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# Palladium(II) Halide Complexes with N-Methyl O-Ethylthiocarbamate

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*The complexes Pd(MTC)$_2$X$_2$ (where MTC = N-methyl O-ethylthiocarbamate; X = Cl, Br, I), [Pd(MTC)$_3$X]X (X = Cl, Br) and [Pd(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 palladium atom. In the solid state the 1:2 adducts have a* trans *square-planar geometry.*

*The 1:4 complexes present an ionic structure where the halide ions are held by strong hydrogen bonding. In benzene the 1:2 adducts are monomers, while the 1:4 complexes release ligand molecules to give the 1:3 and the 1:2 adducts.*

## Introduction

Palladium(II) and platinum(II) halides form with tertiary thiocarbamates and thioamides adducts of general formula $ML_2X_2$ (M = Pd, Pt; X = halide; L = N,N-dimethylthioamide or thiocarbamate) [1–4], where the ligand coordinates through the thiocarbonyl group. When the ligands are primary [5, 6] and secondary [7] thioamides, in addition to the 1:2 adducts also the ionic $[PdL_4]X_2$ complexes have been obtained, because of the stabilization of the halide ions by N···H···X bonding, as found in the analogous compounds $[Pd(NH_2–CS–NH_2)_4]Cl_2$ [8] and $[Pt(EtNH–CS–NH_2)_4]I_2$ [9]. A similar complexing behaviour should be expected with primary and secondary thiocarbamates, although only $C_6H_5NH–CS–OCH(CH_3)_2$ has been reported to form both neutral 1:2 and ionic 1:4 species with platinum(II) chloride [10]. The ligand $C_6H_5NH–CS–OEt$ forms with palladium the chelated complex $Pd(C_6H_5N–CS–OEt)_2$ [11, 12], with platinum the five-coordinate adduct $Pt(C_6H_5NH–CS–OEt)_3Cl_2$ [13]. The primary thiocarbamate complex *trans*-$Pt(NH_2–CS–OCH_2CH_2CH_3)_2Cl_2$ was prepared by reacting $K_2PtCl_4$ and the ligand in water at a molar ratio 1:1, but the investigation was apparently not extended to larger molar ratios [10].

In a previous paper [1] we described the palladium(II) and platinum(II) halide complexes with N,N-dimethyl O-ethylthiocarbamate (DMTC), having formula $M(DMTC)_2X_2$ (M = Pd, Pt; X = Cl, Br, I). The study was successively extended to the title ligand $CH_3NH–CS–OEt$ (MTC), which allows to attain higher stoichiometries and, having only one substituent on the nitrogen atom, can coordinate the metal with one or both the possible isomeric forms.

The present work concerns the MTC complexes of the palladium(II) halides. In addition to *trans*-$Pd(MTC)_2X_2$ (X = Cl, Br, I) and ionic $[Pd(MTC)_4]X_2$ (X = Cl, Br) also the 1:3 complexes have been isolated and characterized. The experimental data do not allow to establish their structures in the solid state, so that either a square pyramidal or, more probably, an ionic $[Pd(MTC)_3X]X$ (X = Cl, Br) arrangement should be supposed.

## Experimental

The starting materials were $K_2PdCl_4$, $K_2PdBr_4$, $PdCl_2(C_6H_5CN)_2$ [14] and $PdX_2$ (X = Cl, Br, I; Alfa Products). MTC was obtained by reacting $C_2H_5O–CS–SCH_2–COONa$ [15] with $CH_3NH_2$ in water [16]. The oily product was separated, dissolved in diethyl ether and washed with cold water to pH = 7. The ethereal layer was dried over anhydrous $Na_2SO_4$. The solvent was removed, the ligand distilled under reduced pressure and stored in nitrogen.

