Spectroscopic Studies and X-ray Crystal Structure Determination of the Complex *cis*-(S-ethylcysteine)platinum(II)dichloride

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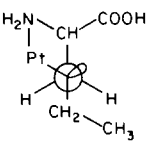
IR, ^1H NMR and ^{13}C NMR spectra of cis-*Pt(S-EtCys)Cl$_2$ have been analyzed and interpreted in favor of a structure in which the ethyl-cysteine ligand coordinates through its S and N atoms. Additionally, the ^1H and ^{13}C NMR spectra show the existence of two diastereomers, differing in their absolute configuration at sulfur. These conclusions were confirmed by a single-crystal X-ray structure determination, which showed the presence of both diastereomers in the unit cell. Crystallographic details:* cis-*Pt(S-EtCys)Cl$_2$ crystallizes in the monoclinic space group* P2$_1$, *with* a = *8.336(6)* Å, b = *10.997(8)* Å, c = *15.097(9)* Å, β = *120.76(3)°*, Z = *4. Final* R *factor = 0.054 for 1842 reflections.*

Introduction

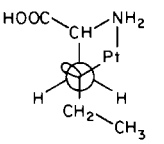
The interaction of sulfur-containing α-amino acids with a variety of metal ions has been the subject of numerous investigations [1–8]. These amino acids contain three potential coordination sites, the sulfur atom, the amino nitrogen atom and the carboxylate oxygen atom. The actual sites of metal–ligand interaction strongly depend upon the pH and the metal-to-ligand ratio in aqueous solution [7, 8].

S-alkyl cysteine complexes of Pt(II) and Pd(II) have also been reported in the literature [9–14], but they are mainly limited to S-methyl cysteine and methionine. Some S-aralkyl cysteines (*e.g.*, S-trityl cysteine) are known to possess antitumour properties [15, 16]. We have therefore undertaken a systematic study of the interaction of S-alkyl and aralkyl cysteine derivatives with Pt(II) [17], in the hope of preparing new Pt complexes which might be potent anticancer agents. These ligands are believed to coordinate to Pt(II) through the S and N atoms [9–14].

The S-methyl cysteine complexes of Pd(II) and Pt(II) exist in solution as different isomers (like *I*a and *I*b), as revealed by ^1H NMR and ^{13}C NMR studies [18–20]. This is due to the different ligand conformations around the chiral sulfur center. The same is true in the crystal structure of the complex of Pd(II) with S-methyl-L-cysteine [21]. The S-methyl-L-cysteine sulfoxide complex [20], however, showed the existence of only one isomer in the solid state.



*I*a



*I*b

In the present paper we report the preparation, spectral properties (conductivity, IR, ^1H NMR, ^{13}C NMR) and the X-ray crystal structure determination of the complex *cis*-S-ethyl-L-cysteine-platinum(II)dichloride, in which the S and N atoms are the coordination sites of the ligand to Pt(II). Two diastereomers are found (*I*a and *I*b), both in solution and in the solid state, due to the chiral sulfur atom.

Experimental

Materials

K_2PtCl_4 was purchased from Johnson Matthey and Mallory Ltd. and S-ethyl-L-cysteine from Fluka A.G.

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Fig. 1. IR spectra of the following compounds in the region 1500–1800 cm^{-1}: (1) S-EtCys (2) Deuterated S-EtCys (3) *cis*-Pt(S-EtCys)Cl_2 and (4) Deuterated *cis*-Pt(S-EtCys)Cl_2.

Preparation of the Complex

The synthesis of the complex *cis*-(S-EtCys)$PtCl_2$ was similar to the literature method [10], but using 0.1–0.5 *N* HCl as solvent, instead of water. The crystals used for X-ray analysis were obtained by slowly cooling and evaporating the solution of equimolar mixtures of K_2PtCl_4 and S-ethyl-L-cysteine, followed by partial solvent removal using a steam bath. Chemical analysis was performed on the samples after drying at 110 °C (under vacuum, over P_2O_5) until sample weight remained constant. *Anal.* Calcd. for $C_5H_{11}NO_2SCl_2Pt$: Pt, 47.00; C, 14.45; H, 2.65; N, 3.37; S, 7.70; Cl, 17.10%. Found: Pt, 46.95; C, 14.57; H, 2.76; N, 3.41; S, 7.68; Cl, 17.17%.

