Complexes of Palladium(II) and Platinum(II) Halides with O-Ethylthiocarbamate

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Introduction

This note follows our previous studies on platinum(II) and palladium(II) halide complexes with N,N-dimethyl O-ethylthiocarbamate (DMTC) [1] and N-methyl O-ethylthiocarbamate (MTC) [2, 3], which act as monodentate through the sulfur atom. The importance of the number of methyl groups bonded to nitrogen on the complex stoichiometry was evident; with both ligands the square-planar 1:2 adducts were isolated, whereas MTC only gave 1:3 and 1:4 complexes. Attempts to prepare the 1:1 derivatives, quite usual with thioureas and thioamides, led to solids in which the ligands seemed to decompose by elimination of the nitrogen methyls; the IR spectra suggested the formation of the NH_2 group. We thought it interesting to have a survey about the complexing behaviour of the primary thiocarbamate $H_2N–C(S)–OEt$(TC) towards MX_2 (M = Pd, Pt; X = Cl, Br, I). This ligand has been reported to form, by reaction with K_2PtCl_4 in ethanol, the complex $[Pt(TC)_4]Cl_2 \cdot C_2H_5OH$ [4], whereas $H_2N–C(S)–OC_3H_7$ in the same solvent gave the 1:2 adduct [5]. With primary thioamides palladium halide complexes having either 1:2 or 1:4 stoichiometry have been isolated [6, 7].

Experimental

PtX_2 and PdX_2 (X = Cl, Br, I) were used as supplied (Alfa Products). TC was prepared by reaction of $C_2H_5O–C(S)–SCH_2–COONa$ [8] with ammonia in H_2O [9]; upon cooling white crystals separated, which were washed with cold water, dissolved in ethyl ether and dried over anhydrous Na_2SO_4. The pure product was isolated by removing the solvent under reduced pressure.

Preparation of the Complexes

$M(TC)_2X_2$

$Pt(TC)_2X_2$ (X = Cl, Br, I) and $Pd(TC)_2X_2$ (X = Br, I) were prepared by stirring the solid halide in an acetone solution of TC (molar ratio 1:2) at room temperature. In two hours the salts dissolved almost completely; the respective complexes were isolated by addition of n-hexane (yields 70–80%). In the same conditions $PdCl_2$ gave red solids having variable analytical data. $Pd(TC)_2Cl_2$ was isolated by stirring a suspension of $PdCl_2$ in a benzene solution of TC (molar ratio 1:2); the solid turned slowly to yellow-orange and the reaction was completed in 15 h. The analogous bromo- and iodo-derivatives could also be obtained by the same method. $M(TC)_2Cl_2$ (M = Pt, Pd) were also prepared by mixing benzene solutions of *trans*-$M(DMTC)_2Cl_2$ [1] and TC (molar ratio 1:2); the initial precipitate was $[M(TC)_4]Cl_2$, which slowly reacted with the residual DMTC complex to give the 1:2 TC derivatives in 20 h. PtI_2 and TC in benzene at a molar ratio 1:2 (20 h) gave $Pt(TC)_2I_2$ in a beige form, whereas from acetone a pink solid was isolated.

The 1:2 complexes are soluble in acetone, DMSO, water (where the iodo-derivatives are poorly soluble), CH_2Cl_2; they are insoluble in benzene (the iodo derivatives dissolve slightly) and hydrocarbons. In water and ethanol the complexes undergo a more or less rapid decomposition, especially evident for the palladium derivatives, to give red solutions. $Pd(TC)_2Cl_2$ is unstable also in the solid state; all the reported data were taken with two days from preparation.

$M(TC)_3X_2$

$Pd(TC)_3X_2$ (X = Cl, Br) were prepared by stirring a suspension of the halide in a benzene solution of TC (molar ratio 1:3; reaction time 5 h); $Pt(TC)_3Cl_2$ by dissolving the salt in an acetone solution of TC (molar ratio 1:3) and by adding n-hexane after 2 h. Reaction of $PtBr_2$ and TC (molar ratio 1:3) either in acetone or in benzene gave a mixture of 1:2, 1:3 and 1:4 derivatives. The solubilities of the 1:3 complexes resemble those of the 1:2 analogues.

