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ZINC(II) COMPLEXES WITH NITROGEN DONOR CHELATING LIGANDS

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ABSTRACT

Complexes of zinc (II) thiocyanate with nitrogen donor chelating ligands like orthophenanthroline, 5-nitroorthophenanthroline, 2, 9-dimethylorthophenanthroline, 2, 2'-dipyridyl, and 8-aminoquinoline have been synthesized and characterized by elemental analysis, infrared spectra and conductance measurements. Although in the synthesis of the complexes 1:1 metal:ligand ratio was maintained all the ligands form 1:2 metal complexes of the type $Zn(NCS)_2(AA)_2$ except 2, 9-dimethylorthophenanthroline which forms 1:1 complex, $Zn(NCS)_2(2,9\text{-dimethylorthophenanthroline})$. The complexes are insoluble in common non-coordinating solvents and do not melt sharply. The infrared spectral data indicate the presence of bridging thiocyanate bonding. The complexes are soluble in coordinating solvent, dimethylsulfoxide and exhibit molar conductance values attributable to 1:1 electrolyte. The breaking of the polymeric structure occurs in dimethylsulfoxide and formation of complexes of the type $[Zn(NCS)(DMSO)(2,9\text{-dimethylorthophenanthroline})]NCS$ and $[Zn(NCS)(DMSO)(AA)_2]NCS$ is suggested. The reaction of zinc (II) thiocyanate with ethanolic solution of biguanide leads to the isolation of bis (biguanide) zinc(II).

INTRODUCTION

THE ligands orthophenanthroline, 5-nitroorthophenanthroline, 2,9-dimethylorthophenanthroline, 2,2'-dipyridyl and 8-aminoquinoline contain N-C-C-N chelating group in common and are known to form mono, bis and tris complexes with metal ions^{1,2}. In the literature there is no record of mono complexes of these ligands with zinc(II) thiocyanate and the work described here deals with such complexes. The presence of thiocyanate groups in the complexes gives an added opportunity to find out the nature of bonding of the thiocyanate groups in the complexes. We reacted zinc(II) thiocyanate and the above heterocyclic amine ligands in 1:1 ratio in ethanolic medium, and, only in the case of 2,9-dimethylorthophenanthroline, we were able to prepare the desired mono complex. In all other cases (orthophenanthroline, 5-nitroorthophenanthroline, 2, 2'-dipyridyl and 8-aminoquinoline) we obtained bis complexes. A similar reaction with biguanide $[H_2N-C(=NH)-NH-C(=NH)-NH_2]$ led to the isolation of bis (biguanide)

zinc(II). The complexes have been characterized by elemental analysis, conductance and infrared spectral measurements.

EXPERIMENTAL

Materials and Methods

Zinc(II) thiocyanate and 8-aminoquinoline were obtained from Pfaltz and Bauer Inc. (U.S.A.). Orthophenanthroline, 5-nitroorthophenanthroline, 2,9-dimethylorthophenanthroline and 2, 2'-dipyridyl were supplied by G. Frederick and Smith Chemical Co. (U.S.A.). Biguanide was purchased from Aldrich Chemical Co. (U.S.A.). Zinc was estimated complexometrically with EDTA after igniting the complexes to ZnO and dissolving ZnO in dilute HCl. Carbon, hydrogen and nitrogen were determined micro-analytically. Conductance measurements (25° C) were done in DMSO with Radelkis type OK 102/1 conductivity bridge and a dip type cell which was calibrated with KCl solutions. Infrared spectra were recorded in KBr pellets on Perkin Elmer Model 21 and 237 infrared spectrophotometers and

