Inorganica Chimica Acta, 46 (1980) 57–62

N,N-Dimethyl O-Ethylthiocarbamate Complexes of Palladium(II) and Platinum(II) Halides

L. SINDELLARI, G. FARAGLIA, B. ZARLI, P. CAVOLI

Istituto di Chimica Generale dell'Università, Via Loredan 4, 35100 Padua, Italy

A. FURLANI and V. SCARCIA

Istituto di Farmacologia dell'Università, Via Valerio 32, 34100 Trieste, Italy

Received June 28, 1979

Complexes of formula $M(DMTC)_2X_2$ (where M = Pd, Pt; DMTC = N,N-dimethyl O-ethylthiocarbamate; X = Cl, Br, I) have been prepared and studied by visible, IR and ^1H nmr spectroscopy. The ligand acts as sulfur donor towards the metal atom. The complexes have generally a trans *square-planar geometry. Whereas the structure of solid $Pd(DMTC)_2Cl_2$ could not be determined, in solution a* trans *configuration is suggested. Cis-$Pt(DMTC)_2X_2$ (X = Cl, Br) have been also isolated, which in solution slowly isomerize to* trans.

The compounds have been tested for possible cytotoxic effects.

Introduction

Palladium(II) and platinum(II) halides form with thiourea and N-substituted thioureas compounds having various stoichiometries, such as MLX_2 [1–5], ML_2X_2 [1–3, 6, 7] and ML_4X_2 [1, 2, 4–7–9], where M = Pd or Pt; L = ligand; X = halide. Thioamides H_2N-CS-R give generally 1:4 complexes [10–12], while with N,N-dimethylthioamides a series of palladium complexes of formula PdL_2X_2 has been prepared [13–15]. However a few compounds of these metals with thiocarbamate esters have been reported. The ligand C_6H_5NH-CS-OEt forms with platinum the five-coordinate adduct PtL_3Cl_2 [16]; with palladium this ligand acts as bidentate giving $Pd(C_6H_5N$-CS-$OEt)_2$ [17], where the metal atom attains an approximately planar configuration through deprotonated nitrogen and sulfur [18]. N-Allylthiocarbamates give adducts of formula PdL_2Cl_2 and $MLCl_2$ (M = Pd or Pt) [17]; in $Pd(CH_2CHCH_2$-NH-CS-$OCH_3)Cl_2$ the ligand acts as bidentate through the sulfur atom and the olefinic double bond [19]. Except for ref. [2] where coordination through the nitrogen is suggested, the above reported ligands have been found to bind *via* thiocarbonyl group. Metal–sulfur bond has been confirmed in the four-coordinate ionic complexes $Pd(NH_2$-CS-$NH_2)_4Cl_2$ [20] and $Pt(EtNH$-CS-$NH_2)_4I_2$ [21] by X-ray studies.

As a part of a study on the complexing behaviour of the ligands RR'N-CS-OEt (where R = R' = H; R = H, R' = CH_3; R = R' = CH_3) by varying the number of the substituents to the nitrogen, this paper reports the preparation and properties of the complexes $M(DMTC)_2X_2$ (where M = Pd, Pt; DMTC is the title ligand; X = Cl, Br, I). Owing to the wide interest on the antitumor activity of palladium [22, 23] and platinum [24, 25] complexes, the prepared compounds have been tested for possible cytotoxic effects.

Experimental

The starting materials were K_2PtX_4 (X = Cl, Br) [26], K_2PdX_4 (X = Cl, Br) [27], and $PdCl_2(C_6H_5$-$CN)_2$ [28] (M.p. = 120–1 °C, far IR spectrum as in ref. [29]). DMTC was obtained from $EtOCS_2K$ and $(CH_3)_2NH$ in water [30], extracted by ethyl ether, dried over anhydrous Na_2SO_4. The solvent was removed and the ligand distilled under reduced pressure and stored in nitrogen. Benzene and n-hexane were distilled from Na.

