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NATURE OF SELENOCYANATE BONDING IN THE COMPLEXES OF $MM'(NCSe)_4$ ($M=Co, Ni, Zn, Cd$; $M'=Zn, Cd, Hg$); WITH LEWIS BASES (PART II)

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NATURE OF SELENOCYANATE BONDING IN THE COMPLEXES OF $MM'(NCSe)_4$ ($M = Co, Ni, Zn, Cd; M' = Zn,$ Cd, Hg); WITH LEWIS BASES (PART II)

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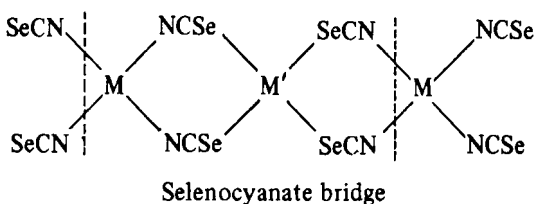
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Complexes of $[MM'(NCSe)_4]$ ($M = Co, Ni, Zn, Cd; M' = Zn, Cd, Hg$) with certain ligands (L), viz., ethylenediamine(en), isonicotinic acid hydrazide(inh), 3-aminopyridine(apy), pyridine(py), pyrazine 2-carboxamide(pza), pyrazine 2-3-dicarboxamide(pzd) and tetrahydrofuran(thf) have been synthesized and characterized. Their molar conductance, magnetic moments, infrared and electronic spectral studies indicate that these complexes are of three types: (i) cationic-anionic, viz., $[ML_6][M'(NCSe)_4]$ ($M = Ni, M' = Cd, L = inh; M = Cd, M' = Hg, L = py$; and $M = Zn, M' = Cd, Hg; L = en$); (ii) monomeric bridged, viz., $L_4M(NCSe)_2M'(SeCN)_2$ ($M = Co, Ni; M' = Cd, Hg; L = pzd$); (iii) polymeric bridged, viz., $>(SeCN)_2L_2M(NCSe)_2Hg(SeCN)_2 <$ ($M = Co, Ni; M' = Zn, Cd, Hg; L = thf, pza$ and apy). The nature of bonding in these complexes has been related to the softness difference of M and M' and the basicity of the ligands.

INTRODUCTION

In our earlier communication,¹ the softness values ($E_n \ddagger$) of M and M' were calculated in $MM'(NCSe)_4$ ($M = Co, Ni, Zn; M' = Zn, Cd, Hg$), and the difference of softness values ($\Delta E_n \ddagger$) were related to the stability of the selenocyanate bridge of $MM'(NCSe)_4$ with respect to their reaction with pyridine and its derivatives.



In this communication we have discussed the following – (i) The $\Delta E_n \ddagger$ values have been related with the stability of the selenocyanate bridge with respect to a new set of ligands, viz., tetrahydrofuran, pyrazine 2-carboxamide, pyrazine 2-3-dicarboxamide and ethylenediamine. These ligands have different basicities and some of them are bulky. Hence, the study of the effects of these two factors on the stability of selenocyanate bridge is interesting. (ii) A new set of tetraselenocyanate where $M = Zn, Cd$; and $M' = Cd, Hg$; have been allowed to react with the ligands discussed in the earlier communication.¹

EXPERIMENTAL

Materials and Manipulations

All manipulations were made as described earlier.¹

Synthesis of the Complexes

$CoHg(SeCN)_4 \cdot 2thf$ and $CoCd(SeCN)_4 \cdot 2thf$ were prepared by separately stirring 20 mmol. each of $CoHg(SeCN)_4$ and $CoCd(SeCN)_4$ with 50 ml. of anhydrous tetrahydrofuran for 48 h. In each case a pink mass was obtained which was filtered, washed with tetrahydrofuran and dried in vacuum. $CoZn(NCSe)_4 \cdot 4thf$ was similarly prepared.

All other complexes were prepared by stirring a solution or suspension of 20 mmol. of $MM'(NCSe)_4$ and the ligand in 20 ml of methanol for 8 h. The resulting compounds were filtered, washed with the solvent and dried in vacuum.

All physical measurements and analysis of the complexes were made as described earlier.¹

RESULTS AND DISCUSSION

On the basis of the structure of the complexes we have divided our study into three groups.

