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Zinc(II) complexes of sulfinamides—II. t-Butyl *N*-(hydroxyphenyl) and t-butyl *N*-(*o*-aminophenyl) sulfinamoyl acetates

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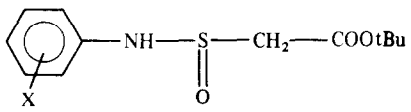
Abstract—The $ZnBr_2$ complexes of the four title sulfinamoylesters were formed and investigated by NMR and i r techniques The stoichiometry of the complexes greatly depends on the position of the amino or hydroxyl substituents on the aromatic ring Nevertheless, the occurrence of a tetracoordinated zinc atom is suggested for all the complexes

1 INTRODUCTION

In our preceding paper [1] the complexation with $ZnBr_2$ and $ZnCl_2$ of t-butyl *N*-phenyl sulfinamoylacetate **V** and other related compounds was examined A stoichiometry of 2L Zn(II) and a tetrahedral arrangement around the zinc atom were found

The $ZnBr_2$ complexes of the four phenyl substituted ligands **I–IV** are now studied, the slightly soluble $ZnCl_2$ complexes are not detailed herein



X = *o* – NH_2 **I**
o – OH **II**
m – OH **III**
p – OH **IV**
H **V**

These ligands (**I–IV**) possess in each case a new potential coordinating site on the phenyl ring and various Zn(II) complexes can be expected

Such compounds, especially **I** and **II**, are strong inactivators of coniferyl alcohol dehydrogenase, a zinc-containing metalloenzyme [2], and this complexation study was initiated to model roughly the enzymatic site, as previously done by JAGODZINSKI and PETITCOLAS [3] for horse liver alcohol dehydrogenase

2 EXPERIMENTAL

2 1 *Synthesis of sulfinamoylesters*

t-Butyl bromoacetate (69 mmol) and zinc chips (77 mmol) activated by iodine crystal were refluxed in dimethoxyethane (70 cm^3) After 1/2 h heating, the reaction mixture turned cloudy On refluxing 4 h more the bromozincic derivative yielded up to 90% Then, the reaction medium was cooled to 0°C and the appropriate sulfinylamine (30 mmol) in solution in dimethoxymethane (50 cm^3) was introduced dropwise under magnetic stirring

The mixture was stirred at 0°C 1/2 h more Then, it was hydrolysed at the same temperature with 20% aqueous ammonium chloride and extracted with ether Ether was removed and the sulfinamoyl acetates obtained in 50–60% yield after successive recrystallization from ether petroleum ether (50 50)

t-Butyl N-(O-*aminophenyl*) *sulfinamoylacetate* **I** (*m p* 87°C) ^{1}H NMR (ppm, $CDCl_3$) = 7 2–7 7 (m, 5H), 3 78 (s, 2H), 3 59 (s, 2H), 1 52 (s, 9H)

t-Butyl N-(O-*hydroxyphenyl*) *sulfinamoylacetate* **II** (*m p* 118°C) ^{1}H NMR (ppm, $CDCl_3$) 7 2–6 8 (m, 5H), 6 5 (s, 1H), 3 8 (s, 2H), 1 48 (s, 9H)

t-Butyl N-(m-*hydroxyphenyl*) *sulfinamoyl acetate* **III** (*m p* 100°C) ^{1}H NMR (ppm, $CDCl_3$) 7 8–7 9 (m, 2H), 7 4–6 6 (m, 4H), 3 95 (s, 2H), 1 45 (s, 9H)

t-Butyl N-(p-*hydroxyphenyl*) *sulfinamoylacetate* **IV** (*m p* 136°C) ^{1}H NMR (ppm, $CDCl_3$) 8 0 (s, 1H), 7 0–6 6 (m, 5H), 3 8 (s, 2H), 1 5 (s, 9H)

2 2 *Preparation of zinc complexes*

They were prepared as previously reported [1] Lower concentrations (0 01 M) and ultrasonic assistance are useful for the solubilization of compound **IV**

2 3 *Spectra*

^{1}H NMR spectra were performed on a Bruker WH90 for solutions in $CDCl_3$ with Me_4Si as internal reference Infrared spectra were recorded on Beckman IR9 and Perkin-Elmer 683 spectrometers in KBr pellets for solids and in 0 05 M $CHCl_3$ solution by using NaCl 0 5 mm cells in the 4000–400 cm^{-1} frequency range and polyethylene cells in the 600–200 cm^{-1} range

3 RESULTS AND DISCUSSION

3 1 *Stoichiometry of the complexes*

As previously reported [1] the break point of the curve $\Delta\delta_i = f(\rho[Zn]/[L])$ for CH_2 and NH protons gives information about the stoichiometry of the complex (see Fig 1 for the CH_2 proton) The plot for the unsubstituted *N*-phenyl compound **V** is drawn as a comparative model Thus, the following stoichiometries are obtained

