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INVESTIGATIONS ON ORGANOZINC COMPOUNDS
XII*. COORDINATION CHEMISTRY OF ORGANOZINC COMPOUNDS RZnX: ORGANOZINC COMPOUNDS OF THE TYPE EtZnNPhCSZ**

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SUMMARY

The coordination chemistry of the organozinc–nitrogen compounds EtZnNPhCSZ ($Z=H$, Me, OMe, SMe and NPh_2) has been studied. Whereas the benzene-insoluble EtZnNPhCSH appears to be a coordination polymer, all the other compounds occur as dimers in benzene solution. A structure with four-coordinate zinc and three-coordinate sulphur and nitrogen atoms seems plausible for these compounds in solution. The occurrence of thiocarbonyl coordination is supported by the PMR data. The compound with $Z=SMe$ decomposes into EtZnSMe and PhNCS above 15°. With pyridine, monomeric 1/1 complexes are formed ($Z=Me$, OMe, SMe). The 1/1 Py complex of EtZnNPhCSH is more likely dimeric. $EtZnNPhCSNPh_2$ forms a 1/2 complex with Py. All the compounds readily form monomeric 1/1 complexes with *N,N,N′,N′*-tetramethylethylenediamine (TMED) some of which may contain five-coordinate zinc.

INTRODUCTION

As shown in the preceding paper in this series[1], the nature of the group Z has a profound influence on the coordination behaviour of organozinc–nitrogen compounds EtZnNPhCOZ. Whereas the zinc atoms in $RZnNPh_2$-dimer[2] and $RZnN{=}CPh_2$-dimer[3] are necessarily three-coordinate, replacement of a Ph group in $EtZnNPh_2$ by the group COZ causes the zinc atom to increase its coordination number to four by further coordination involving the COZ group. Compounds RZnNPhCOZ have been found to occur in solution as trimers ($Z=OMe$ and NPh_2), as tetramers ($Z=Me$[1], Et[4] and Ph[4]), or as higher associates ($Z=H$[1]). Whereas in the presence of pyridine or TMED the carbamate ($Z=OMe$) and urea ($Z=NPh_2$) derivative readily break down with the formation of monomeric pyridine (1/2) and TMED (1/1) complexes, the amide derivatives ($Z=H$, Me) yield binuclear Py and

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* For part XI see ref. 1.

** Part of this research has been communicated at the XIth Intern. Conf. on Coordination Chemistry, Haifa, September 1968.

TMED complexes which as appears from spectral evidence contain a bridging N=C=O group[1,4].

Earlier studies by one of us showed that in organotin chemistry substitution of a carbonyl by a thiocarbonyl group has structural implications[5,6]. *E.g.* addition of Et_3SnH or Et_3SnOMe to PhNCX (X=O, S) yields compounds containing a Sn–N bond, if X=O, and a Sn–S bond, if X=S (*e.g.* $Et_3SnNPhCOH$ and $Et_3SnSCH{=}NPh$[5]). As part of our general study of organozinc coordination chemistry[7] we have extended our study of compounds EtZnNPhCOZ to the thiocarbonyl analogs EtZnNPhCSZ (Z=H, Me, OMe, SMe, NPh_2). Moreover, we wished to study the nature of the products formed by the addition of organozinc alkoxides and amides to isothiocyanates[8].

