The Vibrational Spectra of Complexes with Planar Monothiooxamides. III. The Palladium(II) Complexes of Neutral Monothiooxamides

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PLEASE SCROLL DOWN FOR ARTICLE

THE VIBRATIONAL SPECTRA OF COMPLEXES WITH PLANAR MONOTHIOOXAMIDES - PART III [1]. THE PALLADIUM(II) COMPLEXES OF NEUTRAL MONOTHIOOXAMIDES

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ABSTRACT

The new complexes *trans*-[PdX$_2$(H$_4$MTO)$_2$] (X= Cl, Br, I), *trans*-[PdX$_2$(H$_3$MMTO)$_2$] (X= Cl, Br, I), *trans*- [PdX$_2$(SH$_3$)$_2$] (X= Cl, Br), [Pd(H$_4$MTO)$_4$]Cl$_2$ and [Pd(H$_3$MMTO)$_4$]Cl$_2$, where H$_4$MTO = monothiooxamide, H$_3$MMTO = N$_{(O)}$-methylmonothiooxamide and SH$_3$ = N$_{(S)}$-methylmonothiooxamide, have been prepared. The complexes were

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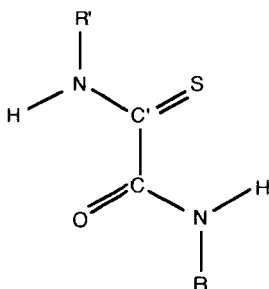* Authors to whom correspondence should be addressed.

characterized by elemental analyses, conductivity measurements, X-ray powder patterns, thermal methods and spectroscopic (UV/VIS, FT-IR, Laser-Raman) studies. The vibrational analysis of the complexes is given using NH/ND and CH_3/CD_3 isotopic substitutions. Monomeric square planar structures are assigned for the complexes in the solid state. The neutral monothiooxamides behave as monodentate ligands coordinating through their thioamide sulfur atom. The complex $[Pd(SH_2)_2]$ was isolated during the thermal decomposition of trans - $[PdCl_2(SH_3)_2]$.

INTRODUCTION

The development of amide and thioamide coordination chemistry and spectroscopy is a central theme in transition-metal chemistry [2-4]. Research in this area ranges from solution of pure spectroscopic [5] and chemical problems [6] to biological modeling applications [7] and advanced materials chemistry [8-11]. Our involvement in the amide/thioamide chemistry stems from a desire (i) to understand the factors that influence the bonding of amide and thioamide groups to metal ions, and (ii) to study in detail the spectroscopic properties, especially vibrational spectra, of the complexes formed.

Over the last fifteen years, we have been reporting our efforts towards developing the coordination chemistry and vibrational spectroscopy of oxamide ($H_2NCOCONH_2$) [12-17] - and dithiooxamide ($H_2NCSCSNH_2$) [3,18-21]-based ligands, with [12-15] or without [3,16-21] additional donor sites, mainly with d^7, d^8, d^9 and d^{10} transition metal ions. In contrast to the obtained large body of knowledge, complexes of ligands with both amide and thioamide groups have not been investigated. The simplest class of ligands, which belongs to this family,is monothiooxamides (Fig. 1).

Complexes of monothiooxamides could offer unique features in terms of structural, physical and spectroscopic properties. This has prompted us [1,22,23] to begin a systematic study of the coordination chemistry of planar monothiooxamides with a special attention to vibrational spectra. In Parts I [1] and II [22] of this series we have reported on the vibrational spectra of Ni(II), Pd(II), Pt(II), Cu(II) and Zn(II) complexes with singly and doubly deprotonated N,N'-dimethylmonothiooxamide and $N_{(S)}$-

R = R' = H ; monothiooxamide (H$_4$MTO)

R = R' = CH$_3$; N,N'-dimethylmonothiooxamide (LH$_2$)

R' = H, R = CH$_3$; N$_{(O)}$-methylmonothiooxamide (H$_3$MMTO)

R' = CH$_3$, R = H ; N$_{(S)}$-methylmonothiooxamide (SH$_3$)

FIG. 1. The general formula of the monothiooxamides used in our studies and their abbreviations.

methylmonothiooxamide; the monoanions LH$^-$ and SH$_2^-$ coordinate in a bidentate chelating fashion *via* the sulfur atom of the deprotonated thioamide group and the oxygen atom of the neutral amide group, while doubly deprotonated L^{2-} and SH^{2-} behave as bis-bidentate S,N/N,O-bridging ligands giving polymeric structures. In order to redress the complete lack of characterized complexes with *neutral* monothiooxamides, we have undertaken a combined preparative and spectroscopic investigation of Pd(II) complexes with the neutral ligands shown in Fig.1. We herein describe the results of this study.

EXPERIMENTAL

All manipulations were performed under aerobic conditions. Elemental analyses, physicochemical measurements and spectroscopic techniques were carried out by published methods [3, 20, 22].Details for the syntheses of monothiooxamides can be found elsewhere [24].

The complexes *trans*-[PdX$_2$(ligand)$_2$] were all prepared similarly. A total of 2.0 mmol of PdX$_2$ (X = Cl, Br, I) was dissolved in 2 ml of the corresponding concentrated HX (X = Cl, Br, I) acid; hydrochloric (37%), hydrobromic (48%) and hydroiodic (57%) acids were used. To this solution was slowly added a solution of the appropriate monothiooxamide (4.0 mmol) in 12 ml of glacial CH$_3$COOH. Precipitates formed almost immediately and the reaction mixtures were kept stirring at room temperature for about 10 min. All solids were collected by filtration, and washed with CH$_3$COOH (2 x 3 ml), EtOH (3 x 5 ml) and Et$_2$O (4 x 10 ml). No further purification was undertaken and the products were dried *in vacuo* over P$_4$O$_{10}$. Yields were in the 30-50 % range.

