Structural Characterization of Platinum(II)–Methionine Complexes in Aqueous Solution

Tomasz Grochowski * and Krystyna Samochocka
Department of Chemistry, Warsaw University, Zwirki i Wigury 101, Warsaw, Poland

The presence of isomeric complexes formed in aqueous solutions of platinum(II)–methionine systems has been demonstrated. Proton and ^{13}C NMR spectroscopy was found useful for the characterization of such structures and for obtaining the quantitative contributions of the different isomers. Formation of a trimethionine complex was detected and importance of this molecule in the isomerization from *trans* to *cis* geometry was postulated. A method of obtaining dimethionineplatinum(II) complexes enriched in *cis* isomers was developed and the products of this reaction were characterized.

The discovery that the $[PtCl_4]^{2-}$ complex ion binds preferably to the methionine (Met) residues in proteins [1] aroused an interest in platinum(II)–methionine compounds. However, there have been few reports on the structural characterization of platinum(II) complexes containing methionine and chloride ligands.[2–4] The chelate $[PtCl_2(Met)]$ was synthesised, isolated and characterized by the use of IR and NMR spectroscopy. Two platinum(II) complexes containing *N*-acetylmethionine ligand were also investigated.[5,6] They were characterized by NMR spectroscopy and it was concluded that co-ordination occurred only through the sulfur atom. The other platinum(II) complexes containing thioether ligands (*i.e.* *S*-methylcysteine) were studied by the use of multinuclear NMR spectroscopy.[7] Platinum(II)–methionine complexes containing ammonia ligands were investigated as models of the protein-bonded anticancer agent *cis*-diamminedichloroplatinum(II). The co-ordination of methionine to the hydrolysed form of this complex has been shown to involve different mechanisms.[8] Since four labile chloride ligands are present in the first co-ordination sphere of $[PtCl_4]^{2-}$ the number of complexes which may originate with methionine is expected to be greater than with *cis*-$[PtCl_2(NH_3)_2]$.

In this study four systems were studied by ^1H and ^{13}C NMR spectroscopy: aqueous solutions of $K_2[PtCl_4]$ and methionine in 1:1 (I), 1:2 (two different methods of preparation, II and III) and 1:3 ratio (IV). The isomeric structures of complexes were characterized, and the yields of each form estimated.

Results and Discussion

The three functional groups of the methionine ligand, the thioether, the amine and the carboxylic acid, are all likely to co-ordinate to Pt^{2+}. Two types of chelation in platinum(II)–methionine complexes have been reported: (*i*) through sulfur and oxygen [8] (S,O chelate); (*ii*) through sulfur and nitrogen [2–4,8] (S,N chelate). Complexes of methionine, or its derivatives, bonded only through sulfur (S monodentate) have also been synthesised.[5–10] Each structure can be identified based on literature NMR spectral data (Table 1). The chemical shift of the methine (CH-α) proton in the ^1H NMR spectrum was considered as the decisive criterion for differentiation of isomeric species.

In the spectrum of the S,O-chelate complex this signal is strongly shifted downfield from δ 4.24 (due to free methionine) to δ 5.33 and 5.58 (two isomers).[8] Thus, the ^1H NMR signals of such a chelate can easily be distinguished.

Table 1 Literature NMR data for platinum(II) complexes with methionine or its derivatives

Complex[a] (donor atom)	CH_3S		CH		Ref.
	^1H	^{13}C	^1H	^{13}C	
$[PtCl_2(Met)]$ (S,N)	2.56 2.60	22.22	2.45	57.26	4
$[Pt(NH_3)_2(Met)]^{2+}$ (S,N)	2.53 2.54	20.11 20.47	3.75 3.91	56.09 58.15	8
$[Pt(NH_3)_2(Met)]^{2+}$ (S,O)	2.45 2.47	— —	5.33 5.58	— —	8
$[Pt(NH_3)_2(Met)_2]^{2+}$ (S)	2.64	—	—	—	8
$[PtCl_3(amet)]^-$[b] (S)	2.27	20.80	—	51.7	5
trans-$[P + Cl_2(amet)_2]$ (S)	2.33	19.2	—	51.4	6
cis-$[PtCl_2(amet)_2$ (S)	2.46	20.8	—	51.4	6

[a] amet = *N*-Acetylmethionine. [b] ^3J(Pt–H) 49.6 Hz.

