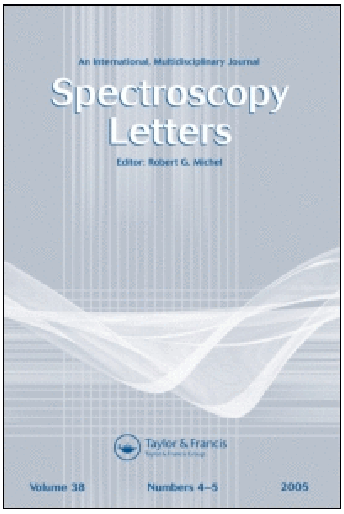

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Synthesis and Spectroscopic Studies of Metal (II) Tetracyanonickelate Complexes with 1,3-Thiazolidine-2-thione

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SYNTHESIS AND SPECTROSCOPIC STUDIES OF METAL (II) TETRACYANONICKELATE COMPLEXES WITH 1,3-THIAZOLIDINE-2-THIONE

Key words: IR and Raman spectra, 1,3-thiazolidine-2-thione, Hofmann-type complexes

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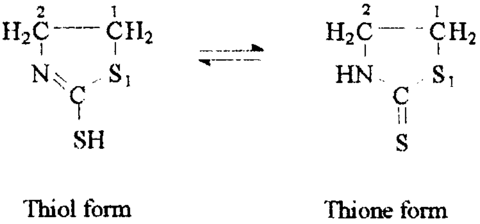
ABSTRACT

Two new Hofmann-type complexes, M (1,3-thiazolidine-2-thione)$_2$ Ni(CN)$_4$ (where M = Ni and Cd), were synthesized and characterized by elemental analysis, magnetic susceptibility data, IR and Raman Spectroscopy. Their structure consist of planar infinite polymeric layers of $\{M\text{-}Ni(CN)_4\}_\infty$. 1,3-thiazolidine-2-thione coordinated to M atom above and below this layers is monodentate and S-bonded in these complexes.

INTRODUCTION

Compounds like 1,3-thiazolidine-2-thione (tt), containing a secondary thioamide group are of considerable interest as ligands since they provide potential bonding for metal ions in many physiological systems[1]. It is also important in flotation process and in photographic industry[2] .

The ligand exhibits thiol- thione tautomerism.


Thiol form
Thione form

The absence of a ν(S-H) at about 2500 cm^{-1} and the presence of ν(N-H) in the range of 2890-3310 cm^{-1} strongly suggest that the thione form to be predominant tautomer in the solid state[3]. The ligand contains three different reaction centers, namely cyclic nitrogen and sulphur atoms and thiocarbonyl sulphur atom. It appears from previous papers[4-8] that in neutral medium this ligand coordinates through the imido nitrogen or thione sulphur atoms; when operating in basic medium the monoanion (tt^-) bonds via cyclic nitrogen and exocylic sulphur atoms.

We have prepared two new bis(1,3-thiazolidine-2-thione)metal(II) tetracyanonickelate complexes (abbreviated to M-Ni-tt), $M(tt)_2 Ni(CN)_4$ (M = Ni and Cd), to decide the site of coordination and to examine the chelating behavior of the ligand in Hofmann-type complexes. Spectral studies suggest that the ligand behaves as a monodentate ligand, coordination occuring through the thioketonic sulphur atom.

There is no complete vibrational spectroscopic study on tt complexes of transition metals in the literature. In this study, detailed vibrational assignment of tt in our complexes were carried out on the basis of normal coordinate analysis of tt.

EXPERIMENTAL

1,3-thiazolidine-2-thione was purchased from Merck and recrystallized from hot water.

$M(tt)_2Ni(CN)_4$ were prepared by dissolving 1 mmol of $K_2Ni(CN)_4$ in a small volume of hot anhydrous MeOH containing 2,2-dimethoxypropane as a dehydrating agent. To this solution, 2 mmol of the ligand and 1 mmol of the metal halide dissolved in anhydrous MeOH was added respectively. The reaction mixture was stirred for two days at room temperature. The product obtained was filtered and washed with dry ethanol and dried in a vacuum dessicator.

$Cd(tt)Cl_2$ was prepared as described by De Flippo et al[9]. The composition of these known complexes were checked by metal analysis (not reported here).

Infrared spectra were taken on a FTIR-Nicolet 10 spectrometer in KBr disc. Raman spectra were recorded on Jobin Yvon 4100 spectrometer. Magnetic susceptibility measurement were performed by Gouy Method at room temperatures.

