

Palladium Complexes with 3-Thiomorpholinone: Preparations and Reactions

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Some reactions between palladium compounds and 3-thiomorpholinone (T) were examined, the compounds PdCl_2T_2 and PdBr_2T_2 being isolated in solid state. The reaction between PdBr_4^{2-} and T is quantitative and may be followed by means of conductometric or high-frequency titrations; the compound PdCl_2T_2 is fairly soluble in water and hydrolyses to form the compound $\text{Pd}(\text{OH})_2\text{T}_2$. Spectrophotometric study of the system formed from PdCl_4^{2-} and T reveals that the compound PdCl_2T_2 is formed instantaneously and then reacts with the excess of PdCl_4^{2-} to form PdCl_3T^- . The reaction follows a second order mechanism. The instability constants of the two compounds and the rate constant are calculated at 25°C. The 3-thiomorpholinone compounds of Palladium and Platinum are examined by means of I.R. spectrophotometry and the resultant spectra are discussed. The results of the enquiry suggest that this category of compounds is most likely to have a square trans-planar configuration in which the ligand is bonded to the metal via sulphur.

Introduction

In an earlier work¹ the Authors studied some reactions between Platinum compounds at varying stages of oxidation and 3-thiomorpholinone (=T) as ligand, the compounds PtCl_2T_2 (yellow), PtBr_2T_2 (orange), and $\text{Pt}(\text{Ph}_3\text{P})_2\text{T}_2$ (white) being isolated in solid state.

The reactions between the compounds PtCl_4^{2-} and PtBr_4^{2-} and T are quantitative and can be followed by means of high-frequency titrations; the first gives a single equivalent point for the molar ratio of 1:2 between the reagents while the second gives two distinct equivalent points for the molar ratios of 1:1 and 1:2. This led one to suspect the presence in solution of a monosubstituted compound PtBr_3T^- , later verified by polarography. The complex PtBr_4^{2-} has in fact two distinct and reproducible reduction waves; with the addition of the ligand a third, intermediate wave appears, from which the coordination of the ligand in the complex may be calculated as 1.04.

The compound PtCl_2T_2 can also be obtained starting from PtCl_2^{2-} ; in this case T-uptake is 3 moles and high-frequency titration gives one distinct equivalent point for a molar ratio of 1:3. While two

moles of ligand are used in the substitution the third is obviously necessary for the reduction of the metal. The reaction is accompanied by an increase in acidity. By means of pH measurements it was possible to demonstrate that the reaction follows a second order mechanism which might well be attributable to the reduction stage.

Reflux reaction of the compound $\text{Pt}(\text{Ph}_3\text{P})_4$ (prepared from PtCl_4^{2-} and triphenylphosphine) with T in CHCl_3 solution yielded the compound $\text{Pt}(\text{Ph}_3\text{P})_2\text{T}_2$ which can be recrystallized from alcohol, is white in colour and very stable. This product is not electrolytic and is monomeric in alcohol solution.

In the present paper some reactions between compounds of Palladium and 3-thiomorpholinone are examined.

Experimental Section

1. *Reaction with K_2PdCl_4 .* A solution of 2 millimoles of T dissolved in 1.3 ml of water is added dropwise and under stirring at 40 °C to a solution of 1 millimole of K_2PdCl_4 dissolved in 2 ml of water. The reaction is very fast and is characterised by a rapid discoloration (from red to yellow) and by the separating out of a gold-yellow, powdery product. The solution remains deep yellow; the yield is about 90%. The product, which corresponds to PdCl_2T_2 , is diamagnetic, very stable and fairly soluble in H_2O .

2. *Reaction with Na_2PdCl_6 .* By letting 1 millimole of Na_2PdCl_6 react with an excess of T under the same experimental conditions as at 1) above a yellow product is obtained, identified as PdCl_2T_2 . During the reaction the colour changes from red to yellow and pH decreases considerably.

3. *Reaction with K_2PdBr_4 .* By letting 1 millimole of K_2PdBr_4 react with 2 millimoles of T, dissolved in the minimum amount of water, complete discoloration of the solution is obtained together with the separating out of PdBr_2T_2 , which is diamagnetic, orange in colour, very stable and insoluble. The reaction is quantitative (Rqd: 496 mg; found: 499 mg).