### *Preparation of the Complexes*

#### *Pd(MTC)$_2$Cl$_2$*

$PdCl_2$ (0.63 mmol) was dissolved under stirring in a benzene solution of the ligand (2.5 mmol in 5 ml). The compound precipitated by addition of n-hexane to the deep-red solution. An identical product was isolated by dissolving $PdCl_2(C_6H_5CN)_2$ in a benzene solution of MTC (molar ratio 1:2). The compound precipitated slowly from the deep-orange solution. When the reaction was carried out in $CH_2Cl_2$ (0.5 mmol of $PdCl_2$ and 1 mmol of MTC in 10 ml) a green solution was obtained, which turned quickly to deep-orange. The solid, isolated by adding n-hexane, was identical to those prepared by the above reported

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

| Compound | Colour | M.p. °C (dec.) | C% | H% | N% | Hal% |
|---|---|---|---|---|---|---|
| $Pd(MTC)_2Cl_2$ | orange | 134 | 23.3 | 4.0 | 6.7 | 17.4 |
| | | | (23.1) | (4.3) | (6.7) | (17.1) |
| $Pd(MTC)_2Br_2$ | orange | 136 | 18.9 | 3.6 | 5.4 | 31.9 |
| | | | (19.0) | (3.6) | (5.5) | (31.7) |
| $Pd(MTC)_2I_2$ | red-brown | 142 | 16.0 | 3.1 | 4.5 | 42.5 |
| | | | (16.0) | (3.0) | (4.7) | (42.5) |
| $[Pd(MTC)_3Cl]Cl$ | orange | 116 | 27.1 | 4.9 | 7.9 | 13.3 |
| | | | (27.0) | (5.1) | (7.9) | (13.2) |
| $[Pd(MTC)_3Br]Br$ | red-orange | 109–12* | 23.1 | 4.0 | 6.7 | 25.8 |
| | | | (23.1) | (4.3) | (6.7) | (25.6) |
| $[Pd(MTC)_4]Cl_2$ | yellow | 109 | 29.4 | 5.5 | 8.5 | 10.8 |
| | | | (29.3) | (5.5) | (8.6) | (10.8) |
| $[Pd(MTC)_4]Br_2$ | orange-yellow | 92 | 25.7 | 4.7 | 7.3 | 21.5 |
| | | | (25.9) | (4.8) | (7.5) | (21.5) |

*The solid begins to release ligand around 95 °C.

methods, but it darkened in time, although the IR spectra and the analytical data remained unchanged. After five months the colour was brown, M.p. ≅120 °C. The compound is soluble in acetone, $CH_2Cl_2$, $CHCl_3$; slightly soluble in benzene and ethanol; insoluble in diethyl ether, n-hexane, water.

*$Pd(MTC)_2X_2$ (X = Br, I)*

The complexes were prepared by dissolving $PdX_2$ (0.3 mmol) in a $CH_2Cl_2$ solution of MTC (0.6 mmol in 5 ml) and by adding n-hexane to the deep-orange bromide and the deep-red iodide solution. The solubilities are similar to those of the chloro-complex.

*$[Pd(MTC)_3X]X$ (X = Cl, Br)*

The complex $[Pd(MTC)_4]X_2$ was dissolved in the minimum amount of benzene. After addition of n-hexane until turbidity, crystals precipitated overnight.

*$[Pd(MTC)_4]Cl_2$*

The yellow-orange product precipitated after addition of n-hexane to the deep-red benzene solution of $PdCl_2$ (0.56 mmol) and ligand (3.38 mmol in 5 ml). Carrying out the same reaction at a molar ratio 1:4, the product was $Pd(MTC)_2Cl_2$. At a molar ratio 1:6, but in a larger benzene volume, mixtures of solids were obtained. Pure $[Pd(MTC)_4]Cl_2$ was also prepared by gradual addition of $K_2PdCl_4$ (1.53 mmol) to a MTC solution in absolute ethanol (7.1 mmol in 10 ml) at about 40 °C. KCl was filtered off and the solution evaporated to dryness. The oily residue was washed with diethyl ether, dried *in vacuo*, and recrystallized from absolute ethanol containing a few drops of ligand (at 50 °C). The compound is soluble in benzene, acetone, $CH_2Cl_2$, ethanol; slightly soluble in water; insoluble in diethyl ether and n-hexane.

*$[Pd(MTC)_4]Br_2$*

The compound was prepared by adding n-hexane to a benzene solution of $PdBr_2$ (0.45 mmol) and MTC (3.6 mmol in 5 ml). By operating at a molar ratio 1:6, a mixture of not characterized products was obtained. By reacting $K_2PdBr_4$ and MTC in methanol, with the procedure used for the chloro-complex, a less pure product was isolated.