For the preparation of the 1:4 ionic complexes [Pd(H$_4$MTO)$_4$]Cl$_2$ and [Pd(H$_3$MMTO)$_4$]Cl$_2$, a solution of PdCl$_2$ (2.0 mmol) in 2 ml of 37% hydrochloric acid was added dropwise to a stirred solution of the free ligand (9.0 mmol) in 20 ml of glacial CH$_3$COOH. Upon addition of PdCl$_2$ yellow precipitates were obtained. Stirring was continued for 15 min. The precipitates were collected by filtration, washed with CH$_3$COOH (2 x 5 ml), EtOH (2 x 10 ml) and copious amounts of Et$_2$O, and dried *in vacuo* over P$_4$O$_{10}$. Yields were *ca.* 60%.

The deuterated compounds were prepared exactly as described for the normal complexes using PdCl$_2$, normal ligands and deuterated solvents (CH$_3$COOD, DCl, DBr, DI). The precipitates were washed only with CH$_3$COOD and CD$_3$OD. The CD$_3$-complexes were prepared as described above for the normal complexes using the CD$_3$-forms of H$_3$MMTO and SH$_3$.

RESULTS AND DISCUSSION

Preparation and Properties of the Complexes

The prepared complexes are listed in Table 1 with their elemental analyses, colours and molar conductivity values.

Firstly, we comment on the synthetic points which present a special interest.

The formation of Pd(II) complexes with *neutral* monothiooxamides is feasible only in acidic solvent mixtures (HX-CH$_3$COOH). The use of

TABLE 1

Colours, Elemental Analyses and Conductivity Data for the Prepared Complexes

Comp. number	Complex	Colour	Elemental analyses (%)*				$\Lambda_M{}^+$ (S cm^2 mol^{-1})
			Pd	X	C	H	
1	[PdCl$_2$(H$_4$MTO)$_2$]	yellow-orange	27.1	17.3	12.7	2.30	15
			(27.6)	(18.4)	(12.5)	(2.09)	
2	[PdBr$_2$(H$_4$MTO)$_2$]	yellow	23.1	33.4	10.3	1.80	13
			(22.4)	(33.7)	(10.1)	(1.70)	
3	[PdI$_2$(H$_4$MTO)$_2$]	yellow-brown	18.3	44.6	8.5	1.50	dec.
			(18.7)	(44.6)	(8.4)	(1.42)	
4	[PdCl$_2$(H$_3$MMTO)$_2$]	yellow	25.4	17.0	17.3	2.97	18
			(25.7)	(17.1)	(17.4)	(2.93)	
5	[PdBr$_2$(H$_3$MMTO)$_2$]	yellow	20.7	31.1	13.9	2.65	9
			(21.2)	(31.8)	(14.3)	(2.41)	
6	[PdI$_2$(H$_3$MMTO)$_2$]	yellow-brown	18.2	43.0	12.1	2.08	dec.
			(17.8)	(42.5)	(12.1)	(2.03)	
7	[PdCl$_2$(SH$_3$)$_2$]	yellow	24.9	16.8	17.2	3.05	29
			(25.7)	(17.1)	(17.4)	(2.93)	
8	[PdBr$_2$(SH$_3$)$_2$]	orange	20.6	32.1	14.0	2.57	21
			(21.2)	(31.8)	(14.3)	(2.41)	
9	[Pd(H$_4$MTO)$_4$]Cl$_2$	yellow	17.7	12.0	16.3	2.71	145
			(17.9)	(11.9)	(16.2)	(2.72)	
10	[Pd(H$_3$MMTO)$_4$]Cl$_2$	brownish yellow	16.1	10.4	22.1	3.80	164
			(16.4)	(10.9)	(22.2)	(3.73)	

* Theoretical values are in parentheses.

+ Values of molar conductivity for *ca.* 10^{-3} M solutions in DMF at 25°C; the conductivities of some solutions change with time.

X = Cl, Br, I; dec. = decomposition.

strongly acidic media prevents formation of complexes with the monoanionic form of the ligands [1, 22], by shifting the equilibrium : neutral ligand $\rightleftharpoons$ monoanionic form + H$^+$ towards the undissociated forms. With LH$_2$, however, no complexes with the neutral form of the ligand could be obtained.
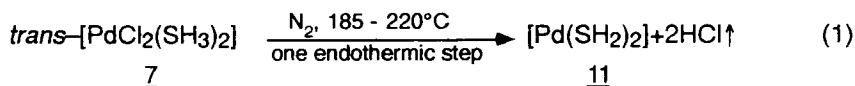
The 1:2 *trans* complexes can be synthesized directly from the [PdX$_4$]$^{2-}$ ions by reaction with H$_4$MTO, H$_3$MMTO and SH$_3$. The isolation of *trans* (and not *cis*) complexes can be explained by the fact that the ligands have a greater *trans effect* compared to X$^-$[25]. The failure to isolate *trans* - [PdI$_2$(SH$_3$)$_2$] is attributed to steric effects; electronic reasons may also be involved.

