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COMPLEXES OF ORGANOMETALLIC COMPOUNDS

XXXII. THE COORDINATION CHEMISTRY OF MONOPHENYLTHALLIUM(III) WITH TRI- AND TETRADENTATE LIGANDS

L. PELLERITO, ROSALBA CEFALÙ and G. RUISI
Istituto di Chimica Generale, Università di Palermo, 90123 Palermo (Italy)

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SUMMARY

Several new complexes formed by $PhTlCl_2$ with tridentate ligands (with ONO and SNO donor atoms) and a tetradentate ligand (with ONNO donor atoms), have been prepared. The complexes show 1/1 organothallium(III)/Ligand ($=L^{2-}$) stoichiometry. Their nature and configuration are investigated in the solid state by vibrational spectroscopy, and in solution by electronic spectroscopy. The existence of chelation by the dianionic ligands on Tl^{III} is inferred, and suggestions are made concerning the Tl^{III} coordination number and the stereochemistry of the complexes.

INTRODUCTION

In continuation of our researches on complexes formed by organometal moieties with multidentate ligands[1-5], we describe below the synthesis and spectroscopic structural investigations of several new complexes PhTlL, where L^{2-} is a dianion derived from (*i*) the tridentate ligands H_2Aat [2-pentanone-4-(2-benzothiazolinyl)] and H_2Sat [2-(*o*-hydroxyphenyl)benzothiazoline], containing SNO donor atoms; (*ii*) H_2Sab [2,2′-methylidynenitrilodiphenol], containing ONO donor atoms, and (*iii*), the tetradentate ligand H_2Salen (*N*,*N*′-ethylenebissalicylaldimine), containing ONNO donor atoms.

EXPERIMENTAL

Analytical grade reagents and solvents were used, and were purified by recrystallization or distillation, and dried, when necessary, according to standard methods.

The compounds H_2Sat, H_2Aat, H_2Sab, H_2Salen and $PhTlCl_2$ were prepared and crystallized by literature methods[1,6-9]. The complexes PhTlL were synthesized by mixing a solution of the ligand (H_2L) in dry methanol, with sodium methoxide in the ratio 1/2. To the resulting solution, containing the Schiff base in the dianion form, was added a solution of $PhTlCl_2$ in dry methanol.

TABLE 1

ANALYTICAL DATA

Compound	*M.p.* (°C)	*Analysis found (calcd.) (%)*					
		C	*H*	*N*	*O*	*S*	*Tl*
PhTlAat	130 (dec.)	41.86 (41.95)	3.51 (3.31)	2.58 (2.88)	3.28 (3.29)	6.59 (6.57)	42.18 (41.99)
PhTlSat	179–182	43.74 (44.85)	2.71 (2.77)	2.57 (2.75)	3.40 (3.14)	6.28 (6.30)	41.30 (40.17)
PhTlSab	206–208	46.13 (46.32)	2.78 (2.86)	2.77 (2.84)	6.69 (6.49)		41.56 (41.48)
PhTlSalen	185–189	48.16 (48.24)	3.51 (3.50)	5.34 (5.11)	5.81 (5.84)		37.40 (37.31)

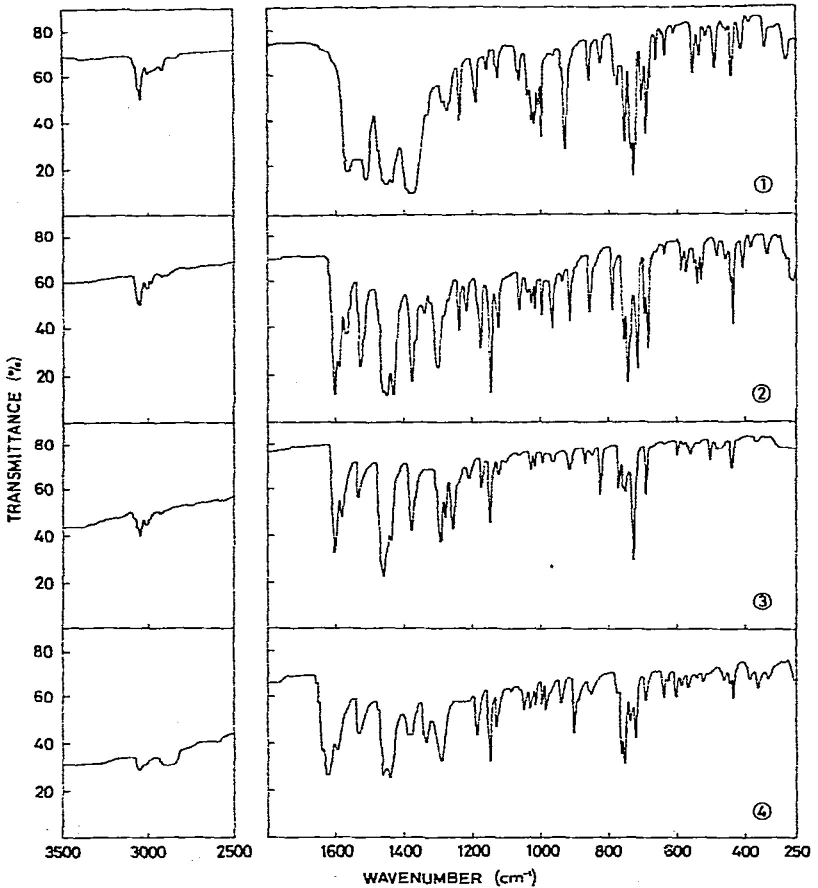


Fig. 1. IR spectra in hexachlorobutadiene (3500–2500 cm^{-1}) and Nujol mulls of the complexes: 1, PhTlAat; 2, PhTlSat; 3, PhTl Sab; 4, PhTlSalen.

