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Complexes of Platinum(II) Halides with Dithiocarbamic Esters

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Abstract

Platinum(II) halides form either 1:1 or 1:2 complexes with dithiocarbamic esters (R_2N–C(S)–SR′). Complexes of both stoichiometries have been obtained with the ligands TMDT (R = R′ = Me) and DMDTE (R = Me; R′ = Et), whereas with TEDT (R = R′ = Et) only the 1:1 adducts were isolated. From IR spectra the complexes of formula PtL_2X_2 (L = TMDT, DMDTE; X = Cl, Br, I) have a *trans* square planar configuration by two halide and two thiocarbonyl sulfur atoms. In the complexes of formula $PtLX_2$, for which a *cis* square planar configuration is suggested, the ligands act probably as bidentate through either thiocarbonyl or thioether sulfur.

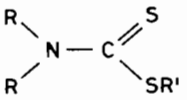
All the complexes have been tested for cytostatic activity on KB cells.

Introduction**

Previously we prepared and characterized some platinum(II) halide complexes with thiocarbamic esters, in order to test them as possible antitumor compounds. The ligands acted as monodentate through the thiocarbonyl group; whereas DMTC gave 1:2 adducts only [1], the homologues bearing either one or two hydrogens at the nitrogen atom, MTC and TC, gave higher stoichiometry complexes too, of general formulas PtL_3X_2 and $[PtL_4]X_2$ (X = Cl, Br) [2, 3]. The DMTC and MTC complexes were tested for cytostatic activity towards KB cells; significant ED_{50} values were observed for *cis*- and *trans*-$Pt(MTC)_2Cl_2$ and $Pt(MTC)_3Cl_2$ [4].

Owing to the importance of sulfur–metal interactions in biological systems, we thought it would be of interest to extend the study to dithiocarbamic esters. The coordination chemistry of this class of ligand has been scarcely studied; as far as we know, only the N,N-dialkyl dithiocarbamic ester derivatives of mercury dihalides have been reported. The complexes have 1:1 stoichiometry, the ligand acting as monodentate through the thiocarbonyl sulfur [5]; from X-ray data $HgCl_2 \cdot (CH_2)_4N$–C(S)–SCH_3 is a chlorine bridged dimer with a distorted tetrahedral arrangement around each mercury atom by one sulfur and three chlorine atoms [6]. Alkylthiuram disulfides act as bidentate towards mercury halides forming 1:1 derivatives [7]; the X-ray structure of $HgI_2 \cdot Me_2N$–C(S)–S–S–C(S)–NMe_2 presents the mercury atom in a distorted tetrahedral coordination by two iodine and two thiocarbonyl sulfur atoms [8]. Thiuram disulfide derivatives and dithiocarbamic salts have received some attention as antagonist of metal intoxication. Interesting relationships between metal redistribution after treatment with either tetramethylthiuram disulfide or sodium diethyldithiocarbamate($NaEt_2dtc$) and biological effect have been observed [9]. Moreover the protective effect of $NaEt_2dtc$ against *cis*-$Pt(NH_3)_2Cl_2$ toxicity has been the object of numerous studies [10].

The present paper reports the preparation and characterization of platinum(II) halide complexes with the ligands



R = R′ = Me	TMDT
R = R′ = Et	TEDT
R = Me; R′ = Et	DMDTE

Preliminary results of an *in vitro* cytostatic activity screening on KB cells are also reported.

Experimental

Reagents were $PtCl_2$ (Johnson Matthey), PtX_2 (X = Br, I; Alfa Products) and K_2PtCl_4 (Johnson Matthey). The ligands, prepared by reacting Na(R_2dtc) and RI (R = Me, Et) in $EtOH/H_2O$ [11], were dissolved in diethylether and dried over Na_2SO_4; the solvent was then removed under reduced

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**Abbreviations used: DMTC, Me_2N–C(S)–OEt; MTC, MeHN–C(S)–OEt; TC, H_2N–C(S)–OEt; R_2dtc, R_2N–CS_2^-.

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pressure. TMDT was recrystallized from n-pentane (m.p., 44–5 °C); DMDTE and TEDT were pale yellow oils. Preparations of complexes were carried out at room temperature; reaction vessels were wrapped in black paper.