C, H and N micro analyses were carried out by using Hewlett-Packard 185 elemental analyzer. Analytical data, room temperature magnetic moments and colour of the complexes are listed in Table 1. No UV-visible and molar conductivity measurement were carried out because of the insolubility of the complex in known solvent.

RESULT AND DISCUSSION

The IR spectra of M-Ni-tt complexes were compatible with each other, so thus only IR spectrum of Cd-Ni-tt complexes was given in Figure 1. Owing to the lack of structural data, the assignment was made by treating the tt molecule (C_s) and the $Ni(CN)_4$ (D_{4h}) ions as isolated units.

1.Vibration of Coordinated 1,3-Thiazolidine-2-Thione

Normal coordinate analysis of tt have been reported by K. Geetharani and D.N. Sathyanarayana[10] to check the empirical assignment and by Davillonova et. al.[11] on the basis of Urey-Bradley force field to assign the complete fundamental vibrations. The tt wavenumbers observed in IR and Raman spectra of M-Ni-tt complexes, together with our measurement on solid tt are given in Table 2. The vibrational wavenumbers and assignment of solid tt taken from Davillonova et. al. are included for comparison. Their nomenclature is followed in assigning the tt modes in our complexes.

TABLE 1

Analytical Results of M-Ni-tt Complexes : Found (Calculated) in %.

Compound	Colour	μ_{eff}	C (%)	H (%)	N (%)
Ni - Ni - tt	Green	3.1 B.M.	22.91 (23.38)	2.00 (1.95)	15.57 (16.37)
Cd - Ni - tt	Cream	Diamagnetic	25.97 (26.12)	2.10 (2.17)	14.05 (13.93)

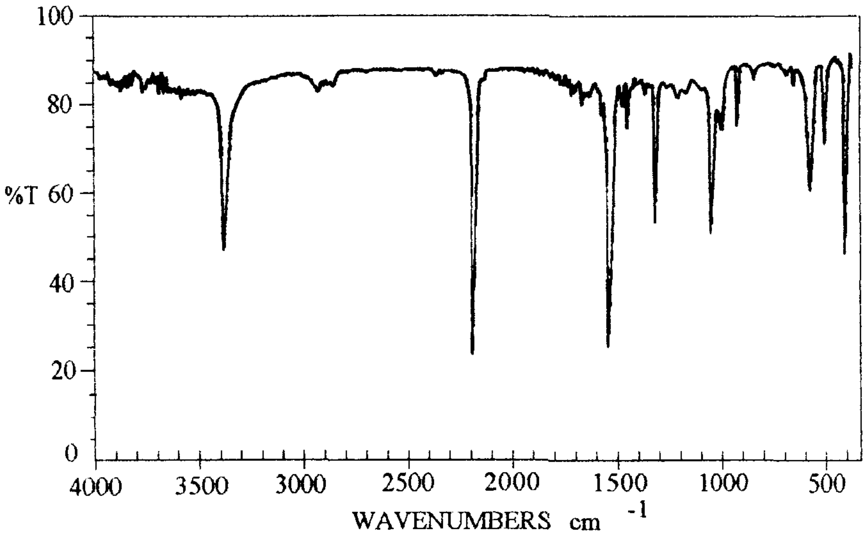


FIG. 1 Infrared spectra of Cd-Ni-tt complex in KBr disk.

We have also prepared and recorded the IR spectrum of the Cd(tt)Cl_2 complex to decide the coordination site in our complexes on the basis of shift of bands. For the purpose of comparison, vibrational wavenumber of Cd(tt)Cl_2 complexes are given in Table 2. In the crystalline state, Kubiak and Glowiak[12] have shown, by using X-ray diffaction technique, that structure of Cd(tt) Cl_2 complex is polymeric, with octahedrally coordinated Cd linked into infinite chains by double Cl bridges, which are further condensed in pairs by Cl bridges. tt ligands are monodentate and S-bonded to the Cd (II) ion. There is also an intermolecular hydrogen bond between the N atom and equatorial Cl atom such as N-H·······Cl.

