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A study of the Reactions of Cysteinatomethylester Platinum(II)-μ-Dichloro Cysteinatomethylester Platinum(II) with Nucleosides

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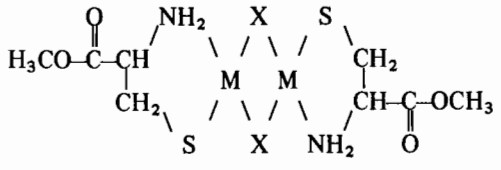
The reactions of the dinuclear complex cysteinatomethylester platinum(II)-μ-dichlorocysteinatomethylester platinum(II), [Pt(O-MeCys)Cl]$_2$, with nucleosides have been studied in aqueous solutions. The isolated complexes correspond to the general formulae [Pt(O-MeCys)(nucl)Cl], where nucl = cytidine (cyd), inosine (ino), guanosine (guo), adenosine (ado), tri- and tetraacetyladenosine (trado, tetado) and triacetylinosine and guanosine (trino, trguo). The complexes were characterized by elemental analyses, conductivity measurements, IR, ^{1}H NMR and ^{13}C NMR spectra. The results indicate that the purine bases coordinate through both N(7) and N(1) with Pt(II), whenever these are available, while cytidine does so through N(3). The Pt–N bond in this case is found weaker as compared to other similar bonds, due to the high trans *influence of the opposite Pt–S bond.*

Introduction

Recently, we reported the reactions of cysteine (Cys) and cysteinemethylester (O-MeCys), with K_2MX_4, where M is Pt(II) and Pd(II) [1]. Among the isolated complexes and based mainly on their IR spectra, the ones of the empirical formulae M(O-MeCys)Cl were assigned dinuclear structures *I*:



I

Similar structures were also proposed for the analogous complexes of cysteine [1–3]. It was further found that the dinuclear Pt(II) complexes of the above formula [Pt(O-MeCys$^-$)Cl]$_2$ reacted readily with nucleosides to form the monomeric species, as follows:

$$[Pt(O\text{-}MeCys^-)Cl]_2 + 2nucl \rightleftharpoons 2[Pt(O\text{-}MeCys^-)(nucl)Cl] \quad (1)$$

where nucl is a nucleoside like, inosine, guanosine, adenosine *etc.* These reactions are worthy to study, because they support the proposed dinuclear structures of the cysteine and derivative complexes. Also, they provide a mixed amino-acid, nucleoside–Pt(II) complex system, which is interesting, due to the antitumor property of the Pt(II) complexes [4]. Similar reactions of dipeptide–Pd(II) complexes with nucleosides and nucleotides have recently been studied mainly with ^{13}C NMR spectroscopy, by Kozlowski *et al.* [5–7].

On the other hand, studies of interactions of different Pt(II) and Pd(II) complexes, used as starting materials, with nucleosides, have shown the N(7) atom of inosine, guanosine, xanthosine, triacetylinosine, triacetylguanosine and tetraacetyadenosine, and the N(1) and N(7) atoms of 9-methyladenine, adenosine and triacetyladenosine as the binding sites with the metals [8–15]. The O(6) of the first nucleosides were also proposed to participate in bonding, either in chelate or polynuclear structures [8, 14a].

In the present paper we report on the [Pt(O-MeCys$^-$)(nucl)X] complexes, isolated from reaction (1), which are characterized and studied with IR, ^{1}H and ^{13}C NMR spectra.

Results and Discussion

All the complexes isolated from reaction (1), correspond to the empirical formulae [Pt(O-MeCys$^-$)-

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TABLE I. Analytical and Conductivity Data of the Complexes.[a]