Methods

(a) The IR spectra were recorded on Perkin-Elmer Model 1337 and 621 spectrophotometers, covering the regions 4000–400 cm^{-1} and 4000–200 cm^{-1} respectively, in KBr pellets or nujol mulls. (b) The ^1H NMR spectra were recorded on a Varian F.T. 80A high resolution spectrometer with DSS as internal reference (when D_2O was used as a solvent) or TMS (when DMSO-d_6 was used as a solvent). (c) The ^{13}C NMR spectra were obtained with a Varian F.T. 80A spectrometer with proton noise-decoupling at 20 MHz. (d) The conductivity measurements were performed using an E365B conductoscope, Metrohm Ltd., Herisau, Switzerland. (e) X-ray diffraction data were collected on a Syntex (Nicolet) $P2_1$ automated diffractometer.

Deuterated Ligand and Complex

These were prepared by treating the ligand with D_2O or preparing the complex directly in D_2O or in 0.5 *N* DCl solution. The handling of samples for IR work was performed under an inert atmosphere.

Results and Discussions

The binding sites proposed for S-alkylcysteine derivatives and methionine are the S and N atoms [10–14, 17–20]. The carboxylate oxygen atom can be excluded as a binding site by the examination of the IR spectra of the complexes in the region 1600–1800 cm^{-1} (Fig. 1). The uncomplexed S-EtCys molecule shows two bands at 1610 and 1570 cm^{-1}, which have been assigned to the NH_3^+ degenerate bending motion and asymmetric COO^- stretching mode [5–8]. This supports a zwitterionic structure for the S-EtCys ligand. Both bands are replaced by one at 1585 cm^{-1} upon deuteration and new bands appear at 1175–1145 cm^{-1} (NH/ND = 1.35).