Table 2 Proton NMR data for methionine in D_2O and $(CD_3)_2SO$ solutions with calculated Δδ corrections (all values in ppm *vs.* $Si(CH_3)_4$ for dmso or 3-(trimethylsilyl)propane-1-sulfonic acid for D_2O)

Atom	δ		Δδ
	In D_2O	In $(CD_3)_2SO$	
CH_3S	2.13	2.02	0.09
CH_2S	2.71	2.49	0.22
CH_2*	2.21	2.53	−0.32
	2.32	2.58	−0.26
CH-α	4.24	3.96	0.28

* ABXY pattern.

For the S,N-chelate complexes the ^1H NMR spectra were recorded in D_2O[8] and $(CD_3)_2SO$.[4] Since the investigated samples were prepared in water solutions, the recalculation of literature spectra for substances dissolved in dimethyl sulfoxide (dmso) was necessary. An approximate procedure based on comparison of spectra for methionine in D_2O and $(CD_3)_2SO$ is proposed. For each ^1H NMR signal the difference $\Delta\delta = \delta_{D_2O} - \delta_{dmso}$ was determined (Table 2). Subsequently, the Δδ corrections were added to the literature values of the chemical shifts for appropriate protons in the spectrum of the S,N-chelate $[PtCl_2(Met)]$ recorded in dmso.[4] The obtained data were considered to correspond to the spectrum of a water solution of the latter compound. Generally, for the S,N chelate the chemical shift of the CH-α proton is lower in comparison to

Table 3 NMR data for platinum(II)–methionine complexes in samples **I–IV**

Sample	Complex (donor atoms)	δ CH_3S	δ CH-α	^3J(Pt–H)/Hz
I	**1a** $[PtCl_3(HMet)]$ (S)	2.41	4.35	50
	1b $[PtCl_2(Met)]$ (S,N)	2.55	3.71	
		2.57	3.83	
	1c $[PtCl_2(Met)]$ [S,O]	2.68	5.45	
II[a]	**2a** *trans*-$[PtCl_2(HMet)_2]^{2+}$ (S)	2.55	4.56	45
	2b *cis*-$[PtCl_2(HMet)_2]^{2+}$ (S)	2.56	4.42	
	2c *trans*-$[PtCl(Met)(HMet)]^{2+}$ (S) (S,N)	2.57	4.27	
		2.68	3.80	
	2d *cis*-$[PtCl(Met)(HMet)]^{2+}$ (S) (S,N)	2.60	4.02	
		2.67	3.78	
III	**3a** *cis*-$[Pt(Met)_2]^{2+}$ (S,N)	2.59[b]	3.63	49
	3b *trans*-$[Pt(Met)_2]^{2+}$ (S,N)	2.63	3.76	
IV	**2a** *trans*-$[PtCl_2(HMet)_2]^{2+}$ (S)	2.54	—	
	2b *cis*-$[PtCl_2(HMet)_2]^{2+}$ (S)	2.57	—	
	2c *trans*-$[PtCl(Met)(HMet)]^{2+}$ (S) (S,N)	2.61	—	
		2.68	—	
	2d *cis*-$[PtCl(Met)(HMet)]^{2+}$ (S) (S,N)	2.66	—	
		2.67	—	
	4 $[PtCl(Met)_3]^+$ (S)	2.70	—	
		2.74	—	
	Methionine	2.13	4.24	

[a] It is not possible to ascribe NMR signals to isomers. [b] Doublet signal ($\Delta\delta$ = 0.004 ppm).

Table 4 Carbon-13 NMR data for platinum(II)–methionine complexes in samples I–IV

Sample	δ CH_3S	δ CH-α
I	22.73	53.72
	22.87	54.93
	23.29	55.94
	23.50	56.12
II	21.48	53.31
	21.56	53.38
	21.71	53.43
	22.13	53.59
	22.58	53.75
	22.86	55.46
III	21.11	57.08
	21.22	58.20
	21.67	58.48
	22.04	58.55
IV	21.35	55.07
	21.82	55.23
	21.93	55.33
	22.19	55.48
	22.38	56.47
	22.60	57.12
	22.78	57.57
	23.36	57.79

the spectrum of the free amino acid. The upfield displacement from δ 4.24 (due to methionine) to 3.68[4] (value corrected for water solution) as well as to δ 3.75 and 3.91[8] (two isomeric structures) is sufficient to distinguish the ^1H NMR signals for this isomer.

