

Synthesis and reactivity of coordinated tetradentate dithioacetylacetonate of bivalent transition metal ions

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ABSTRACT

Chelates of tetradentate dithioacetylacetonates of metal(II) and metal(III) have been synthesized in the modified simple method and their reactivity were reported with halogenating agents and α -naphthylisocyanate. The coordinated β -diketonates of transition metal ions showed remarkable reactivity at γ -CH of the ligand moieties. The quasiaromatic character of these coordinated compounds is confirmed by conducting halogenation and α -naphthylisocyanation reaction. The reactivity of dithioacetylacetonates of metal (III) is compared with that of metal (II). The analytical data of the parent and reacted dithio chelate complexes were also studied. The products have been characterized by analytical, IR, NMR and electronic spectral studies. The reactivity among the three different metals in different series of transition metal is also compared and discussed with experimental evidences. **Keywords:** dithioacetylacetonate, bivalent metal ion, trivalent metal ion, α -naphthylisocyanation, halogenations, physico-chemical studies

1. INTRODUCTION

In transition metal chemistry, much attention is being directed towards sulphur as a ligand. The results to date confirm that this atom confers properties on the derived metal complex which are sometimes highly novel and often differ markedly from those of the corresponding oxygen analogues. The unusual versatility of the ligand acetylacetonate in respect to both the number and various types of complex which it forms, encourages the pursuit of its sulphur analogue. Alan R Hendrickson, 1976, has examined the transesterification reactions of bis(O-ethylthiosacetothioacetato)nickel(II), Ni(O-Et.sacsac)₂ with alcohols and secondary amines to provide a variety of new 1,3-dithio complexes. Another new type of mixed ligand complex containing 1,2 and 1,3- dithio ligands has been formed by a ligand scrambling reaction between Ni(sacsac)₂ and [Ni(MNT)₂]₂- to afford [Ni(sacsac)(MNT)].

The dithio derivatives of acetylacetonato complexes are expected to have many interesting properties, but their synthesis were not successful. Martin and Stewart have succeeded in synthesizing dithioacetylacetonate of Ni(II), Co(II) Pd(II) and Pt(II).

Reactions of halogenating reagents with dithioacetylacetonato complexes have already been studied with the successful halogenations of the chelate ring. This reaction is one proof of the aromaticity of the acetylacetonato chelate ring. Thus the halogenations of the dithioacetylacetonato complexes is very interesting, and the chlorination or bromination of the compounds M(sacsac)₂ where M=Ni(II) or Co(II) prepared by the method was examined. The reaction of acetylacetonate with H₂S in the presence of the metal ion led to the isolation³ of the dithioacetylacetonato derivative [Co^{II}(sacsac)₂]. The characterization of this compound as a monomeric square planar species with a spin state S=1/2 and extensive in-plane magnetic anisotropy confirmed that this ligand may confer interesting stereochemical and magnetic properties on coordinated transition metal ions.

The study of iron-sulfur enzymatic systems has caused renewed interest in the metal-sulfur bonding in tervalent transition metal complexes with sulfur donors. Detailed information is available about the electronic structure the structural consequences of varying the crystal field properties of the substituted ligands the d-electron configuration of the metal the effect of solvating molecules and in the case of the Fe(III) derivatives exhibiting high-spin low-spin crossover, the dependence of the magnetic and structural properties on temperature, pressure (A.H.Ewald et al.) and small modifications to the ligands and the crystal lattice.

The above literature study clearly indicated the possibility of getting dimeric nature of dithioacetylacetonate. Therefore we have reported modified procedure of synthesizing bis(dithioacetylacetonato)M(II) where M=Ni(II), Cu(II), Pd(II) and Zn(II) in situ. Several reports on the reactivity of acetylacetonates have been reported. Very less work were reported on the reactivity of monothioacetylacetonate. Compared with acetylacetonates of transition metals, reactivity of dithioacetylacetonato complexes are scanty. Hence dithioacetylacetonato complex of M(II) and M(III) with higher yield was synthesized. For the first time, α -naphthylisocyanation and halogenations reactions were conducted on dithioacetylacetonates.