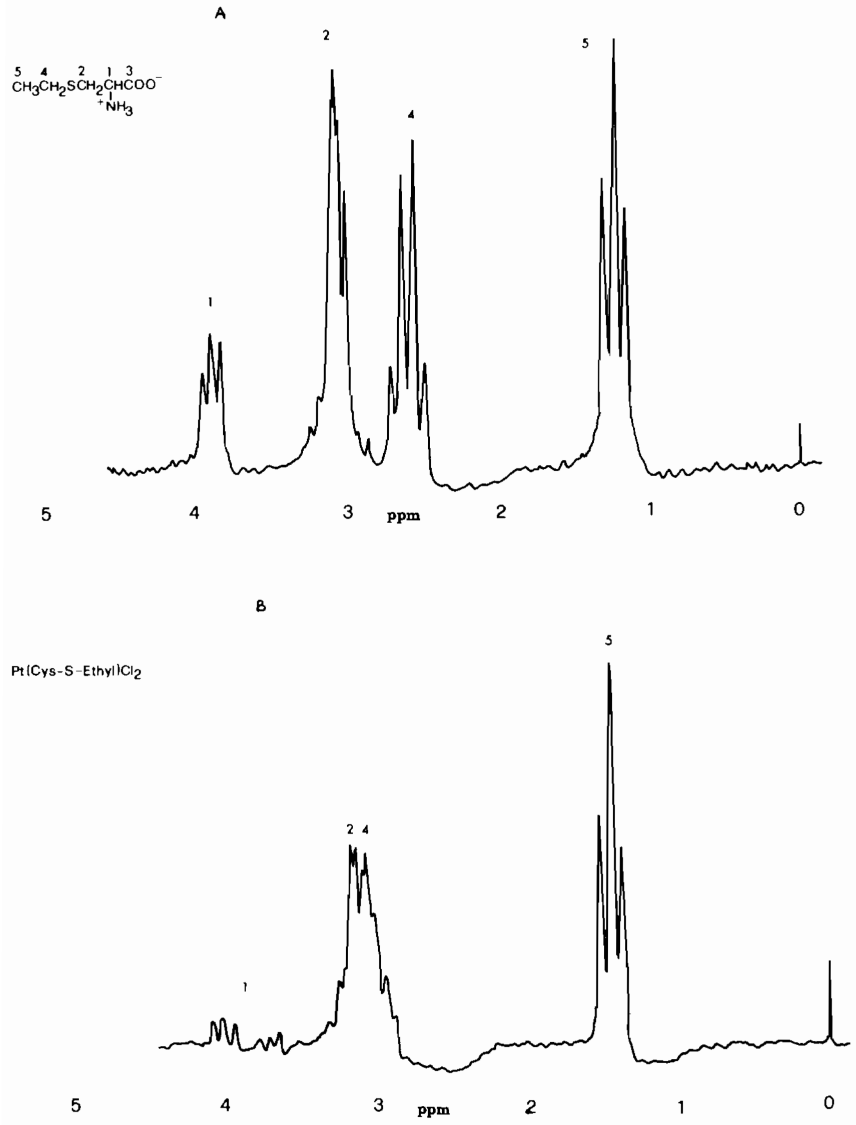
The complex Pt(S-EtCys)Cl_2 also contains two bands in this region at 1703 and 1580 cm^{-1} (Fig. 1), the first of which is due to the ν_{asym}(COOH) of the protonated carboxyl group and the second to the metal-coordinated amino group [6–8]. This second band disappears upon deuteration and a new band appears at 1160 cm^{-1} (NH/ND = 1.37) due to $\delta(ND_2)$. The positions of the ν(COOH) band (>1700 cm^{-1}) and the $\delta(NH_2)$ band (~1600 cm^{-1}) indicate a non-bonded (or free) carboxylate group and the existence of metal binding to the NH_2 group [6–8]. The complex also shows two medium intensity bands at 328 and 310 cm^{-1}, which can be assigned to the two ν(Pt–Cl) motions expected for a *cis* configuration. McAuliffe [11] assumes intermolecular hydrogen bonding of the carboxyl groups in the complex Pt(Met)Cl_2 (where Met is methionine), due to a narrow band observed at 935 ± 15 cm^{-1} which was assigned to the OH out-of-plane deformation vibration. The same assumption can also be made here, since the band at 935 cm^{-1} may be assigned similarly and appears at 630 cm^{-1} in the deuterated complex.

The molar conductance of the title complex is very high in 10^{-3} *M* aqueous solution (Λ_m ~ 300 Mho-cm^2), a value which is consistent with a 1:3 electrolyte. This can be rationalized by the replacement of the two chlorines bound to Pt(II) by two water molecules and the simultaneous ionization of the proton of the free carboxylate group. The compound is not ionic in DMF solution (Λ_m ~ 11 Mho-cm^2).

The ^1H NMR chemical shifts (δ values) of the ligand and the complex can be assigned as follows:

$\overset{5}{C}H_3\overset{4}{C}H_2S\overset{2}{C}H_2\overset{1}{C}H\overset{3}{C}OO^-$
NH_3