TABLE 1

STOECHIOMETRY, MELTING POINTS, ANALYTICAL DATA AND MOLECULAR WEIGHTS OF ORGANOZINC–NITROGEN COMPOUNDS

No.	Compound	M.p. (°C)	Zn (%) found (calcd.)	N (%) found (calcd.)	Molecular weight[c]	
					found (calcd.)	concn. (wt.-%)
(Ia)	$(EtZnNPhCSMe)_2$	105	27.13 (26.76)	5.59 (5.73)	495 (489.2)	3.69
(Ib)	$EtZnNPhCSMe \cdot Py$	70	21.17 (20.20)	7.23 (8.65)	310 (325.5)	4.89
(Ic)	$EtZnNPhCSMe \cdot TMED$	60	18.84 (18.12)	11.64 (11.49)		
(IIa)	$(EtZnNPhCSH)_n$	101	28.06 (28.37)	6.14 (6.09)	[b]	
(IIb)	$(EtZnNPhCSH)_2 \cdot 2\ Py$	[a]	21.31 (21.12)	8.47 (9.05)	443 (619.4)	2.88
(IIc)	$EtZnNPhCSH \cdot TMED$	[a]	17.35 (18.85)	9.04 (9.70)		
(IIIa)	$(EtZnNPhCSOMe)_2$	91	25.36 (25.06)	5.80 (5.38)	520 (521.2)	3.95
(IIIb)	$EtZnNPhCSOMe \cdot Py$	[d]	19.34 (19.24)	7.59 (8.24)	350 (339.7)	1.25
(IIIc)	$EtZnNPhCSOMe \cdot TMED$	55	17.71 (17.35)	11.70 (11.13)		
(IVa)	$(EtZnNPhCSSMe)_2$	[e]			553[f] (553.2)	4.20
(IVb)	$EtZnNPhCSSMe \cdot Py$	[e]			340[f] (353.5)	1.42
(IVc)	$EtZnNPhCSSMe \cdot TMED$	[e]			359[f] (392.8)	1.29
(Va)	$(EtZnNPhCSNPh_2)_2$	226	16.03 (16.44)	6.83 (7.03)	800 (795.8)	2.83
(Vb)	$EtZnNPhCSNPh_2 \cdot 2\ Py$	67	11.68 (11.74)	9.81 (10.07)		
(Vc)	$EtZnNPhCSNPh_2 \cdot TMED$	130	12.13 (12.71)	10.07 (10.89)		

[a] Glass; does not show a well-defined melting point. [b] Insoluble in benzene. [c] Molecular weights were determined by ebulliometry in benzene, unless otherwise stated. Concentration dependency was observed only for compound (IIb). [d] Oil; could not be made to crystallize. [e] Not isolated; made *in situ* for molecular weight determinations. [f] Cryometric determinations.

RESULTS AND DISCUSSION

The compounds EtZnNPhCSZ (Z=H, Me, OMe and SMe) have been prepared by the 1/1 reaction of Et_2Zn with the appropriate HNPhCSZ compound in dilute benzene. A second synthetic route to the thiocarbamate (Z=OMe) is the addition of EtZnOMe to PhNCS[8]. The compounds prepared by the two routes proved to be identical. The thiourea ($Z=NPh_2$) was prepared by the addition route ($EtZnNPh_2$+PhNCS[8]). All compounds are colourless, crystalline, air-sensitive solids, which, with the exception of the thioformanilide derivative (Z=H), are soluble in benzene, but insoluble in aliphatic hydrocarbons.

For each of these compounds the complex-forming behaviour towards pyridine (Py) and *N,N,N',N'*-tetramethylethylenediamine (TMED) has been investigated. The stoechiometry, melting point, molecular weight and analytical data for the various compounds and complexes isolated are given in Table 1.

*N-(Ethylzinc)thioacetanilide, EtZnNPhCSMe (Ia–d)**

In contrast with *N*-(ethylzinc)acetanilide, which is tetrameric[1], this compound is dimeric in benzene. Monomeric 1/1 complexes are formed upon reaction with Py (Ib) and TMED (Ic).

In view of the considerable coupling of vibrations in thioamides[9] (*i.e.* between C=S and C=N) IR spectroscopy has limited value in assigning structures to the compounds (I)–(VI).

PMR data of (Ia–c) are presented in Table 2. The thiocarbonyl group in thioanilides has a very strong anisotropy, *i.e.* a large deshielding effect on its environment. The anisotropy is much stronger than that of a carbonyl group. Accordingly, one would expect the occurrence of thiocarbonyl coordination to zinc to be reflected in the position of the PMR absorptions of the ethyl group bound to zinc, in particular those of the methylene protons. The appearance of $\delta(CH_2Zn)$ at unusually low field for (Ia–c) [*e.g.* $\delta(CH_2Zn)$ for (Ia): 0.81 ppm; for EtZnNPhCOMe: 0.42 ppm[1]] offers strong evidence for the presence of coordinated thiocarbonyl groups in these compounds. For the monomeric 1/1 Py complex (Ib) a structure with four-coordinate zinc seems plausible.

TABLE 2

PMR SPECTRAL DATA OF $(EtZnNPhCSMe)_2$ AND ITS COMPLEXES[a]

No.	Compound	$\delta(CH_2)$	$\delta(CH_3)$	$\delta(CSCH_3)$	$\delta(NCH_3)$	$\delta(NCH_2)$
	HNPhCSMe			2.18, 2.36[b]		
(Ia)	$(EtZnNPhCSMe)_2$	0.81	1.62	2.09		
(Ib)	EtZnNPhCSMe·Py	0.80	1.67	2.22		
(Ic)	EtZnNPhCSMe·TMED	0.44	[c]	2.29, 2.86	2.00	1.80

[a] All PMR spectra were recorded in benzene solution; δ values in ppm downfield fromTMS. [b] Due to rotational isomerism around the N–C bond[10]. [c] Could not be determined exactly, since the triplet appeared as a shoulder on the NCH_2 singlet.

