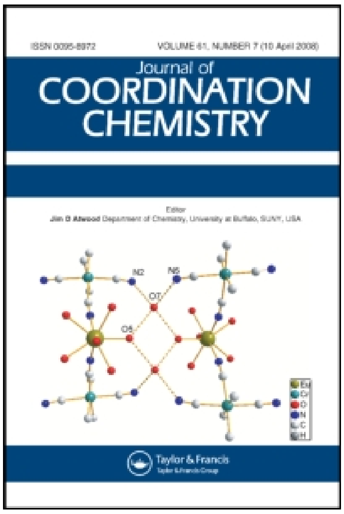

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RHODIUM(III) HALIDE COMPLEXES WITH *N*-METHYL-*O*-ETHYLTHIOCARBAMATE

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N-methyl-*O*-ethylthiocarbamate (MTC) forms with rhodium trihalides the complexes $[Rh(MTC)_3X_3]$ (X = Cl, Br, I), $[RhCl_3.2MTC]$ and $[RhBr_3.MTC]$, which are characterized by electronic, i.r. and ^1H n.m.r. spectra. The ligand acts as a sulfur donor towards the rhodium atom. The i.r. and ^1H n.m.r. data suggest for $[Rh(MTC)_3X_3]$ (X = Cl, Br) an octahedral meridional configuration either in solution or in the solid state; $[Rh(MTC)_3I_3]$ decomposes in most solvents releasing ligand molecules. The complex $[RhCl_3.2MTC]$ contains bridging Rh-Cl bonds. In dimethylsulfoxide all complexes decompose with progressive displacement of the ligand.

INTRODUCTION

The coordination chemistry of rhodium(III) halides with sulfur donors concerns mainly thioethers and sulfoxides. Thioethers (L) gave, along with the octahedral $[RhL_3Cl_3]$ complexes,[1-3] the ionic species $[RhL_{6-x}Cl_x]$ $[RhL_xCl_{6-x}]$, where x = 1,2, having the same 1:3 stoichiometry[4,5]; both ions in $[Rh(SEt_2)_4Cl_2]$ $[Rh(SEt_2)_2Cl_4]$ had a *trans* octrahedal structure.[6] Whereas 1,4-thioxan gave 1:3 adducts,[7] bidentate thioethers could form either polimeric 1:1 or ionic 1:2 complexes.[3,7,8] With dimethyl- and diethylsulfoxide (L') the compounds $[RhL_3'X_3]$ (X = Cl, I) and $Na[RhL_2'Cl_4]$ were prepared.[9-12] In the neutral species two of the three ligand molecules coordinate the metal through the sulfur atom, the last one being bound by the oxygen atom.[13,14] In the ion $[Rh(DMSO)_2Cl_4]^-$ both *trans* ligand molecules behave as sulfur donors.[15,16] Rhodium(III) halides could also coordinate more than three sulfoxide molecules, giving the species $[Rh(DMSO)_nX_{6-n}]^{n-3}$, where n = 2-5 and X = Cl,Br.[17,18] Various 1:3 mixed complexes of the type $[RhL_x(DMSO)_{3-x}Cl_3]$, where L is dimethylsulfide,[19] pyridine *N*-oxide[20] and amines[10] have been reported; in particular $[Rh(DMSO)py_2Cl_3]$ has a meridional octahedral structure with the pyridine molecules in a *cis* position, and shows a remarkable activity towards some sarcomas.[21] Promising biochemical data were also observed for complexes with amines,[22] dithiocarbamate[23] and 2-mercaptothiazoline.[24,25]

We thus thought it to be of interest to investigate the complexing behaviour of rhodium trihalides towards various thiocarbamic esters of general formula RR'N-C(S)-OEt, with a view to prepare either simple or mixed complexes. As a first study, this paper reports some complexes with $CH_3NH\text{-}C(S)\text{-}OC_2H_5$ (*N*-methyl-*O*-ethylthiocarbamate, MTC) whose platinum(II) halide adducts display an appreciable *in vitro* cytotoxic activity towards KB cells.[26,27]

EXPERIMENTAL

Reagents were $RhCl_3$ (Ventron), $RhBr_3.3H_2O$ (Fluka) and MTC (prepared as in *ref.* 28). Anhydrous solvents were used for measurements and recrystallizations.