When heated *in vacuo* at 100 °C for about 1 h, $[Pd(MTC)_4]Cl_2$ loses two ligand molecules. The residue has analytical and IR data identical to those of $Pd(MTC)_2Cl_2$, but is different in colour (hazel-brown) and melting point (about 120 °C). In the same conditions $[Pd(MTC)_4]Br_2$ gives $Pd(MTC)_2Br_2$, M.p. = 135 °C.

Attempts to prepare the 1:4 iodo-complex by reacting $PdI_2$ with an excess of MTC in benzene (up to a molar ratio 1:20) gave always the poorly soluble 1:2 adduct.

### *Measurements*

The IR spectra in the region 4000–180 $cm^{-1}$ were recorded on a Perkin Elmer Mod. 580 B Infrared Spectrophotometer, using Nujol mulls between KBr or polythene disks and for solutions 0.5 mm KBr cells. A Beckman IR 11 Spectrophotometer was used in the 300–100 $cm^{-1}$ region. Conductivities of $10^{-3}$ *M* acetone or *sym*-dichloroethane solutions were measured at 25 °C by a LKB Conductivity Bridge Mod. 3216 B. Electronic spectra were taken at 25 °C by a Beckman DK2A Spectrophotometer. Molecular weight measurements were made at 37 °C by a Mechrolab Mod. 302 vapor pressure Osmometer.

TABLE II. Infrared Bands in the 3500–3000 $cm^{-1}$ and 1650–1530 $cm^{-1}$ Regions of MTC and Complexes.

| | | | | | | |
|---|---|---|---|---|---|---|
| MTC (film) | | | 3280s,br | | 3070w | 1535s,br |
| MTC (10% $Cl_2C{=}CCl_2$) | 3455m | 3420m | 3240m,br | | 3080w | 1560s; 1520s |
| MTC (0.2 *M* benzene) | 3405sh | 3378s | 3250vw | | – | – |
| $Pd(MTC)_2Cl_2$ | | | | 3180m | 3110m,s | 1588s |
| $Pd(MTC)_2Cl_2$ (benzene) | | | | 3200 | – | 1588s |
| $Pd(MTC)_2Br_2$ | | | 3258s | 3200sh,w | 3110vw | 1563s |
| $Pd(MTC)_2I_2$ | | | 3262s | 3220sh,w | 3110vw | 1558s |
| $Pd(MTC)_2(SCN)_2$[a] | | | | 3190m,s | 3115m | 1578s |
| $[Pd(MTC)_3Cl]Cl$ | | | | 3180sh | 3095m | 1602s; 1580sh |
| $[Pd(MTC)_3Br]Br$ | | | | 3180br | 3100br | 1598s; 1575sh |
| $[Pd(MTC)_4]Cl_2$ | | | | 3150sh[b] | 3040sh[b] | 1580s; 1540sh,br |
| $[Pd(MTC)_4]Cl_2$ (benzene) | 3410sh | 3390m | | 3170sh,br | – | 1605s; 1585sh,m |
| $[Pd(MTC)_4]Br_2$ | | | | 3140sh[b] | 3095m[b] | 1580s; 1545sh,br |
| $[Pd(MTC)_4]Br_2$ (benzene) | 3410sh | 3390m | | 3170sh,br | – | 1600s; 1585sh,s |

[a] Ref. [23]. [b] Shoulders of a broad band at 2950 $cm^{-1}$ (in Voltalef 10S mulls).

The Van't Hoff factor was calculated as $i = \Delta R_c/\Delta R_b$ where $\Delta R_c$ is the experimental osmometric value for a given concentration of complex, and $\Delta R_b$ is the value for an identical concentration of standard (benzil). The $^1H$ nmr spectra were recorded at 27 °C using a Bruker Spectrospin HFX-10 90 MHz Spectrometer and a Varian FT80A NMR Spectrometer.

