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SHORT COMMUNICATIONS

SYNTHESIS AND INFRARED STUDY OF SOME PHENYLSULFONATO ADDUCTS.AN EXAMPLE OF C-S BOND CLEAVAGE

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ABSTRACT. $SnBu_2Cl_2.2L$, $2SnMe_2Cl_2.3L$, $2H_gCl_2.3L$ and $MnCl_2.3L.2H_2O$ were synthesized ($L = PhSO_3Me_4N$); the structures proposed on the basis of their infrared spectra are discrete, the phenylsulfonate acting as a monodentate or a bidentate ligand. A particular behaviour of $PhSO_3^-$ acting as SO_3^{-2} in the presence of $SbCl_3$ has been established; in the complex obtained $[2SbCl_3.SO_3(Me_4N)_2]$, the sulfite acts as a bidentate ligand.

INTRODUCTION

Complexes and derivatives containing substituted anions such as FSO_3^- (1-4), $C_nH_{2n+1}SO_3^-$ (5,6), $p\text{-}CH_3C_6H_4SO_3^-$ (7), $CF_3SO_3^-$ (8) and $SO_3C_5H_4N^-$ (9) have been reported. In a recent study, Hathaway (10) reported the main results obtained on oxoanions ligands. Studies on SO_4^{2-} acting as a polydentate ligand have been carried out in our laboratory by Sall (11). The absence of study on $PhSO_3^-$ acting as ligand led us to synthezise new phenylsulfonato adducts, the structures of which are suggested on the basis of their infrared spectra.

EXPERIMENTAL

All reagents were obtained from Merck Co. and used without further purification. Elemental analysis were performed by the "service central d'analyses" CNRS Vernaison, France. Infrared spectra were scanned as nujol mulls on a PE 580 spectrophotometer, using CsI plates.

The salt $PhSO_3Me_4N.H_2O$ (abbreviated as L hereafter) was obtained by mixing stoichiometric amounts of $PhSO_3H$ and a 10% water solution of Me_4NOH. The solution was stirred overnight, then the water was removed under vacuum at 50°C. The resulting powder was recrystallized from absolute ethanol.

-$SnBu_2Cl_2.2L$ (A), $2SnMe_2Cl_2.3L$ (B), $2HgCl_2.3L$ (C): The solutions obtained on mixing ethanolic solutions of the metal chloride and L in the ratio 2:3 gave, after slow evaporation, colourless crystals which were washed with acetone and dried under vacuum.

-$MnCl_2.3L.2H_2O$ (D): Ethanolic solutions of $MnCl_2$ and L were mixed in the ratio 1:2. Under slight heating a white precipitate was obtained, filtered off, washed with ethanol and dried under vacuum.

-$2SbCl_3.SO_3(Me_4N)_2$(E): The mixture of ethanolic solutions of $SbCl_3$ and L in the ratio 2:1 gave, a white precipitate while stirring.

RESULTS AND DISCUSSION

The infrared spectra of $PhSO_3Me_4N.H_2O$ and the titled adducts are summarized in Table 1.

Adducts A. The bands due to $\nu asSnC_2$ and $\nu sSnC_2$, often used in organotion IV compounds to choose between a linear or bent SnC_2 group (12) are obscured by the strong bands due to δSO_3; the presence of $\nu asSnCl_2$ at 330 cm^{-1} indicates a *cis* conformation for $SnBu_2Cl_2$. The suggested structure is an octahedron with monodentate phenylsulfonates occupying *trans* positions.

Table 1. Vibrational data of titled phenylsulfonato adduct (the phenyl and methyl bands are omitted).

