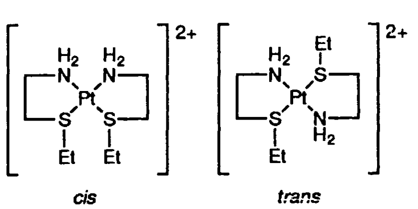
Compound	NH_2			SCH_2CH_3	
$[PdCl_2(esea)]$			5.12		1.42
$[PtCl_2(esea)]$ *a*			5.60		1.31
b		6.21w	5.60s	1.33w	1.31s
$[PtBr_2(esea)]$ *a*			5.64		1.33
b		6.17s	5.64w	1.36s	1.33w
$[Pt(esea)_2][PtCl_4]$ *c*	6.81	6.30		1.33	
d		6.24		1.34	1.31vw
e		6.24w	5.62s	1.35w	1.33s
$[Pt(esea)_2][PtBr_4]$ *a*	6.50w	6.16s	5.65w	1.33 (br)	
b		6.17s	5.62w	1.35s	1.33w
$K[Pt_2Cl_5(esea)]$ *a*			5.59		1.33
b		6.21w	5.60s		1.31s
$K[Pt_2Cl_5(ambo)]$[f]			5.0 (br)		2.50, 2.46w[g]
$K[Pt_2Br_5(ambo)]$[f]			5.0 (br)		2.53[g]

[a] Spectrum recorded immediately after sample dissolution. [b] After 5 h. The spectrum does not change within 1 week. [c] Saturated solution immediately after preparation. [d] Saturated solution within 10 min. [e] Pale yellow solution formed within 3 d. [f] The OH signal superimposes with the NH_2 resonance. [g] SCH_3 proton signals of co-ordinated ligand (free ambo; SCH_3, δ 2.01; NH_2, 2.70; OH, 3.89).

one of the sulfur atoms, to the second platinum atom bearing two chlorines and one PEt_3 molecule.[35]

Infrared Spectra.—Absorptions above 3000 cm^{-1} for the esea complexes originate from ν(NH) vibrations of the co-ordinated amino group. The related bands, for $[Pt(esea)_2][PtCl_4]$ at 3205s, 3174 (sh), 3117w and 3085w cm^{-1}, are slightly shifted to higher energy for $[PtCl_2(esea)]$ [3225s, 3194 (sh), 3103w cm^{-1}]. The $\delta(NH_2)$ vibrations occurs as one band (1563m cm^{-1}) for the ionic complex, whereas two bands (1571m and 1546w cm^{-1}) are observed for $[PtCl_2(esea)]$. The spectra of the bromo-analogues show a similar trend, apart from some small band shifts. The spectra of $K[Pt_2X_5(ambo)]$ (X = Cl or Br) are identical above 3000 cm^{-1} and contain, along with the ν(NH) absorptions at 3240m, 3207m, 3136w cm^{-1}, a strong ν(OH) band at 3440 cm^{-1}. The related $\delta(NH_2)$ absorptions are halide dependent (X = Cl, 1586; X = Br, 1595w and 1580 cm^{-1}). As expected for a *cis* geometry, the spectra of $[MX_2(esea)]$ (M = Pd or Pt) display, in the far-infrared region, two strong absorptions assigned to M–X vibrations (M = Pd, X = Cl, 329 and 305; M = Pt, X = Cl, 329 and 308, X = Br, 221 and 208 cm^{-1}) whereas the square-planar anion in $[Pt(esea)_2][PtX_4]$ gives one strong band at 319 (Cl) or 231 cm^{-1} (Br). As regards $K[Pt_2X_5(ambo)]$, the presence of several bands assignable to platinum–halide vibrations (X = Cl, 351m, 336m, 318s and 301m; X = Br, 247m, 235m, 221s and 189m cm^{-1}) is in accordance with the presence of two platinum moieties. The corresponding ν(Pt–X) absorptions of $[PtX_2(ambo)]$ were at 330 and 324 cm^{-1} for X = Cl, and 223 cm^{-1} for X = Br. Moreover, complexes containing the $[PtX_3L]^-$ anion, in which L = phosphine, arsine or thioether, show more Pt–X bands in the 350–270 (X = Cl) and 250–200 cm^{-1} (X = Br) regions.[36–38]