In view of the special properties of the sulfur donor atom and the meager data available on the thio analogues of β -diketonates, α -naphthylisocyanation and halogenations reactions were conducted on tris(dithioacetylacetonato) M(III), where M= Fe(III), Co(III) and Rh(III) and bis(dithioacetylacetonato)M(II) where M=Ni(II), Cu(II), Pd(II) and Zn(II). In order to find out the aromaticity of the rings and also to know whether stepwise addition at γ -CH takes place, reactions have been studied using controlled amounts of α -naphthylisocyanate and the halogenating agents such as NCS, NBS and pyridinium iodide.

2. EXPERIMENTAL METHODS

Bis(dithioacetylacetonato)metal(II) complexes were prepared by modifying the reported procedure. The purity of the complexes are also verified by their IR and PMR spectroscopic data (S.E.Livingstone et al. and A.Yokoyama et al.).

Preparation of dithioacetylacetonate of M(II) where M= Ni(II), Cu(II), Pd(II) and Zn(II): These complexes were prepared by passing dry HCl gas for 1 hour through 300ml of 5% ethanolic solution of acetylacetonone. Cooled to -78°C . The HCl was replaced by H_2S gas and the bubbling continued for $\frac{1}{2}$ hour. Upon addition of 0.1mole of metal chloride dissolved in 400ml of 1:1 water-ethanol solution, the characteristic coloured chelate immediately precipitated. The products were crystallized.

Preparation of di- α -naphthylamido substituted derivatives of dithioacetylacetonate of Ni(II), Cu(II), Pd(II) and Zn(II). $\text{M}^{\text{II}}(\text{S}_2\text{AA}.\alpha\text{-C}_{10}\text{H}_7\text{NCO})_2$: Di- α -naphthylamido substituted derivatives of dithioacetylacetonate of M^{II} were prepared by taking $\text{M}^{\text{II}}(\text{S}_2\text{AA})_2$ (0.01mole) in dry benzene and α -naphthylisocyanate (0.02mole) was added dropwise and the mixture was refluxed till the precipitates were obtained. The precipitate was filtered, washed in dry benzene and dried.

Preparation of dichloro substituted derivatives of dithioacetylacetonate of Ni(II), Cu(II), Pd(II) and Zn(II). $\text{M}^{\text{II}}(\text{S}_2\text{AA}.\text{Cl})_2$: Dichloro derivatives of dithioacetylacetonate of M^{II} were prepared by taking $\text{M}^{\text{II}}(\text{S}_2\text{AA})_2$ (0.01mole) and dropwise mixing with N-chlorosuccinimide (0.02mole) in dry benzene (50ml). The mixture was refluxed till the precipitates were formed. The precipitate obtained was filtered off and washed with dry benzene and then finally dried over vacuum.

Preparation of dibromo substituted derivatives of dithioacetylacetonate of Ni(II), Cu(II), Pd(II) and Zn(II). $\text{M}^{\text{II}}(\text{S}_2\text{AA}.\text{Br})_2$: To a solution of the parent complex $\text{M}^{\text{II}}(\text{S}_2\text{AA})_2$ (0.01mole) in dry benzene, N-bromosuccinimide (0.02mole) was added dropwise and the dibromo derivatives of metal(II)dithioacetylacetonate precipitates were obtained. The mixture was refluxed till the precipitates were formed. The precipitate obtained was filtered off and washed with dry benzene and then finally dried over vacuum.