TABLE I
 Analytical results and molar conductance data

Complexes	Colour	M.P.	% Nitrogen		% Selenium		% mercury or cadmium		% cobalt, nickel or zinc		% Co+Cd, Co+Zn or Zn+Cd	Molar conductance (cm ² mhos/mol) (λ M) M/1024
			Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.		
[Ni(inh) ₆] [Cd(SeCN) ₄]	Yellow	180(d)	21.8	20.9	22.4	23.1	8.0	8.3	4.2	4.6	—	130
[Zn(py) ₄] [Cd(SeCN) ₄]	White	185(d)	12.2	11.9	34.6	35.2	—	—	—	—	16.7	135
[Cd(py) ₄] [Hg(SeCN) ₄]	White	210(d)	10.7	11.2	30.1	29.7	19.1	18.9*	—	—	—	110
[Zn(en) ₃] [Hg(SeCN) ₄]	White	120(d)	17.9	17.5	34.1	35.2	21.6	22.6	7.5	8.1	—	135
[Zn(en) ₃] [Cd(SeCN) ₄]	White	130(d)	18.0	17.8	40.7	41.4	—	—	—	—	23.3	125
(pzd) ₂ Ni(NCSe) ₂ Hg(SeCN) ₂	Green	190(d)	20.8	21.3	23.5	23.9	14.9	15.4	4.4	4.6	—	51
(pzd) ₂ Co(NCSe) ₂ Hg(SeCN) ₂	Pink	170(d)	20.8	21.3	23.5	24.3	14.9	14.7	4.4	4.3	—	38
(pzd) ₂ Ni(NCSe) ₂ Cd(SeCN) ₂	Green	180(d)	22.3	21.9	25.2	24.8	8.9	8.4	4.7	5.0	—	54
(pzd) ₂ Co(NCSe) ₂ Cd(SeCN) ₂	Pink	175(d)	22.3	21.7	25.2	24.9	—	—	—	—	14.1	60
>(SeCN) ₂ (pza) ₂ Ni(NCSe) ₂ Hg(SeCN) ₂ <	Violet	230(d)	14.3	14.8	27.0	26.5	17.1	16.7	5.0	5.3	—	40
>(SeCN) ₂ (pza) ₂ Co(NCSe) ₂ Hg(SeCN) ₂ <	Pink	165(d)	14.3	14.0	27.0	27.5	17.1	17.4	5.0	4.9	—	43
>(SeCN) ₂ (pza) ₂ Ni(NCSe) ₂ Cd(SeCN) ₂ <	Violet	185(d)	15.5	15.1	29.2	30.4	12.1	11.8	6.4	6.3	—	52
>(SeCN) ₂ (pza) ₂ Co(NCSe) ₂ Cd(SeCN) ₂ <	Pink	180(d)	15.5	15.9	29.2	28.9	—	—	—	—	19.1	50
>(SeCN) ₂ (thf) ₂ Co(NCSe) ₂ Hg(SeCN) ₂ <	Pink	140(d)	6.8	7.1	38.4	39.1	24.3	23.8	7.2	7.4	—	—
>(SeCN) ₂ (thf) ₂ Co(NCSe) ₂ Cd(SeCN) ₂ <	Pink	165(d)	7.6	7.3	43.0	43.5	—	—	—	—	22.7	—
>(SeCN) ₂ (thf) ₂ Co(NCSe) ₂ Zn(thf) ₂ (SeCN) ₂ <	Pink	170(d)	6.7	6.8	38.0	38.4	—	—	—	—	20.8	—
>(SeCN) ₂ (apy) ₂ Co(NCSe) ₂ Cd(SeCN) ₂ <	Pink	180(d)	14.4	13.9	40.6	41.2	—	—	—	—	21.9	35

(d) = decomposes * = % mercury a = m.-thanol medium b = D.M.F. medium c = methanol +en medium

Cationic-Anionic Complexes

[Ni(inh)₆] [Cd(SeCN)₄], [CdL₄] [Hg(SeCN)₄] (L = py) and [Zn(en)₃] [M(SeCN)₄] (M = Cd, Hg); The molar conductances of these complexes in methanol (Table I) indicate that they are 1:1 electrolytes. The electronic spectra and magnetic moments of the nickel(II) complexes, as discussed later, indicate that nickel(II) is in octahedral configuration in [Ni(inh)₆] [Cd(SeCN)₄]. Infrared spectra of these complexes show one strong band in the CN stretching region in the range 2090–2105 cm⁻¹. This indicates the presence of only Se-bonded selenocyanates.^{9,10} The bands assigned to γCSe and δNCSe are in the ranges 535–610 cm⁻¹ and 380–400 cm⁻¹, respectively. The positions of these bands also support the presence of Se-bonded selenocyanates.^{9,11-12,14} On the basis of these results we can propose a cationic-anionic structure to these complexes.