The direction of the shifts in the position of all the bands in the spectra of the complexes are the same indicating that the binding pattern in these complexes must be similar. A comparison of the IR and Raman spectra of the ligand and the complexes brings about the following facts to light.

a) The $\nu_{(NH)}$ in the complexes are shifted towards lower wavenumbers of about 50 cm^{-1} using as reference the value of 3420 cm^{-1} for $\nu_{(NH)}$ for the free ligand in saturated CCl_4 solution[13]. A negative shift of this magnitude strongly suggest that these complexes are not N-bonded. Because the $\nu_{(NH)}$ shows a negative shift of 300 cm^{-1} in the N-bonded complexes such as $Co(tt)_2X_2$ [14] and $Cr(tt)_3X_3$ [15] (X=Cl, Br, I). The shifting of the position of $\nu_{(NH)}$ in our complexes could be explained on the assumption that metal ions are bonded to the thiocarbonyl sulphur only and hence, there would be a slight shift of electron density from nitrogen towards the sulphur. Comparison of the spectrum of ligand with that of the Cd(tt)Cl_2 complexes shows a negative shift of the order of 160 cm^{-1} in NH stretching frequency. This shift can be explained due to hydrogen bonding between the hydrogen of the NH and halogen of the metal halide.

b) The strong and sharp band at 1089 cm^{-1} of the ligand having major contribution from exocyclic CS stretching $\nu_{(C=S)}$, is absent in the spectra of the complexes. We things that this band shifts to the lower frequency region with complex formation through S donor atom and overlaps with the strong band around 1054 cm^{-1} of free tt.

c) The strong band at 585 cm^{-1} of the ligand, having contributions from ν (C_1S_1) + δ(CS) + ring def., shifts to higher wave number indicating that the

TABLE 2

Vibrational wavenumbers of 1,3-thiazolidine-2-thione in the M-Ni-tt complexes

Assignments[a] (PED %)	tt			Ni-Ni-tt		Cd-Ni-tt	$Cd(tt)Cl_2$
	IR[a]	IR	R	IR	R	IR	IR
A' ν NH (100)	3130	3135 m	3130 m	3380 vs	-	3368 vs	3260 s
ν_N CH_2 (99)	2960	-	2963 m	-	-	-	-
ν_S CH_2 (99)	2845	2852 w	2853 w	-	-	-	-
ν CN(45) δ NH(33)	1510	1520 vs	1513 m	1520 vs	1521 w	1522 vs	1510 vs
δ_N CH_2 (86)	1448	1455 m	1457 s	1458 w	-	1460 w	-
δ_S CH_2 (94)	1430	1437 m	1437 s	1436 w	-	1438 m	1437 m
δ NH (46) ν CN(36)	1345	1347 s	-	1347 w	-	1347 w	1347 m
w_S CH_2 (43) w_N CH_2 (41)	1290	1295 vs	1295 s	1310 vs	1307 w	1311 s	1304 s
w_S CH_2 (37) w_N CH_2 (29) ν CC(21)	1250	1252 s	1255 m	1260 w	-	1259 w	1250 w
ν CS(43) ring def. (15) ν CS_1 (12)	1085	1089 s	1089 m	-	-	-	-
ν C_2N(44) ν CC(22) w_N CH_2 (14)	1047	1050 vs	1046 s	1054 vs	1056 w	1051 vs	1045 vs
ν CC(47) ν C_2N(20)	933	933 s	932 m	928 m	927 w	929 s	931 s
ν C_1S_1 (47) ring def. (36)	655	653 s	650 m	-	-	-	655 w
ν C_1S_1 (54) δ CS(13) ring def. (11)	585	585 s	587 vs	592 vs	589 m	591 vs	603 br, s
ν C_1S_1 (35) r.d. (5) ν CS_1 (12) ν CS(11)	545	541 s	543 m	524 m	-	522 m	531 s
ring def. (78)	434	432 s	435 vs	b	-	b	428 s
A" ν_N CH_2 (100)	2998	-	2982 s	-	2996 w	-	-
ν_S CH_2 (100)	2882	-	-	2863 w	2866 w	2862 w	-
t_N CH_2 (66) t_S CH_2 (27)	1203	1204 s	-	-	-	-	1190 s
t_S CH_2 (73) t_N CH_2 (27)	1160	1162 m	-	-	-	-	1140 w
ρ_N CH_2 (41) ρ_S CH_2 (38) ΔNH (12)	999	997 s	1002 m	1003 w	-	1002 w	990 s
ρ_N CH_2 (49) ρ_S CH_2 (43)	850	849 m	-	853 w	-	854 w	856 w
ΔNH (81) ρ_S CH_2 (15)	700	699 s	702 m	668 w	665 w	670 w	680 w
ΔCS (77) τ ring (12) ΔNH (10)	434	432 s	-	b	-	b	428 s

a: Taken from ref.[11], ν = stretching, δ = deformation, Δ = out of plane deformation, ρ = rocking, w = wagging, t = twisting and τ = torsion. The subscripts N and S refer to nitrogen and sulphur to which CH_2 group is linked; b: Obscurred by the vibrations of sheet structure.