TABLE I
The analytical and conductance data of zinc(II) complexes^a

Complex	Stoichiometry	%Zn	%C	%H	%N	Λ_m ohm ⁻¹ cm ² mole ⁻¹
Zn(NCS) ₂ (ophen) ₂	ZnC ₂₆ H ₁₆ N ₆ S ₂	Found: 11.8 Reqd. : 12.01	57.3 57.67	3.3 2.96	15.8 15.53	70.0
Zn(NCS) ₂ (5-nitrophen) ₂	ZnC ₂₆ H ₁₂ N ₆ O ₄ S ₂	Found: 10.7 Reqd. : 10.30	51.1 49.44	2.7 2.22	17.2 17.74	58.2
Zn(NCS) ₂ (2, 9-dimephen)	ZnC ₁₆ H ₁₂ N ₄ S ₂	Found: 16.4 Reqd. : 16.71	49.8 49.36	3.7 3.08	14.0 14.39	50.0
Zn(NCS) ₂ (dipy) ₂	ZnC ₂₂ H ₁₆ N ₆ S ₂	Found: 13.2 Reqd. : 13.18	53.9 53.55	3.8 3.24	17.4 17.04	66.5
Zn(NCS) ₂ (8-amq) ₂	ZnC ₂₀ H ₁₆ N ₆ S ₂	Found: 13.4 Reqd. : 13.90	51.5 51.17	4.0 3.41	17.9 17.91	60.4
Zn(biguanide) ₂	ZnC ₄ H ₁₂ N ₁₀	Found: 25.0 Reqd. : 24.53	18.7 18.11	4.8 4.53	52.9 52.83	..

^a Abbreviations: ophen = orthophenanthroline; 5-nitrophen = 5-nitroorthophenanthroline; 2,9-dimephen = 2,9-dimethylorthophenanthroline, dipy = 2, 2'-dipyridyl; 8-amq = 8-aminoquinoline.

each spectrum was calibrated with a polystyrene film.

General Method of Preparation of the Complexes

Zinc(II) thiocyanate (0.003 mole) was dissolved in 15 ml 95% ethanol and was filtered. To the filtrate, an ethanolic (95%) solution of the appropriate ligand (0.003 mole in 20 ml) was added. The mixture was refluxed for 30 min. The separated precipitates were filtered, washed with 95% ethanol and dried under vacuum at room temperature. Yield = 40–60%.

The analytical and conductance data of the complexes are given in Table I. The infrared spectral data of the complexes are presented in Tables II and III.

RESULTS AND DISCUSSION

The complexes are synthesized by the reaction of zinc(II) thiocyanate and bidentate ligands in ethanol. The analytical data indicate that 1:1 complex is formed in case of 2,9-dimethylorthophenanthroline. In the case of the other heterocyclic amines, viz., orthophenanthroline, 5-nitroorthophenanthroline, 2,2'-dipyridyl and 8-aminoquinoline, 1:2 complexes of the type Zn(NCS)₂(AA)₂ (where AA = heterocyclic amine) are formed. The complexes are insoluble in common non-coordinating organic solvents and conductance measurements in non-coordinating solvents were not possible. However, the complexes are soluble in coordinating solvents like dimethylsulfoxide

TABLE II
Infrared spectral data of zinc(II) complexes^a

	ν (C–N) str.	ν (C–S) str.	ν N–C–S bend
Zn(NCS) ₂ (ophen) ₂	2060s	792 m 752 m	480 m
Zn(NCS) ₂ (bipy) ₂	2060 s	798 m	478 m
Zn(NCS) ₂ (nitrophen) ₂	2055 s	750 m	482 m
Zn(NCS) ₂ (2,9-dimephen)	2060 s	785 m	483 m 450 m
Zn(NCS) ₂ (8-amq) ₂	2078 s	785 m	465 m

^a Abbreviations: s, strong; m, medium. All bands are in cm⁻¹.

(DMSO) and we recorded the conductance of the complexes in 0.001 M solution in DMSO. The complexes are not soluble beyond the concentration 0.001 M in DMSO at 25°C. The molar conductance values of the complexes are in the range 50–70 ohm⁻¹ cm² mole⁻¹ in DMSO. The values are indicative of 1:1 electrolyte in this solvent⁸. The insolubility of the complexes in common solvents and failure to melt sharply give an indication of polymeric nature of the complexes,

TABLE III

Infrared spectral data of biguanide and Zn (biguanide)₂

Biguanide	Zn (biguanide) ₂	Possible assignments
3300 s	3150 s	ν (NH ₂)
1625 s	1644 s	NH def.
1540 s}	1512 s}	N-C-N str.
1420 s}	1368 s}	
	1252 s	ring vibration
1200 s	1108 w	δ (NH) and ν (CN)
1100 s		δ (NH) and ν (CN)
1030 m	1062 m	ν (CN)
915 w	945 s	ν (CN)
	895 s	
	765 w	
	738 w	π (NH)
655 w	695 w	π (NH) and δ (N-C-N)

Infrared spectral data of the complexes (discussed later) indicate the presence of bridging thiocyanate groups. In coordinating solvent DMSO, the polymeric nature of the complex is broken and presumably the complexes of the type [Zn(NCS) (DMSO) (2,9-dimethylorthophenanthroline)] NCS and [Zn(NCS) (DMSO) (AA)₂] NCS (where AA = orthophenanthroline, 5-nitroorthophenanthroline, 2,2'-dipyridyl and 8-aminoquinoline are formed.