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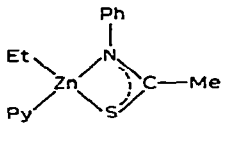
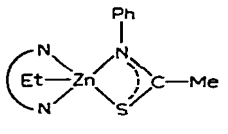
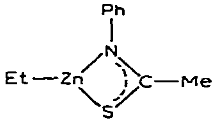
* Numbers correspond with those in Table 1.

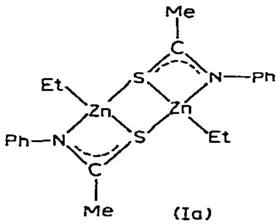

(Ib)


(Ic)

Since the TMED absorptions for (Ic) indicate the presence of a normal chelating ligand (*cf.* refs. 1 and 12) this complex might be five-coordinate. The presence of two bands attributable to the $CSCH_3$ protons points to the presence of non-equivalent methyl groups. Several conformations may be postulated for either a trigonal bipyramidal or a square pyramidal structure.

The behaviour of (Ia) towards Py and TMED strongly suggests that the dimer is built up from two units (A). A structure with four-coordinate zinc and three-coordinate sulphur and nitrogen atoms seems plausible:


(A)


(Ia)

The formation of two coordinate bonds by sulphur is not at all unusual. *E.g.* zinc diethyldithiocarbamate is a dimer in the solid state with five-coordinate zinc and two of the four sulphur atoms being three-coordinate[13].

The energy barrier for rotation around the N–C bond in *e.g.* dimethylthioformamide is about 8 kcal/mol higher than in dimethylformamide[14] indicating that the polar form $>\overset{+}{N}=\overset{|}{C}-X^{-}$ (X = O, S) contributes considerably more to the structure in thioamides than in amides. The resulting high electron density at the sulphur atom will make it a powerful electron donor, whereas the electron-donating capacity of the nitrogen atom will be accordingly smaller.

N-(Ethylzinc)thioformanilide, EtZnNPhCSH (IIa–c)

This compound is insoluble in non-coordinating solvents, but readily soluble in benzene in the presence of complexing ligands like Py or TMED, indicating that it is probably a coordination polymer.

TABLE 3

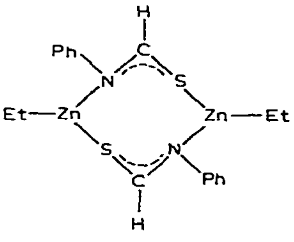
PMR SPECTRAL DATA OF COMPLEXES OF $(EtZnNPhCSH)_n$

No.	Compound	$\delta(CH_2)$	$\delta(CH_3)$	$\delta(CSH)$	$\delta(NCH_3)$	$\delta(NCH_2)$
	HNPhCSH			9.98, 10.12[a]		
(IIb)	$(EtZnNPhCSH)_2 \cdot 2$ Py	0.81	1.65	9.59		
(IIc)	EtZnNPhCSH·TMED	0.59	1.70	9.27	2.17	1.90

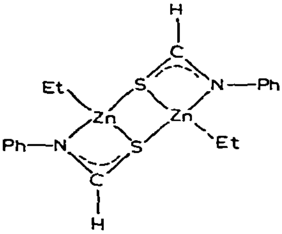
[a] Due to rotational isomerism around the N–C bond[11].

The Py complex (IIb) has 1/1 stoechiometry and its molecular weight shows concentration dependence in boiling benzene solution (see Table 1). The molecular weight determinations suggest that (Ib) is a dissociating dimeric complex. Similar to the thioacetanilide derivative, reaction of (IIa) with TMED affords a 1/1 complex (IIc). PMR data are presented in Table 3.

The unusually high value of $\delta(CH_2Zn)$ for (IIb) (0.81 ppm) and (IIc) (0.59 ppm) as compared with the corresponding complexes of *N*-(ethylzinc)formanilide (*i.e.* 0.26 ppm in the TMED complex[1]) suggest that the thiocarbonyl groups in (IIb) and (IIc) are coordinated. The coordination behaviour of $(EtZnNPhCSH)_n$ towards Py seems to indicate that the polymer is built up from dimeric sub-units as previously observed for $(EtZnNPhCOH)_n$[1]. These will be of type (A) rather than type (B), since B-type dimers would not be expected to coordinate further, whereas the A-type dimers do contain coordinately unsaturated zinc:



(A)



(B)

Polymeric (IIa) might then consist of dimer units A connected via Zn–S or Zn–N coordinate bonds.

