Platinum(II) Halide Complexes with N-Methyl O-Ethylthiocarbamate

G. FARAGLIA, L. SINDELLARI, B. ZARLI and I. AGNOLETTI

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

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The complexes trans-Pt(MTC)$_2$X$_2$ (where MTC = N-methyl O-ethylthiocarbamate; X = Cl, Br, I), cis-Pt(MTC)$_2$Cl$_2$, Pt(MTC)$_3$X$_2$ (X = Cl, Br) and [Pt(MTC)$_4$]X$_2$ (X = Cl, Br) have been prepared and characterized by visible, IR and ^{1}H NMR spectroscopy. The ligand acts as sulfur donor towards the platinum atom. The 1:3 complexes are monomers in benzene, whereas the 1:4 complexes are totally dissociated to give the 1:3 compounds and free ligand. Benzene solutions of the 1:2 chloro-adducts present a multispecies equilibrium, discussed on the basis of the IR and ^{1}H NMR data.

Introduction

Recently we started a research program directed towards synthesis and characterization of complexes of platinum(II), palladium(II) and mercury(II) with the sulfur donors N,N-dimethyl O-ethylthiocarbamate (DMTC) [1, 2], and N-methyl O-ethylthiocarbamate (MTC) [3, 4]. A part of this study was to test the cytotoxic effects of the palladium and platinum complexes [5], in order to correlate the activity of compounds containing metal–sulfur bonds with that of the widely reported metal–nitrogen complexes. The palladium and platinum halide complexes with DMTC have general formula M(DMTC)$_2$X$_2$ (M = Pd, Pt; X = Cl, Br, I); the palladium adducts have a *trans* configuration, as shown by X-ray analysis of the chloro- and bromo-derivatives [6, 7]. With platinum chloride both the *cis* and *trans* isomers were isolated, as confirmed by X-ray data [8, 9]. Platinum bromide gave easily the *trans* form, whereas the *cis* isomer was isolated with difficulty, owing to a rapid *cis* to *trans* isomerization [1]. With MTC as ligand palladium halides formed the *trans* 1:2 adducts and the 1:4 ionic complexes [Pd(MTC)$_4$]X$_2$ (X = Cl, Br), having the stoichiometries usually found when the ligands were primary and secondary thioamides [10–12]. In addition complexes with a 1:3 stoichiometry have been isolated, for which an ionic structure of the type [Pd(MTC)$_3$X]X (X = Cl, Br) was supposed in the solid state; in benzene or in acetone the experimental

data were in favour of the formation of a labile five-coordinate intermediate, with subsequent release of ligand to give the 1:2 adduct [3]. As far as we know, the existence of five-coordinate complexes of palladium(II) and platinum(II) halides with monodentate ligands has been proved by X-ray analysis only for some compounds with tertiary phosphines [13–15]. Their distorted tetragonal pyramidal structure consists generally of a roughly planar arrangement of one halogen and three phosphorus atoms around the metal, whereas the second halogen, lying in an elongated apical position, has an appreciably ionic character. By reaction of K$_2$PtCl$_4$ with N-phenyl O-ethylthiocarbamate Kukushkin *et al.* obtained a complex of formula PtL$_3$Cl$_2$, to which, on the basis of far IR spectra, it was assigned a trigonal-bipyramid structure [16]. Owing to the importance of five-coordinate species in the mechanism of isomerization of square-planar platinum complexes [17, 18], a detailed study with the ligands MTC and TC(H$_2$N-CS-OEt) was undertaken.

This paper reports the preparation and characterization of the MTC complexes with PtX$_2$ (X = Cl, Br, I), and the study of their behaviour in benzene and in acetone.

Experimental

The starting materials were PtX$_2$ (X = Cl, Br, I: Alfa Products) and MTC, prepared as in ref. [3].

Preparation of the Complexes

cis-Pt(MTC)$_2$Cl$_2$

PtCl$_2$ (1.6 mmol) dissolved slowly in a benzene solution of MTC (3.26 mmol in 25 ml) giving an orange solution. After 5 h the small amount of unreacted halide was filtered away. By adding n-hexane an orange oil separated, which, by shaking, gave bright-yellow crystals of the compound. By standing overnight the solution separated a mixture of *cis*-Pt(MTC)$_2$Cl$_2$ and Pt(MTC)$_3$Cl$_2$. The *cis* compound dissolves easily in acetone, CH$_2$Cl$_2$ and abs. ethanol, slowly in benzene. It is insoluble in ethyl

ether and n-hexane. By recrystallization from benzene/, CH_2Cl_2/ and acetone/n-hexane the compound is essentially unchanged.