The ^1H and ^{13}C NMR spectra of the S-monodentate complex in the methine (CH-α) proton and carbon regions exhibit greater similarity to the spectra of the free ligand than to those of the chelate complexes. The same ^{13}C chemical shift of the CH-α carbon for *N*-acetylmethionine complexes and for the free ligand was considered as a decisive argument in favour of S-monodentate structures for those platinum(II) compounds.[5,6] When the formation of the latter compound was complete

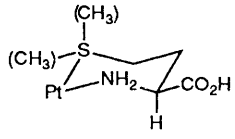


Fig. 1 Two possible orientations of the CH_3S methyl group at the six-membered ring of the S,N-chelate platinum(II)–methionine complex

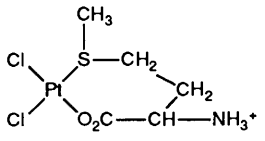
the singlet due to the methyl (CH_3S) group was shifted 0.31 ppm downfield and split into a 1:4:1 pattern due to coupling with ^{195}Pt nuclei. Since, the ^{13}C NMR chemical shift of the CH-α methine carbon is unaffected by co-ordination of sulfur to platinum, it is concluded that the ^1H NMR peak of the methine proton is also unperturbed by co-ordination.

Square-planar platinum(II) complexes containing two methionine ligands may exist in two isomeric geometrical forms: *cis* and *trans*. The coupling constant between the ^{195}Pt and ^1H (CH_3S) nuclei ^3J(Pt–H) differs for *trans* S–Pt–S and *cis* (Cl–Pt–S or N–Pt–S) complexes (about 49 Hz for *cis* and about 45 Hz for *trans*).[11–13]

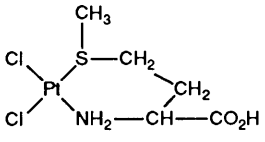
Structures of the Platinum(II)–Methionine Complexes.—In sample I. The ^1H and ^{13}C NMR spectra of sample I at pH 2 reveal the presence of four isomeric structures (Tables 3 and 4). The chemical shift of the CH-α proton, δ 5.45, indicates the presence of the S,O-chelate complex **1a**. Two peaks at δ 3.71 and 3.83 represent the S,N-chelate structure **1b**, differing in the orientation of the S–CH_3 bond in the six-membered ring (Fig. 1) because the equatorial position of carboxylic group had already been established.[4,8] The major signal in ^1H NMR spectrum of sample I, in the methine (CH-α) proton range, at δ 4.35, confirms the presence of the S-monodentate complex **1c**. From the integration of the ^1H NMR spectrum the isomer ratio S monodentate:S,N chelate:S,O chelate was estimated to be 2.5:1:1. The coupling constant ^3J(Pt–H) = 50 Hz for the prevailing signal of the CH_3S protons (at δ 2.41) is almost equal to the value (49.6 Hz) of (*N*-acetylmethionine)trichloroplatinate(II) which has the *trans* Cl–Pt–S structure.[5]

The assignment of the ^1H NMR peaks of the CH_3S protons was based on a comparison of the intensities of these signals with those of the methine (CH-α) protons.