The monomeric TMED complex (IIc) may be five-coordinate, since the PMR spectrum is in accord with the presence of a normal chelating TMED ligand (*cf.* refs. 1 and 12).

O-methyl N-(ethylzinc)thiocarbanilate, EtZnNPhCSOMe (III a–c)

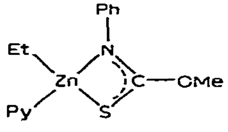
Contrary to EtZnNPhCOOMe which is trimeric[1], this compound is a dimer in benzene (no concentration dependence). Its coordination behaviour resembles that of $(EtZnNPhCSMe)_2$ in that both with Py (IIIb) and with TMED (IIIc) monomeric 1/1 complexes are formed. Relevant PMR data are given in Table 4.

TABLE 4

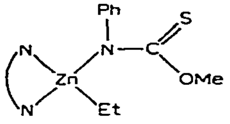
PMR SPECTRAL DATA OF $(EtZnNPhCSOMe)_2$ AND ITS COMPLEXES

No.	Compound	$\delta(CH_2)$	$\delta(CH_3)$	$\delta(OCH_3)$	$\delta(NCH_3)$	$\delta(NCH_2)$
	HNPhCSOMe			3.71		
(IIIa)	$(EtZnNPhCSOMe)_2$	0.89	1.60	3.19		
(IIIb)	EtZnNPhCSOMe·Py	0.90	1.75	3.82		
(IIIc)	EtZnNPhCSOMe·TMED	0.25	1.50	3.76	1.90	1.76

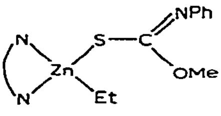
The low-field positions of $\delta(CH_2Zn)$ in both (IIIa) and the Py complex (IIIb) suggest thiocarbonyl coordination in these compounds. However, in the TMED complex (IIIc) $\delta(CH_2Zn)$ has a much lower value which might indicate that upon complexation with TMED the thiocarbonyl coordinate bonds are broken. The values of $\delta(CH_3N)$ and $\delta(CH_2N)$ are in accord with the presence of a chelating TMED ligand (*cf.* refs. 1 and 12). Although the structure of the Py complex (IIIb) seems unambiguous, a second structure containing a Zn–S rather than a Zn–N bond cannot be excluded for the TMED complex:



(IIIb)



(IIIc)



(IIId)

The UV spectrum of HNPhCSOMe shows an absorption at 275 nm which can be assigned to a n–π^* transition of the C=S group[15]. It is to be expected that coordination of the C=S group causes a hypsochromic shift of this band, since the non-bonding electron pairs of the sulphur are no longer freely available for excitation (*cf.* the effect of hydrogen bonding on the position of the n–π^* transition of carbonyl derivatives[16]). In fact, in the ethylzinc derivative (IIIa), the thiocarbonyl band has shifted to 260 nm. However, when this compound is complexed with TMED, the band shifts back to 275 nm, *i.e.* the position of the same band in HNPhCSOMe which has a free thiocarbonyl group. These results favour structure (IIIc) for the TMED complex.

A dimeric structure with three-coordinate sulphur atoms as proposed for (Ia) seems plausible for (IIIa). The weakness of the Zn–S coordinate bonds in this compound will be connected with the $-I$ inductive effect of the OMe group which is stronger than its mesomeric effect.

Methyl N-(ethylzinc)dithiocarbanilate, EtZnNPhCSSMe (IVa–c)

This compound like its carbonyl analogue[1] which decomposes above 5°, has limited thermal stability, decomposition occurring above 15° according to:

$$\text{EtZnNPhCSSMe} \rightarrow \text{EtZnSMe} + \text{PhNCS}$$

The characterization of the decomposition products was carried out as described for the carbonyl analogue[1]. The reaction of EtZnSMe with PhNCS in the presence of TMED is incomplete after 24 hours, whereas the same reaction with PhNCO is instantaneous:

$$\text{EtZnSMe} + \text{PhNCS} + \text{TMED} \rightarrow \text{EtZnNPhCSSMe}\cdot\text{TMED}$$

Compound (IVa), which proved to be sufficiently stable to allow cryometric determination of its molecular weight, was found to be dimeric in benzene (no concentration dependence). Monomeric 1/1 complexes are formed with Py (IVb) and