trans-Pt(MTC)$_2$Cl$_2$

The slow reaction of $PtCl_2$ (0.8 mmol) and MTC (1.6 mmol) in acetone (3 ml) led to a pale-yellow compound, which, after 16 h, was filtered and washed with acetone. By addition of n-hexane, the solution separated a small fraction of *cis* isomer. If n-hexane was added to a solution of $PtCl_2$ and MTC in CH_2Cl_2 (molar ratio 1:2, reaction time, 4 h) a mixture of both the isomers, richer in *trans*, was obtained. *Trans*-Pt(MTC)$_2$Cl$_2$ is soluble in CH_2Cl_2, slightly soluble in acetone and benzene, insoluble in ethanol, water and ethyl ether.

trans-Pt(MTC)$_2$Br$_2$

Was prepared either in acetone, following the method used for *trans*-Pt(MTC)$_2$Cl$_2$, or in benzene, stirring overnight a suspension of $PtBr_2$ (0.6 mmol) in a benzene solution of MTC (1.2 mmol in 5 ml). It is soluble in CH_2Cl_2, slightly soluble in acetone and benzene.

trans-Pt(MTC)$_2$I$_2$

PtI_2 (0.35 mmol) and MTC (0.74 mmol in 15 ml of benzene) gave a yellow solution (reaction time 16 h), from which the compound precipitated after addition of n-hexane. It is soluble in acetone, CH_2Cl_2 and benzene. By operating at molar ratios up to 1:6, the product was always the same.

Pt(MTC)$_3$Cl$_2$

$PtCl_2$ (1.3 mmol) dissolved easily in a CH_2Cl_2 solution of MTC (4.0 mmol in 5 ml); after 20 min, 70 ml of n-hexane were added to the orange-yellow solution, from which yellow-green crystals separated overnight. By operating in the same conditions, but adding n-hexane after 16 h, immediate precipitation of *cis*-Pt(MTC)$_2$Cl$_2$ was observed (yield $\cong$ 50%); on time the solution separated fractions of the 1:3 complex. The compound was also prepared either in acetone or in benzene (molar ratio 1:3); it is soluble in CH_2Cl_2, acetone, benzene, ethanol; slightly soluble in water.

Pt(MTC)$_3$Br$_2$

$PtBr_2$ (0.4 mmol) was allowed to react with an acetone solution of MTC (1.4 mmol in 12 ml). After 4 h the small amount of unreacted halide was filtered off, and 60 ml of n-hexane were added to the yellow-orange solution. Golden-yellow crystals of the compound separated overnight. It was also prepared by adding n-hexane to: (a) a solution of $PtBr_2$ (0.6 mmol) and MTC (2.0 mmol) in 4 ml of CH_2Cl_2; (b) a very concentrated solution of [Pt(MTC)$_4$]Br$_2$ in acetone. The complex is soluble in benzene,

acetone, CH_2Cl_2; slightly soluble in ethanol, insoluble in water.

[Pt(MTC)$_4$]Cl$_2$

$PtCl_2$ (1.0 mmol) dissolved easily in a benzene solution of MTC (6.3 mmol in 10 ml); by addition of n-hexane the yellow solution separated a small amount of a colourless oil, which was discarded. Successive fractions of n-hexane allowed to isolate the white-greenish compound. If the reaction in benzene was performed at a molar ratio 1:4, the product was a mixture of the 1:3 and 1:4 complexes. [Pt(MTC)$_4$]Cl$_2$ dissolves in benzene and CH_2Cl_2 giving yellow solutions; it is slightly soluble in acetone and water. By heating *in vacuo* at 100 °C this compound does not change to the 1:2 adduct, differing from the analogous [Pd(MTC)$_4$]Cl$_2$; the IR spectrum of the residual solid indicates a partial decomposition, with progressive enhancement of a band around 305 cm^{-1}, probably assignable to ν(Pt—Cl).

[Pt(MTC)$_4$]Br$_2$

The greenish-white compound was isolated by adding, within 20 min, n-hexane to the orange CH_2-Cl_2 solution of $PtBr_2$ (0.7 mmol) and MTC (4.3 mmol in 7 ml). It is soluble in benzene, CH_2Cl_2 and acetone, giving yellow solutions; slightly soluble in methanol. The compound was also prepared by operating in benzene at a molar ratio 1:6.