It is difficult to say that out of the two bases, e.g., ligand and selenocyanate, which will coordinate to M[Co(II), Ni(II), Zn(II)] and which to M'[Zn(II), Cd(II), Hg(II)]. The softness (E_n‡) calculations as presented earlier,¹ however, indicate that Cd²⁺ and Hg²⁺ will link to Se-end of selenocyanate hence the anion will be [Cd(SeCN)₄]²⁻ or [Hg(SeCN)₄]²⁻. The cation will, therefore, be [Ni(inh)₆]²⁺, [Zn(en)₃]²⁺ or [Zn(py)₄]²⁺. In [Cd(py)₄] [Hg(SeCN)₄], mercury being softer will coordinate to selenocyanate through soft Se-end and cadmium to pyridine which is a borderline base.^{4,5}

Group Theoretical Support

The proposed structure may also be supported by group theoretical calculations. In such a case the ions [Ni(inh)₆]²⁺ and [Zn(en)₃]²⁺ will belong to O_h and the ions [CdL₄]²⁺ and [M(NCSe)₄]²⁻ to T_d points groups. We have calculated the number of normal modes and the symmetry species for these point groups. The comparison of calculated and observed number of bands also support the proposed formula.

The fundamentals γ₁, γ₂ and γ₅ are assigned to CN stretching, CSe stretching and NCSe bending frequencies, respectively. The positions of these bands depend upon the nature of selenocyanate bonding.⁹⁻¹¹ When the bonding takes place through Se-end of selenocyanate these bands appear in the ranges, 2090–2105 cm⁻¹, 535–600 cm⁻¹ and 375–410 cm⁻¹, respectively. Since the observed bands are in this very region we believe that

selenocyanate is selenium bonded in these complexes.^{9-11,22} All these modes belong to the symmetry species T_2 . The presence of only one band in each region in our complexes show that T_2 are not split.

The fundamental γ_3 which belongs to T_2 symmetry is assigned to $M-S_4$ ($M = Cd, Hg$) stretching modes and the fundamental γ_4 to $Ni-L_6$, $Zn(LL)_3$ or $Cd-L_4$ stretching modes. In $Ni(II)$ and $Zn(II)$ complexes γ_4 belongs to T_{1u} and in $Cd(II)$ complexes to T_2 symmetry.

Monomeric Bridged Complexes

$(pzd)_4 Co(NCSe)_2 Hg(SeCN)_2$, $(pzd)_4 Ni(NCSe)_2 Hg(SeCN)_2$, $(pzd)_4 Co(NCSe)_2 Cd(SeCN)_2$ and $(pzd)_4 Ni(NCSe)_2 Cd(SeCN)_2$; Molar conductances of these complexes in dimethylformamide indicate that they are non-conducting in nature. The electronic spectral band positions and spectral parameters indicate that $Co(II)$ and $Ni(II)$ are in an octahedral environment. The Bohr magneton values also support the octahedral configuration of these complexes. The infrared spectra show the presence of three bands in νCN and γCSe regions indicating the presence of two types of selenocyanate groups. In γCN region two bands are observed in the range $2110-2135\text{ cm}^{-1}$ which are assigned to bridged selenocyanates.^{9,10} The third band which is observed in cadmium complexes at 2095 cm^{-1} and in mercury complexes at about 2105 cm^{-1} , is assigned to se-bonded terminal selenocyanate. In γCSe region two bands are observed, one in the range $570-600\text{ cm}^{-1}$ due to selenium bonded terminal selenocyanates and the other in the range $615-625\text{ cm}^{-1}$ due to bridged selenocyanates.⁹⁻¹¹ In $\delta NCSe$ region only one band is observed, in the range $408-415\text{ cm}^{-1}$, due to instrumental limitations. The positions and number of these bands further support the presence of bridged and terminal selenium bonded selenocyanates.^{1,9-13,22} On the basis of these results two structures Figure 1 and Figure 2 can be proposed.