For the uncomplexed ligand (Fig. 2A), the triplet at 1.24 ppm is due to the protons of the CH_3 group, and the quartet at 2.62 ppm to the C_4 methylene protons. The multiplet at 3.06 ppm can be assigned to the C_2 methylene protons and the triplet at 3.90 ppm to the C_1 methine proton [4, 10]. In the ^1H NMR spectrum of the Pt complex in D_2O solution (Fig. 2B) there is only one triplet assigned to the methyl group protons at 1.35 ppm [while in DMSO-d_6 solution (Fig. 2C) there are two triplets at 1.60 and 1.64 ppm]. In D_2O solution (Fig. 2B) there are also two triplets at 4.02 and 3.72 ppm, assigned to the methine protons C*1* of the two isomers (*1*a and *1*b). We cannot distinguish the two sets of protons in the multiplet with maxima at 3.08 and 3.17 ppm, assignable to the C_4 and C_2 methylene protons. The two sets of C_1 methine protons shift downfield by 0.12 ppm and upfield by 0.18 ppm respectively. The two maxima of the C_4/C_2 multiplet and the CH_3 protons are observed downfield by 0.46 and 0.12 ppm, indicating a simultneous S,N involvement in bonding with Pt(II) [10, 18–20].



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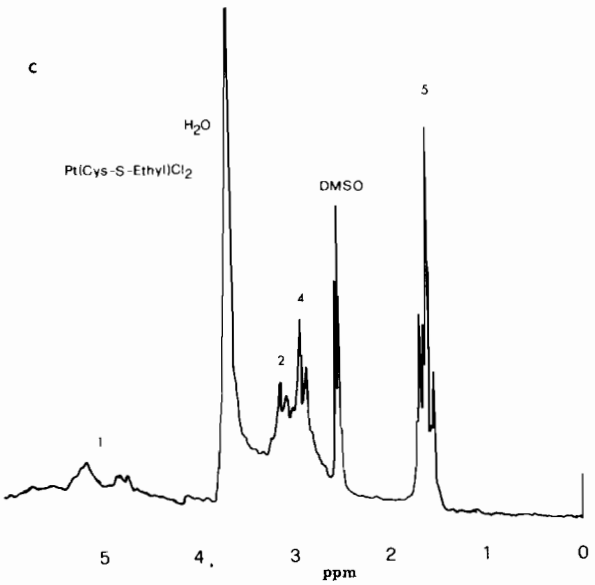

Fig. 2. ^{1}H NMR spectra of the compounds (A) S-EtCys in D_2O (B) *cis*-Pt(S-EtCys)Cl_2 in D_2O and (C) *cis*-Pt(S-EtCys)Cl_2 in DMSO-d_6.

The presence of the two diastereomers (*I*a and *I*b) as well as the nature of the coordination sites are better seen in the ^{13}C NMR spectra of the ligand and the complex (Fig. 3). The ^{13}C NMR spectrum of the ligand was recorded in D_2O and that of the complex in DMSO-d_6, due to the low solubility of the latter in D_2O and of the former in DMSO-d_6. The assignment of the ligand carbon atoms are: 55.16 ppm for C_1, 33.11 ppm for C_2, 174.50 ppm for C_3, 27.00 ppm for C_4 and 15.33 ppm for C_5 (Fig. 3A). All the ^{13}C NMR signals of the complex *cis*-Pt(S-EtCys)Cl_2, except the carbonyl C_3 at 172.89 ppm, show up as double peaks: the C_1 atoms appear at 65.67 and 65.17 ppm; C_4 at 35.72 and 36.76 ppm; and C_5 at 16.78 and 17.52 ppm (Fig. 3B). The peaks corresponding to C_2 (~39.6 ppm) appear under the DMSO-d_6 signals and do not show up clearly. For each pair of resonances given above, the first one listed has more than twice the intensity of the second.

The chemical shift differences are ~10.5 ppm for C_1, ~6 ppm for C_2, ~9 ppm for C_4 and ~1.7 ppm for C_3 and C_5. The ^{13}C NMR clearly show the presence of two species in solution, presumably due to the two diastereomers around the chiral sulfur center (*I*a and *I*b), as proposed by Kozlowski *et al.* [18–20] for the Pd(II) and Pt(II)-S-methyl-L-cysteine systems.

The complexes of Pd(II) and Pt(II) with S-methyl-L-cysteine sulfoxide do not show the presence of two isomers in the solid state. However, in solution, the former complex shows isomerization in the ^{1}H NMR immediately after dissolution, while the isomers of the latter appear only after 3 days [20].