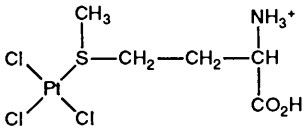
In sample II. The ^1H and ^{13}C NMR spectra of sample II at pH



1a



1b



1c

2 show the presence of six differently bonded methionine moieties in the bis(methionine)platinum(II) complexes (Tables 3 and 4). Because the chemical shifts of the CH-α proton (δ 4.02–4.56) and carbon (δ 53.31–53.59) are similar to analogous signals in the spectrum of the unco-ordinated ligand (δ 4.24 for ^1H and δ 53.93 for ^{13}C), the predominance of the S-monodentate structures is evident. However, two broad proton signals at δ 3.76 and 3.81 reveal the presence of the S,N-chelate complex. Thus, six differently bonded ligand molecules participate in formation of four complexes: *trans*-(S monodentate)$_2$ **2a**, *cis*-(S monodentate)$_2$ **2b**, *trans*-(S monodentate)(S,N chelate) **2c** and *cis*-(S monodentate)(S,N chelate) **2d**. For the semicyclic structures, **2c** and **2d**, two isomers are formed which differ in the orientation of the S–CH_3 bond as already explained. The overlapping signals of the *trans* and *cis* isomers result in broadening of the CH-α proton peaks for the S,N-chelate structures.

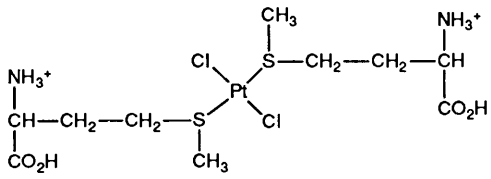
The isomer ratio (S monodentate)$_2$:(S monodentate)(S,N chelate) was evaluated to be about 7:3 based on integration of ^1H spectra. At more neutral pH 5 the ratio changed to 6:4.

The coupling constant ^3J(Pt–H) = 45 Hz for the prevailing signal of CH_3S protons at δ 2.56 corresponds to the *trans* S–Pt–S geometrical isomer. Since, the coupling constant was observed in the 100 MHz spectrum it was not possible to unambiguously assign the *trans* structure to any of the three signals at δ 2.55, 2.56 and 2.57. The predomination of *trans* geometry, because of the absence of satellite lines with a coupling constant near 50 Hz, was a general conclusion.

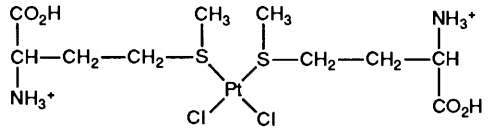
The assignment of the signals for the methyl protons was based on literature data[8] for the S-monodentate complex $[Pt(NH_3)_2(Met)_2]$. In the ^1H NMR spectrum of this molecule the signal of the CH_3S protons occurs at δ 2.64. An analogous peak in the spectrum of sample II was detected at δ 2.68 (200 MHz), but at the highest resolution (500 MHz) it was split into two signals at δ 2.677 and 2.681, corresponding to *trans* and *cis* isomers. An analogous change in the chemical shifts of the methyl protons of the S-monodentate mono- and di-methionine platinum(II) complexes (from δ 2.41 to 2.68) has been reported[5] in the case of *N*-acetylmethionine complexes (from δ 2.27 to 2.45).

In the ^{13}C NMR spectrum of bis(*N*-acetylmethionine)-dichloroplatinum(II) differences between *cis* and *trans* isomers were observed.[6] The chemical shift of the CH_3S carbon atom is lower for the *trans* (δ 19.2) than for the *cis* isomer (δ 20.8), while the value for the CH_2S methylene carbon is, by contrast, lower for the *cis* isomer (δ 34.9 *vs.* 35.1). Based on these facts, ^{13}C NMR signals could be assigned to particular isomeric structures. The signals of methyl carbon atoms near δ 21 (21.48 and 21.56) indicate a *trans* structure while those shifted about 1.6 ppm downfield (near δ 23: 22.58 and 22.86) indicate a *cis* isomer. Since the proposed assignment is based on spectral data for the acyclic S-monodentate complex, the four NMR peaks listed above are assumed to originate from methionine moieties bonded only through sulfur.