Preparation of the Complexes

trans-*$Pt(DMTC)_2X_2$ (X = Cl, Br)*

To a concentrated aqueous solution of K_2PtX_4 the ligand (molar ratio 1:3) in ethanol was added giving an oil which crystallized slowly. The crude product, dried *in vacuo*, was recrystallized from benzene–hexane. The same compound was obtained by varying the metal to ligand molar ratio from 1:1 to 1:6.

cis-*$Pt(DMTC)_2Cl_2$*

A mixture of K_2PtCl_4 and DMTC in 95% ethanol (molar ratio 1:3) was allowed to stand at room temperature for three days; the deep orange solution was evaporated at reduced pressure, the residue dried

in vacuo and recrystallized from benzene–hexane. An orange solid, pure *cis* by far IR, was obtained (M.p. = 93–4 °C). By varying the molar ratio from 1:2 to 1:5 and the time of standing from one to three days, generally mixtures of *cis* and *trans* isomers were obtained, which were separated by repeated benzene–hexane crystallizations. Various pure *cis* solid fractions (controlled by elemental analysis and far IR) having different melting points and slightly different IR spectra in the 700–500 cm^{-1} region were isolated.

cis-*Pt(DMTC)$_2$Br$_2$*

By reaction of K_2PtBr_4 and ligand (molar ratio varying from 1:2 to 1:5; reaction time from one hour to seven days) *cis–trans* mixtures were normally obtained, operating as described above for the *cis*-chloro-complex. In one instance the pure product was isolated in a very small amount.

trans-*Pt(DMTC)$_2$I$_2$*

To an aqueous solution of K_2PtCl_4 and KI (molar ratio 1:10) gently heated for about 5 min, DMTC (molar ratio 1:3) was added giving a dark oil which crystallized slowly. The crude product, washed with ethyl ether, was recrystallized from benzene–hexane.

Pd(DMTC)$_2$Cl$_2$

A benzene solution of $PdCl_2(C_6H_5CN)_2$ and ligand (molar ratio 1:3) was allowed to stand for 15 min. Brown crystals of the complex separated by addition of hexane. The same compound has been obtained from K_2PdCl_4 and DMTC either in water or in methanol, following the procedures used in the preparation of both the *cis* and *trans* platinum complexes.

trans-*Pd(DMTC)$_2$Br$_2$*

A solution of K_2PdBr_4 and ligand (molar ratio 1:3) in methanol was evaporated to dryness; the oily residue was extracted with benzene. The compound crystallized by adding hexane.

trans-*Pd(DMTC)$_2$I$_2$*

The dark solid obtained from K_2PdCl_4 and KI in water (molar ratio 1:10) was dried *in vacuo* and added to a benzene solution of the ligand (molar ratio K_2PdCl_4 to ligand 1:4). The solution was filtered and by adding hexane pale-brown crystals of the complex precipitated. The solid tends to release the ligand with progressive formation of $Pd(DMTC)I_2$, characterized by elemental analysis. The last compound also formed by ageing of benzene solutions of Pd($(DMTC)_2I_2$ or in attempts to recrystallize it from benzene–hexane.

The IR spectra in the region 4000–400 cm^{-1} were recorded on a Perkin-Elmer Mod. 621 Infrared Spectrophotometer using Nujoll mulls between KBr plates. Far IR spectra were run on a Beckman IR 11 Spectrophotometer using either Nujol mulls or benzene solutions between polythene plates. Molecular weights were measured at 37 °C in benzene by a Mechrolab Mod. 302 vapor pressure Osmometer. Conductivities of 10^{-3} *M* acetone or dichloroethane solutions were measured at 25 °C by a LKB Conductivity Bridge Mod. 3216B. The ^1H nmr spectra were recorded at 27 °C on a Bruker Spectrospin HFX-10 90 MHz Spectrometer. The chemical shifts in deuterated solvents were measured against tetramethylsilane as internal standard; for benzene solutions the solvent signal was uesed as internal shift reference. The chemical shifts are all given from tetra-

TABLE I. Analytical Data of the Complexes (the calculated values are in parentheses).

Compound	Colour	M.p. °C	C%	H%	N%	Hal%
trans-Pt(DMTC)$_2$Cl$_2$	pale-red	118–9	22.7 (22.5)	4.2 (4.1)	5.4 (5.3)	13.1 (13.3)
cis-Pt(DMTC)$_2$Cl$_2$	orange-yellow	93–4	22.1	4.2	5.3	13.2
trans-Pt(DMTC)$_2$Br$_2$	dark-red	118–9	19.4 (19.3)	3.6 (3.5)	4.5 (4.5)	25.7 (25.7)
cis-Pt(DMTC)$_2$Br$_2$	yellow-brown	[a]	19.5	3.6	4.6	25.5
trans-Pt(DMTC)$_2$I$_2$	brown	120–1	16.3 (16.8)	3.3 (3.1)	3.8 (3.9)	36.1 (35.5)
Pd(DMTC)$_2$Cl$_2$	brown	127–8	26.8 (27.0)	4.8 (5.0)	6.3 (6.3)	16.2 (16.0)
trans-Pd(DMTC)$_2$Br$_2$	brown	126–7	22.6 (22.5)	4.1 (4.1)	5.3 (5.3)	30.3 (30.0)
trans-Pd(DMTC)$_2$I$_2$	brown	122–4	19.0 (19.2)	3.7 (3.5)	4.4 (4.5)	40.8 (40.6)