Measurements

The IR spectra were registered by a Perkin Elmer Mod. 580 Spectrophotometer (Nujol mull betweeen CsI discs; benzene solutions in 0.5 mm KBr cells) in the 4000–350 cm^{-1} region; by a Beckman IR 11 Spectrophotometer (Nujol mulls or benzene solutions between polythene plates) below 400 cm^{-1}. Electronic spectra of solids (Nujol mulls on paper) were obtained with a Beckman DK2A Spectrophotometer; solution spectra with a Cary 15 Spectrophotometer. The ^{1}H NMR spectra were registered at about 27 °C by a Varian FT 80A NMR Spectrometer. Osmometric measurements were carried out at 37 °C by a Knauer Mod. 11 Vapor Pressure Osmometer. The Van't Hoff factor was calculated as $i = \Delta R_c / \Delta R_b$, where ΔR_c is the experimental osmometric value for a given concentration of complex (by F.W.), and ΔR_b is the value for an identical concentration of standard (benzil). Conductivities were measured by a LKB Conductivity Bridge Mod. 3216B.

Results and Discussion

The complexes are reported in Table I, along with the analytical data and the Van't Hoff *i* values

TABLE I. Analytical Data (the calculated values are in parentheses) and Van't Hoff i Values.

Compound	Colour	M.p. °C (dec.)	C%	H%	N%	Hal%	Solvent	i 1.0×10^{-2} M	0.5×10^{-2} M	0.25×10^{-2} M
cis-Pt(MTC)$_2$Cl$_2$	bright yellow	102	19.0 (19.0)	3.4 (3.7)	5.5 (5.6)	14.0 (14.1)	benzene	0.87	0.86	0.87
							acetone	0.98	1.00	1.00
$trans$-Pt(MTC)$_2$Cl$_2$	pale yellow	121	19.0	3.5	5.5	14.1	benzene	–	0.88	0.88
							acetone	0.98	1.01	1.00
$trans$-Pt(MTC)$_2$Br$_2$	beige	122–3	16.1 (16.2)	3.0 (3.1)	4.6 (4.7)	26.7 (26.9)	benzene[a]	–	–	–
							acetone	0.96	0.95	0.96
$trans$-Pt(MTC)$_2$I$_2$	pink-yellow	127–8	14.0 (14.0)	2.6 (2.6)	4.1 (4.1)	– (36.9)	benzene	1.00	0.96	0.99
							acetone	1.02	1.04	1.01
Pt(MTC)$_3$Cl$_2$	yellow-green	119–20	23.3 (23.1)	4.1 (4.4)	6.7 (6.7)	11.8 (11.4)	benzene	1.04	1.00	1.02
							acetone	1.48	1.60	1.74
Pt(MTC)$_3$Br$_2$	bright-yellow	117–8	20.2 (20.2)	3.8 (3.8)	5.9 (5.9)	22.7 (22.4)	benzene	1.09	1.03	1.13
							acetone	1.72	1.85	1.93
[Pt(MTC)$_4$]Cl$_2$	greenish white	117	26.0 (25.9)	4.8 (4.9)	7.5 (7.5)	9.6 (9.6)	benzene	1.98	2.08	2.06
							acetone[b]	2.37	2.56	2.65
[Pt(MTC)$_4$]Br$_2$	greenish white	116	23.2 (23.1)	4.4 (4.4)	6.7 (6.7)	19.3 (19.2)	benzene	1.93	1.99	1.99
							acetone	2.50	2.59	2.70

[a]Scarcely soluble in benzene. [b]The reported values are for concentrations: 0.75×10^{-2}, 0.37×10^{-2}, 0.19×10^{-2} M.

measured in solution of benzene and acetone. The square-planar complexes of formula Pt(MTC)$_2$X$_2$ have been isolated in the *trans* form when X = Cl, Br, I; the *cis* isomer has been obtained only when X = Cl. As already observed for palladium [3], the platinum complexes having 1:3 and 1:4 stoichiometries can be isolated only when X = Cl, Br; in fact reacting PtI$_2$ with a large excess of MTC in benzene, the product is always the 1:2 adduct.

The i values in acetone indicate that the 1:2 compounds are monomers in this solvent; the 1:3 and 1:4 complexes undergo a progressive ligand release on diluting, as it happened with the palladium analogues [3]. All the complexes are non-electrolytes in acetone ($10^{-2}-10^{-3}$ M solutions) also if a large excess of ligand is added. The osmometric and conductometric data are in accordance with a total transformation of the 1:4 species to give free ligand and 1:3 complexes, which in turn dissociate to give the 1:2 adducts, the effect being more evident for X = Br. The 1:4 palladium derivatives had in acetone $i \cong 3$, indicating that the main species at concs. $< 10^{-2}$ M was the 1:2 adduct. In acetone and benzene solutions MTC behaves as a monomer at least for concs. lower than 4×10^{-2} M.