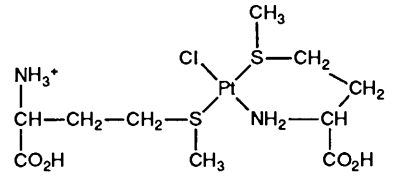
In sample III. On the basis of ^1H and ^{13}C NMR spectra at pH



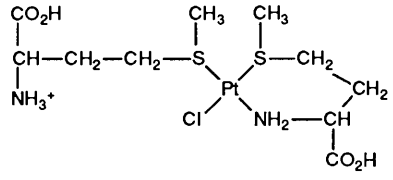
2a



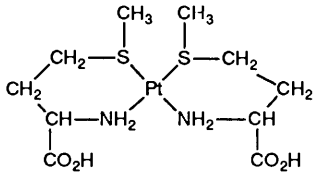
2b



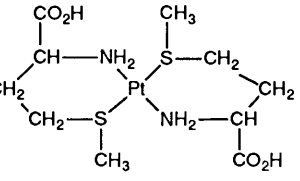
2c



2d



3a



3b

5.5 four differently bonded methionine moieties were found in sample III (Table 3 and 4). The chemical shift of the CH-α proton peaks (δ 3.63 and 3.76) indicates S,N-chelate structures. The coupling constant ^3J(Pt–H) = 49 Hz for the prevailing ^1H NMR signal of the CH_3S protons (δ 2.59) shows the predomination of the *cis* geometrical isomer in the sample. Four structures are ascribed to the *cis* **3a** and *trans* **3b**, S,N-chelate isomers of the bis(methionine)platinum(II) complex, each having two different orientations of the S–CH_3 bond.

The assignment of *cis* and *trans* structures to the methine CH-α proton signals was based on a comparison of integral intensities for methine and methyl proton peaks. The ratio of the *cis* to *trans* isomers is evaluated to about 4:3.

In sample IV. Comparison of the ^1H NMR spectra of samples IV and II (both at pH 2) in the CH_3S proton region showed only one change. Two signals at δ 2.70 and 2.74 appeared when excess of methionine, indicated by the peak at δ 2.13, was added. The spectrum of a sample containing $K_2[PtCl_4]$ and L-methionine in a 1:2.5 ratio also showed these signals (Fig. 2). Since, the formation of trisubstituted complex has been reported[10] in the case of the platinum(II)–dimethyl sulfide system containing excess of ligand, it was concluded that $[PtCl(Met)_3]^+$ (all ligands S monodentate) was formed. In the spectrum of $[PtCl(SMe_2)_3]^+$ two peaks due to CH_3S methyl protons are present: that at δ 2.62 corresponds to two dimethyl sulfide molecules in mutual *trans* position, while that at δ 2.63 originates from one SMe_2 molecule in *trans* position to chloride and *cis* to the remaining sulfide ligands. In the spectra of *cis*- and *trans*-$[PtCl_2(SMe_2)_2]$ complexes these peaks are placed at

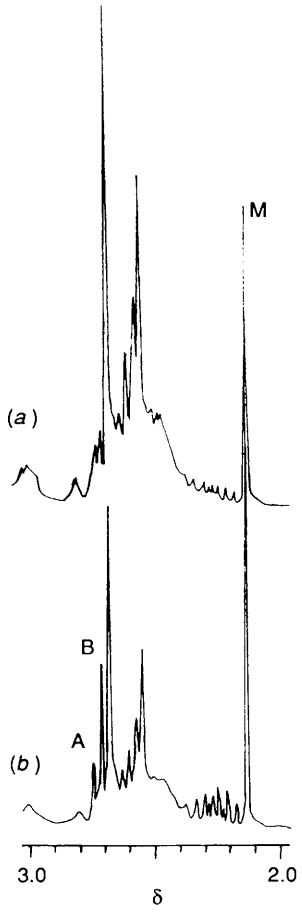
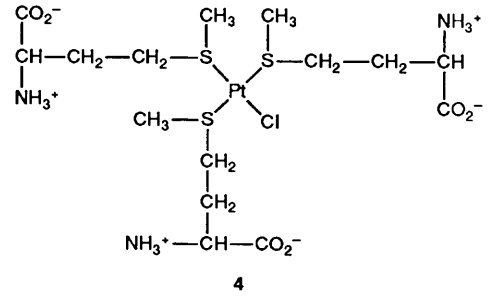


Fig. 2 Proton NMR spectra of samples with $[PtCl_4]^{2-}$:methionine ratio = 1:2.5 (*a*) and 1:3 (*b*). A,B = Methyl proton signals of the trimethionine complex; M = methyl proton signal of free methionine ligand



4

δ 2.54 and 2.44, respectively. This downfield shift of the CH_3S proton signals agrees with observed differences between the spectrum of platinum(II)–dimethionine (δ 2.59 and 2.68) and –trimethionine complexes (δ 2.70 and 2.74). The major peak at δ 2.70 corresponds to two *trans* bonded ligands, the minor peak at δ 2.74 to the *cis*. Comparison of ^{13}C and ^1H NMR spectra shows the presence of eight differently bonded methionine molecules in system IV. Six amino acid moieties, which are characterized by the same spectral parameters as for sample II, belong to four complexes **2a**–**2d**, while the remaining two non-equivalently co-ordinated ligands are contained in compound **4**.