## Results and Discussion

The analytical data of the complexes are reported in Table I. For palladium iodide only the adduct having 1:2 stoichiometry has been isolated. The tendency of palladium iodide to give complexes with low stoichiometries was also observed with N-methyl thiobenzamide [7], which forms only 1:2 adducts, and for $Pd(DMTC)_2I_2$, which loses one ligand molecule to form $Pd_2(DMTC)_2I_4$ [1]. All the prepared compounds are non-electrolytes in benzene, acetone and $CH_2Cl_2$. The 1:2 chloro- and bromo- derivatives are monomeric in those solvents, whereas the 1:4 complexes dissociate, the extent being larger for the bromo-derivative. The complex $[Pd(MTC)_4]Cl_2$, ionic in the solid state, is very soluble in benzene, where the Van't Hoff *i* factor varies from 2.0 for a 2.1 × $10^{-2}$ *M* solution, to 2.23 for a 2.6 × $10^{-3}$ *M* solution, owing to a complete formation of the soluble 1:3 intermediate

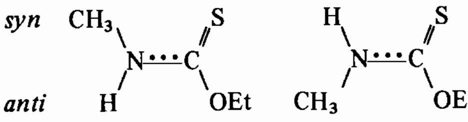
$$[Pd(MTC)_4]Cl_2\ (solid) \rightarrow Pd(MTC)_3Cl_2 + MTC\ (benzene)$$

$Pd(MTC)_3Cl_2$ is the predominant species in concentrated benzene solutions (see $^1H$ nmr and IR data and the method of preparation) whereas in diluted solution a further dissociation occurs according to the reaction

$$Pd(MTC)_3Cl_2 \rightleftarrows Pd(MTC)_2Cl_2 + MTC$$

and at concentrations of $[Pd(MTC)_4]Cl_2$ lower than 5 × $10^{-4}$ *M* the species in solution is mainly $Pd(MTC)_2Cl_2$ (see visible spectra). An analogous behaviour is observed in acetone and *sym*-dichloroethane, where the 1:4 complex dissociates in a larger amount than in benzene. The *i* factor for $[Pd(MTC)_4]Br_2$ in benzene varies from 2.15 (2.0 × $10^{-2}$ *M*) to 2.52 (2.5 × $10^{-3}$ *M*). The corresponding 1:3 complex is the most important species in very concentrated solutions; by diluting, progressive precipitation of the scarcely soluble 1:2 adduct occurs, whereas the species in solution is essentially the 1:3 complex stabilized by an excess of ligand.

MTC, either pure liquid or in solution, consists of a mixture of the two isomers(I) and (II)



(I) (II)