Preparation of diiodo substituted derivatives of dithioacetylacetonate of Ni(II), Cu(II), Pd(II) and Zn(II). $\text{M}^{\text{II}}(\text{S}_2\text{AA}.\text{I})_2$: Diiodo derivatives of dithioacetylacetonate of M^{II} were prepared by taking $\text{M}^{\text{II}}(\text{S}_2\text{AA})_2$ (0.01mole) and pyridinium iodide (0.02mole) in dry benzene (50ml). The mixture was refluxed till the precipitates were formed. The mixture was refluxed till the precipitates were formed. The precipitate obtained was filtered off and washed with dry benzene and then finally dried over vacuum.

Analysis: Carbon, Hydrogen, oxygen, nitrogen, sulfur, halogen and the metal content in each of the complexes are found out and listed in the analytical data table.

Physicochemical techniques: The results of IR and PMR spectral studies are presented in tables and the representative spectra are shown.

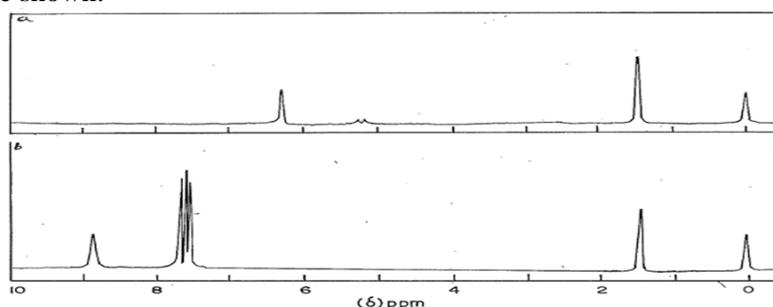


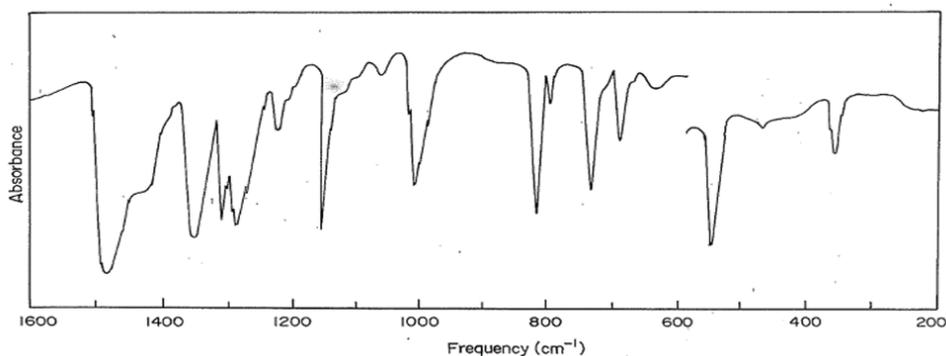
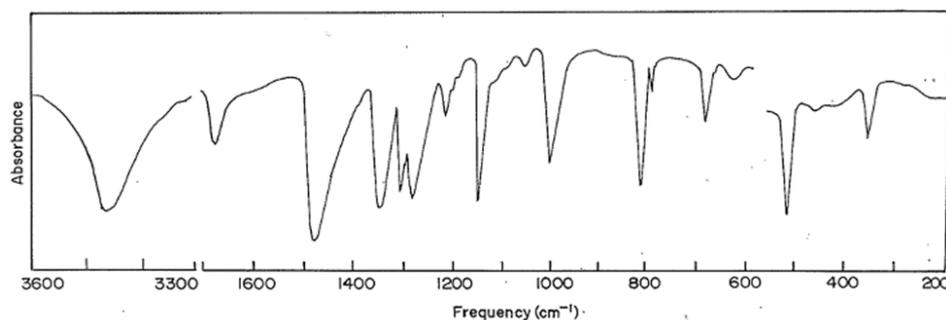
Figure.1. ^1H FT NMR Spectra of (a) $\text{Ni}(\text{S}_2\text{AA})_2$ (b) $\text{Ni}(\text{S}_2\text{AA}.\alpha\text{-C}_{10}\text{H}_7\text{NCO})_2$