In benzene $trans$-Pt(MTC)$_2$I$_2$ seems to be a monomer, whereas both the chloro-isomers have $i \cong 0.9$, independent of concentration. The i value lower than one is not the result of an intermolecular association, but is probably due to the presence of a multi-species equilibrium in solution, which is better observed by the ^{1}H NMR spectra.

Differing from the 1:3 palladium complexes, the corresponding platinum complexes are monomeric species in benzene; in fact in the examined concentration range, it is $i \cong 1$. In the same solvent the white [Pt(MTC)$_4$]X$_2$ complexes dissolve slowly to give yellow solutions, which, being $i \cong 2$, should contain the stable 1:3 species and free ligand.

The IR spectra of the *trans* 1:2 adducts (Table II) show, in the ν(N–H) region, a strong halide dependent band around 3250 cm^{-1} and a weak one around 3110 cm^{-1}, the last being probably a 2ν (C–N) overtone; the complex cis-Pt(MTC)$_2$Cl$_2$ presents two equally intense absorptions at 3280 and at 3240 cm^{-1}. In the 1:3 and 1:4 complexes the broad N–H bands fall at lower frequencies in respect to the 1:2 adducts, suggesting the formation of hydrogen bonds towards halogen atoms, as observed in the palladium analogues [3].

The band of MTC at 1535 cm^{-1}, assigned as mainly ν(C–N) with a small δ(N–H) contribution, shifts in all the complexes to higher frequencies, as expected for coordination through the sulfur atom [1–4 and refs. therein]. In order to identify the species in solution, the spectra of the 1:3 and 1:4 complexes have been made also in benzene. The IR data are in accordance with the osmometric

TABLE II. Infrared Bands in the 3500–3000 cm^{-1} and 1650–1550 cm^{-1} Regions.

cis-Pt(MTC)$_2$Cl$_2$	$\begin{cases} 3280s \\ 3240s \end{cases}$	3200sh,vw	3120vw	1588vs,br	1565sh,s
trans-Pt(MTC)$_2$Cl$_2$	3260s	3180sh,w	3120sh,w	1568vs	
trans-Pt(MTC)$_2$Br$_2$	3250m	3200sh,vw	3110sh,w	1562vs	
trans-Pt(MTC)$_2$I$_2$	3245s		3110vvw	1558vs	
Pt(MTC)$_3$Cl$_2$[a]		3150sh	3100m,br	1595s,br	1580sh,s
Pt(MTC)$_3$Br$_2$[a]		3180m,br	3110m,br	1595s,br	1577sh,s
[Pt(MTC)$_4$]Cl$_2$[b]		3180sh,br[c]	3040sh,br[c]	1580s,br	1550sh,m
[Pt(MTC)$_4$]Br$_2$[b]		3150sh,br[c]	3080sh,br[c]	1580s,br	1550sh,m

[a]In benzene: 1605s, 1585sh,w.   [b]In benzene: 3410sh, 3390m, 3170sh,br, 1605s, 1585sh,w.   [c]Shoulders of a broad band at 2950 cm^{-1} (in Voltalef 10S mulls).

results: in fact the 1:3 complex bands are similar to those of Nujol mulls (Table II), whereas the 1:4 complexes show around 1600 cm^{-1} the bands due to the 1:3 species and at 3390m, 3410sh cm^{-1}, the bands of free MTC.

Below 800 cm^{-1}, where ν(CS), δ(NCS) and π(NH) are found, the 1:2 adducts stronger bands fall around 625 cm^{-1}, as in trans-Pd(MTC)$_2$X$_2$ (X = Br, I) [3]; the spectra of the 1:3 and 1:4 complexes are similar to those of the palladium analogues. Trans-Pt(MTC)$_2$-Cl$_2$ presents a strong band at 325 cm^{-1}, assigned to ν(Pt–Cl); the cis isomer two bands of comparable intensity at 315, 300 cm^{-1}. The corresponding frequencies for trans- and cis-Pt(DMTC)$_2$Cl$_2$ were at 327 cm^{-1} and 317, 306 cm^{-1} respectively; in benzene the trans form spectrum was unchanged (328 cm^{-1}) whereas a slow cis to trans isomerization was observed for the cis form. Cis-Pt(MTC)$_2$Cl$_2$ in benzene presents a strong band at 324 cm^{-1}, with a broad shoulder around 310 cm^{-1}; saturated solutions of trans-Pt(MTC)$_2$Cl$_2$, obtained by heating up to 50 °C, have an identical spectrum, suggesting that both the compounds reach a similar equilibrium situation. The spectra in Nujol of Pt(MTC)$_2$X$_2$ (X = Br, I) have only one ν(Pt–X) band; respectively at 238 and 186 cm^{-1}, indicating a trans configuration, as in the DMTC derivatives. The ν(Pt–X) in the 1:3 complexes fall at 319 cm^{-1} (X = Cl) and 226 cm^{-1} (X = Br).

