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COMPLEXES OF ORGANOMETALLIC COMPOUNDS

XXXVII. MÖSSBAUER AND OTHER STUDIES ON ADDUCTS OF ORGANOTIN(IV) CHLORIDES WITH *N,N'*-ETHYLENEBIS(SALICYLIDENEIMINATO)-NICKEL(II)

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Summary

Novel 1/1 adducts have been obtained from the complex *N,N'*-ethylenebis-(salicylideneiminato)nickel(II) (NiSalen) with di- and mono-organotin(IV) chlorides, and their solid state configuration investigated by Mössbauer, IR and electronic spectroscopy and magnetic measurements. In coordinated NiSalen the square planar structure is maintained around Ni^{II}, and the coordination to tin involves three-coordinate phenolic oxygens. The environment of Sn^{IV} is judged to be octahedral in both types of compounds. A *trans*-R_2, *cis*-Cl_2 configuration is advanced for $R_2SnCl_2NiSalen$.

Introduction

Earlier researches on the interaction of organotin compounds with multidentate bases produced evidence for the existence and structure of the molecular complexes R_2SnSalen [*N,N'*-ethylenebis(salicylideneimine) = H_2Salen], where $Salen^{2-}$ coordinates Sn^{IV} as "*cis*"-tetradentate in a *trans*-R_2 octahedral type structure [1, 2], as well as of the polymeric (in the solid state) 1/1 adducts $R_nSnCl_{4-n}\cdot L$ [L being H_2Salen and *N,N'*-ethylenebis(acetylacetoneimine)], where the neutral ligand acts as bis—monodentate bridging organotin halide units [3—6]. The present paper describes a subsequent study on organotin(IV) chloride—Ni^{II}Salen systems, in which the nickel complex should behave as a neutral bidentate ligand through its phenolic oxygen atoms, in accord with previous findings [7, 8]. Novel 1/1 adducts R_nSnCl_{4-n} NiSalen (R = Me, Ph; n = 1, 2) have been made, and their configuration studied by Mössbauer, IR, and electronic spectroscopy and magnetic measurements in the solid state. Species in solution were investigated by PMR and electronic spectroscopy.

Experimental

Analytical grade reagents (C. Erba, Milano) were used throughout, and were purified and dried where necessary by standard procedures.

The ligand H_2Salen was prepared as described elsewhere [9]. The complex Ni^{II}Salen was prepared by treatment of $Ni(CH_3COO)_2$ (20 mmol in 30 ml of H_2O) with H_2Salen (20 mmol in 300 ml of C_2H_5OH); the red-brown precipitate was repeatedly recrystallized from $CHCl_3$. M.p. 345° (uncorrected, measured by a Leitz hot plate instrument). The adducts R_nSnCl_{4-n}NiSalen were synthesized by 1 h reflux under N_2 of CH_2Cl_2 solutions of NiSalen (2 mmol in 60 ml) and R_nSnCl_{4-n} (Fluka and Alfa Inorganics; 2 mmol in 50 ml); red-brown solids were obtained on cooling, and were dried and stored under vacuum. Analytical data are shown in Table 1. Elemental analyses were carried out at the Istituto di Chimica Farmaceutica, Università di Padova, except for Ni and Sn, which were determined gravimetrically in our laboratory by standard methods [10].

The Mössbauer spectra were measured on samples kept at liquid N_2 temperature [using a AERE (Harwell) cryostat], with a R.T. $Ba^{119}SnO_3$ source

TABLE 1

DATA FOR R_nSnCl_{4-n}NiSalen ADDUCTS

(A) Analysis found (calcd.) (%)

Compound	M.p. (°C)	C	H	N	O	Ni	Sn	Cl
Me_2SnCl_2NiSalen	≈277(dec.)	39.90 (39.69)	3.81 (3.70)	5.18 (5.14)	5.91 (5.87)	10.26 (10.78)	21.98 (21.79)	12.96 (13.02)
Ph_2SnCl_2NiSalen	≈224(dec.)	50.34 (50.28)	3.57 (3.62)	4.06 (4.19)	4.82 (4.78)	8.35 (8.78)	18.17 (17.75)	10.44 (10.60)
$MeSnCl_3$NiSalen	≈299(dec.)	35.87 (36.13)	3.00 (3.03)	4.83 (4.96)	5.79 (5.66)	9.89 (10.39)	21.63 (21.00)	18.99 (18.82)
$PhSnCl_3$NiSalen	≈245(dec.)	42.28 (42.13)	3.20 (3.05)	4.37 (4.47)	5.20 (5.10)	9.36 (9.60)	18.75 (18.93)	16.83 (16.96)