The failure to isolate the bromide and iodide salts of [Pd(H$_4$MTO)$_4$]$^{2+}$ and [Pd(H$_3$MMTO)$_4$]$^{2+}$ can be explained by the HSAB theory [26]. The Br$^-$ and I$^-$ ions are softer bases than Cl$^-$ and , so, they have a stronger tendency to coordinate to Pd(II) which is a soft base. Another reason for the isolation of chloride salts and the non-isolation of bromides and iodides may be the strength of the hydrogen bonds. In the chloride salts, the hydrogen bonds are stronger [20, 24] and this favours the formation of ionic compounds when an excess of ligand is present. The non-formation of the ionic compounds [Pd(LH$_2$)$_4$]Cl$_2$ and [Pd(SH$_3$)$_4$]Cl$_2$ is attributed to the steric hindrance caused by the presence of four secondary thioamide groups around Pd(II).

The complexes are microcrystalline or powder-like, stable in atmospheric conditions and soluble only in DMF and DMSO. The 1:4 complexes have a moderate solubility in H$_2$O; however, their aqueous solutions are not stable having a tendency for hydrolysis.The X-ray *powder* diffraction patterns indicate that each product represents a definite compound, which is not contaminated with starting materials or species with other stoichiometries. The data indicate the formation of three groups of isostructural compounds; the first group includes complexes 1 - 3, the second complexes 4, 5 and 6, and the third includes complexes 7 and 8. The low molar conductivities of the 1:2 complexes in DMF reveal that both anions are bonded to Pd(II) [27]. The values of 9 and 10 lie in the range observed for 1:2 electrolytes [27]. All the prepared complexes are diamagnetic.

The thermal decomposition of the Pd(II) compounds was studied using mainly TG/TDG techniques. The data for the complexes of H_4MTO (1-3, 9) and H_3MMTO (4-6, 10) present no special interest as their decomposition is characterized by rather complex degradation mechanisms. These complexes decompose without the formation of stable intermediates; also, no stoichiometric compounds could be assigned to the curves' inflections. For both H_4MTO and H_3MMTO 1:2 complexes, the thermal stability sequence– as indicated by the temperature of initial mass loss – is chloro complex < bromo complex < iodo complex. Also for a given ligand the thermal stability sequence is : 1:4 complex < 1:2 complex, i.e. complex 9 is thermally less stable than complex 1, and 10 less stable than 4. These trends are in accord with IR spectoscopy (vida infra) which shows that the strength of the intermolecular N–H···X hydrogen bonds follows the opposite sequences, i.e. iodo complex < bromo complex < chloro complex and 1:2 complex < 1:4 complex; stronger hydrogen bonds result in easier (in terms of energy) formation and elimination of HX upon heating and, thus, in less stable complexes.

The two 1:2 complexes of SH_3 (7, 8) decompose via the stoichiometric [Pd$(SH_2)_2$] intermediates; in the case of 7 this intermediate is stable and, thus, it was isolated by the temperature-arrest technique in nitrogen atmosphere and studied. The TG/DTG curves of 7 show an one-step first mass loss between 185 and 220 °C, which corresponds exactly (found : 17.4%, calc. 17.6%) to the release of two moles of HCl per mole of [PdCl$_2$(SH$_3$)$_2$]. A TG plateau is reached at 225 °C up to 267 °C. The stable product (compound 11), obtained after a TG experiment up to 245 °C by keeping the heating rate at 1 °C min^{-1}, was isolated and studied using the same physical and spectroscopic methods with those used for the study of the other complexes. The isolated solid is diamagnetic and behaves as a non-electrolyte in DMF. We repeated the experiment using the deuterated form of 7 as a starting material and obtained the deuterated form of 11 for

$$trans\text{-}[PdCl_2(SH_3)_2] \xrightarrow[\text{one endothermic step}]{N_2,\ 185\text{ - }220°C} [Pd(SH_2)_2]+2HCl\uparrow \qquad (1)$$

$$\underline{7}\underline{11}$$

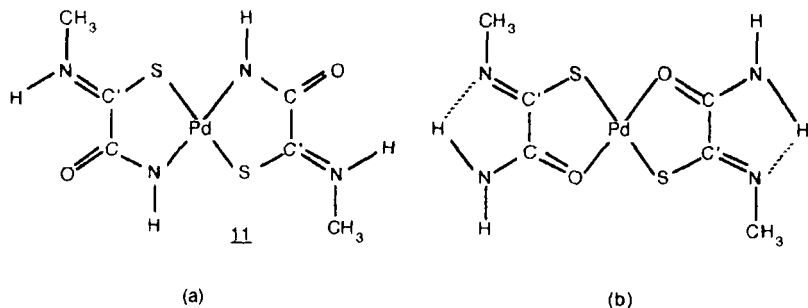comparative spectroscopic studies. The vibrational study proved (vide infra)

FIG.2. The square planar *trans* structures of the two linkage isomers of [Pd(SH$_2$)$_2$] (and other mesomeric forms); for further discussion, see text.

compound 11 to have the *trans* square planar structure shown in Fig. 2a. It is worth noting that the dark yellow compound 11 has been isolated in pure form from a solid-state reaction, whilst attempts for its preparation from solution were unsuccessful and led [1] to the isolation of a linkage isomer of 11 (Fig. 2b). The activation energy E_a of the formation of 11 was determined by the variable-heating rate method proposed by Flynn and Wall [28]; full experimental and theoretical details of this method have also been given by us in refs. 22 and 29. The average E_a value is 179.7 kJ mol^{-1}. This value is somewhat higher than in the cases of HCl elimination from *cis*-[PdCl$_2$(TH$_2$)], where TH$_2$ are various dithiooxamides [29]; the difference may be due to the fact that a monomeric complex is formed in the present case, while stable polymers result from the thermal decomposition of the dithiooxamide complexes. The product 11 starts to decompose at 270 °C and transforms into pure metallic Pd at 500 °C (found residue : 25.2 %, calc. 25.7%).