4. *Reaction with $\text{Pd}(\text{Ph}_3\text{P})_4$.* The compound $\text{Pd}(\text{Ph}_3\text{P})_4$ was prepared using the method proposed by L. Malatesta and M. Angoletta² starting with warmed Ph_3P and $\text{Pd}(\text{NO}_3)_2$ in benzene solution. This com-

(1) D. De Filippo and C. Preti, *Gazz. Chim. It.* 98, 64 (1968).

pound of Palladium (0) was allowed to react with 2 moles of T, refluxing in chloroform for about 2 hours. A yellow, microcrystalline product is obtained which is very stable and was recrystallised from alcohol (found: Pd% 13.33; C% 51.08; H% 3.62; P% 5.83).

5. High-frequency and conductometric titrations.

The reactions between PdCl_4^{2-} and PdBr_4^{2-} and T can be followed by means of high-frequency or conductometric titrations. The titrations were carried out at $25^\circ\text{C} \pm 0.1$ with concentrations of the order of $2 \cdot 10^{-3} M$ and using a $0.1 M$ solution of T as titrating reagent. Under these conditions titrations are rather slow (4-5 hours) as individual readings are carried out at equilibrium.

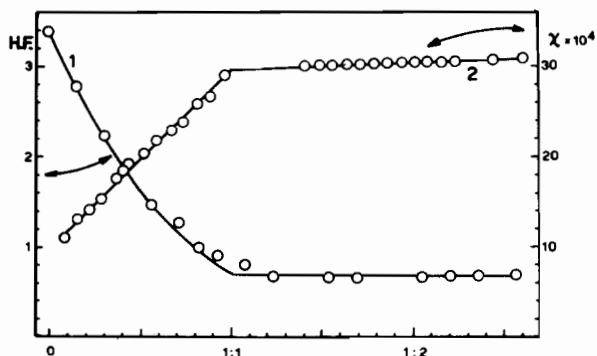


Figure 1. H.F. and conductometric titrations of PdCl_4^{2-} with T.

High-frequency and conductometric titrations of PdCl_4^{2-} with T are shown in Figure 1; they show a distinct equivalent point for the molar ratio of 1 : 1. Under the experimental conditions adopted the solid product PdCl_2T_2 does not separate out. The titrations of the compound PdBr_4^{2-} , however, show an equivalent point for a molar ratio of 1 : 2 (Figure 2).

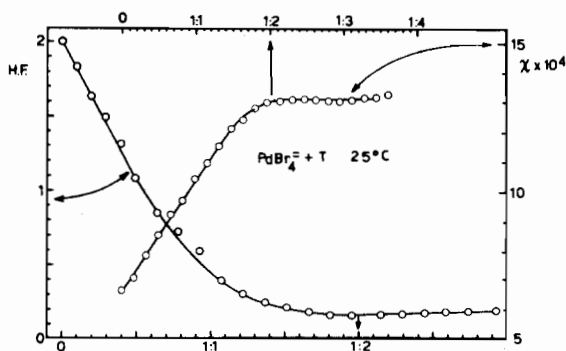


Figure 2. H.F. and conductometric titrations of PdBr_4^{2-} with T.

6. pH measurements and conductivity. Measurements of pH and conductivity were carried out on aqueous solution of PdCl_2T_2 in concentrations ranging between $1 \cdot 10^{-3} M$ and $3 \cdot 10^{-5} M$ (Temp. $25^\circ\text{C} \pm 0.1$) using a WTW bridge and a digital G.P. pHmeter.

(2) L. Malatesta and (Miss) A. Angoletta, *J. Chem. Soc.*, 1186 (1956).

The pH of the solutions examined ranges between 2.7 and 4.4; equivalent conductivity corresponds to about $770 \text{ cm}^2 \text{ ohm}^{-1}$.

Taking the ratio $[\text{H}^+] / [\text{PdCl}_2\text{T}_2]$ the value obtained falls between 2.1 and 1.80; the equivalent conductivity value obtained, however, is very nearly twice that of hydrochloric acid under the same experimental conditions.

When a $10^{-3} M$ solution is titrated with $0.1 N$ NaOH a titration curve is obtained which is typical of a strong acid with an equivalent point for the molar ratio of 1 : 2.