Preparation of the Complexes

$PtLX_2$

$Pt(TMDT)X_2$ (X = Cl, Br) were prepared by stirring a PtX_2 suspension in a 0.2 M CH_2Cl_2 solution of TMDT (molar ratio 1:2.1). The reaction went on gradually forming a red solution and a yellow solid, which was filtered, washed with CH_2Cl_2 and n-hexane and dried *in vacuo* (X = Cl: yield, 55%; reaction time, 90 min. X = Br: y., 70%; r.t. 2 h). When the residual CH_2Cl_2 solutions were either evaporated to dryness or treated with n-hexane, orange solids were isolated which, by IR spectra and elemental analyses, were identified as the dimeric species $[Pt(Me_2dtc)X]_2$ containing a small amount of $Pt(TMDT)_2X_2$ (X = Cl, Br). These species were also present as side products, insoluble in the reaction solvent, when preparations were carried out in benzene and in chloroform. Attempts to isolate the iodo-derivative by reacting PtI_2 and TMDT in various solvents yielded generally mixtures of $Pt(TMDT)I_2$ and $Pt(TMDT)_2I_2$.

$Pt(DMDTE)X_2$ (X = Cl, Br) were obtained in CH_2Cl_2 at the experimental conditions reported above for the TMDT derivatives (X = Cl: y., 57%; r.t., 4 h. X = Br: y., 58%; r.t., 2 h) whereas $Pt(TEDT)X_2$ (X = Cl, Br, I) were prepared by reacting PtX_2 with 0.2 M benzene solutions of TEDT (molar ratio 1:2.1). The compounds, insoluble in benzene, were obtained in high yields (75–80%); reaction times were 20 h (Cl), 18 h (Br) and 28 h (I). The TMDT and DMDTE derivatives are insoluble in the common solvents; the TEDT complexes dissolve slightly in dichloromethane and acetone. All the 1:1 complexes dissolve with decomposition in dimethylsulfoxide (DMSO); they are insoluble in water.

PtL_2X_2

$Pt(TMDT)_2X_2$ (X = Cl, Br, I) were prepared by reaction of PtX_2 and TMDT in acetone (molar ratio 1:12; 1.1 M ligand); after an initial formation of the insoluble 1:1 species, the solid gradually transformed into the 1:2 complexes (X = Cl: y., 40%; r.t., 28 h. X = Br: y., 55%; r.t., 17 h. X = I: y., 70%; r.t., 24 h). The residual deep red solutions, evaporated to dryness, gave orange solids which, when kept under acetone for a few days, changed to the yellow $[Pt(Me_2dtc)X]_2$ (X = Cl, Br). The solid 1:2 complexes decompose with the time; the IR spectrum of a 45 days old $Pt(TMDT)_2Cl_2$ sample shows some bands characteristic of $[Pt(Me_2dtc)Cl]_2$.

$Pt(DMDTE)_2X_2$ (X = Cl, Br) were obtained by reaction of PtX_2 with a 2 M acetone solution of the ligand (molar ratio 1:20; y., 45%; r.t. 3 days).

Reactions of PtX_2 with TEDT were carried out in various solvents, at molar ratios up to 1:20; the solid fraction was the corresponding 1:1 complex, whose amount decreased with the increasing of ligand concentration. The deeply coloured solutions contained probably the 1:2 species, which could not be induced to crystallize either by adding n-hexane or by evaporating the solvent. In both cases red oils separated.

Except for the insoluble $Pt(TMDT)_2I_2$, the 1:2 complexes dissolve slightly in dichloromethane and acetone ($conc_{max} \simeq 5 \times 10^{-3}$ M). The initially transparent solutions separate the corresponding insoluble 1:1 derivatives in a short time. They decompose in DMSO as the 1:1 complexes.

$[Pt(Me_2dtc)X]_2$

Samples of good purity were obtained as side products in the $Pt(TMDT)_2X_2$ preparation, as reported above. Moreover the chloro-derivative was prepared by stirring a $PtCl_2$ suspension (0.4 mmol) in an acetone solution of $Na(Me_2dtc)\cdot 2H_2O$ (0.45 mmol in 4 ml). The reaction went on in heterogeneous phase with probable initial formation of $Pt(Me_2dtc)_2$, which reacted progressively with the residual $PtCl_2$. Within 24 h the solid product was essentially $[Pt(Me_2dtc)Cl]_2$ with traces of $PtCl_2$ and $Pt(Me_2dtc)_2$. IR. ν(CN): 1560 cm^{-1} (X = Cl); 1565 cm^{-1} (X = Br).

The IR spectra were recorded on a Perkin-Elmer Mod. 580 spectrophotometer (Nujol mulls between CsI discs) in the 4000–350 cm^{-1} region; by a Beckman IR 11 spectrophotometer (Nujol mulls between polythene plates) in the 400–200 cm^{-1} region.