X-ray Analysis of cis-*[S-EtCys]PtCl*$_2$

Crystallographic work was carried out to provide unambiguous proof that this complex exists in two

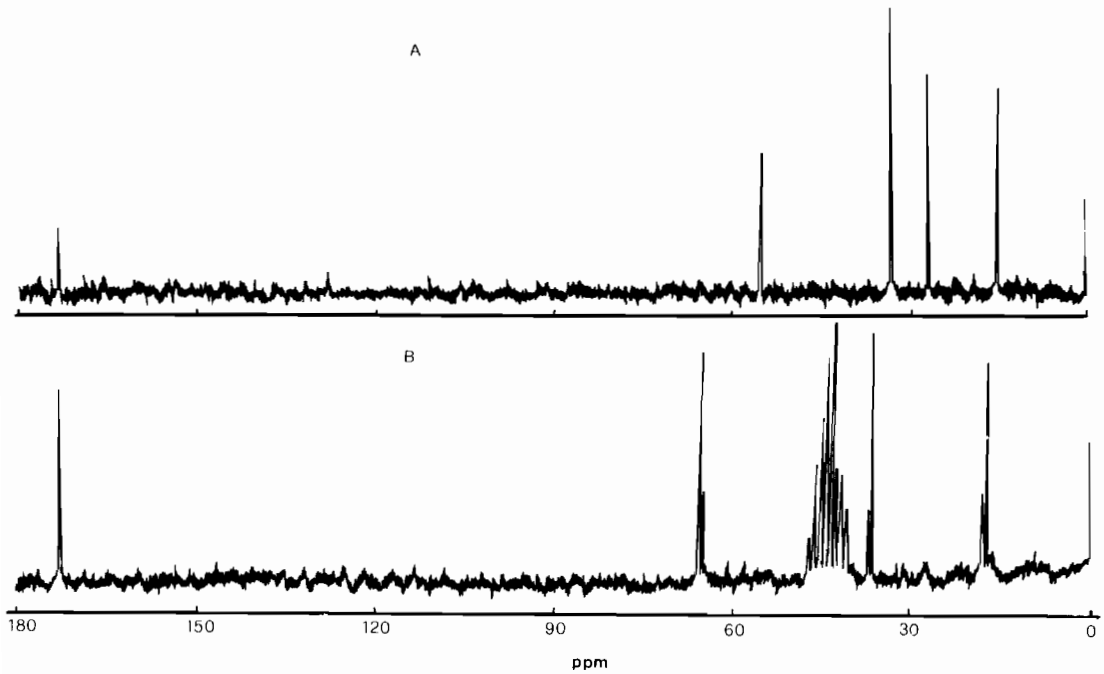

Fig. 3. ^{13}C NMR spectra of the compounds (A) S-EtCys in D_2O and (B) *cis*-Pt(S-EtCys)Cl_2 in DMSO-d_6. The large multiplet in the region 40–50 ppm is due to DMSO-d_6.

TABLE I. Final Atomic Parameters for *cis*-Pt(S-EtCys)Cl_2.