having the N-methyl group in *syn* or in *anti* position, in respect to the sulfur atom. Whereas the corresponding carbamates RNH–CO–OEt show at room temperature free rotation about the C–N bond [17, 18], MTC is present in both the isomeric forms. In fact the thiocarbonyl group enhances the double bond character of the C–N bond. The IR spectrum of liquid MTC in the $\nu$(N–H) region (Table II) shows a broad band at 3280 cm$^{-1}$ indicating intermolecular hydrogen bonding, weakened in solution of tetrachloroethylene or benzene. In the examined solvents two bands above 3400 cm$^{-1}$ are observed, assigned to the $\nu$(N–H) of the two isomers [19]. The strong band at 1535 cm$^{-1}$, split in tetrachloroethylene, should be assigned mainly to $\delta$(N–H), as suggested on the basis of a study on the deuterated derivative of $CH_3$-NH–CS–$OCH_3$ [19]. The assignment seems more probable as mainly $\nu$(C–N), as found for N,N'-dimethyldithiooxamide [20] and other secondary thioamides [21]. Therefore the weak band at 3070 cm$^{-1}$ should be the first $\nu$(C–N) overtone. In the 1:2 complexes the $\nu$(C–N) band shifts towards higher frequencies in respect to the free ligand suggesting coordination through the sulfur atom [1]. The shift, larger for the chloride adduct, follows the trend already observed in the mercury halide complexes with N,N-dimethyldithiocarbamate esters [22]. From X-ray data $Pd(MTC)_2(SCN)_2$ [23] has a *trans* square-planar structure with the metal coordinated by four sulfur atoms, two from the ligands and two from the thiocyanato groups. The ligand is present only with the *anti* isomer (II) and forms strong intermolecular hydrogen bonds involving the nitrogen atom of the thiocyanato groups. In the $\nu$(N–H) region the spectra of $Pd(MTC)_2(SCN)_2$ and $Pd(MTC)_2Cl_2$ are quite similar (two medium bands below 3200 cm$^{-1}$) and differ from those of the bromo and iodo analogues which exhibit one strong band around 3260 cm$^{-1}$. In all the 1:2 adducts MTC coordinates probably with one of its isomers; in the bromo- and iodo-derivatives the hydrogen bonding should be weaker. Hydrogen bonding is observed also for the 1:3 complexes ($\nu$(N–H) around 3100 cm$^{-1}$) and the 1:4 ones ($\nu$(N–H) around 2950 cm$^{-1}$) as well as for the similar N-methylthiobenzamide complexes [7]. In benzene the1:1 complexes dissociate giving free ligand (bands around 3400 cm$^{-1}$) and the 1:3 adducts which have the $\nu$(C–N) band at higher frequencies (1600 cm$^{-1}$) than the corresponding 1:2 and 1:4 derivatives. The ligand bands in the 800–500 cm$^{-1}$ region (Table III) are due to $\nu$(C–S), $\delta$(N–C–S) and $\pi$(N–H) [19–21]. The 1:2 thiocyanate and chloride adducts, whose spectra are very similar, show a strong band around 740 cm$^{-1}$. In the bromo- and iodo-adducts, this band is very weak and a new strong band is observed around 620 cm$^{-1}$. In the Pd–Cl stretching region two medium bands at 345 and 318 cm$^{-1}$ have been found for $Pd(MTC)_2Cl_2$. The analogous $Pd(DMTC)_2Cl_2$ was found to have two bands at 345 cm$^{-1}$ and at 325 cm$^{-1}$ in Nujol mull and only the band at 345 cm$^{-1}$ in benzene [1] suggesting a *trans* arrangement around the palladium atom, successively confirmed by X-ray data [24]. The low solubility of $Pd(MTC)_2Cl_2$ did not allow the far IR spectra to be taken in benzene, but the spectral

TABLE III. Infrared Bands in the 800–180 cm$^{-1}$ Region (Pd–Halogen and Pd–S (thiocyanate) frequencies are in italics).

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Pd(MTC)_2Cl_2$ | 815vw | | 745s | 720m | | 635m | | 538mw | 478ms | | 380w | *345m*[a] | *318ms*[a] | | 260vvw | 223m | 190vvw |
| $Pd(MTC)_2Br_2$ | 820vw | | 735sh | 718mw | | 640sh | 625s | 533w | 478mw | | 380w | | 328vw | | *261m* | 224vw | 190vvw |
| $Pd(MTC)_2I_2$ | 820w | | 735sh | 722m | | 640sh | 614s | 538w | 478mw | | 380w | | 328vw | | 270vvw | *227w* | 190w |
| $Pd(MTC)_2(SCN)_2$ | 821w | 755sh | 741s | 720m | 705w[b] | 638m | | 533w | 478ms | 433m[b] | 383w | | 325w | *288s* | 260vvw | | 182mw |
| $[Pd(MTC)_3Cl]Cl$ | 807m | 772m | | 721m | 695w | 638m | | 535w | 470s | 415w | 382sh | 360w | 333w | *308m* | | 240vw | 220sh |
| $[Pd(MTC)_3Br]Br$ | 812w | 770vvw | | 720m | 690sh | 636m | | 533w | 468s | 413vvw | | 368w | 324w | | 275vvw | *242m* | 224vvw |
| $[Pd(MTC)_4]Cl_2$ | 805ms | 775m | | 720w | 695w | 638m | | 537w | 474s<br>468s | 417m | 380w | 362m | 330w | | | 240vw | 220sh[c] |
| $[Pd(MTC)_4]Br_2$ | 805w | 772ms | 748w | 721m | 695w | 635m | | 536w | 472s<br>462s | 415m | 380w | 362m | 330w | | 275vvw | 240vw | 220vw |

[a] See text. [b] Assigned to SCN group, ref. [23]. [c] Shoulder of a broad band centered at 164 cm$^{-1}$.