The benzene solutions of Pt(MTC)$_3$Cl$_2$ have the same green–yellow colour as the freshly prepared solid, and present a strong absorption at 321 cm^{-1}; the shape and intensity of this band should indicate a similar structure either in the solid state or in solution. According to the IR and osmometric data, in the 1:3 complexes a five-coordinate arrangement around the platinum atom is probably attained. Also if either a trigonal-bipyramidal or a square-pyramidal conformation with an apical ligand cannot be excluded, the most probable structure could be similar to that of the 1:3 phosphine derivatives, dis-

torted square-pyramidal with a longer apical halide bond.

The compounds could be formulated also as [Pt(MTC)$_3$X]X, but the similarity of the spectra in solid and in benzene, where the 1:3 complexes are monomers, allows to prefer the formulation as neutral molecules.

The complexes [Pt(MTC)$_4$]X$_2$ (X = Cl, Br) do not show any band assignable to metal–halogen bonds, as expected for an ionic structure. In benzene [Pt-(MTC)$_4$]Cl$_2$ presents a strong band at 321 cm^{-1}, which supports the formation of Pt(MTC)$_3$Cl$_2$.

In all the complexes the ν(Pt–S) is probably the weak absorption around 270 cm^{-1}, as found in the other thiocarbamate derivatives [1, 3].

The electronic spectra of the freshly prepared solids are reported in Table IV. The absorptions at higher wavelengths in the 1:2 and 1:3 complexes, assigned to d–d transitions, are in accordance with the spectrochemical series. The two ionic 1:4 complexes have identical spectra, which do not change when aged solids are used. On contrary the colour of the solid 1:2 and 1:3 complexes changes with time, while the samples maintain the initial analytical data and IR spectra.

The solution spectra of either fresh or aged chloro complexes are reported in Table V. The extinction coefficients of the freshly prepared complexes are in favour of an essentially square-planar coordination around the platinum atom; the spectra of aged solids show a progressive increasing of the extinction coefficients with time, either in benzene or in acetone. The position of the maxima and the extinction coefficient values are only approximate, due to the broadness of the bands.

The ^{1}H NMR data of the complexes in d$_6$-benzene are in Table VI. In this solvent MTC shows two resonances either for the N–CH$_3$ protons (doublets at 2.59(67%) and 2.17 ppm) or for the methyl protons of the ethyl group (triplets at 1.03 (stronger) and 1.00 ppm), owing to the presence of both the syn

TABLE III. Infrared Bands in the 800–150 cm^{-1} Region (Pt–Halogen Frequencies are in italics).

cis-Pt(MTC)$_2$Cl$_2$[a]	815w	720m	685m,br		623ms	533m	480m				*315–300s*		220vvw	174w,br
trans-Pt(MTC)$_2$Cl$_2$[a]	820w	720mw		640m,sh	628ms	532mw	480mw		380vw		*325ms*	275vvw	220vvw	176w,br
trans-Pt(MTC)$_2$Br$_2$	818w	719w		640m,sh	625ms	532w	480mw		385vw		*332w*	270vw,br 238m	220vvw 200vvw	172w,br
trans-Pt(MTC)$_2$I$_2$	818w	719w		635sh	621ms	533mw	480mw		385vw		*332vw*	275vw,br	186w	165w,br
Pt(MTC)$_3$Cl$_2$[b]	813w	730m,br	690w	633mw		532w	{ 478m 466m	415vvw		354w	*319s*			165w,br
Pt(MTC)$_3$Br$_2$	810w	721m	690m	633m		533w	{ 478m 466m	415vw		352w		275vvw	226m	
[Pt(MTC)$_4$]Cl$_2$[b]	820m	775m 718w	691w	632m		531w	473m	417w	385vw	362	*335w*			
[Pt(MTC)$_4$]Br$_2$	820w	780m 718w	692w	632m		535w	477m	417w	385vvw	367vvw	*333vw*			

[a]In benzene cis- and trans-Pt(MTC)$_2$Cl$_2$ have the same spectrum: 324s, 310sh,br. [b]In benzene both Pt(MTC)$_3$Cl$_2$ and [Pt(MTC)$_4$]Cl$_2$ present an identical band at 321 cm^{-1}.