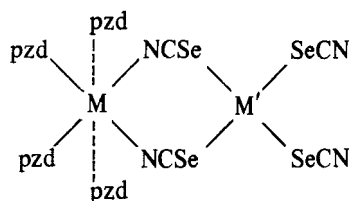


FIGURE 1

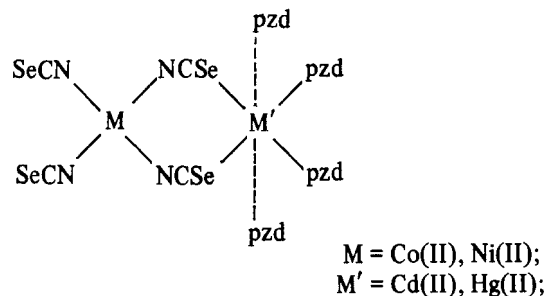


FIGURE 2

The structure of these complexes as proposed in Figure 1 is more probable on the following grounds:

- The $Co(II)$ and $Ni(II)$ are in octahedral configuration.
- The softness values^{4,5} of $Cd(II)$ and $Hg(II)$ have more preference for selenium end of selenocyanate.
- The pzd , which shows coordination through ring nitrogen,² will prefer to link to $Co(II)$ and $Ni(II)$ in comparison to $Cd(II)$ and $Hg(II)$ according to HSAB theory.⁸

Group Theoretical Support

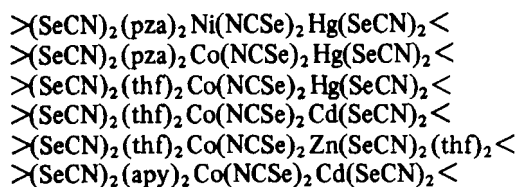
The proposed structure may again be supported by group theoretical calculations. Such a structure will belong to C_{2v} point group. Since the symmetry is low, only a very weak support can be extended on this account. The support presented on this ground is therefore, only additional. The number of *ir* active modes and their symmetry species have been calculated for this point group.

There are eighteen *ir* active modes which are all non-degenerate. The fundamentals γ_1 , γ_3 and γ_{13} have been assigned to CN stretching, CSe stretching and NCSe bending modes of the bridged selenocyanate unit. The fundamentals γ_2 , γ_4 and γ_{14} are assigned to CN stretching, CSe stretching and NCSe bending mode of terminal selenocyanate groups. The fundamentals γ_5 , γ_6 , γ_7 and γ_8 are assigned to $Hg-SeCN$ or $Cd-SeCN$ (terminal), $Hg-SeCN$ or $Cd-SeCN$ (bridged), $M-N$ and $M-L$ stretching modes respectively. The fundamentals γ_9 and γ_{10} are assigned to $Hg-Se_4$ or $Cd-Se_4$ deformations. The fundamentals γ_{11} , γ_{12} and γ_{15} are assigned to $Hg-SeCN$ and $M-NCSe$ deformations. The fundamentals γ_{16} and γ_{17} are assigned to $M-N_2$ and $M-L_4$ deformations. All these fundamentals belong to A_1+B_1 , A_1+B_2 , $2A_1+B_1+B_2$ or $2A_1$ symmetry species. The number of calculated and observed bands are in good agreement, which provide an additional support to the proposed structure.

Polymeric Bridged Complexes:-

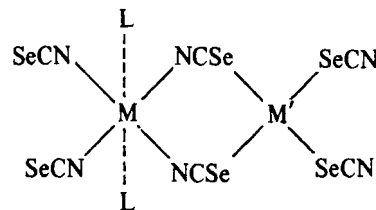
TABLE II
Electronic spectral band assignments, spectral parameters and B.M. values