$[M(TC)_4]X_2$

$[Pt(TC)_4]Cl_2$ was obtained by stirring a $PtCl_2$ suspension in an acetone solution of TC (molar ratio 1:4; 2 h); $[Pd(TC)_4]Cl_2$ by dissolving $PdCl_2$ in an acetone solution of TC (molar ratio 1:9) and

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adding n-hexane after 2 h. Both compounds precipitate immediately by mixing benzene solutions of *trans*-$M(DMTC)_2Cl_2$ (M = Pd, Pt) and TC (molar ratios going from 1:2 to 1:10). $[M(TC)_4]Br_2$ were prepared from the halide and TC in benzene (M = Pt: molar ratio 1:10, reaction time 15 h; M = Pd: 1:6, 3h). The platinum 1:4 complexes are soluble in DMSO, ethanol, water; poorly soluble in acetone and CH_2Cl_2, and insoluble in Et_2O and benzene; the palladium analogues are soluble in H_2O, DMSO, EtOH, acetone and CH_2Cl_2, and slightly soluble in benzene and Et_2O.

$[M(TC)_4]X_2 \cdot 2H_2O$

The platinum derivatives were obtained by reaction of halide and ligand in benzene (X = Cl, molar ratio 1:6; X = Br, 1:10) for three days; the progressive formation of the hydrated forms was followed by IR. The palladium bromide complex was prepared by dissolving $[Pd(TC)_4]Br_2$ in CH_2Cl_2, adding an excess of TC until the formation of a yellow precipitate, and stirring the suspension for 3 d. The solubilities are similar to those of the anhydrous complexes.

$[M(TC)_4]X_2 \cdot 2TC$

The complexes were isolated in benzene from PtX_2 (X = Br, I) and $PdBr_2$ in a concentrated TC solution (molar ratio 1:20, reaction time 5 h). The solids were filtered and dried *in vacuo*; if washed with benzene or Et_2O they release TC to give the 1:4 bromoderivatives and $Pt(TC)_2I_2$. In similar conditions MCl_2 (M = Pt, Pd) gave the anhydrous 1:4 compounds.

Measurements

Instruments and procedures were as in ref. [3]; thermogravimetric analyses were carried out in air on a NETZSCH mod. STA. 429 Thermobalance; magnetic susceptibilities were measured in the solid phase at room temperature by the Gouy method.

Results and Discussion

As is evident from Table I, palladium and platinum halides give with TC complexes having stoichiometries 1:2 (X = Cl, Br, I), 1:3 (X = Cl, Br) and 1:4 (X = Cl, Br) Along with the anhydrous 1:4 species, solids containing two additional water and TC molecules have been isolated*. Differing from the DMTC and MTC derivatives, the TC complexes are generally insoluble in benzene; they dissolve in acetone, where osmometric and conductometric measurements were carried out. The Vant' Hoff *i* values were determined in the concentration range 2×10^{-2}–1×10^{-3} *M*; in Table I the value for a 5×10^{-3} *M* solution of each complex is reported. All the complexes behave as non-electrolytes in acetone. In this solvent the 1:2 adducts seem to be monomers, except for $Pd(TC)_2I_2$, whose *i* values, varying from 1.25 (1.2×10^{-2} *M*) to 1.54 (1.5×10^{-3} *M*), suggest ligand releasing to give the probably dimeric 1:1 derivative, as previously observed in benzene for PdL_2I_2 (L = DMTC, MTC) [1, 2]. Besides $Pd(TC)_2Cl_2$ is an unstable compound which, if kept *in vacuo*, turns from orange-yellow to reddish brown in a few days. The 1:3 and 1:4 complexes dissociate in acetone to give TC and the 1:2 adducts, the effect being more evident for the palladium derivatives, as for the MTC analogues. $[M(TC)_4]X_2 \cdot 2L$ (L = H_2O, TC) behave in acetone as the anhydrous 1:4 analogues, the main species in solution being the 1:2 complex. The compounds having two additional TC molecules were prepared in heterogeneous conditions from the halide in a very concentrated benzene solution of the ligand (molar ratio 1:20); a 1:6 compound was isolated also for PtI_2, which shows no tendency to form 1:3 and 1:4 complexes with either MTC or TC. As far as we know no complex in which platinum(II) and palladium(II) halides coordinate six monodentate ligands has been reported; compounds of the type $[PtL_6]X_2$ have been obtained when L = thioxane and X = nitrate, picrate [10]. Recently $Pt[SC(NH_2)_2]_4Cl_2$ has been found to coordinate one additional thiourea molecule probably through NH····S bonds; $[PtL_4]Cl_2$ (L = thiourea, alkylthiourea) can sum two alkylammonium chloride molecules by NH···Cl bonds [11, 12]. The ability of nickel(II) to give hexacoordinated molecular ions was instead evident in the compounds $Ni[SC(NH_2)_2]_6X_2$ [13, 14].