7. UV-Visible spectrophotometric measurements.

Figure 3 shows the spectra of the compound PdCl_2T_2 , thiomorpholinone and the compound PdCl_4^{2-} in the region $200\text{-}700 \text{ m}\mu$. As can be seen, PdCl_4^{2-} shows maximum absorption between $440\text{-}460 \text{ m}\mu$, while PdCl_2T_2 reaches its peak at $370 \text{ m}\mu$.

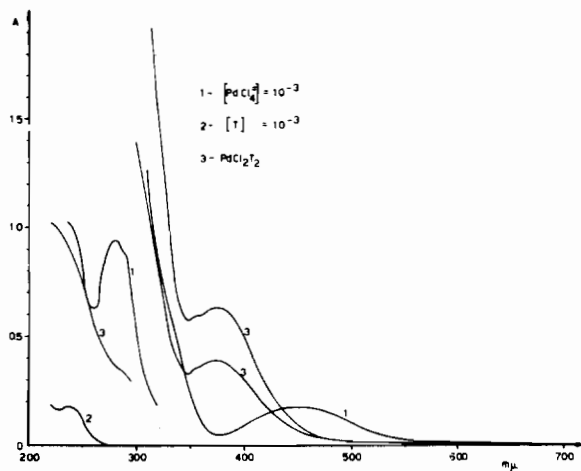


Figure 3. UV-Visible spectra: $[\text{PdCl}_4^{2-}] = 10^{-3} M$, $[\text{T}] = 10^{-3} M$, $[\text{PdCl}_2\text{T}_2] = 2 \times 10^{-3}$ and $1.33 \times 10^{-3} M$.

All measurements were carried out at $25^\circ\text{C} \pm 0.1$ in a solution of hydrochloric acid (pH approx. 1; $[\text{HCl}]/[\text{PdCl}_2\text{T}_2]$ approx. 150 : 1) so as to inhibit hydrolysis.

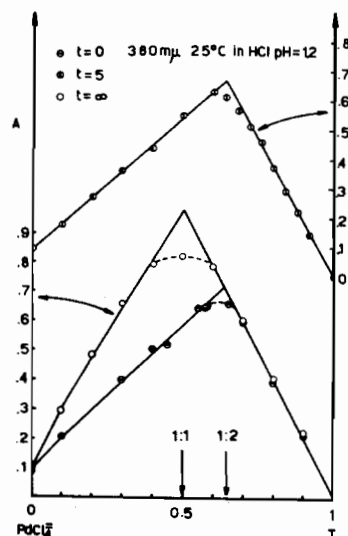


Figure 4. $\text{PdCl}_4^{2-}/\text{T}$ system examined by continuous variation method (time in hours).

Table I.

Compound	Colour	Solub.	Yield %	Pd		C		H	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
PdCl_2T_2	yellow	$10^{-3} M^b$	90	25.8	26.2	23.3	23.3	3.8	3.4
$\text{PdCl}_2\text{T}_2^a$	yellow	$10^{-3} M^b$	90		26.0		23.2		3.4
PdBr_2T_2	orange	insolub.	100	21.1	21.3	19.4	19.8	2.8	3.2

^a Obtained from Na_2PdCl_6 . ^b From spectrophotometric measurements.

From the spectrophotometric measurements was calculated the solubility of the compound yielded, at 25 °C and pH=2, by 57.4 γ/ml of Palladium (Table I). The PdCl_4^{2-} -T system was studied by the continuous variations method at 25 °C (Figure 4); immediately after the mixing of the reagents the maximum absorbance corresponds to the molar ratio 1:2. Absorption of solutions containing an excess of PdCl_4^{2-} increases in time, however, so that, at infinity, maximum absorbance is obtained for the molar ratio of 1:1. The absorption of solutions containing an excess of T remains constant. When the system PdCl_2T_2 -Cl⁻ is examined by the same method it is seen that the absorption of the solutions varies linearly from PdCl_2T_2 100% to Cl⁻ 100%, under which conditions it is zero, and remains constant in time. The variation in time of the absorption of solutions containing an excess of PdCl_4^{2-} was recorded using $2 \times 10^{-3} M$ solutions of PdCl_4^{2-} and T in 0.1 M HCl together with the ratios of (A) 60:40 and (B) 70:30 (Figure 5). Measurements were also carried out with pH = 2 and 3.