coordination take place via exocyclic sulphur. Because sulphur donating character of thioamide molecules has been established either by a lowering of the ν (CS) band (as shown above) or by a raising of the δ (CS) band of the coordinated ligand [3]. As shown in Table 2, similar shifts are observed in the $Cd(tt)Cl_2$ molecules.

d) The characteristic thioamide bands, namely I, II and III at 1520 vs, 1295 vs and 997 s cm^{-1} of the free ligands are observed either as the same position or small positive shift, however, thioamide bands IV at 699 cm^{-1} shift to lower wave number due to complexes formation which indicates the non-involvement of the ring sulphur and NH group[8]. The bands III and IV are considerable reduced in intensity on complexation.

e) The band at 541 cm^{-1} in free ligand undergoes downward shifts as verified in S-bonded complexes of tt [15]. The strong band at 432 cm^{-1} of the ligand is masked by the strong band around 426 cm^{-1} of the sheet vibration of the complexes.

2.$Ni(CN)_4$ Group Vibrations

In Hofmann-type complexes studied previously[16-18], the Ni atom in $Ni(CN)_4$ is square-planar surrounded by the carbon ends of four CN ions. Therefore, it is reasonable to assume that our complexes also have square-planar $Ni(CN)_4$ moeities. In order to assign the bands attributable to $Ni(CN)_4$ ions in the spectra of our complexes, we refer to the work of Mc Coullogh et. al.[19] who presented vibrational data for the salts $Na_2Ni(CN)_4$ in the solid state and assigned the fundamental vibration of the isolated $Ni(CN)_4$ ions on the basis of D_{4h} symmetry. These are given in Table 3 for comparison with the assignments for groups in our complexes and 3-chloropyridine complexes[20]. Vibrational wave numbers of $Ni(CN)_4$ mode of our complexes appear to be much higher then those of free $Ni(CN)_4$ ion as shown in Table 3. This upwards shifts, especially, at $\nu_{(CN)}$ and $\delta_{(Ni-CN)}$ mode explained as mechanical coupling between the M-N and C-N stretching vibrations and observed with various Hofmann-type complexes. The vibrations of the Ni-CN-M sheet structure for our complexes are found to be similar to Hofmann's 3-chloropyridine complexes, showing that the $[M\text{-}Ni(CN)_4]_\infty$ layers have been preserved.

CONCLUSION

The analytical results indicate that these complexes have two ligands molecules in the unit cells. Spectral results also show that the tt molecules behave as

TABLE 3

The wavenumbers (cm^{-1}) of Ni(CN)4 group vibrations in M-Ni-tt complexes

Assignment		$Na_2Ni(CN)_4$[a]	M-Ni-3-ClPy[b]		M-Ni-tt	
			Ni	Cd	Ni	Cd
ν_1 A_{1g}	ν(CN)	2149 vs	(2186vs)[c]	(2175 vs)	(2186 vs)	-
ν_4 B_{1g}	ν(CN)	2141 s	(2174 s)	(2165 s)	(2176 s)	-
ν_8 E_u	ν(CN)	2132 s 2128 s	2164 s	2155 s	2163 vs	2149 vs
	$\nu(^{13}CN)$	2087 w	2130 w	2115 vw	2129 vw	2113 vw
ν_9 E_u	ν(Ni-CN)	543 w	555 w	548 w	d	d
ν_{12} A_{2u}	π(Ni-CN)	448 w	456 m	445	d	d
ν_{10} E_u	δ(Ni-CN)	433 s 421	441 s	420 vs	441 s	426 s

a : Taken from ref.[19], b : Taken from ref.[20], c : Raman bands are given in paranthesis, d : Obscured by the fundamental vibrations of the ligand.

monodentate ligands and coordination occurs via exocyclic S atom to Cd(II) and Ni(II) atoms in our complexes. Because Cd(II) ion, being soft, should prefer to bond to soft donor atom such as sulphur. Effective magnetic moments of Ni-Ni-tt complexes are around 3.1 B.M. This value fall within the normal range for octahedral stereochemistry around Ni(II) complexes. These results are similar to those for Hofmann-type complexes[16-18].

On the basis of above observation, the following structures can be attributed to these complexes that their structure consist of layers of two-dimensional polymeric sheets formed from $Ni(CN)_4$ ions bridged by $M(tt)_2$ cations. In each sheet the Ni atoms are surrounded by four carbon atoms of cyanide anions in a square-planar environment. The M atoms have six-coordination with four nitrogen ends of bidentate CN ligands in plane and two suphur donor atom of tt molecules up and down this plane. The sheets are stacked on top of another by means of the force between the tt molecules.

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