[a] On heating variable quantities of the *trans* isomer are formed.

methylsilane. Electronic spectra were taken at 25 °C by a Beckman DK2A Spectrophotometer. For the solid compounds Nujol mulls on Whatman No. 1 paper were employed.

The spectral data in solution (Tables II, III and IV) are of freshly prepared samples.

Results and Discussion

The complexes (Table I) have formula $M(DMTC)_2X_2$ (where M = Pd, Pt and X = Cl, Br, I). Attempts to isolate 1:4 complexes by using an excess of ligand were unsuccessful, whereas compounds $[ML_4]X_2$ are easily prepared when the ligand is O-ethylthiocarbamate or its N-methyl derivative [31]. For the chloro- and bromo-complexes of platinum with DMTC both the *cis* and *trans* forms, possible in a square-planar arrangement, have been isolated. From molecular weight measurements the chloro- and bromo-complexes are monomers in benzene. All the adducts are non-electrolytes in acetone and in dichloroethane. The *trans*-$Pt(DMTC)_2Cl_2$ has been obtained in two crystalline modifications having the same melting point and identical behaviour in solution, but slightly different spectra in the 700–400 cm^{-1} region (Table II). Analogous to that reported for *cis*-complexes of Pt(II) with N-methyl imidazole [32], a number of crystalline modifications with different melting points are possible for *cis*-$Pt(DMTC)_2Cl_2$. We did not perform detailed experiments on the crystallization parameters; the data reported in this paper concern the product having M.p. = 93–4 °C.

All the platinum adducts are soluble in chloroform; in benzene the solubility of the *trans* complexes is considerably higher than that of the *cis* forms; the behaviour reverses in acetone where *trans*-$Pt(DMTC)_2I_2$ is almost insoluble. The *trans* isomers of platinum are insoluble in water and slightly soluble in methanol; *cis*-$Pt(DMTC)_2Cl_2$ presents an appreciable solubility in the last solvent, but decomposes in a short time giving a yellow solid (not characterized). The solubility of the chloro- and bromo-complexes of palladium resembles that of the *trans* isomers of platinum; freshly prepared *trans*-$Pd(DMTC)_2I_2$ dissolves easily in benzene or acetone, but in solution and more slowly in the solid state loses ligand molecules giving a brown compound of formula $Pd(DMTC)I_2$. Attempts to prepare the 1:1 complex starting from $PdCl_2(C_6H_5CN)_2$ and DMTC in benzene suggested an initial formation of this complex, followed in solution and in the solid state by decomposition of the ligand. Further experiments in this field will be performed in order to assess the best conditions to prepare the probably dymeric 1:1 adducts and the reasons of their instability.

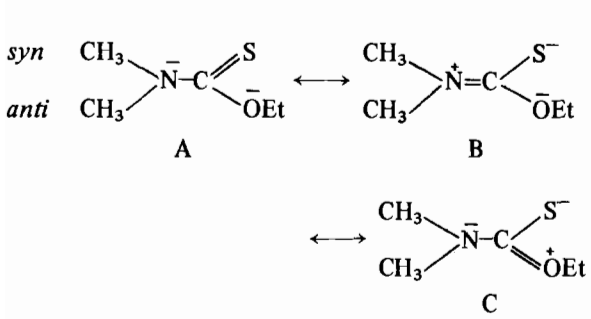
TABLE II. Infrared Bands in the region 700–180 cm^{-1} (the metal–halogen stretching frequencies are underlined).