Compound	C%	H%	N%	Pt%	Cl%	Λ_M in DMF	Melting Points °C
[Pt(O-MeCys)(ino)Cl]	26.86 (26.55)	3.40 (3.16)	11.52 (11.06)	30.60 (30.82)	5.30 (5.61)	24	215 *D*
[Pt(O-MeCys)(trino)Cl]	31.95 (31.63)	3.71 (3.43)	9.50 (9.23)	27.30 (27.70)	4.95 (4.68)	26	198 *D*
[Pt(O-MeCys)(guo)Cl]	25.60 (25.93)	3.02 (3.24)	13.28 (12.97)	30.50 (30.10)	5.90 (5.48)	23	225 *D*
[Pt(O-MeCys)(trguo)Cl]	30.85 (31.02)	3.24 (3.49)	10.48 (10.86)	25.50 (25.20)	4.86 (4.59)	25	185
[Pt(O-MeCys)(ado)Cl]	26.85 (26.59)	3.55 (3.32)	13.60 (13.30)	31.10 (30.87)	5.95 (5.62)	25 (100 H_2O)	190 *D*
[Pt(O-MeCys)(trado)Cl]	31.25 (31.67)	3.80 (3.56)	11.40 (11.09)	25.98 (25.74)	4.95 (4.69)	26	180
[Pt(O-MeCys)(tedado)Cl]	32.80 (33.01)	3.35 (3.63)	10.80 (10.50)	24.75 (24.38)	4.85 (4.44)	27	175 *D*
[Pt(O-MeCys)(xao)Cl]	25.52 (25.89)	3.35 (3.08)	10.30 (10.79)	29.70 (30.06)	5.82 (5.47)	25	220 *D*
$[Pt(O\text{-}MeCys)Cl]_2(ado)$	21.42 (21.68)	2.70 (2.91)	10.30 (9.84)	39.50 (39.15)	7.50 (7.13)	15 (50 H_2O)	195 *D*

[a]trino = triacetyl inosine, trguo = triacetyl guanosine, trado = triacetyl adenosine, tetado = tetraacetylanosine, *D* = decomposition. The numbers in parentheses represent the calculated values.

TABLE II. IR Data of the Compounds.[a]

Compound	ν(C=O) acetyls	$\delta(NH_2) + \delta(NH_3)$	ν(Pt–Cl)	$\nu(NH_2)$	ν(C=O) rings	$\delta(NH_2)$ rings	ν(C=C) + ν(C=N) rings	ν(C=O) sugar acetyls
O-MeCys·HCl	1726vs	1564m	–	2900–3400vs,br	–	–	–	–
$[Pt(O\text{-}MeCys)Cl]_2$	1733 vs	1576m 1620m	315m	3200sbr	–	–	–	–
[Pt(O-MeCys)(guo)Cl]	1740s	1633s 1588s	329m	3200–3400vs,br	1694s	1633s	1500 s 1539 s 1588 s	–
[Pt(O-MeCys)(ino)Cl]	1738s	1635s	355m?	3200–3400vs,br	1695vs	–	1569 m 1592 m	–
[Pt(O-MeCys)(trguo)Cl]	1741s	1631s 1594s	333m	3200–3400vs,br	1695vs	1631s	1500 m 1537 m 1594 m	1741
[Pt(O-MeCys)(GMP)Cl]	1739s	1639s 1596s	333m	3200–3400vs,br	1694vs	1639s 1596s	1500 m 1533 m	–
[Pt(O-MeCys)(trino)Cl]	1740s	–	330m	–	1690s	–	1550 m 1580 m	1740
[Pt(O-MeCys)(ado)Cl]	–	1640s	330m	3200–3400vs,br	–	1640s	1562m 1590 m	–
[Pt(O-MeCys)(trado)Cl]	1740s	1640s	330m	3200–3400vs,br	–	1640s	1537 m 1585 m	1738

[a]s = strong, m = medium, vs = very strong, br = broad.

(nucl)Cl] as their analytical results indicate. In the case of ado we have also obtained a second complex of the formula $[(Pt(O\text{-}MeCys)Cl)_2(ado)]$. The molar conductances of the complexes, in DMF solutions rather indicate 1:1 electrolytes, which could only be explained with the displacement of the chlorine atom by a solvent molecule (Table I):

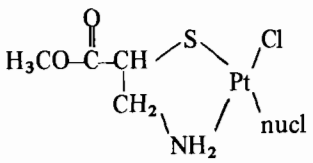
$$[Pt(O\text{-}MeCys^-)(nucl)Cl] + DMF \rightleftarrows [Pt(O\text{-}MeCys^-)(nucl)(DMF)]Cl \quad (2)$$

In the case of ado, the complex [(Pt(O-MeCys)(ado)-Cl] has a Λ_M = 100 mhos in water solutions (1:1 electrolyte), while the complex $[(Pt(O\text{-}MeCys)Cl)_2$-(ado)] a Λ_M value of about 50 mhos.

TABLE III. ^{1}H NMR Chemical Shifts of the Compounds in ppm (δ).