The final decomposition residue of 1-10 was metallic Pd or a mixture of Pd and PdS.

Solid-State Electronic Spectra

Table 2 gives details of the solid-state (diffuse reflectance) spectra of the Pd(II) complexes with neutral monothiooxamides. Assignments have been

TABLE 2

Solid- State Electronic Spectral Data (10^3 cm^{-1}) in the 29400-11200 cm^{-1} region for the Pd(II) Complexes

Complex	d–d*		LMCT+	MLCT++
1	17.30,	20.11	22.16	24.47
2		20.42	22.32	25.70
3	17.09 sh,	20.36	22.19	24.75
4	17.41,	20.18	22.21	24.13
5	17.35,	20.37	22.38	25.00
6	17.12 sh,	20.61	22.47	24.87
7	18.00,	21.00	22.80	24.67
8	17.83,	20.87	22.87	25.13
9	n.o.		23.21	28.50
10	19.52		22.98	27.99

* The lower energy band is probably due to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition under D_{4h} symmetry, while the higher energy band is probably due to the $^1A_{1g} \rightarrow {}^1E_g$ transition (D_{4h}).

+ Ligand-to-metal charge transfer $^1A_{1g} \rightarrow {}^1B_{2u}$, $^1B_{3u}$ transition.

++ Metal-to-ligand charge transfer $^1A_{1g} \rightarrow {}^1B_{2u}$ transition.

sh = shoulder; n.o. = not-observed.

given by studying literature for Pd(II) complexes with sulfur ligands [30, 31]. Square planar structures are assigned for the complexes on the basis of their d-d frequencies [30, 31]. The LMCT and MLCT transitions were assigned according to the work of Clark and Turtle [31].

The Vibrational Spectra of the Complexes in the Solid State

The full vibrational analysis of the free ligands has been published [24, 32, 33]. Although several attempts were made (using a spinning cell and the two Ar^+ laser lines at 514.5 and 488.0 nm), it was possible to obtain satisfactory Raman spectra only for the complexes 7 and 9. Tables 3, 4 and 6 summarize the most characteristic and diagnostic fundamentals of the H_4MTO and H_3MMTO complexes, and compound 11, respectively. The full vibrational analysis of 7 and 8 is given in Table 5. Fig. 3 illustrates the mid-IR spectra of trans -[PdX$_2$(H$_4$MTO)$_2$] (X = Cl, Br, I).

The assignments have been given in comparison with the data obtained for the free ligands [24, 32, 33] and for complexes containing amide [12-17] or thioamide groups [3, 19-21], and have been assisted by NH/ND- and CH_3/CD_3-isotopic substitutions.The spectroscopic discussion will be confined only to the most important features in relation to the coordination modes of the ligands and to the structures of their complexes.

Considering the amide functions of the complexes, the spectra show the typical bands of neutral primary (1, 2, 3, 7, 8, 9) and trans -secondary (4, 5, 6, 10) amide groups [13, 34, 35]. The absence of large systematic shifts of the amide $\nu_{as}(NH_2)$, $\nu_s(NH_2)$, $\nu(NH)$, $\delta(NH_2)$, $\delta(NH)$, $\rho(NH_2)$, $\omega(NH_2)$, $\tau(NH_2)$, $\pi(NH)$, $\nu(CO)$ and $\nu(CN)$ bands in the vibrational spectra of the complexes, compared with the frequencies of these modes in the spectra of the corresponding free ligands, implies that there is no interaction between the amide groups and Pd(II).

The bands with $\nu(C'S)$ character in the spectra of the complexes are situated at lower frequencies than for the free ligands, whereas the $\nu(C'N)$ vibration shows a significant frequency increase. These shifts are consistent with thioamide sulfur-coordination [19-21]. On coordination via sulfur, the positively charged palladium ion stabilizes the negative charge on the sulfur atom. The thioamide function now occurs in its polar resonance form (Fig. 4) and, thus, the double bond character of the C'N bond increases, while the

<u>TABLE 3</u>

Diagnostic Infrared Fundamentals (cm^{-1}) of the Complexes *trans*-[PdX$_2$(H$_4$MTO)$_2$] (X=Cl, Br, I) and [Pd(H$_4$MTO)$_4$]Cl$_2$