Compound	I	II	III	IV	V
Zn L	1 1	1 1	2 1	1 2	1 2

Compounds **I** and **II** are, respectively, substituted by *ortho* NH_2 or OH groups showing 1 1 stoichiometries

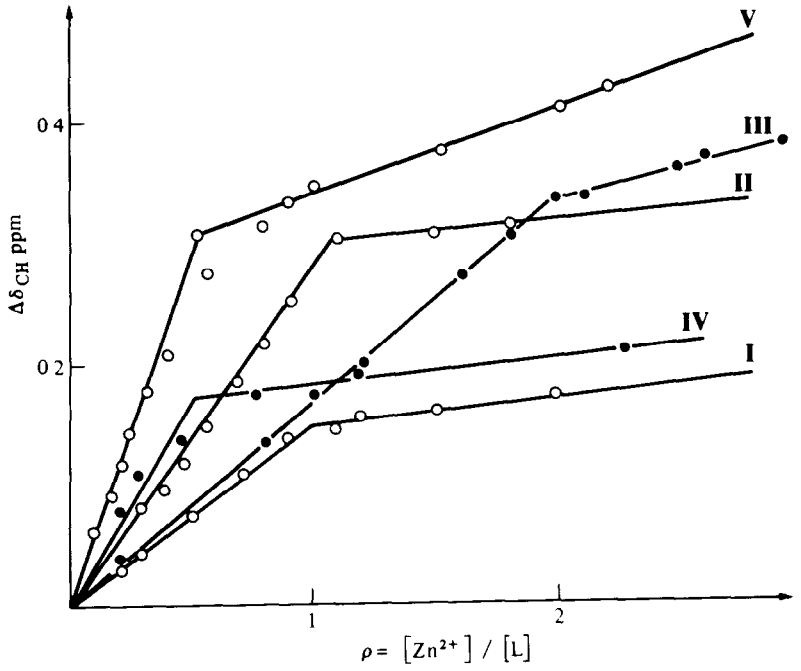
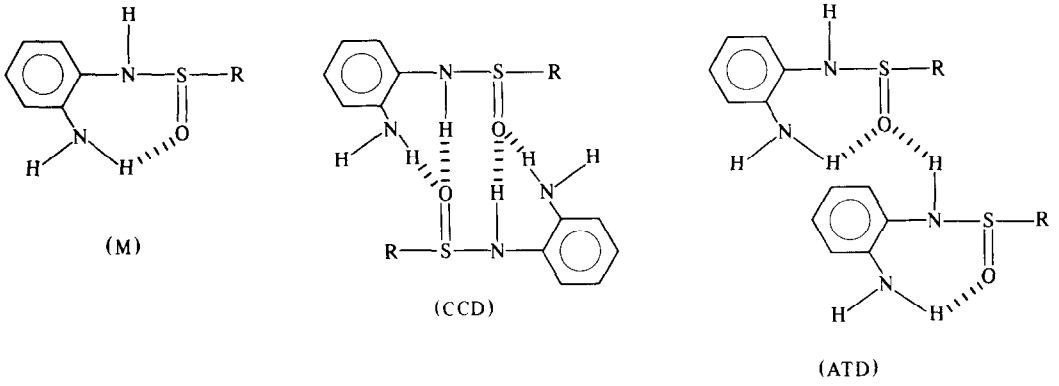


Fig 1 ^{1}H Chemical shift variation ($\Delta\delta_{CH}$) as a function of $\rho = [Zn^{2+}]/[L]$ in $CDCl_3$

Table 1 lists the slopes of the straight lines corresponding to the first part of the curves at low ρ values They are informative about the position of the protons studied with respect to the complexing site Thus, the ratio of the slope for CH_2 and NH protons is 1 5 for V,1 0 for III and 0 4 for I and II By comparison with the unsubstituted reference compound V the OH and NH_2 *ortho* substituents increase the shift effect on the NH sulfinamoyl proton indicating its greater proximity to the metal This effect is less pronounced for the *meta* substitution

amide group The cyclic *cis* (CCD) and acyclic *trans* (ATD) dimeric association patterns suggested for the *N*-phenyl compound V [1] are valuable for I too But the additional intra- (or inter-) molecular chelation NH_2 O=S is also to be considered in monomeric (M) or dimeric forms (R = $CH_2COOtBu$)



3 2 *Infrared study* (*Table* 2)

t-Butyl N-(o-*aminophenyl*) *sulfinamoyl acetate* I Four ν(NH) bands are observed for the ligand in 0 05 M $CHCl_3$ at 3450 and 3350 cm^{-1} and at 3295 and 3260 cm^{-1} The two higher frequency bands can be assigned to the amine group and the other two to the