Compound	H(2)	H(8)	H_1'	CH_2	OCH_3	CH	Solvent
O-MeCys	–	–	–	3.15 (J = 7 Hz)	3.86	4.43 (J = 5.5 Hz)	D_2O
				2.96 (J = 5 Hz)	3.70	4.26	DMSO-d_6
[Pt(O-MeCys)Cl]$_2$	–	–	–	3.03	3.76	4.73	DMSO-d_6
[Pt(O-MeCys)(ino)Cl]	8.16	8.50	6.00 (J = 4 Hz)	3.53	3.85	–	D_2O (1 *M* NaCl)
[Pt(O-MeCys)(ado)Cl]	8.40	8.50	6.20	3.50	3.96	–	D_2O
	8.32	8.50	5.92	–	–	4.53	DMSO-d_6
[Pt(O-MeCys)Cl]$_2$(ado)	8.37	8.57	5.92	–	–	4.50	DMSO-d_6
[Pt(O-MeCys)(guo)Cl]	–	9.16	6.10	–	–	–	D_2O + 1dDCl
[Pt(O-MeCys)(xao)Cl]	–	8.76	6.03	–	–	–	D_2O + 1dDCl
[Pt(O-MeCys)(trado)Cl]	8.35	8.35	6.30	–	–	–	D_2O
[Pt(O-MeCys)(trino)Cl]	8.28	8.69	6.23	–	–	–	D_2O + 1dDCl
ino	8.11	8.22	5.98	–	–	–	D_2O
guo	–	7.80	5.71	–	–	–	DMSO-d_6
ado	7.95	8.17	5.85	–	–	–	DMSO-d_6
xao	–	7.80	5.82	–	–	–	DMSO-d_6
trado	8.02	8.15	6.26	–	–	–	$CDCl_3$
trino	8.03	8.33	6.23	–	–	–	$CDCl_3$

Due to the high *trans* effect of the sulfur atom, the chlorine atom *trans* to it (Structure *I*) would first be expected to labilize and replaced by a nucleoside molecule in reaction (1), producing:



II

IR Spectra

Characteristic IR bands for the complexes and the ligands are given in Table II. The ν(C=O), of the ligand (O-MeCys), shown at 1733 cm^{-1} in the initial complex [Pt(O-MeCys$^-$)Cl], moves to slightly higher frequencies (about 1740 cm^{-1}) in all the [Pt(O-MeCys)(nucl)Cl] complexes and coincides with the ν(C=O) frequency of the sugar acetyls, whenever available [9]. On the other hand, the $\delta(NH_2)$ of the coordinated to Pt(II) aminoacid which is shown at 1620 and 1576 cm^{-1} in the initial complex, may coincide with the $\delta(NH_2)$ motion of the nucleosides, whenever there is one at ~1630–1640 cm^{-1}. However, it can also be assigned to a band near 1590 cm^{-1} present in all the complexes. The ν(C=O) of the exocyclic carbonyl oxygen of ino, guo, xao *etc.* appears at almost constant frequency (1700 cm^{-1}) in the complexes and the free ligands, thus excluding its participation in bonding with Pt(II) [8, 9, 12, 14a]. In the opposite case, it was found at ~1625 cm^{-1}.

Attempts to prepare complexes with O(6) involvement in bonding with Pt(II), using nucleosides possessing an exocyclic keto group at the 6th position in either chelate or polynuclear structures [8, 9, 14a] failed. Usually, this is achieved, following deprotonation of the N(1)–H imino proton, by increasing the pH to slightly alkaline values in the case of Pt(II) [8], or it takes place automatically upon N(7) coordination in the case of Pd(II) [9]. In this way, an O^- is created at the 6th position which interacts with the metals. Increasing the pH of aqueous solutions of the complexes [Pt(O-MeCys)(nucl)Cl] to slightly alkaline values, resulted in the slow hydrolysis of the O-methylester of cysteine [1], as well as the replacement of nucleosides with hydroxyl groups. Again the nucleoside *trans* to the sulfur atom (Structure *II*), is labilized and easily replaced, due to the high *trans* influence of the sulfur atom.