TABLE IV. Electronic Spectra (λ_{max}, nm) of Solid Compounds.

cis-Pt(MTC)$_2$Cl$_2$	341 sh	410 sh,br
trans-Pt(MTC)$_2$Cl$_2$	350 sh	410 sh,br
Pt(MTC)$_3$Cl$_2$	340 sh	392 sh,br
[Pt(MTC)$_4$]Cl$_2$	365 sh	
trans-Pt(MTC)$_2$Br$_2$	365 sh	425 sh,br
Pt(MTC)$_3$Br$_2$	355 sh	400 sh,br
[Pt(MTC)$_4$]Br$_2$	365 sh	
trans-Pt(MTC)$_2$I$_2$		480 sh,br
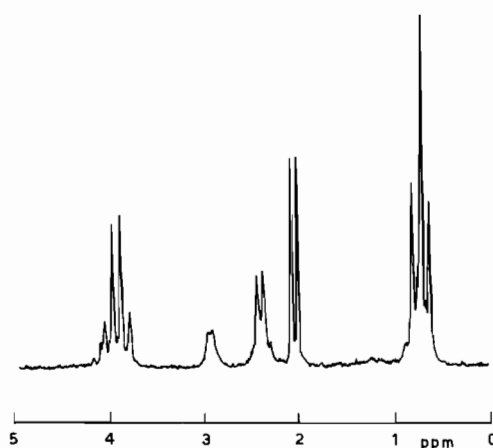
Fig. 1. ^{1}H NMR Spectrum of cis-Pt(MTC)$_2$Cl$_2$ in d$_6$-benzene.

and *anti* forms [3, and ref. therein]. The methylene proton resonances coincide for both the isomers; the related signal is found at 4.40 ppm.

When the ligand coordinates through the sulfur atom, an upfield shift of the ethyl proton resonances has been observed. In deutero-benzene *trans*-Pt(MTC)$_2$I$_2$ presents one signal for each group of protons, at higher fields respect to the corresponding free ligand resonances; the spectrum is similar to those of the 1:2 palladium halide adducts [3]. *Trans*-Pt(MTC)$_2$X$_2$ (X = Cl, Br) are slightly soluble in benzene; the spectra of their saturated solutions resemble that of the iodo-derivative, except for two hardly visible N–CH$_3$ signals downfield in respect to the main one at 2.0 ppm. By heating up to 50 °C, *trans*-Pt(MTC)$_2$Cl$_2$ dissolves giving a spectrum similar to that of *cis*-Pt(MTC)$_2$Cl$_2$, soluble in benzene at room temperature. The spectrum of *cis*-Pt(MTC)$_2$Cl$_2$ (Fig. 1) shows three resonances assignable to N–CH$_3$ protons; the one at 2.03 ppm coincides with that of *trans*-Pt(MTC)$_2$X$_2$ (X = Cl, Br, I), whereas the signal at 2.94 ppm seems to support the formation of the 1:3 complex. The signal around 2.4 ppm has been observed only for benzene so-

TABLE V. Electronic Spectra of $\cong 1 \times 10^{-3}$ M solutions of the Chloro-Complexes (λ_{max}, nm; ϵ_{mol} in parentheses).

Compound	Benzene		Acetone	
cis-Pt(MTC)$_2$Cl$_2$[a]	350(470)	415(170)	350(390)	420(120)
trans-Pt(MTC)$_2$Cl$_2$[a]	350(340)	415(150)	350(340)	420(130)
Pt(MTC)$_3$Cl$_2$[a]	343(380)	400(170)	343(370)	400(140)
[Pt(MTC)$_4$]Cl$_2$[a,b]	343(410)	395(190)	343(370)	400(130)
cis-Pt(MTC)$_2$Cl$_2$[c]	345(780)	410(260)ı60dı	340(780)	417(200)ı60dı
Pt(MTC)$_3$Cl$_2$[c]	345(980)	400 shı50dı	343(1180)	400 sh ı100dı

[a]The spectra were made within a week from the preparation of the compounds.   [b]The spectra of the aged compound (90d) is essentially unchanged.   [c]Spectra of aged solids.

TABLE VI. ^{1}H NMR Spectra of the Complexes in d$_6$-Benzene (t $\simeq$ 27 °C; the chemical shifts are in ppm).