Magnetic susceptibility measurements showed that all the $[M(TC)_4]X_2 \cdot 2L$ solids were diamagnetic, suggesting that the L molecules are out of the coordination sphere. Water in the hydrated complexes was estimated by thermogravimetric analysis. For instance $[Pt(TC)_4]Br_2 \cdot 2H_2O$ loses the water molecules in the range 60–90 °C (H_2O%: Calcd., 4.4; found, 4.5); at higher temperatures the thermogram is similar to that of the anhydrous complex, which seems to release two TC molecules in the 110–130 °C interval whereas $[Pt(TC)_4]Br_2 \cdot 2TC$ begins to release the ligand at about 90 °C.

The IR bands of TC at 3430 and 3140 cm^{-1} (Table I) have been assigned, according to other ligands containing the $H_2N–C(S)–$ group, [15], as $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ respectively; the absorption at 3280 cm^{-1} is probably the first overtone of $\delta(NH_2)$, which is observed at 1640 cm^{-1}. The ν(CN) falls at 1440 cm^{-1}, whereas ν(CS) should contribute to the medium band at about 900 cm^{-1}. The 1:2

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*The analytical data of all the complexes, in good accordance with the assigned formula, have been deposited with the Editor.

TABLE I. IR Data (3500–3000 and 1650–1550 cm^{-1} regions) and Van't Hoff i Values for TC and Complexes.