The 3450 and 3350 cm^{-1} frequencies support the participation of the amino group in hydrogen bonding For instance, *p*-bromoaniline associated with butyl-oxide [4] presents two ν(NH) with the NH group *anti* and *syn*, respectively, at 3473 and 3364 cm^{-1} for the 1 1 complex and 3442 and 3359 cm^{-1} for the 1 2 complex, DMSO gives only the 1 2 complex Similarly, (2-aminophenyl) methyl sulphone intramolecularly hydrogen bonded shows two ν(NH) bands at 3473 and 3367 cm^{-1} while (NH) bands for the *para* derivative are found at 3500 and 3408 cm^{-1} [5]

When $ZnBr_2$ is added, the ν(C=O) and ν(C–O)

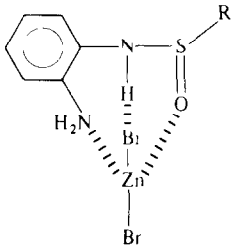
Table 1 Slopes of the straight lines $\Delta\delta_{CH} = f(\rho)$ at low ρ values

	Compound				
	I	II	III	IV	V
CH_2 slope	0 16	0 25	0 17	0 30	0 58
NH slope	0 42	0 64	0 17	—	0 39

bands remain unchanged, but important frequency decreases are observed for (i) the NH stretching bands which now lie in the 3220 cm^{-1} region (broad band with two shoulders at 3310 and 3140 cm^{-1}), a ν(NH) band was found [6] at the same frequency (3220 cm^{-1}) for the p-NH_2-$C_6H_4COC_6H_5$ $ZnBr_2$ complex, (ii) the δ(NH) deformation band ($\Delta\nu$ = 45 cm^{-1}) but only 25 cm^{-1} in the above mentioned amino complex, (iii) the ν(S=O) vibration ($\Delta\nu$ = 70 cm^{-1})

Moreover, two new bands are observed at 475 and 275 cm^{-1} The band at 275 cm^{-1} was considered [1] as a possible ν(Zn–O) and/or ν(Zn–Br) vibration, while the band at 475 cm^{-1} could be assigned to the ν(Zn–N) vibration The frequency of this latter type of vibration greatly varies in the far i r region depending on the structure of the complexes In particular ν(Zn–N) was found at 540 cm^{-1} for the tetrahedral zinc complex with 2-ethylamino 1,3,4-thiadiazole [7], the frequency decreases from tetracoordinated to hexacoordinated Zn(II) as, for instance, in the cases of ammine complexes ν(ZnN) 414 cm^{-1} for $Zn(NH_3)_2Br_2$ but only 294 cm^{-1} for $Zn(NH_3)_6Br_2$ [8]

These i r results and the 1 1 stoichiometry determined by ^{1}H NMR spectroscopy lead us to suggest the following tetracoordinated structure (C) for the $ZnBr_2$ I complex (R = CH_2 COOtBu)



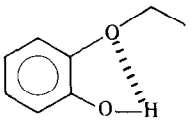
t-Butyl N-(o-*hydroxyphenyl*) *sulfinamoyl acetate* **II** In 0 05 M $CHCl_3$ compound **II** shows a weak free OH stretching vibration at 3600 cm^{-1}, polymeric OH and bonded NH bands at 3250–3380 cm^{-1} On diluting up to 0 005 M the intensity of the 3250–3300 cm^{-1} band decreases while those of the 3600 and 3380 cm^{-1} bands increase

The frequency of the intramolecularly bonded OH vibrator greatly depends [9] on the nature of the proton acceptor and its position inside the molecule

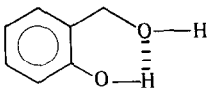
Table 2 Principal i r bands (cm^{-1}) of ligands and their zinc complexes in $CHCl_3$ 0 05 M