[illegible]	A	B	C	D	Assignments	E	Assignments
				1670 w	νH_2O		
1640 w				1645 w			
		1225 vs	1195 vs	1200 vs		1060 m	
1195 vs	1195 vs	1195 vs	1180 vs		$\nu as SO_3$	880 w	νSO_3
1180 sh		1160 vs	1155 vs	1145 s		840 s	
1125 vs	1125 vs	1120 vs	1125 vs	1130 s			
1035 vs	1035 vs	1035 vs	1035 vs	1035 s	$\nu s SO_3$		
765 vs	765 vs	765 vs	765 vs	765 s	$\nu C-S$		
		755 m		755 m			
610 s	610 vs	610 vs	610 vs	610 vs		620 m	
565 s	565 vs	560 vs	565 vs	570 s	νSO_3	550 vs	δSO_3
550 m	550 vs		550 m	550 m		380 w	
		580 m			$\nu as SnC_2$		
		520 w			$\nu s SnC_2$		
480 w	480 w	480 w	480 w	480			
370 w	370 m	370 sh	370 sh	370	ρSO_3		
320 w	320 sh	315 sh	315 w	320			
305 w	305 sh		305 w				
				385	ρH_2O		
				345			
	330 s	290 sh	360 m	280	$\nu M Cl_2$	270 vsb	$\nu Sb Cl$
	275 m	280 s					
	230 w	230 w	230 w	245 w	$\nu M-O$		
				220 w			

vs = very strong; w = weak; s = strong; b = broad; m = medium; sh = should M = Sn, Hg, Mn.

Adduct B and C. The activity of both $\nu asSnC_2$ and $\nu sSnC_2$ (at 580 and 520 cm^{-1}) reveals a bent SnC_2 group ($SnMe_2Cl_2$ has a *cis* conformation). Assuming an octahedral environment for the tin atom as in A, we suggest a discrete structure (Fig.1) containing monodentate and bridged bidentate phenylsulfonates as $pCH_3C_6H_4SO_3$ in its Pt^{II} complexes (7).

In C, $SnMe_2Cl_2$ is replaced by $HgCl_2$; νSO_3 splits into five bands as in B, which suggests a similar structure, the environment of the Hg atom being tetrahedral.

Adduct D. The IR spectrum of D indicates two types of water molecules (two bands due to δH_2O). We can consider them both non-metal bonded and crystallographically different, or one of them metal-bonded and the other non metal-bonded. In the first case, the environment of the Mn atom is a trigonal bipyramid while in the second case an octahedron is obtained. The existence of the two νMnO values can be interpreted in terms of Mn - O apical and Mn - O equatorial distances in the trigonal bipyramid or in terms of Mn - OSO_2Ph and Mn - OH_2 distances in the octahedron.

Adduct E. In the presence of $SbCl_3$, $PhSO_3^-$ has a particular behaviour, turning into a sulfite by C-S bond cleavage. The splitting of νSO_3^- into three bands is consistent with Cs symmetry of the anion. $\nu SbCl_3$ localized at 270 cm^{-1}, obscures νSbO (localized at 245 cm^{-1} in Sb $(SeO_4)_2$ Me_4N (13)). The suggested structure is discrete with a bidentate bridging sulfite.

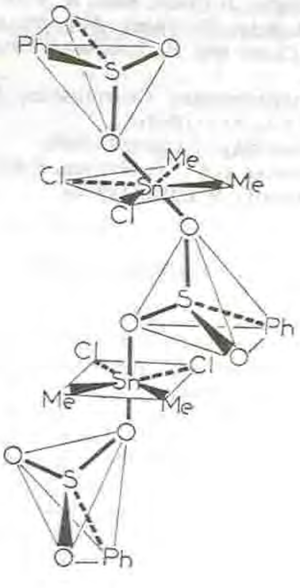

Fig. 1. Suggested structure for $SnMe_2Cl_2.3PhSO_3Me_4N$.

CONCLUSION

All the suggested structures for titled phenylsufonate adducts are discrete, the anion behaving as monodentate or bridging bidentate, while SO_4^{2-} behaves as polydentate (11) and often gives infinite type structures. In the presence of $SbCl_3$, $PhSO_3^-$ reacts as SO_3 , C-S bond cleavage ocuring.

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