TABLE IV. $^1$H Nmr Spectra of MTC and Complexes (the chemical shifts are given in ppm).

| Compound | Solvent | Weight$^a$ | N–$CH_3$ | O–$CH_2$–*$CH_3$* | O–*$CH_2$*–$CH_3$ |
|---|---|---|---|---|---|
| MTC | $C_6H_6$ | 27 | 2.59(67%) | 1.03 | 4.40 |
| | | | 2.17 | 1.00 | |
| | $CDCl_3$ | 60 | 3.08(64%) | 1.30 | 4.50 |
| | | | 2.87 | 1.37 | 4.56 |
| | $(CD_3)_2CO$ | 30 | 2.98(75%) | 1.24 | 4.42 |
| | | | 2.83 | 1.31 | 4.44 |
| $Pd(MTC)_2Cl_2$ | $C_6D_6$ | 3 | 1.98 | 0.69 | 3.90 |
| | $CDCl_3$ | 23 | 2.94 | 1.42 | 4.59 |
| | $(CD_3)_2CO$ | sat.d | 3.00 | 1.45 | 4.62 |
| $Pd(MTC)_2Br_2$ | $C_6D_6$ | sat.d | 1.97 | 0.68 | 3.91 |
| | $CDCl_3$ | 10 | 2.97 | 1.43 | 4.61 |
| $Pd(MTC)_2I_2$ | $C_6D_6$ | sat.d | 2.01 | 0.70 | 3.91 |
| $Pd(MTC)_2(SCN)_2$ | $(CD_3)_2CO$ | sat.d | 3.06 | 1.46 | 4.69 |
| $[Pd(MTC)_3Cl]Cl$ | $C_6D_6$ | 25 | 2.69 | 0.74 | 3.98 |
| | $C_6D_6$ | 5 | 2.59 | 0.74 | 3.98 |
| | | | 2.50w$^c$ | 1.00w$^c$ | 4.34w$^c$ |
| | $CDCl_3$ | 30 | 2.99 | 1.38 | 4.55 |
| | $(CD_3)_2CO$ | 16 | 2.96br | 1.42 | 4.60 |
| | | | | 1.21$^c$ | 4.41$^c$ |
| $[Pd(MTC)_3Br]Br$ | $C_6D_6$ | 25 | 2.69 | 0.75 | 4.03 |
| $[Pd(MTC)_4]Cl_2$ | $C_6H_6$ | 18 | 2.74br | 0.75(80%) | 4.02br |
| | | | 2.65$^c$ | 1.03$^c$ | 4.42$^c$ |
| | $CDCl_3$$^d$ | 25 | 2.97 | 1.38 | 4.53 |
| | $(CD_3)_2CO$ | 12 | 2.95 | 1.42 | 4.60 |
| | | | 3.02$^c$ | 1.21$^c$ | 4.41$^c$ |
| $[Pd(MTC)_4]Br_2$ | $C_6D_6$ | 8 | 2.68br | 0.75(75%) | 4.05 |
| | | | 2.57$^c$ | 1.03$^c$ | 4.40$^c$ |

$^a$Weight (mg) of compound added to 0.5 ml of solvent. $^b$Very weak signals due to free ligand are also present. $^c$Sharp signals assigned to the free ligand. $^d$Free ligand weak signal at 3.07 ppm.

analogies with the DMTC adduct along with a too large band separation, suggest a *trans* arrangement. The 1:2 bromo- and iodo-derivatives show only one $\nu$(Pd–Hal) band at 261 cm$^{-1}$ and at 227 cm$^{-1}$ respectively, indicating a *trans* structure, as already found for $Pd(DMTC)_2Br_2$ by X-ray analysis [25]. In the thiocarbamate and thioamide complexes, the $\nu$(Pd–S) should be around 300 cm$^{-1}$ [1, 7]: in the reported complexes we have tentatively assigned to this vibration mode the weak band near 270 cm$^{-1}$. In the 1:3 compounds the $\nu$(Pd–Hal) falls at 308 cm$^{-1}$ for the chloro- and at 242 cm$^{-1}$ for the bromo-derivative. The presence of only one Pd–Hal absorption could suggest a square planar arrangement around the palladium atom by three ligand molecules and one halide atom, the second being held by hydrogen bonds. In fact the $\nu$(N–H) bands are broad, in respect to the sharp bands of the 1:2 adducts, and resemble in shape and position those of the 1:4 complexes, where the N–H groups are involved in hydrogen bonds with halide ions [7]. The behaviour of the 1:3 complexes in benzene suggests the formation of a five-coordinate intermediate, having probably a square-pyramidal arrangement. In the spectrum of $[Pd(MTC)_4]Cl_2$, identical to that of $[Pd(MTC)_4]Br_2$, the absence of any $\nu$(Pd–Hal) bands strongly indicates an ionic structure in the solid state, as for the similar tetrakis(thiourea)palladium(II) complex [8].