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Preparation of the complexes

[Rh(MTC)$_3$Cl$_3$] and [RhCl$_3$.2MTC]

The reddish orange solution formed by the gradual reaction of MTC (6.0 mmol) with RhCl$_3$ (1.9 mmol dissolved in 10 cm^3 of acetone) separated violet red crystals overnight; they were filtered, washed with acetone and *n*-hexane and identified as [RhCl$_3$.2MTC] (yield $\simeq$10%). By addition of *n*-hexane (10 cm^3) to the acetone solution a dark red oil was obtained, which was decanted from the solution (†) and extracted with benzene. The solid residue was a further fraction of the 1:2 complex (yi. 10%); apparently cubic crystals of [Rh(MTC)$_3$Cl$_3$] (A) precipitated by treating the orange benzene solution with an excess of *n*-hexane (yi. $\simeq$40%). By adding an excess of *n*-hexane to the solution (†) orange needles of [Rh(MTC)$_3$Cl$_3$] (B) precipitated overnight (yi $\simeq$18%). The solids (A) and (B) have analogous analytical data and i.r. spectra, but different melting points; after several recrystallizations from benzene/*n*-hexane, the (A) species was unchanged whereas the (B) species transformed progressively into (A). By operating at higher rhodium chloride to ligand molar ratios, the yield of the 1:2 complex increased slightly ($\simeq$25% at molar ratio 1:5). [Rh(MTC)$_3$Cl$_3$] (either A or B) dissolves easily in benzene, acetone, and chlorinated hydrocarbons; methanol and DMSO solutions turn from orange to pale yellow with time, suggesting progressive decomposition. [RhCl$_3$.2MTC] is soluble in chlorinated hydrocarbons and, by gentle heating, in DMSO (decomposition) but is insoluble in water (as the 1:3 species), acetone, benzene and methanol. The 1:2 complex can be recrystallized from dichloromethane/*n*-hexane.

[Rh(MTC)$_3$Br$_3$] and [RhBr$_3$.MTC]

The acetone solution (6 cm^3) of RhBr$_3$.3H$_2$O (1.0 mmol) and MTC (5.0 mmol) separated overnight a small amount of a brown red solid; it was filtered, washed with *n*-hexane and identified (by elemental analysis and i.r. spectra) as [RhBr$_3$.2MTC]. When washed with either benzene or acetone, this compound released MTC to give the 1:1 complex. The initial acetone solution, treated with *n*-hexane (3 cm^3) separated a brown solid which was filtered and identified as [RhBr$_3$.MTC] (yi $\simeq$15%). The red oil obtained by adding a further 15 cm^3 of *n*-hexane, was separated from the solution (†) and extracted with benzene. The insoluble residue was a further fraction of the 1:1 complex (yi $\simeq$12%). Fractions of [Rh(MTC)$_3$Br$_3$], having identical crystalline shape, i.r. spectra and melting points were isolated by adding an excess of *n*-hexane to either the benzene solution or the acetone solution (†). Solubilities of the 1:3 complex were as for the analogous chloro-derivative, [RhBr$_3$.MTC] is insoluble (or partly soluble with decomposition) in the common solvents.

[Rh(MTC)$_3$I$_3$]

To a solution of [Rh(MTC)$_3$Cl$_3$] (0.5 mmol) and KI (5.0 mmol) in 3 cm^3 of acetone, left standing overnight, *n*-hexane (12 cm^3) was added to give a deep red oil which, treated with benzene/*n*-hexane, gave crystals of [Rh(MTC)$_3$I$_3$] in a low yield ($\simeq$20%). The complex dissolves in benzene, acetone and chlorinated hydrocarbons; the solutions, initially transparent, separate in a short time an unidentified brown solid.

Measurements

Infrared spectra were recorded by using either a Perkin Elmer 580B spectrophotometer (4000-400 cm^{-1}) or a Bruker FTIR (450-100 cm^{-1}) in nujol mulls

TABLE I

Analytical data[a] and infrared frequencies (cm^{-1})[b].