NMR Spectra.—Owing to their low solubility in common solvents, the NMR spectra of the complexes have been measured in deuteriated dimethyl sulfoxide (Table 5). Only the NH_2 and CH_3 (SEt) signals have been reported for the esea complexes, the ethylene multiplets being partly superimposed in the δ 1.8–3.3 range. The chelated structure is retained in this solvent, the SEt and NH_2 signal positions being as expected for S,N co-ordination.[1,26,39] The spectrum of $[PdCl_2(esea)]$ contains one signal for each proton group and is unchanged within 1 week. Conversely, the spectrum of the platinum complex changes with time, indicating the presence of an equilibrium between ionic and neutral species in dimethyl sulfoxide. The proton spectrum of $[PtCl_2(esea)]$, registered immediately after dissolution, contains the broad signal of co-ordinated NH_2 at δ 5.60, the CH_3 triplet being observed at δ 1.31. Three hours after dissolution weak signals are observed at δ 6.21 and 1.33, due to the presence of $[Pt(esea)_2]^{2+}$. The spectrum of $[PtBr_2(esea)]$ shows a similar trend. The signals of the neutral species (δ 1.33 and 5.64) fade with time, the predominant species at equilibrium being the ionic one (δ 1.36 and 6.17). By integration of the NH_2 signals at equilibrium (room temperature) it is found that *ca.* 25% $[PtCl_2(esea)]$ transforms into the ionic species, the corresponding amount being *ca.* 55% for the bromo-derivative under the same conditions. Immediately after dissolution the ionic species presents two NH_2 signals downfield with respect to the signal of the corresponding neutral complex. Since $[Pt(esea)_2][PtCl_4]$ is scarcely soluble in dimethyl sulfoxide, the first spectrum corresponds to a saturated solution. It contains two NH_2 signals (δ 6.81 and 6.30), the downfield one disappearing within 10 min. The ionic species dissolves slowly changing into the 1 : 1 neutral adduct, the final spectrum at equilibrium coinciding with that of $[PtCl_2(esea)]$. The complex $[Pt(esea)_2][PtBr_4]$ is soluble in dimethyl sulfoxide, the initial spectrum showing three NH_2 signals (δ 6.50, 6.16 and 5.65), the downfield one disappearing in a few minutes. Also in this case the final spectrum coincides with that of the neutral adduct $[PtBr_2(esea)]$. Since the $[Pt(esea)_2]^{2+}$ moiety can in principle exist as two isomers, it can be supposed that the NH_2 signals below δ 6.0 for the ionic complexes could originate from the presence in the solid state of both geometric isomers, which interconvert in solution, as observed for the complex $[Pt(MetO)_2]$, the *cis* isomer of which is predominant in aqueous solution.[13]



As regards binuclear complexes, the spectral trend suggests that they decompose in dmso to form the corresponding 1 : 1 adducts along with the $[PtX_3(dmso)]^-$ ion. The spectrum of $K[Pt_2Cl_5(ambo)]$ is identical to that of $[PtCl_2(ambo)]$, showing the signal of co-ordinated NH_2 at δ 5.0, along with two SCH_3 singlets of different intensities which are caused by ligand co-ordination through both the diastereoisomers at the sulfur atom. The $K[Pt_2Cl_5(esea)]$ complex behaves analogously, the spectrum being like that of $[PtCl_2(esea)]$.

The carbon-13 NMR spectrum of $[PdCl_2(esea)]$ contains SEt signals at δ 13.2 (CH_3) and 31.1 (CH_2), the ethylene carbon resonances being at δ 36.3 (CH_2 near sulfur) and 47.4 (CH_2 near nitrogen). The spectrum of the palladium complex does not change with time, confirming the presence of only one species in solution. The spectra of [PtX_2(esea)] were recorded when the equilibrium between the neutral and ionic species was attained (after 1 d at room temperature). The complex [$PtCl_2$(esea)] shows two sets of signals of different intensity, as for the proton spectra. The SEt [CH_3, δ 12.6 (strong), 13.3 (weak); CH_2, 31.1 (strong), 32.1 (weak)] and the CH_2 (near nitrogen) resonances [δ 47.9 (weak), 48.3 (strong)] show satellites due to ^{195}Pt coupling, whereas the CH_2 (near sulfur) resonances [δ 35.6 (weak), 37.7 (strong)] are in part obscured by the solvent multiplet. The intense signals belong to the neutral species. The weak SEt signals of the ionic species are slightly downfield, an opposite shift being observed for the ethylene carbons. The spectrum of [$PtBr_2$(esea)], identical to that of [Pt(esea)$_2$]-[$PtBr_4$] shows a similar behaviour apart from the different intensity of the signal sets.

The fact that the ionic species is preferred in solution for the bromo-derivative could explain the failure in synthesizing the binuclear bromo complex containing esea, which probably requires $[PtBr_4]^{2-}$ to interact with the neutral 1:1 complex. Conversely, binuclear species are easily obtained when the ligand is ambo, the [PtX_2(ambo)] species being stable in dmso solution.

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