trans -[PdX$_2$(H$_4$MTO)$_2$]			[Pd(H$_4$MTO)$_4$]Cl$_2$ *	Assignments +
X = Cl	X = Br	X = I		
3403 m	3409 s	3421 vs	3368 m	ν_{as}(NH$_2$)amide
3312 m	3320 mb	3324 vs	3286 mb	ν_{as}(NH$_2$)thio
3267 mw	3272 w	3275 s	3217 m	ν_s(NH$_2$)amide
3159 w	3156 m	3146 m	3157 wb	ν_s(NH$_2$)thio
			3030 wb	ν(NH)++
			1719 s	ν(CO)
1691 s	1688 vs	1686 vs	1692 s	ν(CO)
1601 s	1595 vs	1590 sh.	1597 m	δ(NH$_2$)amide
1588 s	1587 vs	1587 s	1590 m	δ(NH$_2$)thio
1457 m	1453 s	1444 s	1473 m	ν(C'N)
1380 m	1385 m	1385 m	1394 s	ν(CN)
1242 m	1236 s	1228 s	1220 m	ρ(NH$_2$)thio
1080 m	1079 s	1072 m	1130 w	ρ(NH$_2$)amide
			917 m	ν(CC')
904 m	897 s	891 m	829 m	ν(CC'),ν(C'S)
723 m	724 s	726 s	803 m	ω(NH$_2$)amide,ν(C'S)
649 mb	656 s	655 s	730 s	ω(NH$_2$)thio,δ(NCO)
591 mw	579 m	550 w	567 m	τ(NH$_2$)thio,δ(NC'S)
540 mw	540 s	538 s	545 m	τ(NH$_2$)amide,π(NCO)
336 m	332 s	329 m	340 s	ν(PdS)
			321 s	ν(PdS)
326 s	262 s	232 m		ν(PdX)

* Intense Raman bands appear at : 1595, δ(NH$_2$)amide ; 1475, ν(C'N) ; 1393,ν(CN) ; 1120, ρ(NH$_2$)amide ; 909, ν(CC') ; 747, ω(NH$_2$)thio + δ(NCO) ; 549, τ(NH$_2$)amide + π(NCO) ; 372, ρ(NC'S) ; 336, ν(PdS) and at 330 cm^{-1}, ν(PdS).

+ Assignments have been assisted by NH/ND isotopic substitutions.

++From ammonium-like groups.

b=broad ; m=medium ; s=strong ; sh=shoulder ; v=very ; w=weak.

TABLE   4

Diagnostic Infrared Fundamentals (cm^{-1}) of the Complexes *trans-*[PdX$_2$(H$_3$MMTO)$_2$] (X=Cl, Br, I) and [Pd(H$_3$MMTO)$_4$]Cl$_2$

trans - [PdX$_2$(H$_3$MMTO)$_2$]			[Pd(H$_3$MMTO)$_4$]Cl$_2$	Assignments *
X = Cl	X = Br	X = I		
3276 s	3318 s	3323 s	3247 mb	ν_{as}(NH$_2$)
3165 w		3219 w	3140 wb	ν_s(NH$_2$)
	3171 sb			ν(NH),ν_s(NH$_2$)
3121 m		3153 m	*ca.* 3000 mb +	ν(NH)
1694 s	1690 s	1688 vs	1692 vs	Amide I [ν(CO)]
		1678 vs		Amide I [ν(CO)]
1618 m	1610 s	1591 vs	1642 s	δ(NH$_2$)
			1594 m	δ(NH$_2$)
1523 vsb	1543 mb	1533 sb	1531 vsb	ν(C'N), Amide II
				[ν(CN)+δ(NH)]
1269 w	1274 w	1268 w	1297 w	ρ(NH$_2$)
1207 s	1222 s	1213 s	1221 m	Amide III [δ(NH)+ν(CN)]
1158 m	1157 m	1151 w	1159 m	ν(NR)
1036 w	1045 m	1038 m	1045 w	ρ(CH$_3$), ν(CC')
905 m	922 s	916 m	934 w	ν(CC')
		810 m		ν(C'S), ν(CC')
796 s	801 vs	796 s	802 s	ν(C'S), δ(NCO)
767 mb	758 s	758 s		ν(C'S), δ(NCO)
		688 s	740 wb	ω(NH$_2$)
646 mb	679 mb			ω(NH$_2$), π(NH)
		657 m	662 mb	π(NH)
298 s	288 m	280 w	349 m	ν(PdS)
268 m				ν(PdS)
318 s	259 s	232 m		ν(PdX)

* Assignments for all four complexes have been assisted by NH/ND, CH$_3$/CD$_3$, and *simultaneous* CH$_3$/CD$_3$ and NH/ND isotopic substitutions.

+ From ammonium-like groups.

double bond character of the C'S bond decreases. The frequency of the ν(C'N) vibration lowers in going from $\underline{9}$ to $\underline{1}$ and also from $\underline{10}$ to $\underline{4}$, implying a stronger Pd-S bond in the complexes in which the Pd(II) atom is bonded to four sulfur atoms; this is also confirmed by the higher ν(PdS) frequencies observed in these 1:4 complexes.

The more polar character of the thioamide function explains the lower values of $\nu(NH_2)_{thio}$ and $\nu(NH)_{thio}$ in the complexes, compared with the $\nu(NH_2)_{amide}$ and $\nu(NH)_{amide}$ modes [33].

The 1:4 complexes [Pd(H₄MTO)₄]Cl₂ ($\underline{9}$) and [Pd(H₃MMTO)₄]Cl₂ ($\underline{10}$) are characterized by rather strong intermolecular N–H⋯X hydrogen bonds, involving the thioamide or/and amide groups, as suggested by the position and profile of the NH₂ and NH bands. These bonds result in broad, low-lying (ca. 3000 cm^{-1}) ammonium-like ν(NH) bands with several weak submaxima. Lower frequency $\nu_{as}(NH_2)_{thio}$ and $\nu_s(NH_2)_{thio}$, corresponding with higher frequency $\delta(NH_2)_{thio}$, $\rho(NH_2)_{thio}$, $\omega(NH_2)_{thio}$ and $\tau(NH_2)_{thio}$ modes, are observed for $\underline{10}$ compared to $\underline{9}$. This clearly indicates that the strength of the hydrogen bonds increases from the H₄MTO to the H₃MMTO complex.