Compound	Colour	M.p.°	C%	H%	N%	i.r. frequencies
$[\mathrm{Rh(MTC)_3Cl_3}]$(A)[c]	reddish-orange	137-8	25.4 (25.4)	4.9 (4.8)	7.5 (7.4)	3272m, 3175w, 3110mw; 1597s
$[\mathrm{Rh(MTC)_3Cl_3}]$ (B)[c]	orange	123-5	25.4	4.8	7.4	3272m, 3185 – 3170wbr, 3112mw; 1597s
$[\mathrm{Rh(MTC)_3Br_3}]$	dark-red	124-5	20.6 (20.6)	3.9 (3.9)	5.9 (6.0)	3265sh, 3228m, 3135mw; 1588s
$[\mathrm{Rh(MTC)_3I_3}]$	brown	70-2	17.3 (17.1)	3.3 (3.2)	5.1 (5.0)	3265sh, 3225mw, 3130w; 1578s
$[\mathrm{RhCl_3.2MTC}]$	violet-red	d	21.8 (21.5)	4.0 (4.0)	5.9 (6.3)	3315sh, 3272m, 3195 – 3170wbr, 3110vw; 1592s
$[\mathrm{RhBr_3.MTC}]$	brown	d	10.1 (10.4)	1.8 (2.0)	3.1 (3.0)	3210w, 3130w; 1585s

[a]The calculated values are in parentheses. [b]In the 3500 — 3000 cm^{-1} and 1650 — 1550 cm^{-1} regions. [c]The complex has been isolated in two crystalline forms (see text). [d]The compound does not melt up to 220°.

between KBr and polyethylene discs. ^{1}H n.m.r. spectra were obtained with a Varian FT80A spectrometer and electronic spectra with a Beckman DK2A spectrophotometer. Molecular weights were measured at 30° with a Knauer 11 vapor pressure osmometer. Thermogravimetric data in nitrogen were obtained using a Netzsch STA429 thermoanalytical instrument.

RESULTS AND DISCUSSION

The complexes, reported in Table I along with their analytical data, have been generally prepared by reacting rhodium trihalides with MTC in acetone, except for $[\mathrm{Rh(MTC)_3I_3}]$, obtained by metathesis on the chloro-analogue with KI. $[\mathrm{Rh(MTC)_3Cl_3}]$ was isolated in two forms: (A), reddish orange crystals melting at 137-8°, and (B), orange needles melting at 123-5°, which have analogous i.r. spectra. When recrystallized from various solvents, (B) transforms progressively into (A); for this reason the measurements reported here have been carried out on the (A) species. Along with the 1:3 adducts, lower stoichiometry complexes of formula $[\mathrm{RhX_3.2MTC}]$ (X=Cl, Br) and $[\mathrm{RhBr_3.MTC}]$ were isolated. The 1:2 bromo derivative, when washed with benzene, acetone or dichloromethane, releases MTC to give the 1:1 complex. Owing to its scarce yield and low stability it was not characterized further.

Molecular weight measurements indicate that the complexes $[\mathrm{Rh(MTC)_3X_3}]$ (X=Cl, Br) are monomers in benzene. In this solvent, as well as in acetone and chlorinated hydrocarbons, $[\mathrm{Rh(MTC)_3I_3}]$ slowly decomposes giving insoluble lower stoichiometry species.

The electronic spectrum of $[\mathrm{Rh(MTC)_3Cl_3}]$ in benzene, acetone and 1,2-dichloroethane presents a broad absorption with a maximum around 471 nm ($\varepsilon_{\mathrm{mol}} \simeq 290$), shifted to higher wavelengths for $[\mathrm{RhCl_3.2MTC}]$ ($\lambda_{\mathrm{max}} = 490$ nm in 1,2-dichloroethane). In the same solvents the $[\mathrm{Rh(MTC)_3Br_3}]$ absorbance maximum is at 490 nm ($\varepsilon_{\mathrm{mol}} \simeq 430$).

The ligand bands in the i.r. spectra of the complexes (Table I) indicate coordination through the sulfur atom. The free MTC absorption at 1535 cm^{-1}, assigned as mainly ν(C-N) with a small δ(N-H) contribution in accordance with analogous

TABLE II
Infrared frequencies (600-200 cm^{-1})[a].