TABLE 5

PMR SPECTRAL DATA OF COMPLEXES OF $(EtZnNPhCSSMe)_2$

No.	Compound	$\delta(CH_2)$	$\delta(CH_3)$	$\delta(SCH_3)$	$\delta(NCH_3)$	$\delta(NCH_2)$
(IVb)	EtZnNPhCSSMe·Py	0.86	1.72	2.47		
(IVc)	EtZnNPhCSSMe·TMED	0.42	1.68	2.49	1.91	1.74
	EtZnSMe+PhNCS+TMED	0.39	1.60	2.41	1.91	1.74

TMED (IVc). This coordination behaviour is fully analogous to that of (Ia) and (IIIa). PMR data are shown in Table 5.

The large $\delta(CH_2Zn)$ value of the TMED complex indicates the presence of thiocarbonyl coordination. Apparently, in this compound the donating capacity of the thiocarbonyl group has not been weakened by the relatively small $-I$ inductive effect of the SMe group. For (IVa), a dimeric structure similar to that of (Ia) and (IIIa) is proposed.

N-(Ethylzinc)-N,N',N'-triphenylthiourea, $EtZnNPhCSNPh_2$ (Va–c)

This compound is a dimer in boiling benzene (no concentration dependence). Its coordination behaviour differs from that of (Ia), (IIIa) and (IVa) in that with Py a 1/2 complex $EtZnNPhCSNPh_2\cdot 2$ Py (Vb) is formed. Apparently the coordinate bonds in the molecule are very weak. With TMED a 1/1 complex (Vc) is formed. PMR data of (Va–c) are given in Table 6.

TABLE 6

PMR SPECTRAL DATA OF $(EtZnNPhCSNPh_2)_2$ AND ITS COMPLEXES[a]

No.	Compound	$\delta(CH_2)$	$\delta(CH_3)$	$\delta(NCH_3)$	$\delta(NCH_2)$
(Va)	$(EtZnNPhCSNPh_2)_2$	0.93	1.64		
(Vb)	$EtZnNPhCSNPh_2\cdot 2$ Py	0.87	1.72		
(Vc)	$EtZnNPhCSNPh_2\cdot$TMED	0.48	1.77	1.97[b]	1.97[b]

[a] Spectra are recorded at 70° because of limited solubility of (Va-c) in benzene. [b] Relatively broad band.

The extremely high $\delta(CH_2Zn)$ value (0.93 ppm) of $(EtZnNPhCSNPh_2)_2$—in fact the highest recorded for an ethylzinc compound—contrasts strongly with the excessively low $\delta(CH_2Zn)$ value (0.13 ppm) of $(EtZnNPhCONPh_2)_3$[1]. Although the difference will be mainly caused by the anisotropy of the thiocarbonyl group, environmental influences will also be involved. The high values of $\delta(CH_2Zn)$ in both the Py and the TMED complex suggest that thiocarbonyl coordination is retained and that these compounds, therefore, contain five-coordinate zinc. In the absence of further data a dimeric structure with three-coordinate sulphur, analogous to that of (Ia), is proposed for $(EtZnNPhCSNPh_2)_2$.

EXPERIMENTAL

Experimental techniques have been described in ref. 1.

N-(Ethylzinc)thioformanilide (IIa)

A solution of 0.94 g (6.86 mmole) of HNPhCSH in 40 ml of benzene was added slowly (30 minutes) with vigorous stirring to a solution of 1.18 g (9.57 mmole) of Et_2Zn in 10 ml of benzene at room temperature. During the addition the product slowly precipitated. It was filtered off, washed three times with 10 ml of benzene and dried *in vacuo*.

Methyl N-(ethylzinc)dithiocarbanilate (IVa)

This compound was synthesized via the procedure given in ref. 1 for the synthesis of *N*-(ethylzinc)acetanilide modified only in that the reaction temperature was kept below 10° to prevent decomposition. Also the isolation and all manipulations afterwards were carried out below that temperature.

N-(ethylzinc)-*N*,*N'*,*N'*-triphenylthiourea (Va) was prepared from ethylzinc diphenylamide and phenyl isothiocyanate, as described in ref. 1 for the synthesis of *N*-(ethylzinc)-*N*,*N'*,*N'*-triphenylurea. It was recrystallized from benzene solution.

All other organozinc–nitrogen compounds and their complexes were prepared as described in ref. 1 for the corresponding carbonyl derivatives.

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