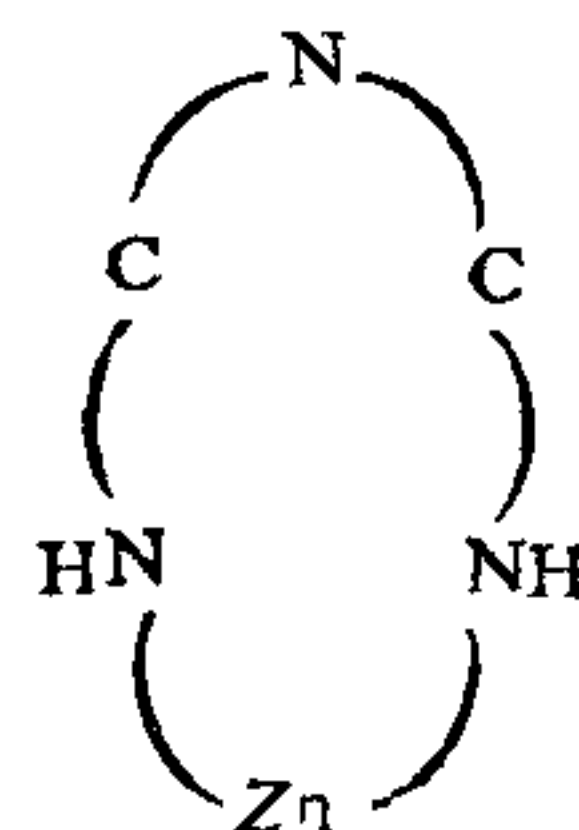
The ambient nature of thiocyanate ion is well established^{4,5}. Zinc(II) ion being intermediate in class *a*-class *b* behaviour, is able to bind to either S or N atoms, depending upon the other ligands present in the molecule. The thiocyanate ion has three fundamental infrared absorption frequencies: the strong band due to the C-N stretch, the weak C-S stretch and the weak N-C-S bend. Infrared spectra have been claimed to indicate the linkage of the thiocyanate groups with the metal ions and a correlation of the thiocyanate bonding type with ranges of the thiocyanate fundamental frequencies is summarized below^{6,7}. The infrared data of the complexes of

	ν (C-N) cm ⁻¹	ν (C-S) cm ⁻¹	ν (N-C-S) cm ⁻¹
NCS	2053	746	486, 471
M-NCS	2050-2100	820-870	475-485
M-SCN	2085-2130	700-760	430-470
M-NCS-M	2045-2165	750-800	440-480

zinc(II) thiocyanate with heterocyclic amines indicate that the thiocyanates are bridged in a polymeric structure^{6,7}. The physical properties, such as insolubility in common non-coordinating solvents and failure to melt sharply also indicate polymeric nature of the complexes. Our complexes do not have C-S stretching frequency below 750 cm⁻¹ and this is indicative of absence of a thiocyanate S-bonded structure. We believe our complexes are thiocyanate bridged polymeric chains with stronger N- than S-bonding⁷.

The intent of this research was to prepare 1:1 complexes of zinc(II) thiocyanate and bidentate NN donor ligands. Only in one case, viz., Zn(NCS)₂ (2, 9-dimethylorthophenanthroline) 1:1 complex was obtained and with all other ligands 1:2 complex, Zn(NCS)₂ (AA)₂ was isolated. The unusual behaviour of 2,9-dimethylorthophenanthroline, can be explained if one considers the steric hindrance of methyl groups in 2,9-dimethylorthophenanthroline⁸.