[Rh(MTC)$_3$Cl$_3$]	600shbr	538w	479m		376w	338sh	*316*s	*294* *287* s		225w
[Rh(MTC)$_3$Br$_3$]		530m	477 470 m	385vvw	374vw		321w		*258*m	235mw
[Rh(MTC)$_3$I$_3$]	590wbr	532m	475m	412vw	372vw		313w		239w	220sh
[RhCl$_3$.2MTC]	600wbr	535w	473m		376w	342m	*322*s	*290*m	274vw	228w
[RhBr$_3$.MTC]		535w	472m		380vvw	340vvw			*258*m	

[a]The Rh-Hal stretching frequencies are in italics.

thioamides.[29,30] is displaced towards higher energies on coordination. In complexes of analogous geometry, for instance *trans*-[M(MTC)$_2$X$_2$] (M=Pd, Pt; X=Cl, Br, I), the shift depends on the halide in the order Cl > Br > I.[26,28] A halide-dependent upward shift is clearly observed in the 1:3 rhodium derivatives. The stronger ν(N-H) absorption in the rhodium complexes (Table I) falls in the 3280-3200 cm^{-1} region, as for the 1:2 palladium and platinum derivatives. The 1:3 rhodium adducts should not contain ionic groups. In fact the stronger ν(N-H) band in the square planar [M(MTC)$_3$X]$^+$ and [M(MTC)$_4$]$^{2+}$ (M=Pd, Pt; X=Cl, Br) species is found below 3200 cm^{-1}, at about 3100 cm^{-1} and 2950 cm^{-1}, respectively.

In the far i.r. spectrum of [Rh(MTC)$_3$Cl$_3$] (Table II and Figure 1) the bands at 313, 294

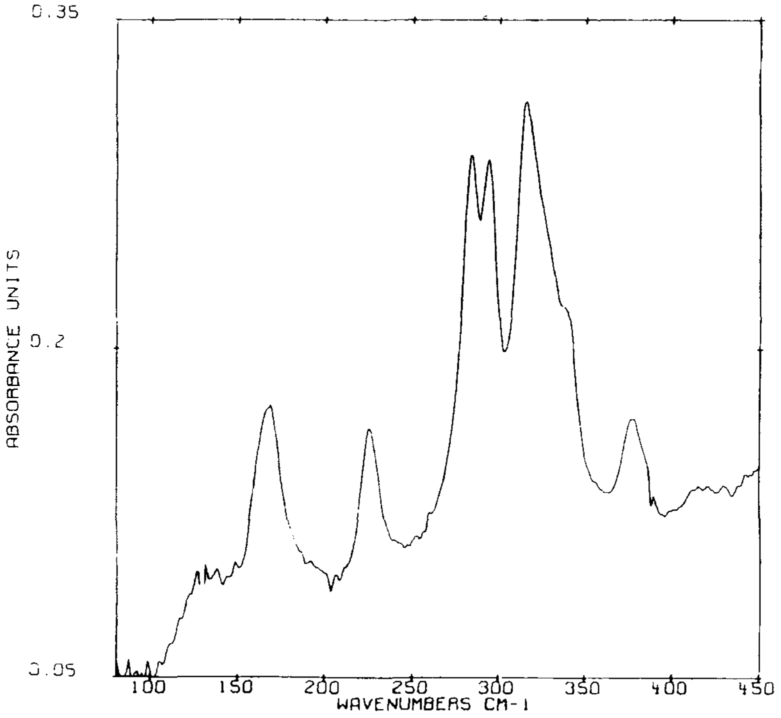

FIGURE 1 Infrared spectrum of [Rh(MTC)$_3$Cl$_3$].