The appearance of a band at ~1640 cm^{-1} for the ado and trado complexes, assignable to the $\delta(NH_2)$ motion of their exocyclic amino group, excluded again the participation of this group to bonding with Pt(II) [10–12]. This had been attributed to the lone pair of electrons of the amino group [10, 12] participation to the ring resonance. Finally, the ν(Pt–

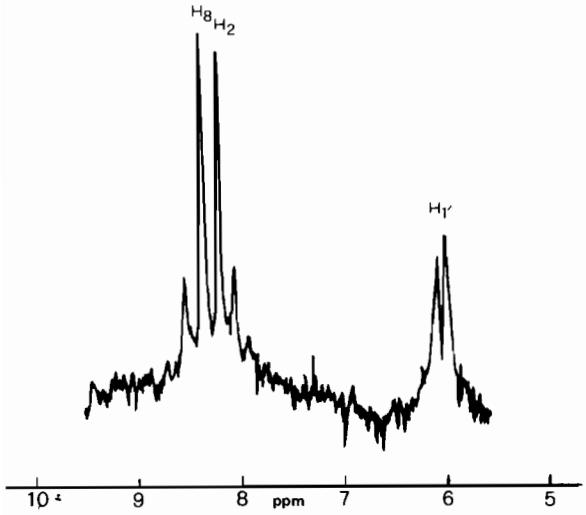


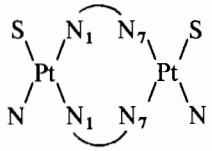
Fig. 1. The ^{1}H NMR spectra of the complex [Pt(O-MeCys)-(ado)Cl]$_2$ in D_2O is shown.

Cl) frequency, which appears at 315 cm^{-1} in the complex [Pt(O-Mecys$^-$)Cl]$_2$ [1] in agreement with the existence of chlorine bridges, moves to higher frequencies (about 330 cm^{-1}) in the monomeric nucleoside derivative complexes (Table II).

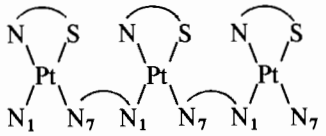
^{1}H NMR Spectra

The O-MeCys·HCl part, of either the ligand, the starting complex [Pt(O-MeCys)Cl]$_2$ and the final complexes [Pt(O-MeCys)(nucl)Cl], is not well resolved in the ^{1}H NMR spectra, in DMSO-d_6 solutions. Especially in the last complexes the O-MeCys bands are not shown clearly, because they coincide many times with the nucleoside resonances. Only the ligand O-MeCys·HCl, in D_2O, shows a triplet at 4.43 ppm, a doublet at 3.15 ppm and a singlet at 3.86 ppm, which are assigned to CH, CH_2 and OCH_3 groups respectively (Table III). The coupling constants are also given.

However, the ^{1}H NMR spectra are very useful in assigning the bonding sites of the nucleosides with Pt(II) [5–15]. The complex [Pt(O-MeCys)(ino)Cl], in D_2O shows two resonances at 8.16 and 8.50 ppm, assigned to H(2) and H(8) respectively. This indicates N(7) coordination of ino with Pt(II), as in other similar cases [8, 11a]. The smaller chemical shift of the H(8) proton resonance upon coordination with Pt(II) in [Pt(O-MeCys)(ino)Cl] (0.28 ppm), as compared to 0.62 ppm in the case for example of *cis*-Pt(ino)$_2$Cl$_2$ [8], may be due to a weaker Pt–N(7) bond the former, lying *trans* to the sulfur atom. In the complex [Pt(O-MeCys)(ado)Cl] both H(2) and H(8) signals are shifted down field almost equally by 0.50 and 0.45 ppm respectively. The spectrum consists of the above two main peaks and also two ^{195}Pt satellites on both sites (Fig. 1). Therefore, every proton is coupled with ^{195}Pt (natural abundance 33%), to give two triplets, where the main peaks coincide with ^{195}Pt satellite [11b]. This indicates simultaneous coordination of both N(1) and N(7) sites of ado with Pt(II) [11b]. Again the chemical shift of both protons is smaller if compared with other Pt(II)–ado complexes (~1 ppm) [10b, d, 11b], obviously due to the high *trans* influence of sulfur, opposite to the coordination site. Simultaneous coordination of N(1) and N(7) also takes place in trado (Table III). This implies dinuclear or polynuclear structures for these complexes as follows:

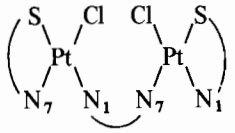


or



III

for the [(Pt(O-MeCys)Cl)$_2$(ado)] complex, the structure



IV

or similar polynuclear ones seem more likely.

The ligands guo and xao also coordinate through N(7) as the shift to higher fields of their H(8) proton resonance indicate. The shift is larger here (0.8–1 ppm). However, this is expected for the spectra recorded in 0.3–0.5 *N* DCl [9]. Also trino coordinates through N(7) with a shift of the H(8) resonance of about 0.35 ppm.