Table.1.Characteristic PMR data of the parent and reacted dithio chelates of metal (II)

Complex	CH_3CS	$\gamma_{\text{C-H}}$	Naphthyl	NH
$\text{Ni}(\text{S}_2\text{AA})_2$	1.57 (s,12)	7.2 (s,2)	-	-
$\text{Ni}(\text{S}_2\text{AA}.\alpha\text{-C}_{10}\text{H}_7\text{NCO})_2$	1.69 (s,12)	-	7.7 (m,14)	8.9 (b,2)
$\text{Ni}(\text{S}_2\text{AA}.\text{Cl})_2$	1.68 (s,12)	-	-	-
$\text{Ni}(\text{S}_2\text{AA}.\text{Br})_2$	1.67 (s,12)	-	-	-
$\text{Ni}(\text{S}_2\text{AA}.\text{I})_2$	1.69 (s,12)	-	-	-
$\text{Pd}(\text{S}_2\text{AA})_2$	2.04 (s,12)	6.43 (s,2)	-	-
$\text{Pd}(\text{S}_2\text{AA}.\alpha\text{-C}_{10}\text{H}_7\text{NCO})_2$	2.03 (s,12)	-	7.8 (m,14)	8.5 (b,2)
$\text{Pd}(\text{S}_2\text{AA}.\text{Cl})_2$	2.05 (s,12)	-	-	-
$\text{Pd}(\text{S}_2\text{AA}.\text{Br})_2$	2.04 (s,12)	-	-	-
$\text{Pd}(\text{S}_2\text{AA}.\text{I})_2$	2.04 (s,12)	-	-	-

Table.2.Characteristic IR spectra (in cm^{-1}) of the parent and reacted dithio chelates of metal (II)

Complex	$\nu_{\text{M-S}}$	$\nu_{\text{C-S}}$	$\pi_{\text{C-H}}$	$\delta_{\text{C-H}}$	Amide	
					ν_{CO}	ν_{NH}
$\text{Ni}(\text{S}_2\text{AA})_2$	510w	825s	705w	1433w	-	-
$\text{Ni}(\text{S}_2\text{AA}.\alpha\text{-C}_{10}\text{H}_7\text{NCO})_2$	505w	835s	-	-	1670s	3420-3350(m,b)
$\text{Ni}(\text{S}_2\text{AA.Cl})_2$	500w	830s	-	-	-	-
$\text{Ni}(\text{S}_2\text{AA.Br})_2$	500w	830s	-	-	-	-
$\text{Ni}(\text{S}_2\text{AA.I})_2$	505w	830s	-	-	-	-
$\text{Cu}(\text{S}_2\text{AA})_2$	410w	845s	705w	1405w	-	-
$\text{Cu}(\text{S}_2\text{AA}.\alpha\text{-C}_{10}\text{H}_7\text{NCO})_2$	420w	850s	-	-	1660s	3410-3350(m,b)
$\text{Cu}(\text{S}_2\text{AA.Cl})_2$	405w	845s	-	-	-	-
$\text{Cu}(\text{S}_2\text{AA.Br})_2$	405w	845s	-	-	-	-
$\text{Cu}(\text{S}_2\text{AA.I})_2$	405w	845s	-	-	-	-
$\text{Zn}(\text{S}_2\text{AA})_2$	405w	850s	700w	1425w	-	-
$\text{Zn}(\text{S}_2\text{AA}.\alpha\text{-C}_{10}\text{H}_7\text{NCO})_2$	415w	860s	-	-	1660s	3410-3340(m,b)
$\text{Zn}(\text{S}_2\text{AA.Cl})_2$	410w	855s	-	-	-	-
$\text{Zn}(\text{S}_2\text{AA.Br})_2$	410w	855s	-	-	-	-
$\text{Zn}(\text{S}_2\text{AA.I})_2$	410w	855s	-	-	-	-
$\text{Pd}(\text{S}_2\text{AA})_2$	450w	725s	820w	1320w	-	-
$\text{Pd}(\text{S}_2\text{AA}.\alpha\text{-C}_{10}\text{H}_7\text{NCO})_2$	460w	735s	-	-	1650s	3430-3330(m,b)
$\text{Pd}(\text{S}_2\text{AA.Cl})_2$	465w	730s	-	-	-	-
$\text{Pd}(\text{S}_2\text{AA.Br})_2$	465w	730s	-	-	-	-
$\text{Pd}(\text{S}_2\text{AA.I})_2$	465w	730s	-	-	-	-