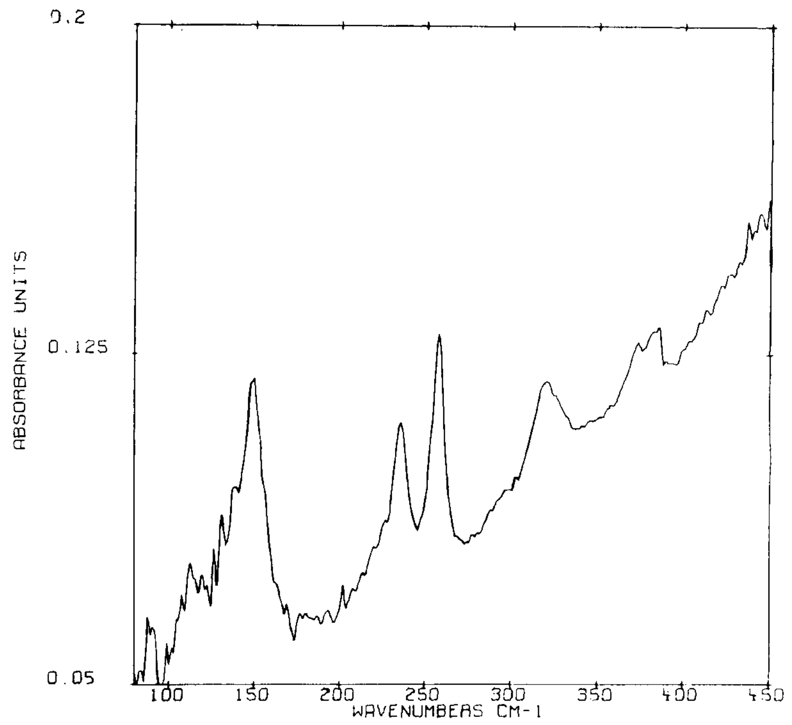

FIGURE 2 Infrared spectrum of $[Rh(MTC)_3Br_3]$.

and 287 cm^{-1} can be assigned as ν(Rh-Cl). The shoulder at 338 cm^{-1} is a halide-dependent band, observed in the chloro- and iodo-derivatives at 321 cm^{-1} and 310 cm^{-1}, respectively. The presence of three i.r. active stretching modes suggests a meridional octahedral configuration for $[Rh(MTC)_3Cl_3]$. Moreover the far i.r. spectrum of this complex is very similar to that of the analogous 1:3 ethylcarbamate (H_2N-C(S)-OEt) complex, whose preliminary crystal structure data are in accordance with *mer* geometry. The far i.r. spectrum of $[Rh(MTC)_3Br_3]$ (Figure 2) is simpler than that of the chloro-derivative, as also observed for *mer*-$[Rh(SMe_2)_3X_3]$ (X=Cl, Br).[31]. The band at 258 cm^{-1} can be assigned as ν(Rh-Br), whereas the one at 235 cm^{-1} could be a ligand band. In fact the chloro- and iodo-analogues show weak absorptions at 225 cm^{-1} and 239 cm^{-1}, respectively. Below 200 cm^{-1} the 1:3 complexes present a medium absorption at 169 cm^{-1} (Cl), 150 cm^{-1} (Br) and 159 cm^{-1} (I). No band clearly assignable to a Rh-I bond was observed in the spectrum of the 1:3 iodo-derivative, except perhaps for a shoulder around 220 cm^{-1}. The spectrum of $[RhCl_3.2MTC]$, showing two Rh-Cl absorptions, a strong one at 322 cm^{-1} and a medium one at 290 cm^{-1} could suggest a dimeric chlorine-bridged configuration.[7] The complex $[Rh(PBut_3)_2Cl_3]_2$ is a chlorine bridged dimer, where one rhodium atom coordinates two *cis* and the other two *trans* chlorines.[32] A dimeric asymmetrical structure was also inferred for $[RhCl_3.2SMe_2]$ from n.m.r. data.[31]

The ^{1}H n.m.r. data for the ligand and complexes in various deuterated solvents are

TABLE III

^{1}H n.m.r. Data (ppm; T ≃ 27°)^a.

Compound	Solvent	NCH_3	NH^b	O-CH_2-CH$_3$	O-CH$_2$-CH_3
MTC	d_6-benzene	2.59(67%)	6.2s^c	4.40	1.03s
		2.17	7.6^c		1.00
[Rh(MTC)$_3$Cl$_3$]	d_6-benzene	2.29s	10.4s	4.12s	0.65s
		2.16	10.6	4.03	0.63
[Rh(MTC)$_3$Br$_3$]	d_6-benzene	2.35s	10.0	4.14s	0.72s
		2.20		4.06	0.69
MTC	d_6-acetone	2.98(75%)	7.9	4.42s	1.24s
		2.83		4.44	1.31
[Rh(MTC)$_3$Cl$_3$]	d_6-acetone	2.90s	9.8	4.63	1.45
		2.87			
[Rh(MTC)$_3$Br$_3$]	d_6-acetone	2.91s	9.3	4.64	1.45
		2.88			
MTC	CDCl$_3$	3.08(64%)	6.5s	4.50s	1.30s
		2.87	7.1	4.56	1.37
[Rh(MTC)$_3$Cl$_3$]	CDCl$_3$	2.91s	9.6s	4.60	1.40
		2.86	9.8		
[Rh(MTC)$_3$Br$_3$]	CDCl$_3$	2.88s	9.2	4.62	1.39
		2.85			
[RhCl$_3$.2MTC]	CDCl$_3$^{d}	2.98	8.9	4.84	1.56
MTC	d_6-DMSO	2.82(75%)	8.9	4.36s	1.21s
		2.66		4.41	1.24
[Rh(MTC)$_3$Cl$_3$]	d_6-DMSO^e	2.9	9.6	4.66	1.41
	d_6-DMSO^f	2.9^{+}	9.7†s	4.66†s	1.41†s
			9.4†	4.62†	1.44†
		2.92s	8.9	4.41s	1.26s
		2.71		4.45	1.29
[RhCl$_3$.2MTC]	d_6-DMSO^g	2.87s	8.9	4.41s	1.25s
		2.71		4.45	1.29