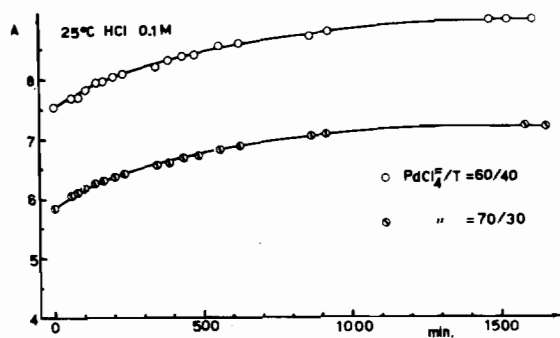


Figure 5. Absorbance measurements vs. time at 380 μ .

8. *Magnetic measurements.* All the compounds examined proved to be diamagnetic.

9. *IR spectrophotometry.* The IR spectra of the Palladium compounds and of the corresponding Platinum compounds were measured working in nujol in the region 4000-600 cm^{-1} , in KCl discs in the region 1000-400 cm^{-1} and between plates of polyethylene in the region 400-200 cm^{-1} , using a Perkin Elmer model 225 Spectrometer, which has a resolution of $\pm 0.5 \text{ cm}^{-1}$. The atmospheric water vapor was removed from the spectrophotometer housing by flushing with dry nitrogen. The spectra are shown in Figure 6 - 8.

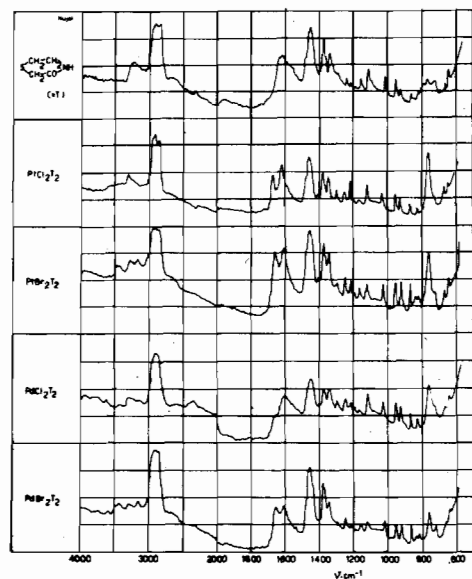


Figure 6. I.R. spectra.

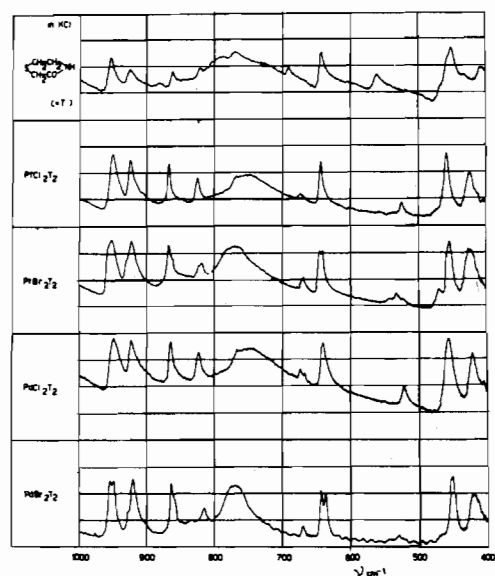


Figure 7. I.R. spectra.

Results and Discussion

The compounds PdCl_4^{2-} and PdBr_4^{2-} react with T in a manner similar to that found for Platinum, and, when working with high concentrations, the solid

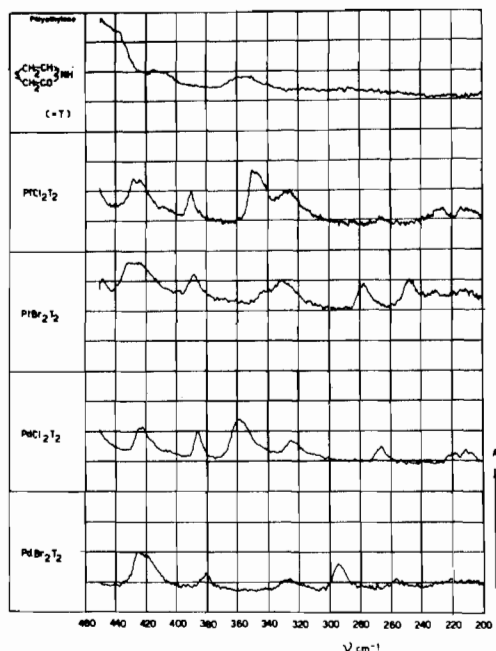
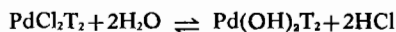


Figure 8. I.R. spectra.

products PdCl_2T_2 (yellow) and PdBr_2T_2 (orange) are separated out, both of which are diamagnetic, the first being fairly soluble in H_2O while the second is insoluble.