**Figure.2.IR Spectrum of $\text{Ni}(\text{S}_2\text{AA})_2$** **Figure.2.IR Spectrum of $\text{Ni}(\text{S}_2\text{AA}.\alpha\text{-C}_{10}\text{H}_7\text{NCO})_2$**

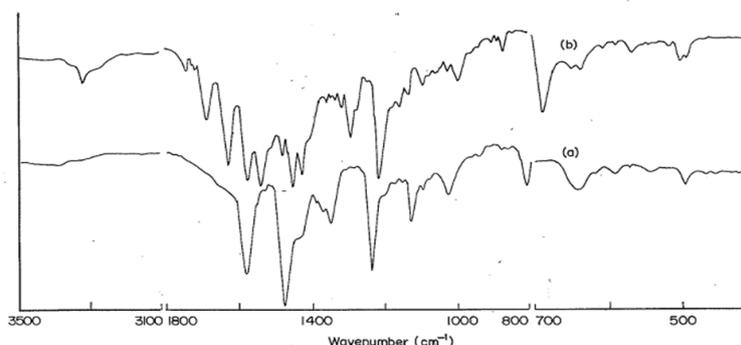


Figure.3.IR Spectra of (a) Co(S2AA)2 (b) Co(S2AA.α-C10H7NCO)2

Table.3.Analytical data of the parent and reacted dithio chelates of Metal (II)