The treatment of alcoholic solution of biguanide with alcoholic solution of zinc(II) thiocyanate led to the synthesis of Zn(biguanide)₂. The infrared spectral data of biguanide and Zn(biguanide)₂ are given in Table III along with the possible band assignments. The N-C-N stretch of biguanide at 1540, 1420 cm⁻¹ is markedly lowered in the complex. The NH def. vibration of biguanide is higher in Zn(biguanide)₂. This shift of the infrared bands is consistent with the nitrogen coordination of the ligand biguanide. A strong band at 1252 cm⁻¹ in Zn(biguanide)₂ is assigned to chelate ring vibration of the following fragment of the molecular structure⁹. This band is absent in the infrared spectrum of biguanide.



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SYNTHESIS AND STRUCTURAL STUDIES OF SOME FIRST ROW TRANSITION METAL COMPLEXES OF ISONICOTINIC ACID HYDRAZIDE

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ABSTRACT

Isonicotinic acid hydrazide (INH) complexes of the types $M(\text{INH})\text{Cl}_2 \cdot n\text{EtOH}$ [where $M = \text{Mn(II)}$, Fe(II) , Co(II) , Ni(II) and Cu(II) and $n = 0$ or 1] $M(\text{INH})_2(\text{NO}_3)_2$ [where $M = \text{Co(II)}$ and Ni(II)] and mixed metal complexes like $\text{HgCo}_2(\text{INH})_2\text{Cl}_6$ and $\text{Ni}(\text{INH})_2\text{HgI}_4$ have been prepared and their nature and structure studied by molar conductance, magnetic susceptibility, electronic, E.S.R. and i.r. spectral measurements. Spin-free octahedral geometry has been proposed for all the complexes except $\text{Mn}(\text{INH})\text{Cl}_2$, $\text{Co}(\text{INH})\text{Cl}_2$ and $\text{HgCo}_2(\text{INH})_2\text{Cl}_6$ for which tetrahedral geometry has been suggested around Mn(II) and Co(II) metal ions.

INTRODUCTION

IN continuation of our earlier work¹ on the complexes of titanium and zirconium tetrahalides with isonicotinic acid hydrazide (INH), we report here the results of our studies on Mn(II) , Fe(II) , Co(II) , Ni(II) and Cu(II) complexes of INH.

EXPERIMENTAL SECTION

Starting Materials

All the chemicals used in this study were of BDH or equivalent quality. Ferrous chloride was freshly prepared as described by Mellor². INH, supplied by Schuchardt Chemical Company, West Germany, was used as such.

Synthesis and Analysis of the Complexes

$\text{Fe}(\text{INH})\text{Cl}_2 \cdot \text{EtOH}$ was prepared under hydrogen atmosphere by mixing together cold ethanolic solutions of the metal chloride and INH in ca 1 : 2 molar ratio. The precipitated complex was filtered in a specially designed vacuum filtering unit, washed with ethanol and dried *in vacuo*. Mn(II) , Co(II) , Ni(II) and Cu(II) complexes were prepared by mixing the hot ethanolic solutions of the metal chloride/nitrate and INH in ca 1 : 2 molar ratio. $\text{HgCo}_2(\text{INH})_2\text{Cl}_6$ was prepared by

adding ca 0.02 mole of cobalt chloride to a mixture of 0.01 mole of mercuric chloride and 0.02 mole of INH in ethanol. $[\text{Ni}(\text{INH})_2]\text{HgI}_4$ was prepared by adding successively ca 0.02 mole of INH and 0.01 mole of nickel nitrate to ca 0.01 mole of K_2HgI_4 in aqueous medium. The complexes, thus obtained, were filtered, washed with ethanol/water and dried at room temperature.

All the complexes were analysed for metal using standard procedures³ while nitrogen, hydrazine, chloride and ethanol contents were estimated as described earlier⁴. Nitrate was determined gravimetrically using nitron reagent. The experimental details pertaining to the molar conductance, magnetic susceptibility, i.r., electronic and e.s.r. spectral measurements were the same as described in our earlier paper⁴. The analytical and electronic spectral data are given in Tables I and II respectively.

RESULTS AND DISCUSSION

The analytical data (Table I) show that INH forms two types of complexes with metal chlorides and nitrates having 1 : 1 and 1 : 2 metal to ligand ratios respectively. All the complexes do not melt upto 250°C. They are insoluble in common organic solvents but with the exception of $\text{Ni}(\text{INH})\text{Cl}_2 \cdot \text{EtOH}$, all of them are fairly soluble in DMSO. The non-melting nature and their

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