Compound	Colour	M.p. °C	i[a]								
$Pt(TC)_2Cl_2$	yellow	[b]	0.95	3430m	3315m	3160vvw				1600sh	1590s
$Pt(TC)_2Br_2$	yellow	[b]	1.02	3420m	3310m	3160vvw				1600sh	1585s
$Pt(TC)_2I_2$	pink[c]	[b]	1.03	3360m	3260m	3160w					1582s
$Pd(TC)_2Cl_2$	orange-yellow	[b]	0.92[d]	3430m	3310m	3175w				1605sh	1595sbr
$Pd(TC)_2Br_2$	orange-yellow	[b]	0.92	3360m	3260m	3175mw				1612sh	1598s
$Pd(TC)_2I_2$	ochre	[b]	1.38	3345m	3240m	3158m	3020vvw				1590s
$Pt(TC)_3Cl_2$	pale-yellow	[b]	1.87		3250mbr	3140mbr	3050shw	1645sh	1620s	1605shs	
$Pd(TC)_3Cl_2$	yellow	[b]	2.02		3270mbr	3120mbr		1632sh	1614s		
$Pd(TC)_3Br_2$	orange-yellow	[b]	1.96[e]	3300sh	3260mbr	3140mbr			1620m	1608s	
$[Pt(TC)_4]Cl_2$	yellowish-white	132	2.73		3250sbr	3180sbr	3040br	1660sh	1638s	1610vs	
$[Pt(TC)_4]Br_2$	yellowish-white	132	2.92		3240sbr		3080sbr	1642sh	1625s	1605s	
$[Pd(TC)_4]Cl_2$	pale-yellow	136	2.95		3200sbr		3040sbr	1658m	1640m	1610s	
$[Pd(TC)_4]Br_2$	yellow	130	–		3240sbr		3080sbr	1640m	1622m	1605s	
$[Pt(TC)_4]Cl_2 \cdot 2H_2O$	yellowish-white	129	[f]	[h]	3250sbr	3180sbr	3040br	1650sh	1628sbr		
$[Pt(TC)_4]Br_2 \cdot 2H_2O$	yellowish-white	129	2.92	[h]	3280sbr	3120sh	3040br	1640sh		1610sbr	
$[Pd(TC)_4]Br_2 \cdot 2H_2O$	yellow	128	2.95[e]	[h]	3250sbr	3120sbr	3080sbr	1640sh		1615sbr	
$[Pt(TC)_4]Br_2 \cdot 2TC$	greenish-white	95	–	3330sh	3240sbr	3140sbr				1610sbr	
$[Pt(TC)_4]I_2 \cdot 2TC$	pale gray	97	4.90[g]	3370sh	3250sbr	3170, 3120w	3060wbr			1612sbr	1600shs
$[Pd(TC)_4]Br_2 \cdot 2TC$	yellow	90	4.95[e]	3340sh	3260sbr	3140sbr				1610s	
TC	white	37	1.00	3430m	3280m	3140m	3050shw	1640m		1610sh	

[a] Van't Hoff i values for 5×10^{-3} M solutions in acetone (37 °C). [b] Slow decomposition with undefined melting point. [c] Prepared in acetone; in benzene a beige form has been isolated. [d] The colour of the solution darkens with time. [e] Values taken within 30′ because i increases with time. [f] Scarcely soluble. [g] In benzene i = 4.35 at the same concentration. [h] H_2O absorption: 3510sh, 3460mbr.

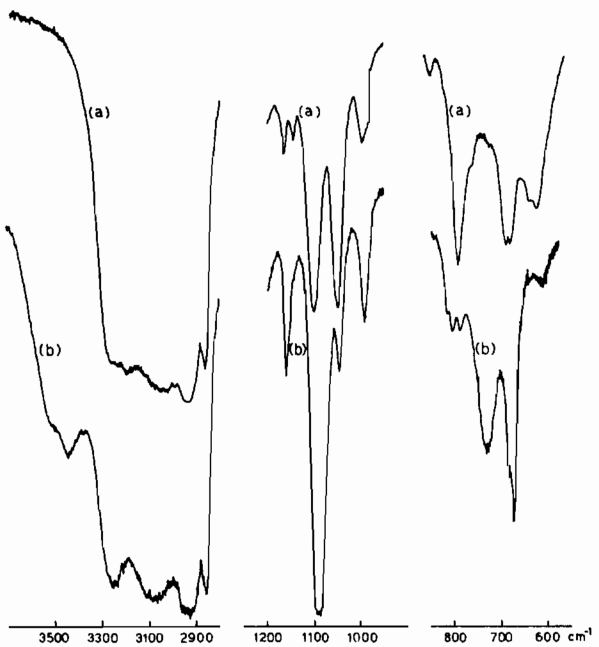

Fig. 1. IR spectra in Nujol: a) $[Pt(TC)_4]Cl_2$; b) $[Pt(TC)_4]Cl_2 \cdot 2H_2O$.