In vitro Cytostatic Activity

The substances have been tested according to Protocols for Screening Chemicals Agents and Natural Products [12]. In brief Minimal Eagle's medium (MEM) [13] supplemented with 10% calf serum was used. 10^5 KB cells, a line derived from a human epidermoid carcinoma of the mouth, were incubated at 37 °C in Leighton tubes. After 24 h the cells were attached to the glass and the compound to be tested, suspended in sterile saline, was then added. Incubation was carried out at 37 °C for 72 h. Cell growth was estimated by counting in the Bürker chambre the viable cells detached from the glass wall with trypsin. The cytostatic activity was expressed as concentration of the compound in μg/ml MEM at which the cells showed a 50% inhibition of growth in relation to the control values (ED_{50}). The statistical evaluation of the results was done by the Student t test.

Results and Discussion

As shown in Table I, the three dithiocarbamic esters form 1:1 complexes with platinum halides, whereas 1:2 complexes have been isolated with N,N-dimethyl esters only. The lower stoichiometry derivatives, generally insoluble in the usual solvents, are easily prepared by reaction of platinum halides with a moderate excess of ligand (molar ratio about 1:2). By increasing progressively molar ratio and ligand concentration, the solid phase is a mixture of 1:1 and 1:2 derivatives, whose relative amount can be estimated roughly by IR spectra (CN absorptions in the 1500–1600 cm^{-1} region). High molar ratios (up to 1:20), elevated ligand concentrations (more than 1 M) and long reaction times are necessary to transform solid mixtures into pure 1:2 adducts. If evaporated to dryness, the red solutions, from which $Pt(TMDT)_2X_2$ have been filtered away, give orange solids, which, after a few days under acetone, transform into the S-demethylated yellow $[Pt(Me_2dtc)X_2]_2$ (X = Cl, Br). The occurrence of S-dealkylation was also observed for palladium and platinum halide complexes with various *ortho*-substituted methylthiophenyl ligands [14 and refs. therein]. The IR spectra of $[Pt(Me_2dtc)Cl]_2$ samples obtained by decomposition are identical to those of samples synthetized from $PtCl_2$ and $Na(Me_2dtc)$: the CN absorption is at 1560 cm^{-1}, close to that of $Pt(Me_2dtc)_2$ (1555 cm^{-1}), whereas the broad band around 310 cm^{-1} is probably the ν(Pt–Cl) of the bridging chlorine atoms, as in the anologous palladium derivatives [15, 16]. Moreover unidentified decomposition products were recovered from the residual solutions of the $Pt(DMDTE)X_2$ and $Pt(DMDTE)_2X_2$ preparations. When platinum halides are reacted with concentrated TEDT solutions, the insoluble 1:1 species separated in a small amount and the deep red solutions contain the main reaction products, probably the 1:2 adducts, which on standing undergo decomposition processes. In fact either evaporation of the solvent or addition of n-hexane yield unidentified orange oils. The 1:2 adducts of Table I, slightly soluble in acetone and in chlorinated hydrocarbons, release easily ligand molecules to form the insoluble 1:1 complexes,

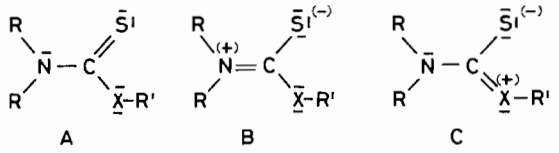
TABLE I. Analytical Data, Infrared Frequencies and *in vitro* Cytostatic Activity.[a]

Compound	Colour	M.p. °C	C%	H%	N%	Hal%	ν(C–N)[b]	ED_{50}(μg/ml)[c]
$Pt(TMDT)Cl_2$	yellow	>270	12.1 (12.0)	2.3 (2.3)	3.4 (3.5)	17.8 (17.7)	1601	>10
$Pt(TMDT)Br_2$	dark yellow	>270	9.7 (9.8)	2.0 (1.9)	2.7 (2.9)	32.8 (32.6)	1599	>10
$Pt(DMDTE)Cl_2$	yellow	>270	14.3 (14.5)	3.0 (2.7)	3.1 (3.4)	17.3 (17.1)	1590	>10
$Pt(DMDTE)Br_2$	hazel	>270	11.9 (11.9)	2.1 (2.2)	2.7 (2.8)	31.8 (31.7)	1590	>10
$Pt(TEDT)Cl_2$	yellow	225–7[d]	19.4 (19.0)	3.3 (3.4)	3.1 (3.2)	16.0 (16.0)	1562	>10
$Pt(TEDT)Br_2$	dark yellow	240–2[d]	15.9 (15.8)	2.8 (2.8)	2.5 (2.6)	29.4 (30.0)	1570	>10
$Pt(TEDT)I_2$	yellow green	169–71[d]	13.6 (13.4)	2.6 (2.4)	2.1 (2.2)	–	1561	3.8
$Pt(TMDT)_2Cl_2$	dark reddish	111–2	18.6 (17.9)	3.2 (3.4)	5.2 (5.2)	13.2 (13.3)	1525	>10
$Pt(TMDT)_2Br_2$	light red	110–1	15.5 (15.4)	3.0 (2.9)	4.4 (4.5)	24.7 (25.5)	1525	2.8
$Pt(TMDT)_2I_2$	hazel	dec.	13.6 (13.4)	2.6 (2.5)	3.8 (3.9)	–	1525	>10
$Pt(DMDTE)_2Cl_2$	dark pink	101–2	21.1 (21.3)	3.9 (3.9)	4.9 (5.0)	12.7 (12.6)	1530	–
$Pt(DMDTE)_2Br_2$	light hazel	88–9	18.2 (18.4)	3.3 (3.4)	4.2 (4.3)	23.2 (24.5)	1525	0.4