Complexes	γ_2		γ_3		10Dq	B'	β	μ_{eff}
	$3A_{2g} \rightarrow 3T_{1g}(F)$	$3A_{2g} \rightarrow 3T_{1g}(P)$	$4T_{1g} \rightarrow 4A_{2g}$	$4T_{1g} \rightarrow 4T_{1g}(P)$				
[Ni(imh) ₂] [Cd(SeCN) ₄]	17000	28570			10450	948	.91	3.0
(pzd) ₂ Ni(NCSe) ₂ Hg(SeCN) ₂	16200	27770			9860	959	.92	3.1
(pzd) ₂ Ni(NCSe) ₂ Cd(SeCN) ₂	16900	28570			10350	961	.92	3.15
>(SeCN) ₂ (pza) ₂ Ni(NCSe) ₂ Hg(SeCN) ₂ <	16500	28600			10000	1006	.96	3.05
>(SeCN) ₂ (pza) ₂ Ni(NCSe) ₂ Cd(SeCN) ₂ <	17200	28570			10500	951	.91	3.0
Complexes	γ_3		γ_5		10Dq	B'	β	μ_{eff}
	$4T_{1g} \rightarrow 4A_{2g}$	$4T_{1g} \rightarrow 4T_{1g}(P)$	$4T_{1g} \rightarrow 4T_{1g}(P)$	$4T_{1g} \rightarrow 4T_{1g}(P)$				
(pzd) ₂ Co(NCSe) ₂ Hg(SeCN) ₂	17545	21740			-	-	-	5.0
(pzd) ₂ Co(NCSe) ₂ Cd(SeCN) ₂	18300	21700			-	-	-	5.1
>(SeCN) ₂ (pza) ₂ Co(NCSe) ₂ Hg(SeCN) ₂ <	18180	21645			-	-	-	4.9
>(SeCN) ₂ (pza) ₂ Co(NCSe) ₂ Cd(SeCN) ₂ <	17850	20900			-	-	-	5.1
>(SeCN) ₂ (apy) ₂ Co(NCSe) ₂ Cd(SeCN) ₂ <	18000	20700			-	-	-	5.0



All these complexes are non-conducting in dimethyl formamide. The colour, B.M. values and electronic spectral band positions (Table II) show that Co(II) and Ni(II) are in octahedral configuration in these complexes.¹⁹ The infrared spectra of these complexes show two bands in γCN region in the range 2100–2155 cm^{-1} , which indicate the presence of only bridged selenocyanates.^{9-10,17} Two bands assigned to γCSe and δNCSe are present in the ranges 560–620 cm^{-1} and 380–405 cm^{-1} , respectively, which also support the presence of only bridged selenocyanate groups.^{9,11-13} One band is observed at about 275 cm^{-1} and two bands in the range 240–265 cm^{-1} , the former is assigned to $\gamma\text{Co-L}$ and the latter to $\gamma\text{Co-NCSe}$.^{11,15-16,20} The presence of these bands indicate that Co(II) is bonded through nitrogen end of selenocyanate bridge. Furthermore, according to HSAB principle nitrogen end of selenocyanate will link to borderline Co(II) or Ni(II) and selenium end to soft Cd(II) and Hg(II).

Pyrazinamide and 3-aminopyridine which show features of coordination through ring nitrogen are borderline base and tetrahydrofuran which show features of coordination through oxygen is a hard base, hence all will coordinate to Co(II), Ni(II) or Zn(II). Hg(II) and Cd(II) are softer hence will have less preference for these bases. On the basis of these observations we can propose the following structures to these complexes:



M = Co(II), Ni(II); M' = Cd(II), Hg(II); L - pza, thf and apy;

FIGURE 3(a)

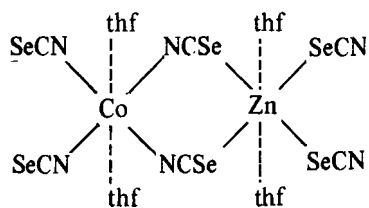


FIGURE 3(b)

Group Theoretical Support

These structures will belong to C_{2v} point group. The number of *ir* active normal modes along with their symmetry species have been calculated. The comparison of calculated and observed number of bands are in good agreement and provide an additional support to the proposed structures. There are 12 *ir* active modes in these complexes. All these active stretching modes are combinations of the species A_1+B_1 , A_1+B_2 and $2A_1+2B_1$. Since these modes consist of combined species they can split to give rise to two bands for each mode.