^{13}C NMR Spectra

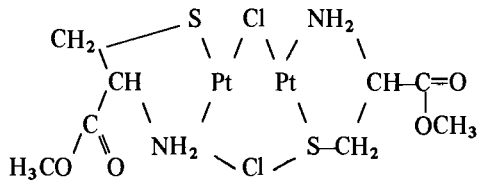
The ^{13}C NMR spectra of O-MeCys·HCl, [Pt(O-MeCys)Cl]$_2$, [Pt(O-MeCys)(ino)Cl], [Pt(O-MeCys)-(guo)Cl], [Pt(O-MeCys)(ado)Cl], and [Pt(O-MeCys)-(cyd)Cl] have been recorded in DMSO-d_6 solutions, in order to gain more information about the structures of the complexes and compare the results with those of ^{1}H NMR spectra. The ^{13}C NMR spectra possess more variables subject to change upon the formation of metal–ligand bonds [5–7, 13b, 14]. The ^{13}C NMR chemical shifts are given in Table IV and Fig. 2. The assignments for the bases have been made

TABLE IV. ^{13}C NMR Chemical Shifts of O-MeCys, $[Pt(O\text{-}MeCys)Cl]_2$ and [Pt(O-MeCys)(nucl)Cl] in ppm (δ).

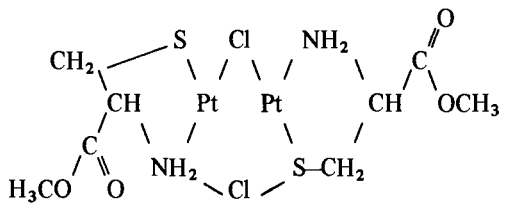
Compound	CH_2	CH	OCH_3	C=O	C_2	C_4	C_5	C_6	C_8	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$
O-MeCys	38.1	52.5	54.1	169.0	–	–	–	–	–	–	–	–	–	–
guo	–	–	–	–	153.9	151.5	117.3	157.0	135.8	87.0	70.6	74.0	85.5	61.8
[Pt(O-MeCys)(guo)Cl]	32.9	63.5	53.1	170.0	154.5	151.8	116.8	157.3	136.4	87.2	70.8	74.2	85.7	61.9
ado	–	–	–	–	152.7	149.4	119.7	156.4	140.3	88.4	71.0	73.9	86.2	62.0
[Pt(O-MeCys)(ado)Cl]	33.0	63.5	53.0	170.0	152.3	149.7	119.9	156.3	140.8	88.6	71.2	74.1	86.3	62.2
cyd	–	–	–	–	155.7	165.7	94.2	141.7	–	89.5	69.7	74.2	84.4	61.0
[Pt(O-MeCys)(cyd)Cl]	33.0	63.8	53.0	170.2	154.5	164.7	94.9	143.0	–	89.6	70.8	74.5	84.5	61.1
[Pt(O-MeCys)Cl]	32.6	63.7	53.4	170.4 171.3	–	–	–	–	–	–	–	–	–	–

by Jones *et al.* [16] and Uesugi *et al.* [17]. Those of the ligand O-MeCys and the complexes were made mainly based on off-resonance experiments.

Thus, the assignments of O-MeCys are as follows: The 38.1 ppm resonance is assigned to the methylene (CH_2), the 52.5 ppm to the methine (CH), the 54.1 ppm to the (OCH_3) and the 169.0 ppm to the C=O carbon resonances. These appear as triplet, doublet, quadruplet and singlet respectively in the off-resonance spectra, in the complex [Pt(O-MeCys)Cl] the CH_2 signal shifts up field by 5.5 ppm, while the CH signal is the most down field shifted by 11.2 ppm. The OCH_3 signal is found upfield by 0.7 ppm, while the C=O resonance is found as a doublet, down field by 1.4 and 2.3 ppm. This split into two peaks of the C=O carbon resonance, may be due to different arrangement of the group $-COOCH_3$, with respect to the plane of the two metals in the dimer (Structures *V* and *VI*).