Compound	mg/0.5 ml	N–CH$_3$	O–CH$_2$–CH$_3$	O–CH$_2$–CH$_3$
cis-Pt(MTC)$_2$Cl$_2$	20	2.03(40%) 2.41(45%) 2.94(15%)[a]	0.68 0.75[a]	3.90 4.05[a]
trans-Pt(MTC)$_2$Cl$_2$	sat.[b]	2.02 2.1vvw 2.9vvw	0.75	3.84
	16[c]	2.04(45%) 2.32(33%) 2.4vvw 2.9(21%)	0.70 0.74	3.90 3.92
trans-Pt(MTC)$_2$Br$_2$	14[c]	2.04 2.16vvw 2.90vvw	0.70	3.87
trans-Pt(MTC)$_2$I$_2$	8	2.01	0.67	3.85
Pt(MTC)$_3$Cl$_2$[d]	40	2.80w 2.85	0.69w 0.74	3.88w 4.04
Pt(MTC)$_3$Br$_2$[d]	50	2.81w 2.85	0.71w 0.76	3.89w 4.01
[Pt(MTC)$_4$]Cl$_2$[d]	30	2.84w 2.89	0.69w 0.73	3.86w 4.02
		2.12w 2.65	1.00w 1.04	4.40
[Pt(MTC)$_4$]Br$_2$[d]	28	2.82w 2.90	0.62w 0.72	3.84w 3.97
		2.02 2.54	0.98w 1.00	4.35

[a]This series of signals coincides with the stronger series in Pt(MTC)$_3$Cl$_2$.   [b]A very.weak singlet at 0.54 ppm is also observed. [c]The solid was allowed to dissolve by heating up to 50 °C.   [d]The symbol w indicates the weaker between two signals too near to be integrated.
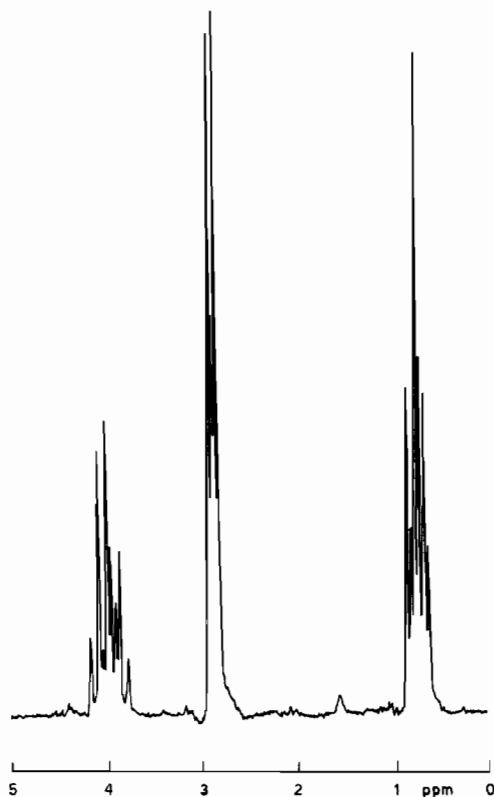
Fig. 2. ^{1}H NMR Spectrum of Pt(MTC)$_3$Cl$_2$ in d$_6$-benzene.

Fig. 3. ^{1}H NMR Spectrum of [Pt(MTC)$_4$]Cl$_2$ in d$_6$-benzene.

lutions of either *trans*- or *cis*-Pt(MTC)$_2$Cl$_2$; the doublets at 2.4 and 2.9 ppm are broad and sometime unresolved; the one at 2.4 ppm present a weak side peak which could be due to a superimposed signal.

The 1:3 complexes present a double series of sharp signals for each group of protons (Fig. 2); the relative amount cannot be determined owing to the partial overlapping. The spectra of [PT(MTC)$_4$]-X$_2$ (X = Cl, Br) show the well resolved signals of the 1:3 complex along with those of the free ligand (25% from integrated areas) in both the isomeric forms (Fig. 3). The two signals for each group of protons in Pt(MTC)$_3$X$_2$ (X = Cl, Br) are possibly due to the *syn* and *anti* forms of the coordinated ligand, although it cannot be excluded that this behaviour depends on two different coordinating situations of the ligand molecules. For instance, if we suppose around the platinum atom an almost planar arrangement by one chlorine and three sulfur atoms, as for the 1:3 phosphine complexes, a different bond length for the sulfur atom *trans* to the chlorine could produce resonances slightly shifted for one of the three ligand molecules. The different stability of the 1:3 platinum complexes with respect
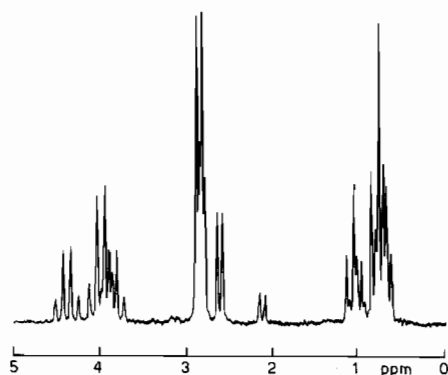
to those of palladium is evident in the ^{1}H NMR data. In fact in the palladium complexes the N–CH$_3$ signals were broad and shifted about 2.7 ppm; on diluting the free ligand resonances became evident. Returning to the behaviour in benzene of *cis*- and *trans*-Pt(MTC)$_2$Cl$_2$, the combined ^{1}H NMR and far-IR data would be in favour of an equilibrium between the *trans*- (2.0 ppm) and *cis*- (2.4 ppm) species. The signal at 2.9 ppm, characteristic of the 1:3 species is hardly due to a reaction