Weaker hydrogen bonds are present in the 1:2 *trans* halo complexes, as deduced from the frequencies of the relevant NH₂ and NH bands which clearly show that the strength of the hydrogen bonds follows the sequences $\underline{1}<\underline{9}$ and $\underline{4}<\underline{10}$, *i.e.*, for a given ligand, 1:2 complex<1:4 complex. For example, the ρ(NH₂) and π(NH) modes for $\underline{10}$ at 1297 and 662 cm^{-1}, respectively, shift to 1269 and 646 cm^{-1} in $\underline{4}$; these shifts indicate [19] stronger hydrogen bonding interactions in $\underline{10}$. The relative strength of the intermolecular hydrogen bonds in the H₄MTO complexes $\underline{1}$ and $\underline{9}$ is nicely demonstrated in the frequency of the pure ν(CN) vibration, which is situated at a higher frequency in $\underline{9}$ (1394 cm^{-1}) than in $\underline{1}$ (1380 cm^{-1}). The higher frequency for the 1:4 complex $\underline{9}$ is in accord with a larger contribution of the polar resonance form to the structure of the amide function, due to stronger hydrogen bonding [21].

According to the positions of the NH₂, NH stretching and deformation bands, for a given monothiooxamide ligand the hydrogen bonding strength in the 1:2 complexes increases according to the series I<Br<Cl, as expected [19, 20]; however, this trend is not clearcut for some deformation modes.

TABLE 5

The Vibrational Analysis ($4000 - 200$ cm^{-1}) of the Complexes *trans*-[PdX$_2$(SH$_3$)$_2$]   (X = Cl, Br)

trans-[PdCl$_2$(SH$_3$)$_2$]			trans-[PdBr$_2$(SH$_3$)$_2$]	Assignments[+,++]
Normal (IR)	Normal (Raman)*	Deuterated (IR)		
			3384 s	ν_{as}(NH$_2$)
3290 m			3285 m	ν(NH$_2$)
3222 mb			3238 mb	ν_s(NH$_2$)
3187 m			3184 s	ν(NH)
3053 mb			3123 mb	ν(NH)
2982 m			2987 w	ν(CH$_3$)
2927 m			2941 w	ν(CH$_3$)
		2542 s		ν_{as}(ND$_2$)
		2468 m		ν_s(ND$_2$)
		2360 vs		ν(ND)
1664 s	1657(3)	1681 s	1697 vs	ν(CO)
1579 vsb	1590(9)		1571 vs	δ(NH$_2$), ν(C'N)
		1565 s		ν(C'N)
1450 m		1470 sh	1440 m	δ(CH$_3$)
1434 m	1428(2)	1433 m	1425 w	δ(CH$_3$)
	1403(10)	1406 s		ν(CN), δ(CH$_3$)
1386 w	1375(8)	1390 s		ν(CN), δ(CH$_3$)
1367 m			1372 vs	ν(CN), δ(NH), δ(CH$_3$)
		1210 s		δ(ND$_2$)
1176 sh	1190(1)	1161 m	1175 m	ν(NR')
		1143 w		ν(NR')
		1097 w		ρ(CH$_3$)
			1096 vs	ρ(NH$_2$)
		1062 m		ρ(CH$_3$), ν(CC')
1055 s			1046 s	ρ(CH$_3$), ρ(NH$_2$), ν(CC')
	1052(3)			ν(CC'), ρ(CH$_3$), ρ(NH$_2$)
		1034 m		ν(CC'), ρ(CH$_3$)

TABLE 5 (Contd.)

trans-[PdCl$_2$(SH$_3$)$_2$]			trans-[PdBr$_2$(SH$_3$)$_2$]	Assignments[+],[++]
Normal (IR)	Normal (Raman)*	Deuterated (IR)		
		984 m	989 s	ν(CC')
		938 s		δ(ND), ν(CC')
		905 w		ρ(ND$_2$)
		891 m		δ(ND), ν(C'S)
867 mb		847 mb	857 mb	ν(C'S), ν(CC')
787 m	784(1)			ω(NH$_2$)
		769 m		ν(C'S)
765 mb				π(NH)
			762 vsb	ω(NH$_2$), π(NH)
695 m		690 w	694 vs	δ(NCO)
		662 s		δ(NCO), δ(NC'S)
640 m	641sh		621 m	δ(NC'S)
		621 mb		ω(ND$_2$), δ(NC'S)
		576 m		π(ND)
570 sh			567 sb	τ(NH$_2$), π(NCO)
497 m		497 w		π(NCO), π(NC'S)
		452 s		τ(ND$_2$)
449 m		427 sb	443 m	ρ(NCO), ρ(NC'S)
355 s	357(2)		346 vs	ν(PdS)
		335 vsb		ν(PdS), ν(PdCl)
320 s	321(1)			ν(PdCl)
			265 vs	ν(PdBr)
245 w			240 m	rv
	217(2)			rv, lm
	200(9)	207 m	209 m	rv, lm

* Only the intense Raman bands are tabulated.

[+] Overtones, combination bands and very weak bands have been omitted.

[++] Assignments for both complexes have been assisted by CH$_3$/CD$_3$, and *simultaneous* CH$_3$/CD$_3$ and NH/ND isotopic substitutions.