Compound	Nujol mull											Benzene			
trans-$Pt(DMTC)_2Cl_2$ (I)	665m	642mw	565vvw		528m	470mw	412w		327s		296vvw		244vvw		328s
(II)	665w	638m	560sh	538m		470m	414w		327s		296vvw		244vvw		328s
cis-$Pt(DMTC)_2Cl_2$	665m	640w	565vvw	532m		470mw	414w		317s	306s					324vvw[a]–311s, br
trans-$Pt(DMTC)_2Br_2$	665m	632m		535m	526m	470m	413m	365w	342vw		296w		239s		238s
cis-$Pt(DMTC)_2Br_2$	670m	628m		540m	530m	470mw	410w	365w	345w		300w		221m	213m	239m, br[a]–218m, br
trans-$Pt(DMTC)_2I_2$	665mw	625m		535m		470m	410w	365w	335vw		296w		235vw	199mw	199mw
$Pd(DMTC)_2Cl_2$	675w	635m	565vvw	538m		470m	406vvw	365vvw	346m	325m	297mw		254vw		345m
trans-$Pd(DMTC)_2Br_2$		632m	566vvw	535m		470m	406vvw	365vvw		327w	296w	263m	250sh		264m
trans-$Pd(DMTC)_2I_2$[b]	665w	630w			526m	470m	407w			332vw	296vvw		248vw	222mw	224mw

[a]The intensity of the band (*trans* isomer) increases with time. [b]For the corresponding 1:1 adduct in solid phase ν(Pd–I) is at 223 cm^{-1}.

The IR spectrum of DMTC shows a strong band at 1530 cm^{-1} assigned to the C–N bond stretching vibration, in analogy to the dimethylthioamides [13–15]. In our complexes this band shifts to higher frequencies (1570–80 cm^{-1}), suggesting that the ligand acts as sulfur donor. The band at 865 cm^{-1} in the free ligand, assignable to the C–S stretching, is lowered in the complexes by 5–8 cm^{-1}. The bands in the 700–200 cm^{-1} region have been all reported in Table II because they exhibit some changes when modifications of the same compound are obtained. In complexes of palladium(II) and platinum(II) with thioamides and thioureas the metal–sulfur stretching frequencies have been reported in the 350–250 cm^{-1} region (weak bands). We have tentatively assigned to this vibration mode the weak band at 296–300 cm^{-1}, present either in the solid state or in benzene. The *trans* isomers of platinum and palladium have one metal–halogen stretching band, unchanged in benzene. The *cis* complexes of platinum exhibit in Nujol mulls two bands, as expected in a C_{2v} symmetry, which give rise in benzene to only one unresolved band, whose intensity decreases with time. The progressive formation of the band of the corresponding *trans* isomer suggests a slow isomerization in solution. The solid $Pd(DMTC)_2Cl_2$ presents in the region where the Pd–Cl stretchings are normally found, two bands at 346 and 325 cm^{-1}; the band at 297 cm^{-1} is stronger than in all the other complexes. In benzene the band at 325 cm^{-1} is not observed, whereas the two bands at 345 and at 298 cm^{-1} remain unchanged. The compound is monomeric in benzene so that the spectrum in this solvent would suggest a *trans* configuration. On the basis of these observations, the two bands in the solid state are not definitely indicative of a *cis* structure, which has been suggested for analogous thioamide complexes [15].

The DMTC molecule is a resonance hybrid of the following canonical structures:



If a large contribution of the form B is present, the double bond character of the C–N bond is enhanced leading to hindered rotation and magnetical non equivalence of the N-methyl groups. Whereas for the analogous $(CH_3)_2N$-CO-OEt only one resonance for the $(CH_3)_2N$-protons is observed [33 and ref. therein], the ^1H nmr spectra of DMTC in various solvents (Table III) show two distinct singlets for the methyls in position *syn* and *anti* respectively, the peak separation being larger in benzene. The higher field signal can be assigned to the *anti* group, the lower field one to the *syn* group, following what observed for dithiocarbamates, for instance $(CH_3)_2$-N-CS-SCH_3 [34]. The substitution of the group -SCH_3 with -OCH_3 causes a lower contribution of the structure C, so that the π bonding in thiocarbamates is larger than in dithiocarbamates [35, 36]. All the resonances of free DMTC are in non aromatic solvents at lower field than in benzene. In particular the shift is more marked for the *anti* protons in respect to the *syn* protons: the resonance values in benzene and $CDCl_3$ show a shift of 0.66 ppm (*anti*) and a noticeably lower shift of 0.39 ppm (*syn*). The formation of sulfur bonded complexes enhances the double bond character of the C–N bond leading to a larger separation of the two $(CH_3)_2N$- signals in respect to the free DMTC; in addition the *syn* resonance shifts to lower fields more than the *anti* resonance, as already observed for amides, thioamides and carbamates [33, 37, 38]. For all the adducts in the examined solvents the singlets have a separation larger than for DMTC and the-CH_2- (ethyl) quartet is at lower fields in respect to the free ligand. With exception of benzene where an interaction of the aromatic ring with the N-dimethyl group should be present [39], both *syn* and *anti* protons are at lower fields in respect to the free DMTC, the shift being of the order 0.30 and 0.07 ppm respectively. The signal of the *anti* protons in all the platinum adducts shows two side peaks due to ^{195}Pt–H coupling (J = 10 Hz). For *cis*- and *trans*-$Pt(DMTC)_2X_2$ (X = Cl, Br) the $(CH_3)_2N$-resonances differ slightly in benzene, so that the spectra allow to distinguish the isomers. A freshly prepared equimolar solution of *cis*- and *trans*-$Pt(DMTC)_2Cl_2$ in this solvent shows clearly the different resonances of the isomers; after a day at 37 °C partial *cis* to *trans* isomerization is observed. In $CDCl_3$ only the signals of the *syn* protons differ, whereas in $(CD_3)_2CO$ the two isomers are undistinguishable. The behaviour of the bromo-complexes strongly resembles that of the chloro analogues, although the isomerization reaction in benzene is faster. No evidence of isomeric forms has been found for $Pt(DMTC)_2I_2$, which exists probably only as *trans* either in solution or in the solid state. The ^1H nmr spectrum of $Pd(DMTC)_2Cl_2$ in benzene, taken as quickly as possible, suggests the presence of only one isomeric form in this solvent in accordance with the far IR data. The spectrum of $Pd(DMTC)_2I_2$ in benzene indicates a dissociation equilibrium. In fact three $(CH_3)_2N$- signals are observed: i) a broad resonance around 2.3 ppm ascribed to the *anti* protons of either free or complexed ligand; ii) a signal at 2.95 ppm due to the *syn* protons of the free ligand; iii) a signal at 3.11 ppm relative to the *syn* protons of

TABLE III. ^{1}H Nmr Spectra of DMTC and Complexes (the chemical shifts are given in ppm).

Compound	Solvent	Weight[a]	O-*CH*$_2$-CH$_3$	O-CH$_2$-*CH*$_3$	N(CH$_3$)$_2$[b]
DMTC	C_6H_6	48	4.43	1.03	2.45–2.97
	$CDCl_3$	40	4.50	1.34	3.11–3.36
	$(CD_3)_2CO$	52	4.43	1.29	3.12–3.29
	CCl_4	70	4.41	1.32	3.11–3.30
	CD_3OD	45	4.47	1.30	3.04–3.28
trans-Pt(DMTC)$_2$Cl$_2$	C_6H_6	18	4.93	1.03	2.30*–3.24
cis-Pt(DMTC)$_2$Cl$_2$	C_6H_6	5	4.93	1.03	2.36*–3.30
trans-Pt(DMTC)$_2$Cl$_2$	$CDCl_3$	11	5.00	1.41	3.16*–3.69
cis-Pt(DMTC)$_2$Cl$_2$	$CDCl_3$	16	5.02	1.41	3.16*–3.71
trans-Pt(DMTC)$_2$Cl$_2$	$(CD_3)_2CO$[c]	8	4.97	1.41	3.19*–3.66
trans-Pt(DMTC)$_2$Br$_2$	C_6H_6	15	4.88	1.01	2.30*–3.24
cis-Pt(DMTC)$_2$Br$_2$	C_6H_6	sat.d	4.88	1.01	2.35*–3.31
trans-Pt(DMTC)$_2$Br$_2$	$CDCl_3$	17	4.97	1.41	3.18*–3.69
trans-Pt(DMTC)$_2$Br$_2$	$(CD_3)_2CO$	sat.d	4.94	1.41	3.21*–3.65
trans-Pt(DMTC)$_2$I$_2$[d]	C_6H_6	10	≃4.9	1.03	2.36*–3.26
	$CDCl_3$	21	4.88	1.41	3.18*–3.62
Pd(DMTC)$_2$Cl$_2$	C_6H_6	15	4.73	1.03	2.32–3.20
	$CDCl_3$	20	4.93	1.45	3.19–3.69
	$(CD_3)_2CO$	10	4.84	1.38	3.18–3.59
trans-Pd(DMTC)$_2$Br$_2$	C_6H_6	11	4.78	1.01	2.30–3.15
	$CDCl_3$	12	4.84	1.40	3.16–3.61
	$(CD_3)_2CO$	6	4.84	1.40	3.19–3.61
trans-Pd(DMTC)$_2$I$_2$[e]	C_6H_6	16	≃4.7–≃4.4	1.01	≃2.3–2.95–3.11
	$CDCl_3$	15	4.84	1.44	3.18–3.61
	$(CD_3)_2CO$	6	4.84	1.43	3.22–3.58