Measurements of pH and conductivity carried out on aqueous solutions of PdCl_2T_2 show that this compound is completely hydrolysed at 25°C . Thus the compound $\text{Pd}(\text{OH})_2\text{T}_2$ exists in solution, formed that a result of the reaction:

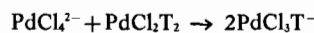


Reversal of hydrolytic balance can be achieved by working at a high concentration of chloride ion. For this reason spectrophotometric measurements were carried out on 0.1 M solutions of HCl.

Examination of the system $\text{PdCl}_4^{2-} - \text{T}$ shows that the disubstituted compound PdCl_2T_2 is that predominant in solution immediately after the mixing of the reagents; at infinity, on the other hand, the mono-substituted compound $\text{K}[\text{PdCl}_3\text{T}]$ is predominant. As has already been observed the absorption of solutions containing an excess of T remains constant in time while that of solutions containing an excess of PdCl_4^{2-} increases regularly until a constant value is reached.

It should also be noted that all the solutions contain a strong excess of chloride ions. If the thiomorpholinone shift were due to these then it would seem logical that the absorption of all the solutions should increase, even of those that do not contain an excess of PdCl_4^{2-} . But the possibility of the reaction being caused by the Cl^- ions is quite out of the question, as is revealed by examination of the system $\text{PdCl}_2\text{T}_2/\text{Cl}^-$ by the continuous variations method. The results show in fact that there is no reaction; absorption varies linearly and remains constant

in time. It is therefore clear that the formation of the compound $\text{K}[\text{PdCl}_3\text{T}]$ is due to the reaction between PdCl_4^{2-} and PdCl_2T_2 , namely:



A kinetic study of this reaction has shown it to be governed by a second order mechanism (Figure 9); the rate constant was 2.34 min^{-1} at $25^\circ\text{C} \pm 0.1$ and $\mu = 0.1$ (A: ratios 60/40, $K = 2.28$. B: ratios 70/30, $K = 2.40$).

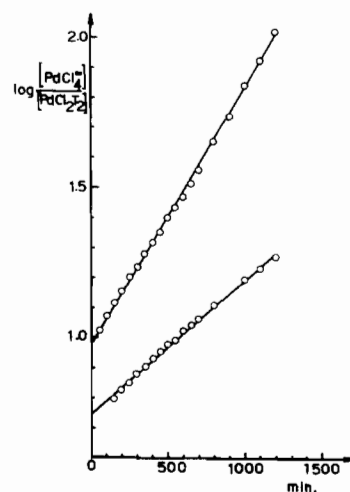
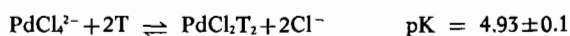
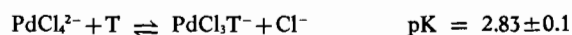


Figure 9. Kinetic study of the reaction between PdCl_4^{2-} and PdCl_2T_2 .

From the absorption data the instability constants of the two compounds were approximately calculated. They proved to be ($25^\circ\text{C} \pm 0.1$; $\mu = 0.1$):



The compound PdCl_2T_2 can be also be prepared starting from Na_2PdCl_6 . In this case the ligand-uptake is 3 moles, as has already been found for the corresponding platinum reaction. This shows that while two moles are used up in the substitution of the chloride ions one mole is used in the reduction of the metal.

This reaction is also accompanied by a perceptible decrease of pH; yet it has been noted that immediately after mixing the reagents pH increases considerably, such increase clearly being dependent on the concentration of thiomorpholinone. It was thus of interest to study the reaction in greater detail so as to describe the mechanism more clearly; in this case it is possible, also as a result of PdCl_2T_2 being more soluble than its corresponding Platinum compound. The results of this enquiry will be reported in a following Note.