	I		II		III		IV	
	L	$ZnBr_2$ L	L	$ZnBr_2$ L	L	$2ZnBr_2$ L	L	$ZnBr_2$ 2L*
ν(OH)			3600 w	3510 m	3600 w	3515 s	3600 m	
			3375	3430 w				
				3380 w	3200 sh	3430 w		
	3450	3310 sh						
ν(NH)	3350							
amine		3220						
ν(NH)	3295		3300		3300 br		3300 br	
amide	3260 sh	3140 sh	3250	3250 br		3230 br		3250 br
ν(C=O)	1725 vs	1725 vs	1723 vs	1721 vs	1727 vs	1729 vs	1725 vs	1726 s
δ(NH)	1625 m	1580 br						
ν(C–N)	1158 s	1155 s	1155 vs	1155	1160	1155	1160 s	1160 s
ν(C–O)	1123 m	1120 m	1125 s	1123	1130	1131		
ν(S=O)	1078 vs		1080 vs		1070 vs		1075 s	
ν(S=O Zn)		1008 s		1008 vs		1008 s		995
ν(S–N)	890 m	920 m	890 w	918 w	965 w	975 w	†	†
ν(Zn–N)		475 m						
Other bands	530 w	540 w		542 w		550 w		
			497 w	532 br	530 w	530 w	510 w	508 m
	462 m	462 w	470 sh	497 w				
		432 w	457 sh	457 m	458 w	460 w	463 w	
			435 s	431 w			430 w	
	390 w		382 w		380 w	380 w	378 w	390 w
	325 m	325 m	323 w	329 w	324 w	324 w	325 w	325 w
ν(Zn Br) or ν(Zn O)		275 m		268 m		265 m		260 m

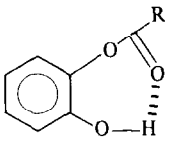
*0 01 M solution
†Very weak bands in this region



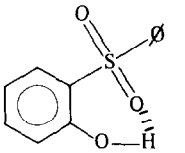
3555 cm^{-1}



3436 cm^{-1}



3380 cm^{-1}



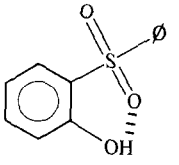
3212 cm^{-1}

A 3380 cm^{-1} value can be in agreement with a ν(OH) related to an OH O=S intramolecular bond and/or with a ν(free NH)

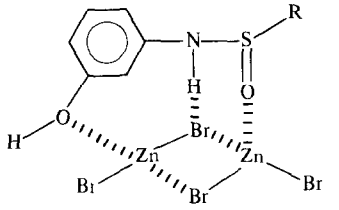
Different forms can be expected for this compound monomeric (M), dimeric (CCD) or (ATD) as for **I**, and polymerics

The ir spectrum of the $ZnBr_2$ complex shows an important lowering of frequency for ν(free OH) and ν(S=O), respectively, 90 and 72 cm^{-1} and the presence of a band at 268 cm^{-1} assigned to ZnO or (and) ZnBr These results and the 1 1 stoichiometry determined by ^{1}H NMR are in agreement with a tetracoordinated structure of the (C) type as previously reported for the sulfinamoylester **I**

t-Butyl N-(m-*hydroxyphenyl*) *sulfinamoyl acetate* **III** Some differences appear between ir spectra of compounds **II** and **III** Thus, in 0 005 $CDCl_3$ a very strong ν(free OH) band is observed at 3600 cm^{-1} and broad bands around 3200 and 3300 cm^{-1} with two shoulders at 3280 and 3320 cm^{-1} These two last frequencies are similar to those assigned to ν(bonded NH) [1] for the unsubstituted compound **V** Consequently, in 0 005 M $CDCl_3$ solution, dimeric forms are expected However, in 0 05 M $CHCl_3$ solution the intensity of the free OH band is very weakened, while that of the broad band at 3200 cm^{-1} is reinforced Thus, S=O HO and S=O HN associations occur In particular, the first type of chelation can be related to the 3200 cm^{-1} frequency, a similar value (3212 cm^{-1}) being found for [9]



The ir spectrum of the $ZnBr_2$ **III** complex shows the following peculiarities (i) no perturbation of ν(C=O) and ν(C–O), (ii) an important lowering of frequency for ν(OH), ν(bonded NH) and ν(S=O), respectively, 85, 70 and 62 cm^{-1}, (iii) a new band in the far ir region at 265 cm^{-1} assigned to ν(ZnO) and/or ν(ZnBr), (iv) a 2 1 $ZnBr_2$ L stoichiometry These facts can be explained by a tetracoordinated zinc(II) provided that $ZnBr_2$ adopts a dimeric form as in the following scheme (R = $CH_2COOtBu$)



t-Butyl β-(p-*hydroxyphenyl*) *sulfinamoylacetate* **IV** This compound is slightly soluble in $CHCl_3$ so that a free OH is observed, the broad ν(NH) band at 3300 cm^{-1} reveals dimeric association as for compound **V** [1] Zn(II) complexes of **IV** and **V** [1] are also comparable For instance, the following facts can be noticed (i) the same 2L $ZnBr_2$ stoichiometry, (ii) no perturbation for ν(C=O), (iii) a large decrease for ν(NH) and ν(S=O), respectively, 50 and 80 cm^{-1} Although the solubilities of the complexes are different, the occurrence of a *para* hydroxyl group greatly increases the insolubility and similar tetracoordinated structures can be suggested for the two complexes

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