(B) Mössbauer T ≈ 77 K

Compound	δ [a]	ΔE [b]	Γ_{av} [c]
Me_2SnCl_2NiSalen	+1.50	4.06	1.09
Ph_2SnCl_2NiSalen	+1.43	3.76	1.13
$MeSnCl_3$NiSalen	+0.90	1.63	1.01
$PhSnCl_3$NiSalen	+0.86	1.38	1.07

(C) Proton Magnetic Resonance in DMSO-d_6, δ(TMS) = 0

Compound	Chemical shifts, δ (ppm)				$J(^{117}SnCH)$ (Hz)	$J(^{119}SnCH)$ (Hz)
	$SnCH_3$	CH_2	Aromatics	=C—H		
NiSalen		3.40 [d]	6.30—7.30	7.82		
Me_2SnCl_2NiSalen	1.00	3.40 [d]	6.30—7.30	7.85	109	114
Me_2SnCl_2	1.00				109.5	114.5
Ph_2SnCl_2NiSalen		[e]	6.30—8.00 [f]			
$MeSnCl_3$NiSalen	0.94	3.40 [d]	6.30—7.34	7.92	129	135
$MeSnCl_3$	0.92				127	133
$PhSnCl_3$NiSalen		3.28 [d]	6.30—7.80	7.85		

[a] Isomer shift, mm·s^{-1}, with respect to an R.T. $BaSnO_3$ absorption spectrum. [b] Quadrupole splitting, mm·s^{-1}. [c] Full width at half height of the resonant peaks, mm·s^{-1}, average. [d] Integrations are difficult owing to an adjacent solvent signal. [e] Fully covered by a solvent signal. [f] Azomethine protons are probably included.

(N.E.N.), operating at constant acceleration, triangular waveform. An Elscint (Haifa) function generator, driving unit and velocity transducer were employed, connected to a Laben (Milano) 400 channel analyzer. Nuclear equipment was from Elscint, including a Ge—Li solid state detector. Velocity calibration was effected by iron spectra taken with ^{57}Co sources (N.E.N.). Data output on a teletype were reduced by an appropriate computer fitting program based on Lorentzian absorption curves. Other details were as reported elsewhere [4]. The Mössbauer parameters are reported in Table 1, and the quality of the spectra is illustrated in Fig. 1a and b.