The compounds of Palladium formerly described and those of like composition previously obtained with Platinum were also studied by means of IR spectrophotometry.

First let it be observed that the characteristic bands of thiomorpholinone in the region 4000-450 cm^{-1} remain unaltered in the compounds. Furthermore, the spectra obtained for the compounds PdCl_2T_2 and PtCl_2T_2 are identical, regardless of whether these substances derived from MCl_6^{2-} or from MCl_4^{2-} . This provides indirect confirmation of what we previously maintained in respect of metal reduction by thiomorpholinone.

In particular, there are no absorption bands in the region 470-630 cm^{-1} except for a weak band present in thiomorpholinone at 562 cm^{-1} which is shifted to 524 cm^{-1} in the chloride compounds and to 532 cm^{-1} in the two compounds containing bromine. This observation excludes the possibility of coordination taking place through the nitrogen and oxygen atoms.

In fact, Nakamoto³ assigns to the metal-nitrogen stretching a wave number of 498 cm^{-1} for the compound $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2 \cdot \text{H}_2\text{O}$ and of 511 cm^{-1} for the compound $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$. In the same way, M. Adams⁴ assigns a weak band falling in the range 510-490 cm^{-1} to this stretching for *trans* compounds of the $\text{MX}_2(\text{NH}_3)_2$ type. The same author draws our attention, furthermore, to the presence of medium-strong bands due to the deformation of the metal-nitrogen bond existing in this type of compound in the range 260-250 cm^{-1} and also points out a band of medium strength just in chloride compounds in the range 230-225 cm^{-1} .

As for the *cis* compounds of the same type metal-nitrogen stretching occurs at 510 cm^{-1} for Platinum compounds at 495 and 476 cm^{-1} for Palladium com-

pounds; a band at 250 cm^{-1} is, however, attributed to bond deformation. In all these areas of the spectrum the compounds studied by us have no absorption bands.

As regards the metal-oxygen stretching Nakamoto³ reports the following values for the compounds $\text{K}_2[\text{PdOX}_2]_2 \cdot 2\text{H}_2\text{O}$ and $\text{K}_2[\text{PtOX}_2] \cdot 3\text{H}_2\text{O}$ (OX=oxalate): 556 and 417 cm^{-1} for Palladium, 559 and 405 cm^{-1} for Platinum. The compounds studied by us do not have absorption bands in these areas either.

With the metal-oxygen and metal-nitrogen bonds thus excluded it follows that thiomorpholinone must be bonded by means of the sulphur atom. This is in agreement with the rule set out by S. Ahrlund, J. Chatt and N. R. Davies,⁵ platinum and palladium being typical metals of Class B. The hypothesis is further supported by the findings of E. Francis and F. A. Cotton⁶ who, in their studies on the compounds of tetrahydrothiophenoxide, found that this ligand is bonded to cobalt, nickel and copper by means of the oxygen atom while in the case of palladium and platinum the bond is effected by means of the sulphur atom.

There are no absolutely certain data available in the literature regarding the assignment of the metal-sulphur stretching band. J. Pluscec and D. Westland⁷ make the following allocations: in the case of palladium, two bands at 330 and 308 cm^{-1} in chloride compounds and one band at 316 cm^{-1} in bromine compounds; in the case of platinum, two intense bands at 350 and 329 cm^{-1} in chloride compounds and two less intense bands at 349 and 324 cm^{-1} in bromine compounds.

	PdCl_2T_2 PtBr_2T_2 PdCl_2T_2 PtBr_2T_2	428 - 422 (s) 431 - 422 (s) 422 (m-s) 426 - 420 (s)	390 (m-s) 388 (m-s) 385 (m-s) 381 (s)	310 (vs) 308 (vs) 308 (vs) 308 (vs)	325 (s-w) 331 (s) 325 (s) 325 (vs) 295 (s)	277 (m-s) 266 (m-w)	247 (s)	
		436 - 422 (s)						
	M = Pt X = Pd							
	MePt EtCl MePt EtBr MePd EtCl MePd EtBr							
	MePt EtCl MePt EtBr MePd EtCl							
	MePt EtCl MePt EtBr							
	MePt EtCl MePt EtBr							

Figure 10. Comparison between absorption bands and hypothesized structures for some complexes of Palladium and Platinum sulphur-bonded.