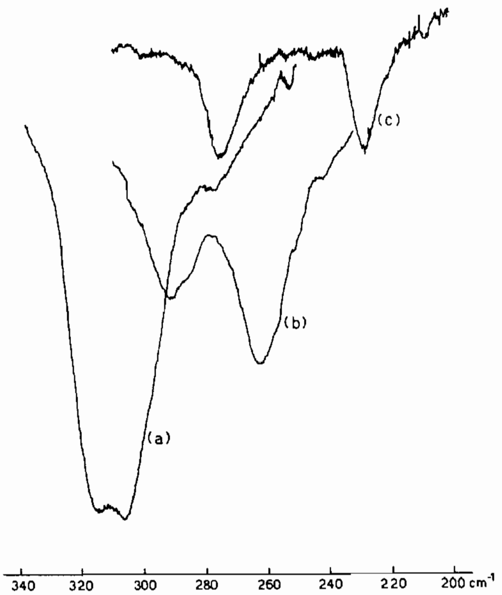

Fig. 2. Far IR spectra in Nujol: a) $Pd(TC)_2Cl_2$; b) $Pd(TC)_2Br_2$; c) $Pd(TC)_2I_2$.

adducts present two halide dependent absorptions beyond 3000 cm^{-1} and one strong band around 1590 cm^{-1}. In the 1:3 and 1:4 complexes the $\nu(NH_2)$ bands are strong and broad and are shifted towards lower frequencies with respect to the 1:2 complexes; the shift being more evident in the 1:4 ones, whose stronger absorption is at about 2950 cm^{-1} (fluorolube mulls). The hydrates show the water absorption at 3510(sh), 3460 (m,br) cm^{-1} (Fig. 1). Around 1600 cm^{-1} the 1:3 and 1:4 derivatives generally present a multi-band spectrum, while $[M(TC)_4]X_2 \cdot 2TC$ has a unique, strong band. The spectral differencies between the anhydrous and hydrated forms are evident in Fig. 1. The anhydrous forms present two bands at 1095, 1045 cm^{-1}; the addition of water (and TC) leads to a noticeable weakening of the lower frequency band, with a parallel increase of the absorption at around 730 cm^{-1} (712 cm^{-1} for TC). The relative intensities of the two bands in the 1100 cm^{-1} region allow control of the formation of $[M(TC)_4]X_2 \cdot 2L$ from the anhydrous forms while the reaction is going on.

The far IR spectra do not allow to assign unambiguously the 1:2 and 1:3 complex structures. Each 1:2 palladium adduct presents two absorptions below 350 cm^{-1} (Fig. 2) (cm^{-1}; Cl: 314, 306; Br: 292, 263; I: 275, 228). Although the chloride spectrum could suggest a *cis* arrangement, the lower frequency absorption of the bromo- and iodo-derivatives coincides practically with that of the respective *trans*-PdL_2X_2 (L = DMTC, MTC; X = Br, I) [1, 2]. The three TC complexes probably have a *trans* structure, the second band being a ligand halide dependent absorption, similar to that observed in $Hg(MTC)_2X_2$ (X = Cl, Br, I) [16]. The complex $Pt(TC)_2Cl_2$ presents two strong bands of similar intensity at 321, 309 cm^{-1}, $Pt(TC)_2Br_2$ a medium band at 220 cm^{-1} with a shoulder at 218 cm^{-1}; $Pt(TC)_2I_2$ has been isolated in two forms, a pink one in acetone (206, 202 cm^{-1}) and a beige one in benzene (206 cm^{-1}). The IR data are in favour of a *cis* arrangement for the chloro- and bromo-derivatives and for the pink iodo-species. In $Pt(TC)_3Cl_2$ the band assignable to $\nu(Pt-Cl)$ falls at 317 cm^{-1}, as in $Pt(MTC)_3Cl_2$ [3], whereas the values for $Pd(TC)_3X_2$ (X: Cl, 334 cm^{-1}; Br, 263 cm^{-1}) differ from those of $Pd(MTC)_3X_2$ (X: Cl, 308 cm^{-1}; Br, 242 cm^{-1}); probably the palladium derivatives have basically a *trans* 1:2 structure with one additional ligand molecule. All the 1:4 complexes do not show any absorption assignable to a metal-halogen bond; in these and in the 1:3 compounds, as in the 1:2 platinum derivatives, the M–S stretching frequency is the weak band around 280 cm^{-1}, as in the DMTC and MTC analogues [1–3].

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