Complex	Colour	Melting Point °C	% Analytical data						
			C	H	S	O	Metal	N	X
Ni(S ₂ AA) ₂	Dark Red	140	37.36 (37.40)	4.35 (4.39)	39.90 (39.93)	-	18.26 (18.28)	-	-
Cu(S ₂ AA) ₂	Green	165	36.80 (36.84)	4.30 (4.33)	39.30 (39.34)	-	19.45 (19.49)	-	-
Zn(S ₂ AA) ₂	Orange Red	168	36.60 (36.64)	4.25 (4.30)	39.10 (39.12)	-	19.90 (19.94)	-	-
Pd(S ₂ AA) ₂	Bright Red	173	32.50 (36.64)	3.80 (3.83)	34.75 (34.78)	-	28.80 (28.850)	-	-
Ni(S ₂ AA.α-C ₁₀ H ₇ NCO) ₂	Greenish brown	150	58.25 (58.28)	4.22 (4.28)	19.40 (19.45)	4.82 (4.85)	8.86 (8.90)	4.21 (4.25)	-
Cu(S ₂ AA.α-C ₁₀ H ₇ NCO) ₂	Pale Green	170	57.80 (57.85)	4.23 (4.25)	19.28 (19.31)	4.80 (4.82)	9.50 (9.56)	4.18 (4.21)	-
Zn(S ₂ AA.α-C ₁₀ H ₇ NCO) ₂	Orange	173	57.65 (57.69)	4.22 (4.24)	19.23 (19.25)	4.78 (4.80)	9.80 (9.81)	4.18 (4.20)	-
Pd(S ₂ AA.α-C ₁₀ H ₇ NCO) ₂	Yellowish red	180	54.30 (54.35)	4.80 (4.00)	18.10 (18.13)	4.50 (4.53)	15.03 (15.05)	3.93 (3.96)	-
Ni(S ₂ AA.Cl) ₂	Yellowish red	145	30.75 (30.79)	3.07 (3.10)	32.85 (32.88)	-	15.00 (15.05)	-	18.15 (18.17)
Ni(S ₂ AA.Br) ₂	Orange Red	148	25.04 (25.08)	2.48 (2.53)	26.75 (26.78)	-	12.22 (12.26)	-	33.33 (33.36)
Ni(S ₂ AA.I) ₂	Scarlet red	152	20.95 (20.96)	2.09 (2.11)	22.35 (22.38)	-	10.19 (10.25)	-	44.26 (44.30)
Cu(S ₂ AA.Cl) ₂	Pale green	168	30.40 (30.42)	3.00 (3.06)	32.45 (32.48)	-	16.02 (16.09)	-	17.92 (17.95)
Cu(S ₂ AA.Br) ₂	Greenish yellow	173	24.80 (24.83)	2.45 (2.50)	26.45 (26.51)	-	13.11 (13.13)	-	33.00 (33.03)
Cu(S ₂ AA.I) ₂	Olive green	175	20.75 (20.79)	2.05 (2.09)	22.15 (22.20)	-	10.07 (11.00)	-	43.88 (43.93)
Zn(S ₂ AA.Cl) ₂	Yellowish red	172	30.25 (30.28)	3.00 (3.05)	32.30 (32.33)	-	16.42 (16.48)	-	17.81 (17.81)
Zn(S ₂ AA.Br) ₂	Orange red	178	24.68 (24.73)	2.45 (2.49)	26.37 (66.41)	-	13.40 (13.46)	-	32.88 (32.91)
Zn(S ₂ AA.I) ₂	Orange red	180	20.68 (20.72)	2.05 (2.09)	22.08 (22.13)	-	11.22 (11.28)	-	43.72 (43.99)
Pd(S ₂ AA.Cl) ₂	Rosy Red	178	27.40 (27.44)	2.70 (2.76)	29.26 (29.30)	-	24.25 (24.31)	-	16.11 (16.19)
Pd(S ₂ AA.Br) ₂	Red	182	22.76 (22.81)	2.25 (2.30)	24.30 (24.35)	-	20.16 (20.20)	-	30.30 (30.34)
Pd(S ₂ AA.I) ₂	Scarlet Red	185	19.32 (19.35)	1.92 (1.95)	20.61 (20.66)	-	17.10 (17.14)	-	40.82 (40.89)

3. RESULTS AND DISCUSSION

The α-naphthylisocyanation and halogenation reactions of Ni(II), Cu(II), Pd(II) and Zn(II) complexes of dithioacetylacetonate with α-naphthylisocyanate in dry benzene produced complexes of stoichiometric ratios of metal : α-naphthylisocyanate /halogenating agent as 1:1 and 1:2. The yields of the formation of the complexes were almost quantitative. The magnetic susceptibility of Ni(II), Pd(II) and Zn(II) indicate them to be diamagnetic, thereby attributing square planar geometry around Ni(II), Pd(II) and Zn(II). The magnetic moment ($\mu_{\text{eff}} = 1.90 \text{ B.M.}$) of the

Cu(II) complexes are in the range expected for the monomeric Cu(II) complexes without magnetic coupling (B.J.Hathaway and A.G. Thomlinson). Although it is difficult to ascertain the stereochemistry of Cu(II) complexes on the basis of magnetic susceptibility data (B.J.Hathaway and D.E.Billing). The reacted Cu(II) thio complexes presumably seem to have a square planar geometry as in the corresponding Ni(II) complexes.