TABLE 6

Diagnostic Infrared Fundamentals of Complex [Pd(SH$_2$)$_2$] (11)*

Normal	Deuterated	Assignments
3296 m		ν(NH)$_{amide}$
3269 mb		ν(NH)$_{amide}$
3162 m		ν(NH)$_{thio}$
3085 mb		ν(NH)$_{thio}$
	2400 m	ν(ND)$_{amide}$
	2257 s	ν(ND)$_{thio}$
1645 vs	1642 vs	ν(CO)
1574 vsb	1568 vsb	ν(C'N)
1426 m	1424 m	ν(CN), δ(CH$_3$)
1410 sh	1402 m	ν(CN), δ(CH$_3$)
1386 m		δ(NH)$_{thio}$, δ(CH$_3$)
1367 m		δ(NH)$_{thio}$
	1361 m	δ(CH$_3$)
1302 m		δ(NH)$_{amide}$
1273 m		δ(NH)$_{amide}$
1176 m	1181 w	ν(NR')
1046 s	1045 s	ν(CC'), ρ(CH$_3$)
1026 m	1022 s	ρ(CH3), ν(CC')
	983 w	δ(ND)$_{amide}$
	912 m	δ(ND)$_{thio}$
856 m	773 w	ν(C'S)
764 sb		π(NH)$_{amide}$, π(NH)$_{thio}$
	634 m	π(ND)$_{amide}$, δ(NC'S)
	571 m	π(ND)$_{thio}$
364 sb	360 sb	ν(PdS), ν(PdN)

* This complex has been prepared by the thermal decomposition of trans-[PdCl$_2$(SH$_3$)$_2$] (see text); the proposed structure of 11 is shown in Fig. 2a.
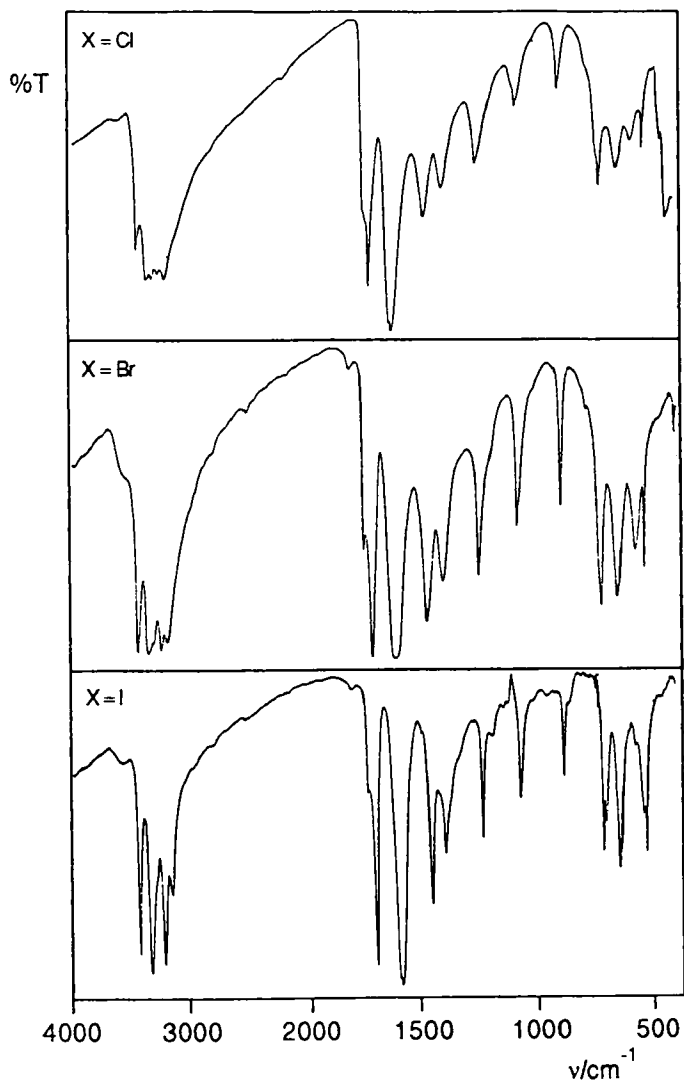
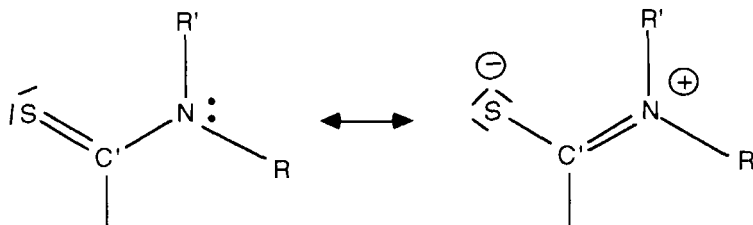FIG. 3. The FT-IR spectra of the complexes *trans*-[PdX$_2$(H$_4$MTO)$_2$] in the 4000-500 cm^{-1} region.

FIG.4. The two canonical forms of the thioamide function.