The synthesis of PhTlSalen was carried out under nitrogen. Analytical results and melting points of the obtained yellow crystalline complexes are listed in Table 1. The complexes are stable when stored under anhydrous conditions. Their low solubility in common organic solvents prevented the determination of their molecular weights, PMR spectra, or conductances.

The vibrational spectra shown in Fig. 1 were recorded with Nujol and hexachlorobutadiene mulls on a Perkin–Elmer model 457 spectrometer. Free ligand spectra agreed with earlier reports[1,4].

The electronic spectra were measured with a Beckman DK 2A spectrophotometer, at 25°, with 1 cm optical path cells and dry methanol as solvent. All compounds obey Beer's law at all the wavelengths studied. The results are listed in Table 2.

TABLE 2

ELECTRONIC ABSORPTION SPECTRA OF PhTlL[a]

Compound	λ	*log a*
PhTlAat[b]	265	
	360	
PhTlSat[b]	231 (sh)	
	258 (sh)	
	281 (sh)	
	302 (sh)	
	350 (sh)	
	425	
PhTlSab	248 (sh)	4.352
	281 (sh)	3.984
	293 (sh)	3.954
	·437	4.061
PhTlSalen	259	4.218
	271	4.079
	345	4.061

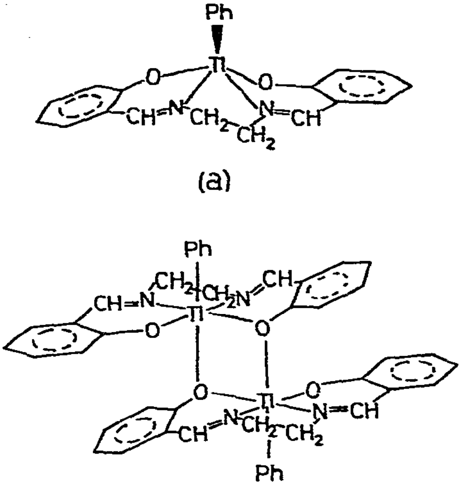
[a] The wavelengths (λ (nm)) and absorptivities (a, $M^{-1} \cdot cm^2$) refer to the band maxima and shoulders (sh). Concentrations range between 3×10^{-5} and 6.5×10^{-5} M. [b] Saturated solution.

DISCUSSION

The vibrational spectra of PhTlL (Fig. 1) essentially coincide with those of the corresponding R_2SnL and R_2PbL compounds[1-4], apart from bands associated with metal–carbon bonds or arising from the vibrational modes of the organic residues bound to the metal. In accordance with detailed discussions reported elsewhere[1-4], it is inferred that L^{2-} ligands, in the Schiff base form, chelate thallium atoms of solid PhTlL through their three and four donor atoms.

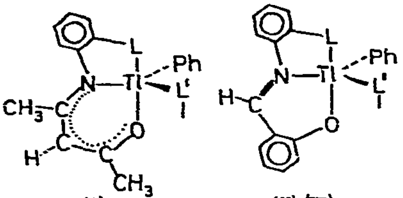
The occurrence of chelation in solution is inferred by inspection of the electronic spectra of Table 2, which show absorption bands at lower energies with respect to those in the free ligand spectrum[1-4].

It seems interesting to speculate on possible structures of PhTlL. When L^{2-} is the dianion of a tridentate ligand, Tl^{III} could be four-coordinated in a distorted tetrahedral environment. This implies that tridentate coordinated L^{2-} ligands lose



(a)

(b)



(I) (II)-(III)

Fig. 2. Generalized structure for compounds PhTlL discussed in the text. (I): PhTlAat, L=S, L'=S or O; (II): PhTlSat, L=S, L'=S or O; (III): PhTlSab, L=L'=O.

Fig. 3. Possible structures for PhTlSalen.

the "planar" structure assumed for the corresponding R_2ML derivatives (R=Me and Ph; M=Sn and Pb)[1,2,5]. If L^{2-} remains "planar" even in PhTlL, the polymeric structures (I)–(III) in Fig. 2 can be suggested, where Tl^{III} is five-coordinated in a trigonal bipyramidal configuration. As for PhTlSalen, the tetragonal pyramid (a) of Fig. 3, with five-coordinated Tl^{III}, seems very likely. On the other hand, a distorted trigonal bipyramidal configuration could arise from an increase of one O–Tl–N angle involving "*trans*" ON [see (a) of Fig. 3]. Furthermore, the oxygen-bridged dimeric structure (b) of Fig. 3, involving six-coordinated Tl^{III} in an octahedral configuration, cannot be excluded "*a priori*".

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