V



VI

The chemical shifts of the nucleosides upon coordination with the metals are not substantial as in other metal–nucleoside complexes [5–7, 13, 14b, 15], possibly due to weak Pt–N(7) bond, lying opposite to the Pt–S bond. Coordination causes negative shift of C_5 (–0.5 ppm) of guo and positive shifts by 0.6 ppm for C_2 and C_8 and 0.3 ppm for C_4 and C_6. The observed shifts are roughly half of those observed by Nelson *et al.* [13b] in Pden-guo complexes, where the C_6, C_4 and C_5 had negative shifts and C_2 and C_8 positive. In our case the C_2 and C_8 are again the most down-field shifted. In cytidine a negative shift by 1.2 and 1 ppm for C_2 and C_4 and a positive one by 0.7 and 1.3 ppm, for C_5 and C_6 respectively, are observed. The analogous shifts found in Pden-Cyd complexes by Nelson *et al.* [13b] were –0.4, –1.5 for C_2 and C_4 and +0.4 and +0.1 ppm for C5 and C_6 respectively. Finally, in the case of ado, we have a negative shift (0.4 and 0.1 ppm) for the C_2 and C_6 atoms and positive shifts by 0.3, 0.2 and 0.5 ppm for the C_4, C_5 and C_8 atoms respectively. Since the C_8 atom is the most down field shifted in the case of guo, the N(7) site is the bonding site, while for cyd is the N(3) with negative shifts of the adjacent carbons [13b]. In the case of ado, both N(1) and N(7) were postulated as bonding sites, since the C_2 and C_6 adjacent to N(1) are shifted up field and the others near to N(7) down field. The O-MeCys carbon signals are observed at almost the same frequency as in the complex $[Pt(O\text{-}MeCys)Cl]_2$, as well as the sugar carbons (see Table IV). The complex [Pt(O-MeCys)(ino)Cl] is not stable in DMSO-d_6 solutions and decomposes easily. Thus, its ^{13}C NMR spectrum is not reported.

Experimental

Materials

The nucleosides and O-methylcysteine were purchased from Fluka Chemical Co. and used without further purification. Potassium chloro platinate (K_2PtCl_4) was from Johnson Matthey and Mallory Ltd.