^{a}The stronger of two very close signals is indicated by s. ^{b}Broad signals. ^{c}For a ≃ 0.2M solution; the resonances shift upfield with dilution. ^{d}The solution is slightly turbid; very weak free ligand signals are also observed. ^{e}Within 10 min from solubilization. ^{f}After 4h; signals of either coordinated (†) or free ligand are present. ^{g}The solid was allowed to dissolve by heating up to 50°.

reported in Table III. At room temperature MTC is a mixture of the *syn* and *anti* isomers

whose relative amount, depending on the solvent, can be estimated from the relative intensities of either NC*H*$_3$ doublets or broad N*H* resonances.[26-28]

The spectrum of [Rh(MTC)$_3$Cl$_3$] in d$_6$-benzene (Figure 3) shows a double series of sharp signals for each proton group. The stronger one is approximately two thirds of the total amount. In accordance with molecular weight data, both series of signals belong to

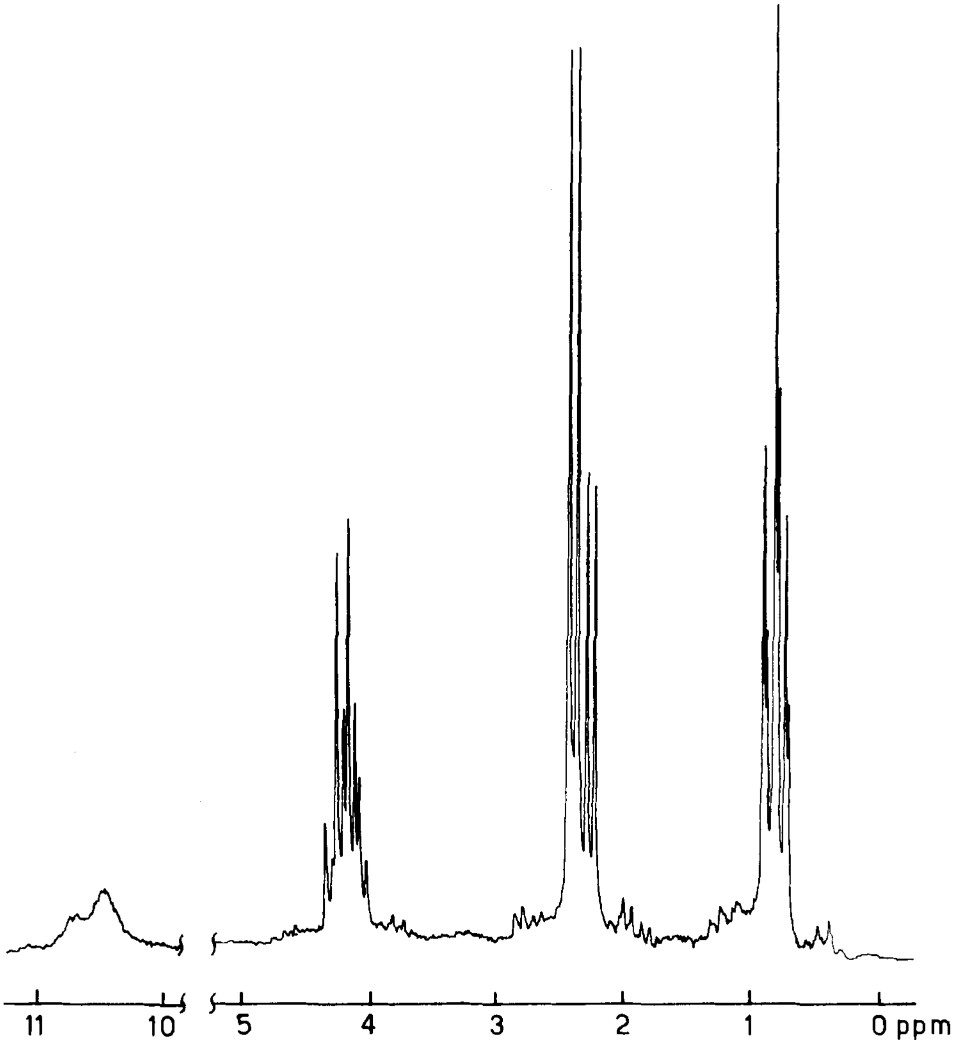

FIGURE 3 ^{1}H n.m.r. spectrum of [Rh(MTC)$_3$Cl$_3$] in d$_6$-benzene.

coordinated ligand. The ethyl group resonances are 0.3 - 0.4 ppm upfield with respect to the corresponding ones of free MTC, with a parallel noticeable downfield shift of the N*H* signals. The complexes $[Pt(MTC)_3X_2[Pt(MTC)_3X_2]$ (X = Cl, Br), for which a tight ion-pair nature was suggested, gave a similar double spectrum in d_6-benzene.[26] Either *mer*-$[Rh(MTC)_3X_3]$ (X = Cl, Br) or the square planar species $[Pt(MTC)_3X]^+$ contain two mutually *trans* MTC molecules, the third one being *trans* to halide; if the sulfur-metal bonds are different, they give rise to different ^1H n.m.r. signals. The spectra of the 1:3 adducts in d_6-acetone and $CDCl_3$ show the sharp signals of the coordinated ligand. In polar solvents all the coordinated MTC resonances shift downfield with respect to those of free MTC.