(A) *Atomic Positions*

	x	*y*	*z*	B (Å^2)
Pt(1)	−0.36748(12)	0.00000(0)[a]	0.11329(7)	
S(1)	−0.1278(8)	0.0863(7)	0.1067(5)	
Cl(1)	−0.6056(10)	−0.0718(8)	0.1326(6)	
Cl(2)	−0.3131(10)	−0.1827(8)	0.0601(5)	
N(1)	−0.4051(23)	0.1664(19)	0.1605(14)	2.1(3)
C(1)	−0.2394(34)	0.2444(28)	0.2036(21)	3.4(5)
C(2)	−0.1580(33)	0.2458(27)	0.1311(19)	2.9(4)
C(3)	−0.2965(32)	0.3829(25)	0.2095(19)	2.7(4)
O(1)	−0.4360(27)	0.4021(21)	0.2073(16)	4.4(4)
O(2)	−0.1630(30)	0.4643(26)	0.2323(19)	5.5(5)
C(11)	−0.1726(37)	0.0756(32)	−0.0226(23)	4.3(5)
C(12)[b]	−0.0166(−)	0.1448(−)	−0.0270(−)	10.0(−)
Pt(2)	−0.35761(12)	0.56619(10)	0.61577(7)	
S(2)	−0.0992(9)	0.4853(8)	0.6344(5)	
Cl(3)	−0.6190(11)	0.6520(8)	0.6115(6)	
Cl(4)	−0.2564(10)	0.7532(8)	0.5943(6)	
N(2)	−0.4441(32)	0.3934(27)	0.6364(19)	4.4(5)
C(4)	−0.3213(36)	0.3050(31)	0.6280(21)	3.6(5)
C(5)	−0.1160(36)	0.3473(27)	0.6855(21)	3.5(5)
C(6)	−0.3566(41)	0.1719(35)	0.6680(24)	4.4(6)
O(3)	−0.2256(26)	0.1107(23)	0.6870(15)	4.6(4)
O(4)	−0.4659(31)	0.1724(26)	0.6944(18)	5.4(5)
C(21)	−0.1574(35)	0.4555(30)	0.5015(21)	3.6(5)
C(22)[b]	0.0033(−)	0.3792(−)	0.5015(−)	10.0(−)

(B) *Anisotropic Thermal Parameters*[c] *(×10^4)*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	137(2)	46(1)	29(1)	−10(2)	55(2)	−8(1)
S(1)	143(11)	57(6)	30(3)	6(14)	53(9)	−4(8)
Cl(1)	233(16)	93(8)	72(6)	−112(20)	169(15)	−37(11)
Cl(2)	234(16)	69(6)	55(5)	−46(18)	106(14)	−51(10)
Pt(2)	132(2)	56(1)	28(1)	10(2)	64(2)	−5(1)
S(2)	145(12)	90(7)	45(4)	−13(16)	83(11)	0(9)
Cl(3)	285(18)	95(8)	57(5)	108(21)	180(15)	68(11)
Cl(4)	200(15)	84(7)	63(5)	−11(18)	106(14)	18(10)

[a]The y coordinate of Pt(1) is fixed at zero. [b]The positions of C(12) and C(22) were measured off a difference-Fourier map; their coordinates could not be refined. [c]The form of the anisotropic thermal ellipsoid is exp $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

diastereomeric forms. *cis*-[S-EtCys]$PtCl_2$ crystallizes in the monoclinic space group $P2_1$, with the following unit cell parameters: a = 8.336(6) Å, b = 10.997(8) Å, c = 15.097(9) Å, β = 120.76(3)°; V = 1189.3 Å^3, ρ(calcd) = 2.32 g cm^{-3} for Z = 4. There are two independent molecules in the unit cell. Two quadrants of data were collected with MoKα X-rays, using a $2\theta/\theta$ scan mode up to a 2θ maximum of 45°. Data processing (which included Lorentz, polarization and absorption corrections) reduced the 2148 independent reflections to a total of 1842 having intensities $>3\sigma(I)$.

The positions of the two Pt atoms were readily obtained from a three-dimensional Patterson map [22]. Considerable difficulty, however, was experienced in locating the rest of the atoms, largely because of pseudo-symmetry effects: the two Pt atoms are nearly related to each other by a centering operation (0.0, 0.5, 0.5) [the actual difference is (0.01, 0.56, 0.50)], and this fact caused a substantial number of spurious features to appear in difference-Fourier maps. Gradually, however, by the slow and judicious addition of atoms to the list of known positions, the phasing improved and the structure was

TABLE II. Distances and Angles in *cis*-Pt(S-EtCys)Cl_2.