[a]Weight (mgr) of compound added to 0.5 ml of solvent. [b]The higher field resonances are ascribed to the protons in position *anti*; for the labelled signals coupling with ^{195}Pt ($J_{^{195}Pt-H}$ = 10 Hz) is observed. [c]In this solvent the spectra of the *trans* and *cis* isomers coincide. [d]Poorly soluble in $(CD_3)_2CO$. [e]In solution free ligand is observed. In benzene: 30% from integrated area; in $CDCl_3$: a weak signal at about 3.3 ppm; in $(CD_3)_2CO$: weak signals at about 3.0 ppm and at 3.27 ppm.

TABLE IV. Electronic Spectra (d–d bands) of the Complexes.[a]

Compound	Solid	Acetone	Benzene
trans-Pt(DMTC)$_2$Cl$_2$	22.12	21.37 (241)	20.96 (214)
cis-Pt(DMTC)$_2$Cl$_2$	22.83	22.47 (310)	22.07 (369)
trans-Pt(DMTC)$_2$Br$_2$	20.62	20.96 (252)	20.74 (233)
trans-Pt(DMTC)$_2$I$_2$	≃20.5sh	≃21.0sh	≃21.0sh
Pd(DMTC)$_2$Cl$_2$	23.2; ≃18.2	22.47 (534); ≃17.6sh	22.42 (530); ≃17.6sh
trans-Pd(DMTC)$_2$Br$_2$	≃21.0; ≃17.2	21.64 (780); ≃17.2sh	21.60 (705); ≃17.2sh

[a]$\bar{\nu} \times 10^{-3}$ cm^{-1} (ϵ_{mol}).

the complexed ligand. The presence of free ligand is also supported by the broad -CH$_2$- (ethyl) quartet at about 4.4 ppm. In deuterated chloroform or acetone the amount of free ligand is of minor importance, suggesting a less pronounced extent of formation of the 1:1 adduct.

The behaviour of the complexes resembles strongly that of the analogous SEt_2 adducts [40]. Whereas $Pd(SEt_2)_2X_2$ (X = Cl, Br, I) and $Pt(SEt_2)_2I_2$ present a *trans* geometry, both *cis*- and *trans*-$Pt(SEt_2)_2X_2$ (X = Cl, Br) are obtained, the *cis*-chloro isomer being converted to *trans* in solution.

The electronic spectra (Table IV) of the complexes are consistent with a square-planar arrangement around the metal. Although the ^{1}H nmr spectra do not allow to differentiate *cis*- and *trans*-Pt(DMTC)$_2$Cl$_2$ in

acetone, so that a fast isomerization could be supposed, the electronic spectra show that both the isomers can exist in this solvent in the form they have in the solid state. In methanol the *cis* isomer presents initially a maximum at 23,500 cm^{-1} (ϵ = 336), the *trans* isomer at 21,500 cm^{-1} (ϵ = 240); the spectra of both the compounds change with time and after three hours the maxima are not present any more.

The cytotoxic activity of the prepared complexes was evaluated *in vitro* on KB cells according to the method of Geran [41]: encouraging results have been obtained with $Pd(DMTC)_2Cl_2$ and *trans*-$Pt(DMTC)_2Br_2$. Because of the insolubility of the compounds in water, they were dissolved in acetone and dimethylsulfoxide prior to administration to the cells, following the usual procedure. Since the activity seems to depend strongly on the solvent used, as already observed [42], more detailed studies have been undertaken which will be the subject of a succeding paper.

Acknowledgement

The Authors thank Mr. R. Salmaso for taking the nmr spectra.

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