All the Dithioacetylacetonates of Ni(II), Cu(II), Zn(II) and Pd(II) are well defined crystalline solids with characteristic colour. The modified procedure gave high yields. Further the parent complexes shows distinct IR spectral and PMR spectral data. All the parent dithioacetylacetonate complex shows characteristic IR frequencies around the region $510-400\text{cm}^{-1}$, $860-725\text{cm}^{-1}$, $830-705\text{cm}^{-1}$ and $1433-1180\text{cm}^{-1}$, which are assignable to $\nu_{\text{M-S}}$, $\nu_{\text{C-S}}$, $\pi_{\text{C-H}}$, and $\delta_{\text{C-H}}$ respectively. Further the parent complexes show all the expected physical constants. To find out the effect of ligational sulphur environment around the metal ion, α -naphthylisocyanation and halogenation reactions were conducted. The π -bonding could hardly be expected between the transition metal ion and the oxygen donor in the case of β -diketonates (J.P.Collman), because oxygen does not possess vacant d-orbital for the back bonding of electrons from the metal ions (A.Yokoyama et al.). However, sulphur analogue of the β -diketone can be expected to be more significant in the metal thio- β -diketonates than in the corresponding β -diketonates. Further electronegativity of S being less than that of oxygen and almost equal to that of carbon. As more S atoms are introduced in the compounds, greater would be the NMR chemical shifts which appear for both vinyl proton and the methane protons. This seems to indicate that thioderivatives may have more reactive γ -CH hydrogen than that of acetylacetonates (S.E.livingstone).

The α -naphthylisocyanation and halogenation reactions carried out were successful and confirmed by the spectral data. All α -naphthylamido substituted derivatives show characteristic frequencies responsible for $\nu_{\text{M-O}}$, $\nu_{\text{C-S}}$ confirming stability of the chelate rings even after the reactions. As expected, the disappearance of bands due to $\pi_{\text{C-H}}$ and $\delta_{\text{C-H}}$ and the signal due to γ -CH in the case of diamagnetic chelates indicate complete substitution at γ -CH of the chelate ring. As expected, α -naphthylamido derivatives exhibit two new bands in comparison with non-substituted complexes. They are free amido $\text{C}=\text{O}$ ($1670-1650\text{cm}^{-1}$) and free amido NH ($3415-3340\text{cm}^{-1}$) respectively. In addition, naphthyl vibration in the region $1600-1580\text{cm}^{-1}$ are also observed in all α -naphthylamido substituted derivatives. Further α -naphthylamido substituted derivatives of Ni(II), Zn(II), Pd(II), Co(III) and Rh(III) show the distinct disappearance of methine proton (γ -CH) signals and NMR spectra of these complexes show NMR signal due to NH around the region $8.2-8.9 \delta$. Further α -naphthyl proton signal appear in the region $7.5-7.8 \delta$. Hence the above IR and PMR data clearly confirm the same results as found in the case of monothioacetylacetonates. All halogenated derivatives confirm the presence of halogen in the substituted product by careful analytical technique with significant disappearance of the IR bands due to $\pi_{\text{C-H}}$, and $\delta_{\text{C-H}}$ and further disappearance of γ -CH NMR signal in all halogenated derivatives. When compared with monothiodiketonates of transition metal ions²⁷, stepwise addition of α -naphthylisocyanate and halogenating agents were not successful. Further the qualitative rate of formation of the reacted products is very low indicating less reactivity. The main feature of this work expected higher reactivity due to complete sulphur ligational environment. But, the spectral results on the qualitative rate of formation of the product indicate clearly less quasiaromatic character of dithio- β -diketonate moiety. Hence dithio- β -diketonate reacts slowly than their monothio analogues. Therefore ligational environment also affects the reaction of coordinated ligand.

4. CONCLUSION

Dithioacetylacetonates of bivalent transition metal ions of Ni, Cu, Pd and Zn showed remarkable activity at γ -CH and the expected reactivity due to complete sulphur ligational environment was successfully proved. The spectral results of α -naphthylisocyanation and halogenation reaction carried out in these complexes confirmed the quasiaromatic character and γ -CH substitution. The reactivity of dithio- β -diketonate of metal (II) has been proved to be slower than the monothio analogues.

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