The FT-IR spectrum of [Pd(SH$_2$)$_2$] (11), which is distinctly different from that of its isomer described earlier [1], clearly shows the simultaneous presence of a neutral secondary thioamide group coordinated *via* the sulfur atom [19-21] and *cis* -secondary amide group binding through the deprotonated nitrogen atom [12,14], *i.e.*, in comparison with the spectrum of its precursor *trans* -[PdCl$_2$(SH$_3$)$_2$] (7), the thioamide bands have remained while the primary amide bands have disappeared. Furthermore, no ν(PdCl) bands could be found in the far-IR region. The low ν(CO) mode is characteristic for the *cis* amide structure and is due to the interaction between the lone-pair electrons of the oxygen atom and the amide hydrogen atom [36]. The ν(CN) mode is at low frequencies, because the palladium-nitrogen bond causes a lower electron density on the nitrogen atom and this results in a decrease of the CN bond strength. The above vibrational properties and the striking simplicity of the mid- and far-IR spectra let us conclude that we must consider the *trans* structure, shown in Fig. 2a, for 11. It may be recalled, at this point, that the FT-IR and Raman spectra of the linkage isomer of 11, shown in Fig. 2b, clearly showed the typical bands for primary amide and tertiary thioamide groups [1].

Assignments of far-IR and low-frequency Raman (only for 7 and 9) bands in Tables 3-5 have been carefully given by studying (i) the frequencies of the internal modes of the free ligands H$_4$MTO, H$_3$MMTO and SH$_3$, (ii) bands principally dependent on X (X = Cl, Br, I) for a given ligand, (iii) bands dependent on the monothiooxamide ligand for a given X, (iv) the variation in band position with deuteration and CH$_3$/CD$_3$ substitution, and (v) extensive

literature reports [1, 21, 22, 37, 38, 39]. The presence of one terminal $\nu(PdX)$ ($X = Cl$, Br, I) vibration (B_{3u} under D_{2h} symmetry) and one $\nu(PdS)$ vibration (B_{2u} under D_{2h} symmetry) in the low-frequency spectra of $\underline{1}$-$\underline{8}$ confirms their *trans* square planar geometry [37-39]. The far-IR spectrum of $[Pd(H_3MMTO)_4]Cl_2$ shows a band of medium intensity at 349 cm^{-1}, assigned to the Pd–S E_u stretching vibration of the square planar $[Pd(H_3MMTO)_4]^{2+}$ ion (point group : D_{4h}) [38]. Two $\nu(PdS)$ bands are observed in the far-IR spectrum of $[Pd(H_4MTO)_4]Cl_2$; this splitting may be due to a deviation of the ideal square planar structure or to a crystal packing effect [37, 39]. The two expected Raman-active $\nu(PdS)$ vibrations (A_{1g}, B_{1g} under D_{4h} symmetry) are observed at 336 and 330 cm^{-1}.

As it has been stated in this paper, the Pd-S bond strength increases on going from *trans*-$[PdCl_2(H_4MTO)_2]$ ($\underline{1}$) to $[Pd(H_4MTO)_4]Cl_2$ ($\underline{9}$) and also from *trans*-$[PdCl_2(H_3MMTO)_2]$ ($\underline{4}$) to $[Pd(H_3MMTO)_4]Cl_2$ ($\underline{10}$). This difference in metal-ligand bond strength is reflected in the frequencies of $\nu(PdS)$, which follow the sequences $\underline{1}<\underline{9}$ and $\underline{4}<\underline{10}$; the difference is, however, much more pronounced in the complexes of H_3MMTO. This trend is due to the symbiotic effect [40], according to which soft ligands flock together in a complex with a soft central metal ion, like Pd(II). So, the tendency towards symbiosis of four soft ligands makes the mixed complexes of definitely soft and hard ligands, *i.e.*, $\underline{1}$ and $\underline{4}$, less stable.

For a given X, the $\nu(PdS)$ vibration shifts to higher frequencies according to the sequence $H_3MMTO<H_4MTO<SH_3$. Electronic factors, such as the large electron releasing effect of the *thioamidic* methyl group in SH_3 and the difference in the withdrawing properties between the primary and secondary *amide* groups, may be responsible for this variation.

CONCLUDING COMMENTS

From the overall study presented, it is concluded that in all the complexes prepared the thioamide sulfur atom is the donor atom to Pd(II), *i.e.*, the neutral monothiooxamides behave as monodentate ligands. Monomeric square planar structures are assigned for the 1:2 and 1:4 complexes in the solid state. The proposed structures are shown in Fig. 5. The nature of the fundamentals of Pd(II) complexes with neutral ligands having both amide
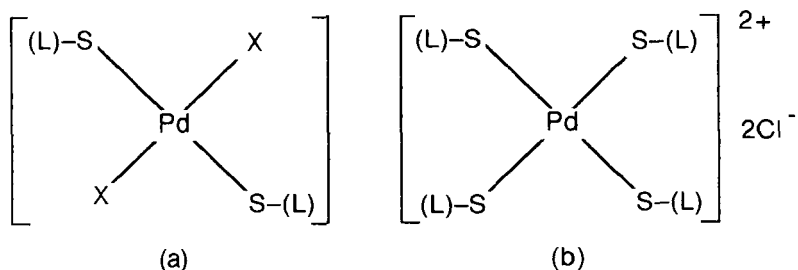
FIG. 5. The proposed square planar structures for the the 1:2 complexes
1 - 8 (a) and the 1:4 ionic compounds 9 and 10 (b). (L)– denotes
the remaining part of the neutral monothiooxamide ligand.

and thioamide functions considering monodentate S-coordination, has also
been discussed here. Work in progress on this interesting class of ligands
reveals that monomeric and dimeric/polymeric transition metal complexes of
neutral monothiooxamides, with various stoichiometries and interesting
structural and spectroscopic properties, can be prepared. The products
obtained to date will be reported in due course.

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