The fundamentals γ_1 , γ_2 and γ_6 which belong to $2A_1+2B_1$ symmetry species, are assigned to CN stretching, CSe stretching and NCSe deformations respectively. The fundamentals γ_3 , γ_4 and γ_5 which belong to A_1+B_2 , $2A_1+2B_2$ and A_1+B_1 symmetry species, are assigned to Co-L, CO-NCSe and Hg-SeCN stretches, respectively. The fundamentals γ_7 to γ_{12} are assigned to Hg-Se₂, Hg-SeCN (A*), Co-N₄ and Co-L₂ deformations, respectively. The bands due to γ_{Co-L} and γ_{Co-N} have been observed in the range 240–275 cm^{-1} , whereas the

bands due to γ_{Hg-Se} have not been observed upto 200 cm^{-1} because they are expected to appear below 200 cm^{-1} .

ELECTRONIC SPECTRAL DISCUSSION

While discussing the structure of various complexes we have indicated that Ni(II) and Co(II) are in octahedral configuration. To extend support to these configurations we have recorded electronic spectra of some of the complexes in methanol and D.M.F. These spectra were also recorded in solid phase by the method prescribed by Lee¹⁸ to check solvolysis. Since there was no difference between the two, we took the spectral bands of the solution spectra, for the purpose of assignments as they were better resolved. The positions of bands as presented in Table II, clearly show that Co(II) and Ni(II) are in octahedral configuration.¹⁹⁻²⁰ The 10 Dq values of nickel complexes were also calculated from positions of γ_2 and γ_3 bands by using the secular equation of Tanabe Sugano.²¹ These values are also typical of octahedral nickel(II) coordinated to nitrogen donor.^{16,19}

CONCLUSION

(i) The softness ($E_n \ddagger$) of M and M' has been calculated by using the Klopman equation.⁵ The difference of softness ($\Delta E_n \ddagger$) of M and M' has been related to the nature of complexes that $MM'(NCSe)_4$ form with pyridine¹ (Table III). $\Delta E_n \ddagger$ value indicates that $CoCd(SeCN)_4$ and $CoZn(NCSe)_4$ should form cationic-anionic or

TABLE III

M/M'	$E_n \ddagger(M)$	$E_n \ddagger(M')$	$\Delta E_n \ddagger(M-M')$	Possible nature of the complexes
Co/Hg	-0.22	-4.86	4.64	Polymeric bridged
Ni/Hg	-0.28	-4.86	4.58	
Zn/Hg	-1.29	-4.86	3.57	
Co/Cd	-0.22	-2.27	2.05	monomeric bridged
Ni/Cd	-0.28	-2.27	1.99	
Zn/Cd	-1.29	-2.27	.98	Cationic-anionic
Co/Zn	-0.22	-1.29	1.07	
Ni/Zn	-0.28	-1.29	1.01	
Cd/Hg	-2.27	-4.86	2.59	

(III) The formation of cationic-anionic type of complexes by $CdHg(SeCN)_4$, where the $\Delta E_n \ddagger$ value is 2.59, is perhaps due to change of M(Cd) from metal of first transition series to second transition.¹

monomeric bridged type of complexes, but they form polymeric bridged complexes with thf and apy. This deviation from general rule can be attributed to ligand effect. Tetrahydrofuran, pyrazine 2-carboxamide and 3-aminopyridine, have comparatively weak basicity hence are unable to rupture the selenocyanate bridge, consequently give rise to polymeric bridged complexes. Contrary to this when the basicity of the ligand is high the selenocyanate bridge is ruptured even when the $\Delta E_n \ddagger$ value is suggestive of polymeric bridged type of complex. For instance, $\text{CoHg}(\text{SeCN})_4^7$, $\text{NiHg}(\text{SeCN})_4^7$, and $\text{ZnHg}(\text{SeCN})_4$ form cationic-anionic complexes with ethylenediamine, $\text{CoHg}(\text{SeCN})_4$ and $\text{NiHg}(\text{SeCN})_4$ have high values for $\Delta E_n \ddagger$ but form monomeric bridged type of complexes with pyrazine 2-3-dicarboxamide instead of forming the expected polymeric bridged type. The change in the nature of these complexes is perhaps due to bulky nature of the ligand which obstruct the formation of polymeric complex.³

(ii) In case of $\text{NiCd}(\text{SeCN})_4$, the $\Delta E_n \ddagger$ value is 1.99, which is at the lowest end of the range prescribed for monomeric bridged type of complexes, hence on slight change in basicity of the ligand, it changes to cationic-anionic type. inh is perhaps a stronger base as compared to pyridine,⁶ hence causes the cleavage of the selenocyanate bridge in this tetraselenocyanate.

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