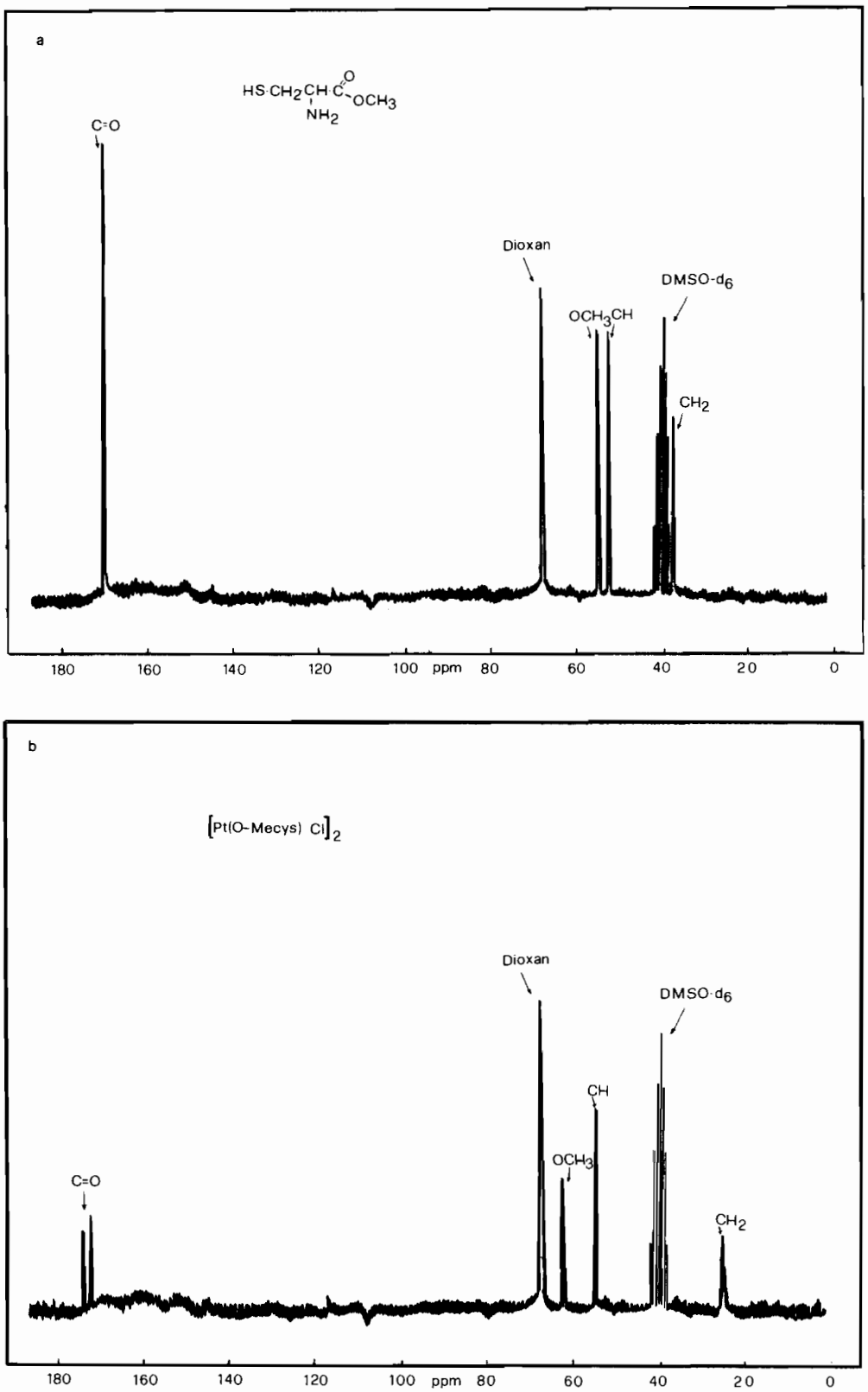
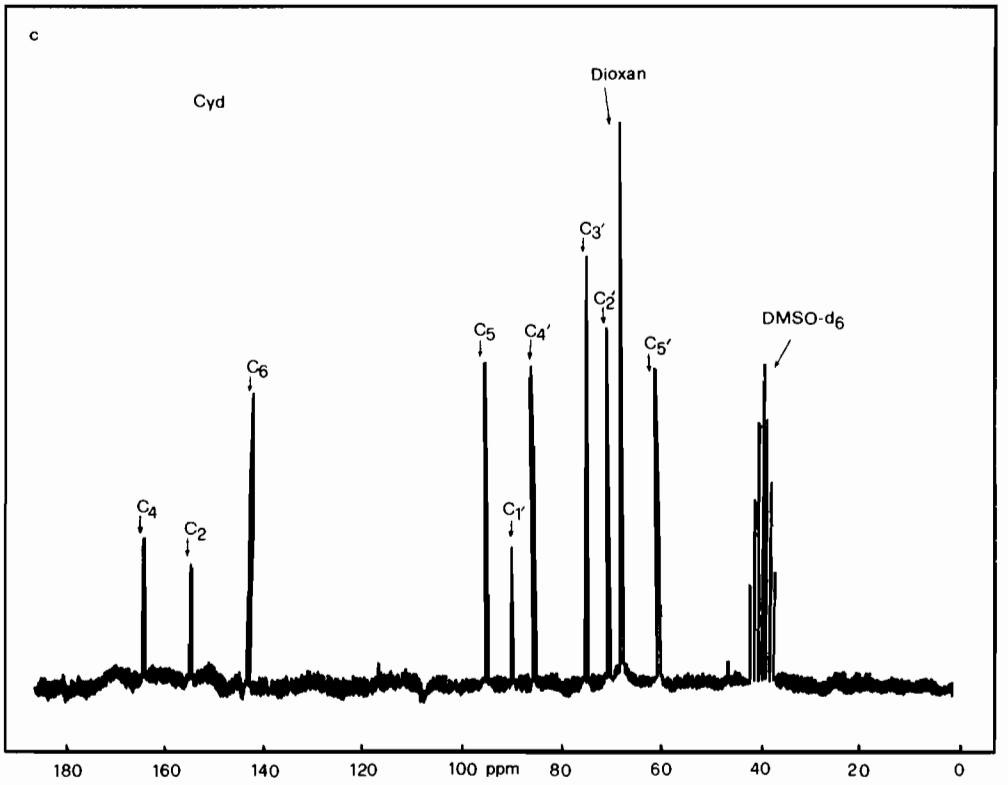


Fig. 2. ^{13}C NMR spectra in DMSO-d_6 of (a) O–cysteinmethylester, O–MeCys, (b) [Pt(O]MeCys)Cl]$_2$, (c) cytidine cyd, and (d) [Pt(O-MeCys)(cyd)Cl].