[a]Against KB cells. [b]Cm^{-1}; very strong. Ligands: TMDT, 1502 cm^{-1}; DMDTE, 1498 cm^{-1}; TEDT, 1488 cm^{-1}. [c]Concentration of complex suspended in saline, which inhibits by 50% the cell growth in respect to controls. [d]At lower temperatures the complexes apparently decompose into orange species.

differing from the $Pt(DMTC)_2X_2$ derivatives, monomeric either in those solvents or in benzene by molecular weight and ^1H NMR data [1].

Useful information about coordination is obtained by correlating the C–N and the Pt–Hal stretching vibrations of the prepared compounds with those of the thiocarbamic ester derivatives. Thiocarbamic and dithiocarbamic ester molecules are resonance hybrids of the canonical formulas (where X = O, S)



A B C

The predominant B contribution hinders the rotation about the C–N bond; the energy of the barriers to rotation has been measured for several molecules by ^1H NMR. The ΔG_{att} values parallel the trend in ν(CN), so that higher barriers correspond to higher ν(CN) values. Barriers to rotation in dithiocarbamic esters are lower than in the corresponding thiocarbamic esters, owing to the greater ability of the sulfur atom to stabilize the positive charge, enhancing the form C contribution. In fact ΔG_{att} is 14.7 Kcal mol^{-1} for TMDT and 17.4 Kcal mol^{-1} for Me_2N–C(S)–OMe [11, 17–19] and is slightly influenced by the alkyl substituents on nitrogen and sulfur, being 14.6 Kcal mol^{-1} for DMDTE and 15.2 Kcal mol^{-1} for TEDT [11, 20]. Accordingly, the ν(CN) value of DMTC (1535 cm^{-1}) is higher than those of TMDT (1502 cm^{-1}), DMDTE (1498 cm^{-1}) and TEDT (1488 cm^{-1}), as is observed for TC (1440 cm^{-1}) and H_2N–C(S)–SMe (1389 cm^{-1}) [3, 21]. When both series of ligands act as monodentate through thiocarbonyl sulfur, the C–N double bond is enhanced, with a parallel ν(CN) shift to higher frequencies with respect to the corresponding uncoordinated molecule. The $\Delta\nu$ values are of the order of 30 cm^{-1} for $HgLX_2$ (L = DMDTE, TMDT) [5] and of 40 cm^{-1} either for $Hg(DMTC)X_2$ [22] or $Pt(DMTC)_2X_2$ [1]. Along with a slightly smaller $\Delta\nu$ ($\simeq$25 cm^{-1}, Table I), the 1:2 complexes here reported show a strong Pt-X absorption (Table II) at the same frequency of the corresponding *trans*-$Pt(DMTC)_2X_2$ [1, 22], which allows to assign to these compounds a *trans* square planar geometry. The 1:1 derivatives show (Table I) a noticeably greater ν(CN) shift, of about 95 cm^{-1} for the N-dimethyl derivatives and of about 75 cm^{-1} for the TEDT ones, owing to the larger inductive effect of the ethyl groups. In these compounds the thioetheral sulfur is clearly involved in coordination, with a consequent decrease of the C form contribution and a parallel increase of the C–N double bond. The IR data do not allow to state whether the bidentate ligands act as chelated or coordinate two platinum atoms. In dithio-anions the $-CS_2$ moiety can afford various behaviours; *e.g.*, palladium and platinum dithioacetates consist of $M_2(dta)_4$ units, where each anion bridges both metal atoms [23, 24], and in $[Pt_2Cl_3(PEt_3)_2(S_2CNMe_2)]$ [25] the chelated dithiocarbamate acts as donor on a second platinum atom. The 1:1 complexes show generally two Pt–X absorptions (Table II), very close to those of *cis*-PtL_2X_2 (L = DMTC, MTC) and *cis*-$PtLX_2$, where L = $RS(CH_2)_nSR$ (n = 2,3) [26]; chelated dithioether is found in $PtLX_2$ (L = 1,2 bis (trifluoromethylthio)propane) by X-ray data [27]. On this basis the 1:1 derivatives here reported have probably a *cis* square planar geometry by chelating dithiocarbamic esters. The weak band around 280 cm^{-1}, common to all complexes of dithio- and thiocarbamic esters, should be associated to Pt–S bond.