(3) N. Nakamoto, Infrared spectra of inorganic and coordination compounds, 1963, John Wiley and Sons Inc., New York, London, Sydney.

(4) D. M. Adams, Metal-ligand and related vibrations, 1967, Edward Arnold Ltd. London.

(5) S. Ahrlund, J. Chatt, and N. R. Davies, *Quart. Revs.*, 265 (1958).

(6) R. Francis and F. A. Cotton, *J. Chem. Soc.*, 2078 (1960).

(7) (Mrs) J. Pluscec and A. D. Westland, *J. Chem. Soc.*, 5371 (1965).

Nakamoto and coworkers,⁸ however, in their studies on dithiocarbamate compounds, attribute a very strong band observed at 375 cm^{-1} and another observed at 388 cm^{-1} to Pt-S stretching; in the case of platinum-dithioxalate compounds, however, they ascribe the bands observed at 436 and 422 cm^{-1} and that observed at 322 cm^{-1} to $\nu(\text{Pt-S})$.⁹ They explain these higher frequencies by attributing them to the fact that the force constant is greater in the dithioxalate-platinum(II) compound than in the dithiocarbamate-platinum(II) compound.

All the spectra of the compounds studied by us do in fact have numerous absorption bands in this area (Figure 10) but very probably none of them corresponds to a pure vibration deriving from the coupling of the different vibrations possible within the plane and outside it.

With regard to halogen-metal stretching, Adam⁴ reports the following values for the *trans* compounds of the type MX_2L_2 : $\text{PdCl}_2(\text{SMe}_2)_2$, 359 cm^{-1} ; $\text{PdCl}_2(\text{SEt}_2)_2$, 358 cm^{-1} ; $\text{PtCl}_2(\text{SEt}_2)_2$, 341.9 cm^{-1} ; $\text{PtBr}_2(\text{SEt}_2)_2$, 253.5 cm^{-1} . For the corresponding diethylsulphide *cis* compounds of platinum bands are observed at 330 and 318 cm^{-1} in the case of chlorine and at 254 - 226 cm^{-1} in the case of bromine.

In the compound PdCl_2T_2 we find a very strong band at 358 cm^{-1} , a value which coincides exactly with the wave number reported in the literature for *trans* compounds, while in the case of the compound PtCl_2T_2 we find a band at 350 cm^{-1} , which is very close to the value predicted. These bands are not present in compounds containing bromine and it therefore seems reasonable to assign them to M-Cl stretching for *trans* type compounds. As regards the

(8) K. Nakamoto, J. Fujita, R. A. Condrate, and Y. Morimoto, *J. Chem. Phys.*, **39**, 423 (1963).

(9) J. Fujita and K. Nakamoto, *Bull. Chem. Soc. Japan*, **37**, 528 (1964).

compound PtBr_2T_2 we observe a band at 247 cm^{-1} as against an average value in literature of $249.8\text{ cm}^{-1} \pm 9$.¹⁰ This band could also be assigned to halogen-metal stretching.

The remaining absorption bands in the region 460 - 200 cm^{-1} (an area in which the ligand does not absorb) should be attributed to interactions between thiomorpholinone and metal and would derive from the coupling of the various possible deformations of the Pt-S bond. The fact that absorption bands may be observed in the range 430 - 420 cm^{-1} , that is to say shifted towards higher energies than those of dithiocarbamate compounds and close to the values observed for dithioxalate compounds, could mean that the M-S bond is particularly strong in the compounds studied by us, as is maintained by Nakamoto.⁹ Such a hypothesis is further supported by the chemical observation that the MX_2T_2 compounds we obtained are formed immediately after the mixing of the reagents, even when working cold, and separate out in a solid state. The possibility of intermolecular interactions taking place due to the contemporaneous presence of the oxygen atom and the NH group should not, however, be overlooked.

In conclusion, it seems reasonable to propose a *trans* configuration for the studied compounds and to suggest that, in them, thiomorpholinone is especially strongly bonded to the metal *via* the sulphur atom.

The preparation and study of the compounds with other metals may perhaps reveal whether this ligand is also capable of establishing coordination bonds with the other donor groups present in the molecule.

Acknowledgment. This work was supported through a grant of C.N.R. (Italian Research Council).

(10) D. M. Adams, J. Ehatt, J. Gerratt, and D. A. Westland, *J. Chem. Soc.*, 734 (1963).