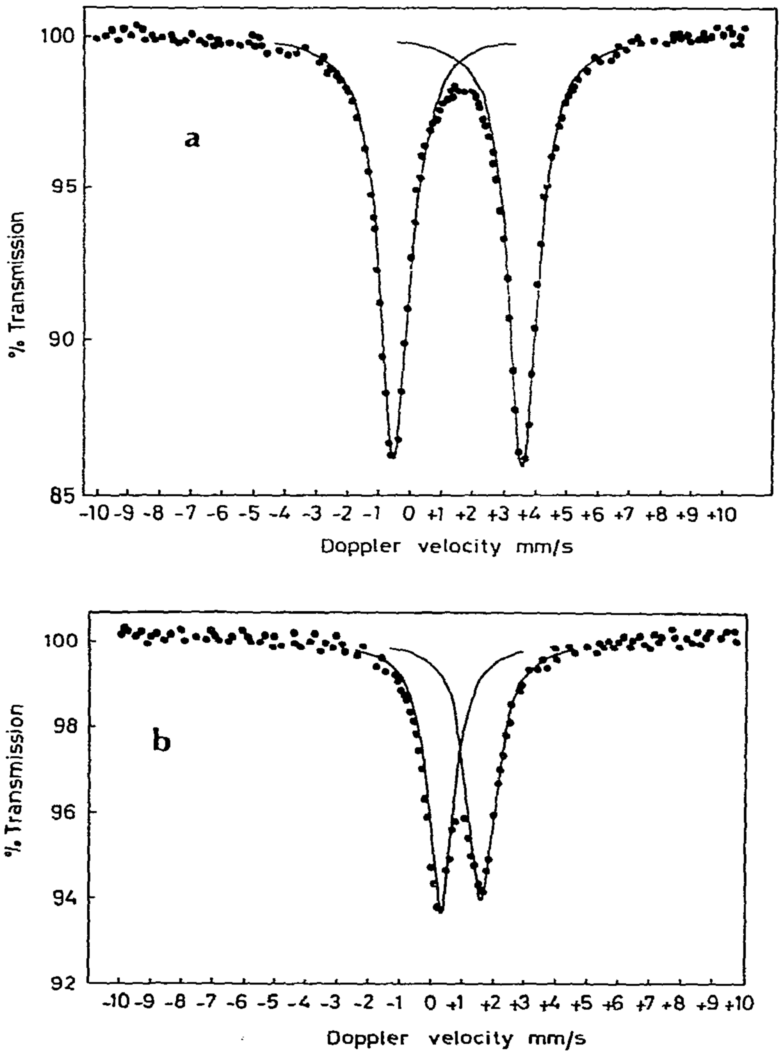

Fig. 1. The Mössbauer spectra of $Me_2SnCl_2NiSalen$ (a) and $PhSnCl_3NiSalen$ (b) at liquid N_2 temperature. Solid curves are computed Lorentzians.

Magnetic data were measured at room temperature by the Gouy method. The infrared spectra were recorded with Nujol mulls between CsI plates on a Perkin—Elmer model 457 spectrometer in the 4000—250 cm^{-1} region. Far IR data (350—80 cm^{-1}) were collected with a Beckman IR 11 instrument on Nujol mulls between polyethylene windows. Some relevant absorptions are listed in Table 2; assignments are made in accord with the literature [7, 8, 11—19]. The electronic spectra in the solid state (diffuse reflectance, blank MgO) and in CH_3CN solution (concentration range 5×10^{-5} to 1.7×10^{-4} M, using 1 cm optical path cells), were recorded with a Beckman DK-2A spectrophotometer and related equipment. The solid state spectra of NiSalen and its R_nSnCl_{4-n} adducts practically coincide (maxima around 400—415 nm, shoulders at 450 and 550 nm), and the same holds for CH_3CN solutions [λ 385 nm (sh), log a = 3.59—3.65; maxima at 405 nm, log a = 3.81—3.87; λ 440 nm (sh), log a = 3.49—3.56; a = absorptivity in $M^{-1} \cdot cm^2$, average]. Beer's law is obeyed (in solution) at the wavelengths of absorption maxima and shoulders (except for the $PhSnCl_3$ adduct, whose spectrum changes slowly with time); a plot of optical density vs. concentration falls on the same straight line for all adducts. PMR spectra were recorded with saturated DMSO-d_6 solutions, with TMS as internal standard, at room temperature, on a Jeol C 60 spectrometer operating at 60 MHz. Results are in Table 1. The assignment of signals is consistent with literature data [9, 20].

Discussion

Coordination to Sn^{IV} by NiSalen through its oxygen atoms is indicated by the shift of ν(C—O) in the solid adducts with respect to the corresponding frequency observed in free NiSalen [7, 8] (Table 2). The fact that our adducts are diamagnetic, and the coincidence of the solid state electronic spectra of the free and the coordinated ligand (see Experimental section), indicate that the coordinated NiSalen maintains its square planar configuration [7, 8].

The Mössbauer parameters of R_2SnCl_2 NiSalen (Table 1) are fully consistent with a *trans*-R_2 octahedral configuration. The latter structure implies isomer shifts [21], δ, greater than 1.20 $mm \cdot s^{-1}$ [22], and quadrupole splittings [21], ΔE, around 4 $mm \cdot s^{-1}$ [22—25]. It follows that the two chlorine atoms covalently bonded to tin(IV) must be in *cis*-positions, which is fully consistent with the occurrence of two IR active $\nu(SnCl_2)$ bands in Me_2SnCl_2NiSalen (Table 2). In this adduct, distortion from the ideal geometry is suggested by the IR absorption at 535 cm^{-1}, the intensity of which indicates that it arises from the $\nu_s(SnC_2)$ mode together with the 520 cm^{-1} free ligand band (Table 2). This implies that the CSnC skeleton is bent in Me_2SnCl_2 NiSalen, and perhaps also in the analogous Ph_2Sn^{IV} derivative. The ideal structure (I), Fig. 2, is assumed to hold for R_2SnCl_2 NiSalen; the non-coplanarity of Ni^{II}- and Sn^{IV}-containing planes reflects the symmetry (tetrahedral ?) of the electronic pairs of three-coordinated NiSalen oxygen atoms [7, 8].