c
Cyd
Dioxan
C3′
C2′
C5
C4′
C5′
DMSO-d6
C6
C4
C2
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180
160
140
120
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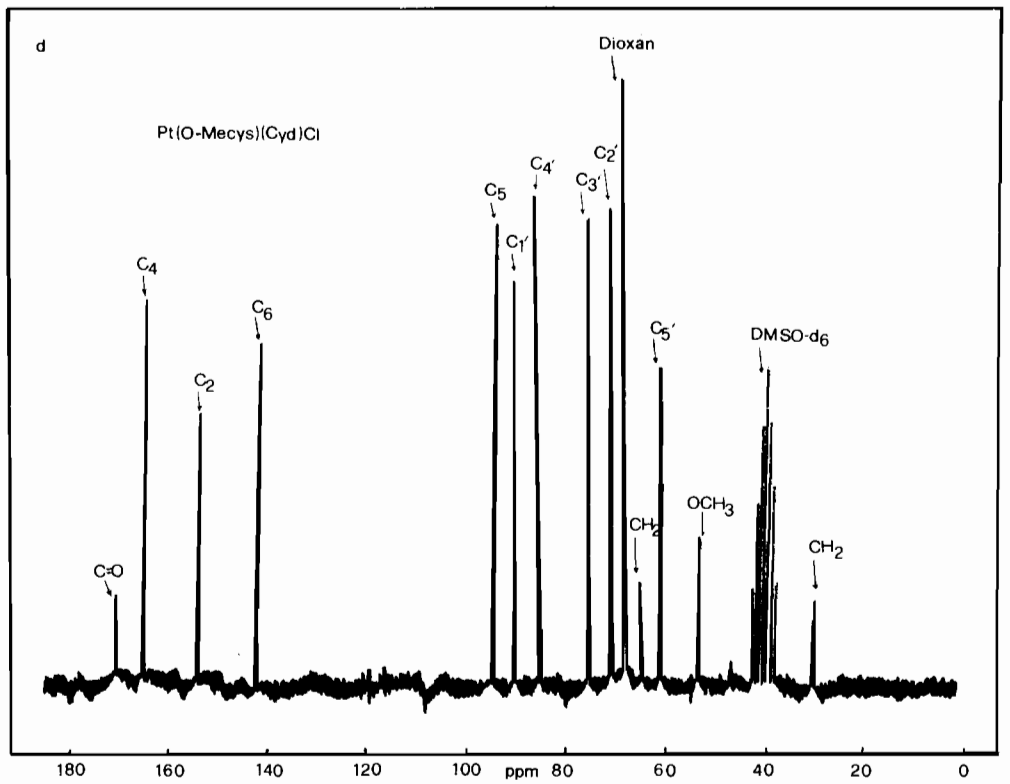
d
Dioxan
Pt(O-Mecys)(Cyd)Cl
C2′
C4′
C3′
C5
C1′
C4
C6
C5′
DMSO-d6
C2
OCH3
CH2
CH2
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180
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Methods

IR spectra were recorded in a Beckman 2050 model spectrophotometer. ^{1}H NMR spectra were recorded on a Varian T 60 spectrometer; TMS was used as internal reference when DMSO-d_6 was used as solvent, while in D_2O, DSS. ^{13}C NMR spectra were obtained on a Varian XL-100 NMR spectrometer operating in Fourier transform mode with proton noise decoupling at frequency of 25.2 MHz . Chemical shifts were measured relative to internal DMSO-d_6 and dioxan and converted to the TMS scale using $\delta^{\text{DMSO-d}_6}$ = +39.6 ppm and δ^{dioxan} = +67.4 ppm. Conductivity measurements were performed using an E365B conductoscope, Metrohm Ltd., Herisau, Switzerland. The melting points were determined on a Fisher John's melting point apparatus and are uncorrected.

Microanalyses

These were performed in the Laboratories of the National Research Foundation of Greece in Athens by Dr. Mantzos.

Preparation of the Complexes

The complex $[Pt(O\text{-}MeCys)Cl]_2$ used as starting material, was prepared as described previously [1]. All the complexes [Pt(O-MeCys)(nucl)Cl] were prepared by mixing equimolar amounts of $[Pt(O\text{-}MeCys)Cl]_2$ and the proper nucleosides in water and heating with stirring at 60 °C over night. For the complex $[(Pt(O\text{-}MeCys)Cl)_2(ado)]$ the stoichiometry was 2:1 = Pt:ado. After cooling, the resulting solutions were evaporated to small volumes and the main products precipitated with excess of acetone and ether (1:3). Preliminary experiments in D_2O showed that the reactions were complete at the end of 10–12 hrs and the products were pure, by recording their ^{1}H NMR spectra. The yields were quantitative.

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