[27,33] The 1:3 complexes show one signal for each proton group, except for two very close NCH_3 doublets of different intensity. Absence of free ligand and electronic spectra similar to those in benzene suggest that the 1:3 chloro- and bromo-derivatives are monomers in these solvents. On the contrary, either in d_6-benzene or $CDCl_3$, $[Rh(MTC)_3I_3]$ shows, along with free MTC signals, almost superimposed resonances of two coordinated species (probably the 1:3 and 1:2 ones). Single sharp signals for each proton group are observed for $[RhCl_3.2MTC]$ solutions in $CDCl_3$, as for *trans*-$[Pd(MTC)_2X_2]$ (X = Cl, Br),[28] supporting the notion that the double signals of the 1:3 adducts are not caused by the ligand isomers. When dissolved in d_6-DMSO, the complexes $[Rh(MTC)_3X_3]$ (X = Cl, Br) give initially a simple spectrum, which progressively changes to a multispecies system. After 6h the main product is free MTC along with only one coordinated species. The spectrum is unchanged after 3d. Possibly DMSO replaces all but one MTC molecule, as observed for the 1:2 and 1:3 platinum complexes.[27] The electronic spectrum of 1.5×10^{-3} M solution of $[Rh(MTC)_3Cl_3]$ in DMSO is initially close to that in benzene; after $\simeq$16h it shows two shoulders at $\simeq$430 nm ($\varepsilon_{mol} \simeq 220$) and 500 nm ($\varepsilon_{mol} \simeq 80$). After heating d_6-DMSO solutions of either $[Rh(MTC)_3Cl_3]$ or $[RhCl_3.2MTC]$ to 50° only free MTC resonances were observed.

Thermal TG and DTA measurements were carried out in order to verify if degradation of the 1:3 complexes allowed the isolation of lower stoichiometry intermediates, as reported for $[Rh(SMe_2)_3Cl_3]$.[34] On the contrary all the 1:3 complexes melt releasing either MTC or halide, the initial weight loss, below 200°, being $\simeq$50% (Cl), $\simeq$52% (Br), $\simeq$49% (I). At higher temperatures progressive slow weight loss takes place, ending at 1100-1200°. $[RhCl_3.2MTC]$ begins to decompose around 130°; afer an initial weight loss of $\simeq$46% (temperature interval 130-220°) and a subsequent one ($\simeq$ 19%; 220-400°), the TG curve resembles that of $[Rh(MTC)_3Cl_3]$.

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