The Mössbauer parameters of $RSnCl_3$ NiSalen (Table 1) are consistent with bonding of the ligand to Sn^{IV}, but, as generally observed for RSn^{IV} derivatives, do not give unequivocal information on coordination number and structure [26]. On the other hand, the fact that the parameters agree with those for octa-

TABLE 2

INFRARED ABSORPTION BANDS IN THE DOUBLE BOND AND 600—80 cm^{-1} REGIONS

NiSalen	NiSalen adducts of				Assignments
	Me_2SnCl_2	Ph_2SnCl_2	$MeSnCl_3$	$PhSnCl_3$	
	1650 vs				
1630 vs	1630 vs	1625 vs	1630 vs	1635 vs	ν(C=N)
1600 s	1600 vs	1600 vs	1600 vs	1600 vs	ν(C=C)
	1560 m	1575 (sh)			
1540 s	1550 s	1550 s	1560 m	1560 m	ν(C—O)
595 m	600 m	600 m	610 m	610 m	
	575 m				$\nu_{as}(SnC_2)$
	565 (sh)				
			572 m		ν(SnC)
550 vvw	550 vvw	560 w	540 m	575 w	
	535 ms				lig[+$\nu_s(SnC_2)$?]
520 m		530 m	520 m	540 m	
485 mw	495 vvw				
467 s	465 s	470 s	473 vs	470 s	
		455 s		445 s	ν(Ph)
430 ms	435 m	440 m	445 m	430 (sh)	
405 s	403 s	405 s	400 s	405 s	
385 vvw	387 w	383 w	380 vvw	385 (sh)	
365 m	365 m	365 m	365 m	365 ms	
355 (sh)	350 w				
330 vw	330 vw	335 vw			
	292 s		313 s	317 s	$\nu_{as}(SnCl_n)$
	256 s		293 s	292 s	$\nu_s(SnCl_n)$
		282 vs (br)			$\nu_{as}(SnCl_2)$ +
		276 (sh)			$\nu_s(SnCl_2)$ +
		263 (sh)			$\nu_{as}(SnPh_2)$
252 vw	250 (sh)		246 w		
				250 mw	lig.+ν(SnPh)
234 vvw				230 w	
		232 vs			$\nu_s(SnPh_2)$
	197 w	200 w		208 w	
	176 (sh)	186 w	180 vw	188 vw	
	166 vs				$\delta(SnCl_2) + \delta(SnC_2)$
			158 m [a]	168 w [a]	$\delta(SnCl_3)$ + lig.
			135 mw [a]	142 m [a]	
		142 m			$\delta(SnCl_2) + \delta(SnC_2)$ + lig.
143 w	140 mw				
	129 (sh)				δ(SnCCl)?
108 w	110 vw	119 vvw	112 (sh)	120 (sh)	
	95 w	108 (sh)			

[a] Limiting peaks of a medium, broad band.

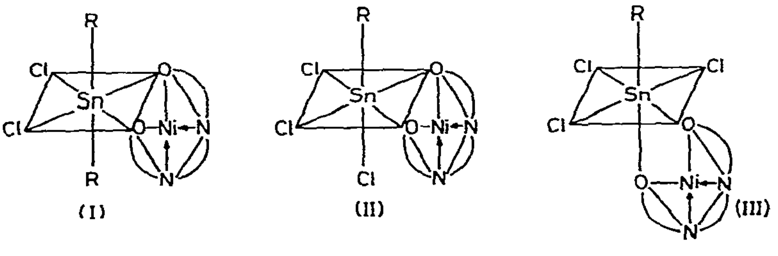

Fig. 2. Structures of R_nSnCl_{4-n}NiSalen adducts.

hedral $RSnCl_3 \cdot 2L$ (L being O or N donor atoms) [26], and by analogy with the behaviour as a bidentate ligand shown by NiSalen in its adducts with R_2SnCl_2, the probable structures (II) or (III) (Fig. 2), seem reasonable. According to group theory predictions, both *fac*- and *mer*-Cl_3 arrangements in (II) and (III) would give rise to three bands in the IR, so no choice between (II) and (III) can be made on the basis of the Sn—Cl vibrations. There is no doubt the two bands at 313—317 and 293—292 cm^{-1} are due to $\nu(SnCl_3)$ vibrations (Table 2). The failure to identify a third Sn—Cl band may be accounted for by the fact that Sn—Cl vibrations are often degenerate [13, 16, 18, 19].

The solution data for our adducts suggest that the parent compounds are formed in CH_3CN and DMSO, apparently in a complete dissociation. This is demonstrated by the electronic spectra (common absorption bands and absorptivities, as well as the linear plots of optical density vs. concentration for all adducts and free NiSalen, see Experimental), which clearly show the presence in solution of uncomplexed NiSalen, and also by the PMR spectra (Table 1), which essentially consist of the superposition of the spectra of free NiSalen and organotin halide.

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