Mechanism of the Isomerization of Platinum(II)–*methionine* (1:2) *Complexes*.—Two samples (II and III) containing dimethionineplatinum(II) complexes are characterized by different compositions of geometric isomers. The procedure which led to sample III enriched in the *cis* isomer started by mixing $K_2[PtCl_4]$ and methionine in a 1:3 ratio. Since the isomerisation of $[PtCl_2(SMe_2)_2]^{2+}$ complexes occurs in the presence of the excess of ligand [11] *via* the unstable trisubstituted species, complex $[Pt(Met)_3]^{2+}$ is thought to be involved in the present system. Indeed a trimethionine compound was formed in sample IV. However, chromatographic separation of the free ligand resulted in decomposition of this unstable compound. Due to the *trans* effect, which is greater for sulfur than for chloride, methionine in *trans* position to another methionine ligand was substituted by chloride ion from the eluent (0.2 mol dm^{-3} NaCl).

Conclusion

Proton and ^{13}C NMR spectroscopy offers great advantage in studying platinum complexes in aqueous solution. Every isomer formed can be identified and its structure established. The spectroscopic data of the studied systems, in which the Pt^{2+} to Met ratio varies from 1:1 to 1:3, shows the formation of a mixture of geometrical and substitutional isomers. Since the initial conditions were suitable for protonation of the amine and carboxylic functional groups of the amino acid ligand, the major products were S-monodentate complexes, but significant amounts of chelate forms were also found. Formation of S,N-chelate complexes due to the high affinity of amine ligands for the Pt^{2+} ion is not surprising, because chelates involving amide nitrogen were obtained also in acidic solution.[14] It would be of much interest to compare the conditions favouring the formation of five- or six-membered rings but only preliminary conclusions can be offered. The five-membered rings are easily formed in the case of amide nitrogen as donor [14–17] even in acidic solution, while six-membered rings are formed, also at low pH, with an amine nitrogen bonded to the Pt^{2+}. Five-membered rings involving amine nitrogen have been reported,[7] but such complexes were obtained at neutral pH.

The spectra of sample IV show the presence of a trimethionine complex which, to our knowledge, has never been identified. The important role in *trans* to *cis* isomerization of this species is in accord with the proposed mechanism of isomerization of platinum(II)–dimethylsulfide complexes.

Experimental

Materials.—The salt $K_2[PtCl_4]$ was obtained [18] from analytical grade $K_2[PtCl_6]$ (POCh Gliwice, Poland). L-Methionine, chromatographically homogeneous, was supplied by Reanal, Hungary. The Sephadex G-10 was obtained from Pharmacia Fine Chemicals.

NMR Measurements.—All spectra were recorded using Bruker AM 500 (500 MHz), Varian Gemini 200 (200 MHz) and Tesla 100 (100 MHz) spectrometers. Residual HDO and TSPA or sodium 4,4-dimethyl-4-silapentane-1-sulphonate were used as internal standards for ^1H NMR spectra, Bu^{t}OH as internal standard for ^{13}C spectra. An internal lock on deuterium from the solvent was used in all measurements. All ^{13}C NMR spectra were proton decoupled. Samples I–IV were dissolved in D_2O before measurements, and allowed to stand for 30 min. The pH of the solutions was about 2.0 for samples I, II and IV, and about 5.5 for III.

UV/VIS Spectra.—The UV/VIS spectra were recorded by use of a Specord UV/VIS spectrophotometer (Carl Zeiss Jena).