The IR bands in the 900–1050 cm^{-1} range have been reported as diagnostic of monodentate or bidentate dithiocarbamic ion and thiuramdisulfide [28]. In this region the prepared complexes show a trend depending on stoichiometry whatever the

TABLE II. Infrared Bands in 600–200 cm^{-1} Region (Pt–Halogen frequencies are in italics).

$Pt(TMDT)Cl_2$	565w	540w		435mw	380w		*325,317*s	282vw	248w		
$Pt(TMDT)Br_2$	565w	535w		430mw	375mw		317m	282vw	252w	*224*ms	*210*ms
$Pt(DMDTE)Cl_2$	562mw	538w		430m	373mw		*324,312*s	290vbr	236m		
$Pt(DMDTE)Br_2$	562mw	538w		430m	370m		337w	286vbr	247vbr	*219*w	*202*s
$Pt(TEDT)Cl_2$	561mw	488w 470m		420m			*325,311*s	280w	228w		
$Pt(TEDT)Br_2$	562mw	488m		418w	375mw			282vw	246w	*218*m	*202*m
$Pt(TEDT)I_2$	560w	470m		418m	380w	360w		280vvw	250vw		
$Pt(TMDT)_2Cl_2$	570w		445mw	429m			*328*s	285w	257vw		
$Pt(TMDT)_2Br_2$	571w		445mw	428m	371vw	352vw		285mw	254w	*236*s	
$Pt(TMDT)_2I_2$	571w		443mw	428m	371vw	352vw		285m	254w	208w	*195*m
$Pt(DMDTE)_2Cl_2$	570w	551w	442m	430m	370w		*327*s	292w	250mw		
$Pt(DMDTE)_2Br_2$	567w	552	445m	430m	380vw	370w	348w	280w		*237*s	224w

halide is. In fact the spectra of all the 1:2 adducts present three bands and those of the 1:1 complexes show only two bands. As an example the spectra of $Pt(TMDT)Cl_2$ and $Pt(TMDT)_2Cl_2$ are reported (Fig. 1).

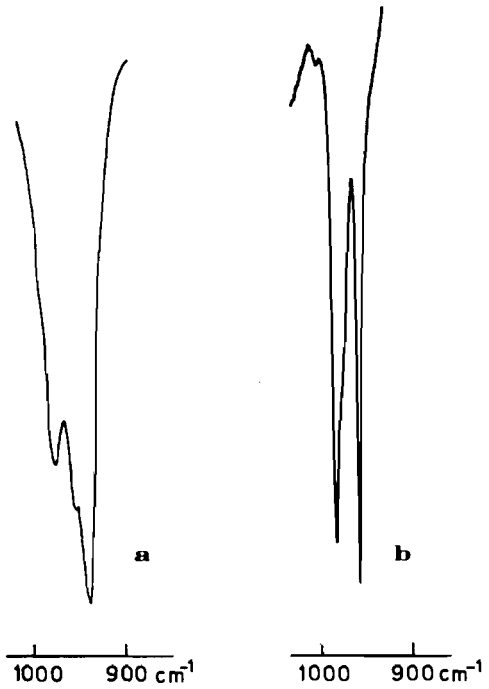


Fig. 1. IR spectra in Nujol of: a) $Pt(TMDT)_2Cl_2$; b) $Pt(TMDT)Cl_2$.

All complexes and ligands were tested for cytostatic activity. We have chosen an ED_{50} of 10 μg/ml as our upper-limit criterion for a significant level of activity. Therefore interesting ED_{50} values were observed for $Pt(TEDT)I_2$, $Pt(TMDT)_2Br_2$ and $Pt(DMDTE)_2Br_2$ only. The ligands were inactive.

Preliminary data indicate cytostatic activity also for some palladium complexes with the ligands here reported.

Acknowledgements

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