The $^1$H nmr spectra of MTC (Table IV) exhibit two resonances for each group of protons. The higher field N–$CH_3$ doublet and the related lower field ethyl group signals have been assigned to the *anti* isomer (II) [26], present for about 30%. The N–$CH_3$ proton resonances shift downfield on going from aromatic to non-aromatic solvents, the shift being larger for the *anti* signals [1, 27, 28]. The spectrum of a 2 *M* $d_6$-benzene solution of ligand shows two broad signals at 7.6 and 6.2 ppm, due to the N–H proton in (II) and (I) respectively, strongly dependent on concentration. In a 0.2 *M* solution the resonances

TABLE V Electronic Spectra of the Complexes *

| Compound | Solid | Benzene | |
|---|---|---|---|
| $Pd(MTC)_2Cl_2$ | 412 | | 412sh(570) |
| $Pd(MTC)_2Br_2$ | 475sh | 340(7500), | 470sh(600) |
| $Pd(MTC)_2I_2$ | 414, 488sh | 405(7500), | 520sh,br |
| $[Pd(MTC)_3Cl]Cl$ | 400sh | | 410sh(590) |
| $[Pd(MTC)_3Br]Br$ | 425sh | 340(7000), | 470sh(600) |
| $[Pd(MTC)_4]Cl_2$ | 450sh | | 420sh(600) |
| $[Pd(MTC)_4]Br_2$ | 450sh | 340(9000), | 470sh(600) |

*$\lambda_{max}$, nm ($\epsilon_{mol}$)

are at 6 7 ppm (II) and 5 4 ppm (I) The N–H signals have not been reported because they are very broad in the complexes The spectra of the 1 2 adducts show one signal for each type of proton suggesting that MTC coordinates with only one of the isomeric forms The influence of ligand stereochemistry on coordination was already observed for $CH_3NH$–CS–$OCH_3$ [29] From benzene to $d_6$-acetone the $N(CH_3)_2$ protons in $Pd(DMTC)_2Cl_2$ undergo shifts of 0 86 ppm (*anti*) and 0 39 ppm (*syn*) [1] The corresponding downfield shift in $Pd(MTC)_2Cl_2$ is 1 02 ppm Concentrated benzene solutions of $[Pd(MTC)_3Cl]Cl$ show one signal for each group of protons, on dilution weak signals of free ligand are observed In d-chloroform the resonances of either free or coordinated ligand coincide, in $d_6$-acetone free ligand is present also for almost saturated solutions The spectrum of $[Pd(MTC)_3Br]Br$ is reported only for concentrated benzene solutions, in fact precipitation of the 1 2 adduct occurs by diluting Benzene solutions of the 1 4 complexes contain free ligand in an amount of about 20% (by integrating the $CH_3$ protons of the ethyl group), the broad signal at about 2 7 ppm (N–$CH_3$) suggests formation of the 1 3 adduct with a rapid ligand exchange The ligand, released in benzene solutions of $[Pd(MTC)_4]X_2$, seems to be in the *syn* form (I), whereas a parallel study now in progress indicates the corresponding platinum(II) complexes release ligand in both the isomeric forms When DMTC [1] or secondary and tertiary ethylcarbamates [27, 28, 30] coordinate through the C=X group (X = O,S), the O–$CH_2$–$CH_3$ proton quartet in benzene is shifted downfield by 0 5 ppm An upfield shift is observed on the contrary in all the MTC complexes, whereas the N–H proton resonances are downfield by about 3 ppm in respect to the free ligand Moreover in aged or heated benzene solutions of the complexes, a sharp singlet of low intensity has been observed around 0 5 ppm, suggesting a slow secondary reaction on time