(A) *Bond Distances* (in Ångstroms)

Pt(1)–Cl(1)	2.289(10)	Pt(2)–Cl(3)	2.344(10)
Pt(1)–Cl(2)	2.293(8)	Pt(2)–Cl(4)	2.308(9)
Pt(1)–S(1)	2.260(7)	Pt(2)–S(2)	2.212(8)
Pt(1)–N(1)	2.05(2)	Pt(2)–N(2)	2.11(3)
N(1)–C(1)	1.47(4)	N(2)–C(4)	1.46(4)
C(1)–C(2)	1.55(4)	C(4)–C(5)	1.54(4)
S(1)–C(2)	1.83(3)	S(2)–C(5)	1.74(3)
C(1)–C(3)	1.61(4)	C(4)–C(6)	1.66(5)
C(3)–O(1)	1.17(4)	C(6)–O(3)	1.19(4)
C(3)–O(2)	1.33(4)	C(6)–O(4)	1.17(5)
S(1)–C(11)	1.79(3)	S(2)–C(21)	1.84(3)
C(11)–C(12)	1.54(–)	C(21)–C(22)	1.58(–)

(B) *Bond Angles* (in degrees)

Cl(1)–Pt(1)–Cl(2)	94.7(4)	Cl(3)–Pt(2)–Cl(4)	92.2(3)
Cl(1)–Pt(1)–S(1)	173.9(3)	Cl(3)–Pt(2)–S(2)	175.1(3)
Cl(1)–Pt(1)–N(1)	88.1(7)	Cl(3)–Pt(2)–N(2)	89.1(8)
Cl(2)–Pt(1)–S(1)	90.9(3)	Cl(4)–Pt(2)–S(2)	88.5(3)
Cl(2)–Pt(1)–N(1)	177.2(7)	Cl(4)–Pt(2)–N(2)	178.7(8)
S(1)–Pt(1)–N(1)	86.3(6)	S(2)–Pt(2)–N(2)	90.2(8)
Pt(1)–N(1)–C(1)	113.6(17)	Pt(2)–N(2)–C(4)	106.1(21)
N(1)–C(1)–C(2)	110.2(21)	N(2)–C(4)–C(5)	112.0(26)
C(1)–C(2)–S(1)	106.6(27)	C(4)–C(5)–S(2)	109.3(21)
Pt(1)–S(1)–C(2)	100.3(10)	Pt(2)–S(2)–C(5)	96.5(12)
Pt(1)–S(1)–C(11)	108.9(12)	Pt(2)–S(2)–C(21)	103.7(11)
C(2)–S(1)–C(11)	107.9(14)	C(5)–S(2)–C(21)	107.0(14)
N(1)–C(1)–C(3)	109.9(23)	N(2)–C(4)–C(6)	106.9(26)
C(2)–C(1)–C(3)	106.1(23)	C(5)–C(4)–C(6)	114.3(24)
C(1)–C(3)–O(1)	119.2(26)	C(4)–C(6)–O(3)	106.0(31)
C(1)–C(3)–O(2)	114.8(26)	C(4)–C(6)–O(4)	115.7(33)
O(1)–C(3)–O(2)	125.2(28)	O(3)–C(6)–O(4)	134.6(36)
S(1)–C(11)–C(12)	107.7(–)	S(2)–C(21)–C(22)	110.1(–)

(c) *Torsion Angles*[a] (in degrees)