Preparation of Samples I, II *and* IV.—To a solution (10 cm^3) of $K_2[PtCl_4]$ (415 mg, 1 mmol for sample I; 207 mg, 0.5 mmol for II; 104 mg, 0.33 mmol for III) in 0.1 mol dm^{-3} HCl was added solid L-methionine (149 mg, 1 mmol). The solution was stirred and allowed to stand for 1 h in the dark. The change of colour from reddish to yellow was complete within this time. The UV/VIS spectra indicate no characteristic $[PtCl_4]^{2-}$ absorption bands. The solution was evaporated *in vacuo* at 35 °C and dried

over P_2O_5. The ^1H and ^{13}C NMR spectral data for samples I, II and IV are listed in Tables 3 and 4.

Preparation of Sample III.—To a solution (10 cm^3) of $K_2[PtCl_4]$ (104 mg, 0.33 mmol) in 0.1 mol dm^{-3} HCl was added solid L-methionine (149 mg, 1.5 mmol). The solution was stirred and allowed to stand for 1 h in the dark. The change of colour from reddish to yellow was complete within this time. The UV/VIS spectra indicate no characteristic $[PtCl_4]^{2-}$ absorption bands. The excess of methionine (indicated by TLC on silica gel plates) was separated on a Sephadex G-10 column using 0.2 mol dm^{-3} NaCl as eluent. All fractions containing platinum complexes were collected, evaporated *in vacuo* at 35 °C and dried over P_2O_5. The ^1H and ^{13}C NMR spectral data for sample III are listed in Tables 3 and 4.

Acknowledgements

This contribution was supported by grant CPBP 01.17 from the Polish Committee of Sciences and Technical Development.

References

1 R. E. Dickerson, D. Eisenberg, J. Varnum and M. L. Kopka, *J. Mol. Biol.*, 1969, **45**, 77.
2 C. A. McAuliffe, *J. Chem. Soc. A*, 1967, 641.
3 C. A. McAuliffe and S. G. Murray, *Inorg. Chim. Acta Rev.*, 1972, **6**, 103, 111.
4 D. Dalietos, A. Furst and D. Theodoropoulos, *Biol. Trace El. Res.*, 1982, **4**, 331.
5 D. D. Gummin, E. M. Ratilla and N. M. Kostic, *Inorg. Chem.*, 1986, **25**, 2429.
6 L. M. Peerey and N. M. Kostič, *Inorg. Chem.*, 1987, **26**, 2079.
7 J. A. Galbraith, K. A. Menzel, E. M. Ratilla and N. M. Kostič, *Inorg. Chem.*, 1987, **26**, 2073.
8 T. G. Appleton, J. W. Connor and J. R. Hall, *Inorg. Chem.*, 1988, **27**, 130.
9 L. Olgemöller and W. Beck, *Chem. Ber.*, 1984, **117**, 1241.
10 M. F. Mogilevkina, V. I. Rar and I. K. Korobeinicheva, *Russ. J. Inorg. Chem.*, 1980, **25**, 1045.
11 R. Roulet and C. Barbey, *Helv. Chim. Acta*, 1973, **56**, 2179.
12 P. L. Goggin, R. J. Goodfellow, S. R. Haddock, F. J. S. Reed, J. G. Smith and K. M. Thomas, *J. Chem. Soc., Dalton Trans.*, 1972, 1904.
13 J. D. Scott and R. J. Puddephatt, *Organometallics*, 1983, **2**, 1643.
14 H. C. Freeman and M. L. Golomb, *Chem. Commun.*, 1970, 1523.
15 G. E. Kirvan and D. W. Margerum, *Inorg. Chem.*, 1985, **24**, 3017.
16 M. F. Mogilevkina, M. V. Sekacheva, I. M. Cheremisina and E. A. Gal'tsova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1976, **21**, 77.
17 M. F. Mogilevkina, V. I. Bessonov and I. M. Cheremisina, *Russ. J. Inorg. Chem. (Engl. Trans.)*, 1973, **18**, 1396.
18 S. E. Livingstone, *The Chemistry of Ruthenium, Rhodium, Palladium, Osmium, Iridium and Platinum*, (Russian Edition), Moscow, 1978, p. 274.

Received 30*th April* 1991; *Paper* 1/02009I