$$2Pt(MTC)_2Cl_2 \rightleftharpoons Pt(MTC)_3Cl_2 + Pt(MTC)Cl_2$$

in fact attempts to prepare the polymeric 1:1 platinum adducts led always to very unstable solids, in which deprotonation and methyl elimination in the CH$_3$NH- group were observed. The ^{1}H NMR data could be explained by assuming the formation of a tight ion-pair of the type Pt(MTC)$_3$Cl$^+$···Pt(MTC)-Cl$_3^-$, where the first moiety resonances coincide with those of the 1:3 complex, whereas the weak signal of the latter species overlaps the 2.4 ppm one. In solutions of *cis*-Pt(MTC)$_2$Cl$_2$, containing variable quantities of Pt(MTC)$_3$Cl$_2$, the N–CH$_3$ signals at 2.0 and 2.4 ppm have about the same relative intensities as in pure *cis*- solutions; the added amount of Pt(MTC)$_3$Cl$_2$ enhances the intensity of the resonance at 2.9 ppm, which appears already broad and unresolved.

The existence of the species PtLCl$_3^-$ has been already observed, for instance in K[Pt(DMSO)Cl$_3$] [19] whose X-ray structure supports the presence of the square-planar anion. The cationic species PtL$_3$Cl$^+$ are present in the salts with non-coordinating anions, for instance [PdCl(PMe$_2$Ph)$_3$][PF$_4$] [15]. The formation of an associated intermediate could also justify the osmometric data of the 1:2 chloro complexes, which present $i \cong 0.9$, at least in the concentration range $10^{-2}–10^{-3}$ M.

Acknowledgements

References

1 L. Sindellari, G. Faraglia, B. Zarli, P. Cavoli, A. Furlani and V. Scarcia, *Inorg. Chim. Acta, 46*, 57 (1980).
2 G. Faraglia, R. Graziani, L. Sindellari, E. Forsellini and U. Casellato, *Inorg. Chim. Acta.,* in press.
3 G. Faraglia, L. Sindellari and B. Zarli, *Inorg. Chim. Acta, 48*, 247 (1981).
4 G. Faraglia, L. Sindellari and B. Zarli, *Inorg. Chim. Acta, 53*, L245 (1981).
5 A. Furlani, V. Scarcia, L. Sindellari, G. Faraglia and B. Zarli, *Experientia,* to be published.
6 R. Bardi, A. M. Piazzesi and M. Munari, *Cryst. Struct. Comm., 9*, 835 (1980).
7 R. Bardi, A. M. Piazzesi and P. Cavoli, *Cryst. Struct. Comm., 9*, 1055 (1980).
8 R. Bardi, A. M. Piazzesi and L. Sindellari, *Inorg. Chim. Acta, 47*, 225 (1981).
9 R. Bardi, A. Del Pra, A. M. Piazzesi and M. Berto, *Cryst. Struct. Comm., 10*, 351 (1981).
10 A. J. Aarts, H. O. Desseyn and M. A. Herman, *Transition Met. Chem., 3*, 144 (1978).
11 A. J. Aarts, H. O. Desseyn and M. A. Herman, *Transition Met. Chem., 4*, 46 (1979).
12 A. J. Aarts, H. O. Desseyn and M. A. Herman, *Bull. Soc. Chim. Belg., 88*, 25 (1979).
13 K. M. Chui and H. M. Powell, *J. Chem. Soc. Dalton,* 1879 (1974).
14 K. M. Chui and H. M. Powell, *J. Chem. Soc. Dalton,* 2117 (1974).
15 W. J. Louw, D. J. A. de Waal and G. J. Kruger, *J. Chem. Soc. Dalton,* 2364 (1976).
16 Ju. N. Kukushkin, V. V. Sibirskaya, V. N. Samuseva, V. V. Strukov, G. B. Avetikyan and G. N. Sedova, *Russ. J. Gen. Chem., 46*, 2203 (1976).
17 R. G. Pearson, W. Louw and J. Rajaram, *Inorg. Chim. Acta, 9*, 251 (1974).
18 D. G. Cooper and J. Powell, *J. Am. Chem. Soc., 95*, 1102 (1973).
19 R. Melanson, J. Hubert and F. D. Rochon, *Acta Cryst., B32*, 1914 (1976).