O(1)–C(3)–C(1)–N(1)	(ψ_1)	19.3	O(4)–C(6)–C(4)–N(2)	(ψ_1)	0.2
O(1)–C(3)–C(1)–C(2)		139.2	O(4)–C(6)–C(4)–C(5)		124.2
O(2)–C(3)–C(1)–N(1)	(ψ_2)	–170.2	O(3)–C(6)–C(4)–N(2)	(ψ_2)	–160.6
O(2)–C(3)–C(1)–C(2)		–50.3	O(3)–C(6)–C(4)–C(5)		–36.5
N(1)–C(1)–C(2)–S(1)	(χ)	–51.9	N(2)–C(4)–C(5)–S(2)	(χ)	–58.6
C(3)–C(1)–C(2)–S(1)		–171.7	C(6)–C(4)–C(5)–S(2)		–179.1
C(1)–C(2)–S(1)–C(11)	(ϕ)	146.1	C(4)–C(5)–S(2)–C(21)	(ϕ)	–66.7
C(2)–S(1)–C(11)–C(12)		67.0	C(5)–S(2)–C(21)–C(22)		–69.9
C(1)–C(2)–S(1)–Pt(1)		32.1	C(4)–C(5)–S(2)–Pt(2)		40.1
C(2)–S(1)–Pt(1)–N(1)		–7.9	C(5)–S(2)–Pt(2)–N(2)		–14.2
S(1)–Pt(1)–N(1)–C(1)		–20.0	S(2)–Pt(2)–N(2)–C(4)		–13.4
Pt(1)–N(1)–C(1)–C(2)		47.2	Pt(2)–N(2)–C(4)–C(5)		42.3

[a]Rotation angles (ψ_1, ψ_2, χ, ϕ) defined according to IUPAC-IUB Commission on Biochemical Nomenclature [*Biochemistry, 9,* 3471 (1970)].

solved. The correct absolute configuration of the two independent molecules could be determined by referring to the known absolute configuration of the α-carbons of the cysteine ligands. The only remaining crystallographic problem is the fact that the terminal carbon atoms of the ethyl groups were disordered and could not be refined. Disorder of ethyl groups is a common crystallographic problem [23] and is often unavoidable. Fortunately, however, the methylene carbon atoms of the ethyl groups were not disordered, and their positions enabled the absolute configurations of the sulfur atoms to be determined

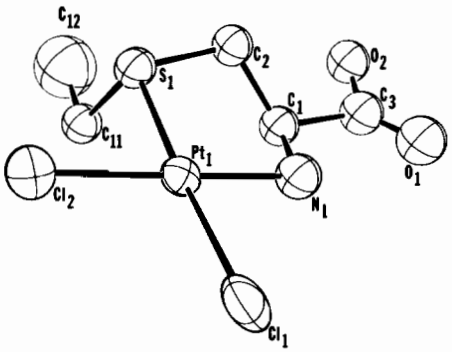

Fig. 4. Molecular plot of one of the two independent molecules of *cis*-Pt(S-EtCys)Cl_2. The absolute configuration of this molecule (and the one shown in Fig. 5) was determined by referring to the known absolute configuration of the α-carbon atom of cysteine.

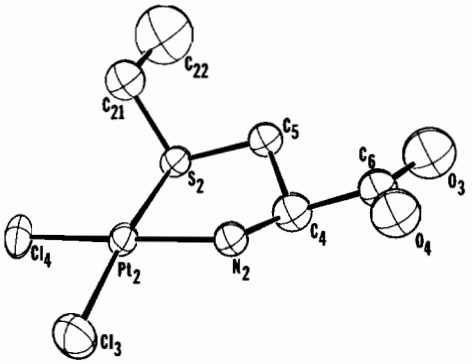

Fig. 5. Molecular plot of the other *cis*-Pt(S-EtCys)Cl_2 molecule. Note that the absolute configuration at S is opposite to that of the molecule shown in Fig. 4.

correctly. The final agreement factor, after least-squares refinement [22], was R = 5.4% for 1842 reflections.

Final atomic parameters are given in Table I, while bond distances, bond angles and torsion angles are listed in Table II. Plots of the two independent molecules are given in Figs. 4 and 5. Distances and angles in this structure have expected values. The chelate rings are in the λ-conformation, as in other metal–cysteine complexes [20, 24, 25]. The main conclusion that can be derived from the structural work is the fact that the two molecules are indeed diastereoisomers (as in *cis*-Pd(S-MeCys)Cl_2) [21], differing only in their absolute configurations at the sulfur atoms. In addition, the N–S bonding model, inferred from IR data, is confirmed.

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