In the electronic spectra (Table V) of the 1 2 compounds the d–d bands position is in accordance with the spectrochemical series The solid 1 4 complexes have identical spectra, indicating an equal structure of the palladium cation In benzene, the low energy bands are poorly resolved shoulders of the charge transfer bands The approximate wavelengths and intensities reported in the Table indicate that in very diluted solutions (less than 8 X $10^{-4}$ *M*) of the 1 3 and 1 4 complexes only the 1 2 species is present

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## References

1 L Sindellari, G Faraglia, B Zarli, P Cavoli, A Furlani and V Scarcia, *Inorg Chim Acta, 46,* 57 (1980)

2 A J Aarts, H O Desseyn and M A Herman, *Bull Soc Chim Belg , 85,* 854 (1976)

3 A J Aarts, H O Desseyn and M A Herman, *Bull Soc Chim Belg , 86,* 581 (1977)

4 A J Aarts, H O Desseyn and M A Herman, *Bull Soc Chim Belg , 87,* 155 (1978)

5 A J Aarts, H O Desseyn and M A Herman, *Transition Met Chem , 3,* 144 (1978)

6 A J Aarts, H O Desseyn and M A Herman, *Transition Met Chem , 4,* 46 (1979)

7 A J Aarts, H O Desseyn and M A Herman, *Bull Soc Chim Belg , 88,* 25 (1979)

8 D A Berta, W A Spofford III, P Boldrini and E L Amma, *Inorg Chem , 9,* 136 (1970)

9 F Bachechi, L Zambonelli and G Macrotrigiano, *Inorg Chim Acta, 17,* 225 (1976)

10 V V Sibirskaya, J N Kukushkin, V V Strukov, V N Samuseva and V G Pogareva, *Russ J Gen Chem , 48,* 1477 (1978)

11 T Tarantelli and C Furlani, *J Chem Soc A,* 1213 (1971)

12 L Gastaldi and P Porta, *Gazzetta, 101,* 641 (1971)

13 J 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)

14 J R Doyle, P E Slade and H B Jonassen, *Inorg Synth , 6,* 216 (1960)

15 B Holmberg, *J Prakt Chem , 71,* 264 (1905)

16 B Holmberg, *Svensk Kem Tidskr , 41,* 254 (1929), *Chem Zentr , 1,* 1926 (1930)

17 G Faraglia, B Zarli, L Sindellari and G Dall'Olio, *Inorg Chim Acta, 19,* 39 (1976)

18 B Zarli, G Casotto, L Sindellari and G Faraglia, *Inorg Chim Acta, 31,* 5 (1978)

19 G C Chaturvedi and C N R Rao, *Spectrochim Acta, 27A,* 65 (1971)

20 H O Desseyn, A J Aarts, E Esmans and M A Herman, *Spectrochim Acta, 35A,* 1203 (1979)

21 H O Desseyn, A J Aarts and M A Herman, *Spectrochim Acta,* 36A, 59 (1980)

22 H C Brinkhoff and J M A Dantzenberg, *Rec Trav Chim , 91,* 117 (1972)

23 R. Bardi, A. Del Pra, A. M. Piazzesi, L. Sindellari and B. Zarli, *Inorg. Chim. Acta*, (1980), in press.
24 R. Bardi, A. M. Piazzesi and M. Munari, *Cryst. Struct. Comm.*, *9*, 835 (1980).
25 R. Bardi, A. M. Piazzesi and P. Cavoli, *Cryst. Struct. Comm.*, (1980), in press.
26 R. A. Bauman, *J. Org. Chem.*, *32*, 4129 (1967).
27 J. Sandström and B. Uppström, *Acta Chem. Scand.*, *21*, 2254 (1967).
28 B. M. Dahl and P. H. Nielsen, *Acta Chem. Sçand.*, *B28*, 1091 (1974).
29 R. A. Bauman, *Tetrahed. Letters*, 419 (1971).
30 B. Zarli, G. Faraglia, L. Sindellari and G. Casotto, *Transition Met. Chem.*, (1980), in press.