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Coordinated tetradentate Dithioacetylacetonate of trivalent transition metal ions – Synthesis and reactivity

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Abstract : Coordinated chelates of tetradentate d i thioacetylacetonates of 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 (III) ions showed remarkable reactivityatγ – CH of the ligand moieties. The quasi aromatic character of these coordinated compounds is confirmed by conducting ha logenation and α – naphthylisocyanation reaction. The activity of dithioacetylacetonates of metal (III) is compared with that of metal (II). The analytical data of the parent and reacted dithiochelate complexes were also studied. The products have been characterized by analytical, IR, NMR and electronic spectral studies. The activity among the three different metals in different series of transition metalis also compared and discussed with experimental evidences.

Keywords : dithioacetylacetonate, α-naphthylisocyanation, halogenations, physico-chemical studies.

Introduction

Coordination of an organic or an inorganic neutral molecule or an ion to a metal ion has a powerful influence on the chemical reactivity of the coordinated species. The presence of the metal ion brings about various changes such as conjugative and inductive effects and steric spatial effects. The term "coordinated ligand reaction" was first coined by Mark M.Jones,[1]according to whom when a system consisting of a metal ion, a ligand and one ormore metal-ligand complexes undergo a reaction, in which the ligand is transformed into one or more compounds.The coordinated ligand reaction has great importance with ample technological implication.[2]

Complexes of β-diketones and related metal chelates undergo many reactions similar to that of aromatic system. The hydrogen atom at the gamma position of the chelate ring can be substituted by a number of electrophilic reagents.[3] The earliest reported reaction of coordinated acetylacetone was due to Reinheln etal.,[4]who obtained tris(bromoacetylacetonato)chromium(III) by the reaction of tris (acetylacetonato) chromium(III) with bromine in chloroform. R.W.Kluiber[5,6] brominated metal acetylacetonates with NBS as brominating agent. Kluiber and Collmanetal., assigned the structure for the brominated complex providing evidence from IR data that the ring γ-CH was substituted by bromine. Several reviews on this topic are available. Currently, much attention is being directed towards sulphur as a ligand in transition metal chemistry.[7]Literature reveals that compounds having thiadiazolenucleus havewide application in the field ofpharmacology. The complexes with sulphur atom confers many properties on the derived compounds such as antimcirobial, antitubercular, antileishmanial, anti-inflammatory,analgesic, CNS depressant, anticonvulsant, anticancer, antioxidant, antidiabetic, molluscicidal, antihypertensive, diuretic, analgesic properties.[8]The sulphur atom substituted metal complex are highly novel and often differ markedly from those of the corresponding oxygen analogues.[9]

Experimental Methods

Preparation of dithioacetylacetonate of M(III) where M= Fe(III), Co(III), and Rh(III)

a. Preparation of dithioacetylacetone

It is prepared by passing a stream of dry HCl gas through a solution of acetylacetone and successively passing H_2S gas for about 20 hours at -50^oC.

b. Preparation of dithioacetylacetonate of Fe(III)

Iron(III) chloride hexahydrate (0.25g) was treated with a solution of dithioacetylacetone(0.5g) in diethylether(30ml). The mixture was stirred at room temperature for 1 hour and was then filtered. The filtrateis vacuum distilled and cooled. A dark red solid was precipitated and recrystallised from petroleum ether.

c. Preparation of dithioacetylacetonate of Co(III)

A solution of dithioacetylacetone (0.5g) in 10ml of diethylether was added to a solution of $CoCl_2.6H_2O$ (0.25g) in 50ml of ethanol. A dark green crystalline solid precipitated immediately. Dark green crystals were obtained upon crystallization from CS_2.

d. Preparation of dithioacetylacetonate of Rh(III)

$RhCl_3$.3H2O (0.25g) was treated with dithioacetylacetone (0.5g) in 50ml of toluene. The reaction mixture was refluxed for 24 hours. After filtering, the red solution was reduced to 15ml by vacuum distillation. Upon cooling dark red crystals were obtained.

Preparation of tri-α-naphthylamido substituted derivatives of dithioacetylacetonate of Fe(III), Co(III), and Rh(III). $M^{III}(S_2AA.\alpha\text{-} C_{10}H_7NCO)_3$

Tri-α-naphthylamido substituted derivatives of dithioacetylacetonate of Fe(III), Co(III), and Rh(III) were prepared by taking $M^{III}(S_2AA)_3$ (0.01mole) in dry benzene and α-naphthylisocyanate (0.03mole) was added dropwise and the mixture was refluxed. The precipitate was filtered, washed in dry benzene and dried.

Preparation of trichloro derivatives of dithioacetylacetonate of M(III) where M= Fe(III), Co(III), and Rh(III). $M^{III}(S_2AA.Cl)_3$

To a solution of the parent complex $M^{III}(S_2AA)_3$(0.01mole) in dry benzene, N-chlorosuccinimide (0.03mole) was added dropwise and the 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 tribromo derivatives of dithioacetylacetonate of M(III) where M= Fe(III), Co(III), and Rh(III). $M^{III}(S_2AA.Br)_3$

Tribromo derivative of dithioacetylacetonate of M(III) were prepared by adding N-bromosuccinimide (0.03mole) dropwise to the parent complex $M^{III}(S_2AA)_3$(0.01mole) in dry benzene. 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 triiodo derivatives of dithioacetylacetonate of M(III) where M= Fe(III), Co(III), and Rh(III). $M^{III}(S_2AA.I)_3$

Triiodo derivative of dithioacetylacetonate of M(III) were prepared by adding pyridinium iodide (0.03mole) dropwise to the parent complex $M^{III}(S_2AA)_3$(0.01mole) in dry benzene. 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.

Physicochemical Techniques

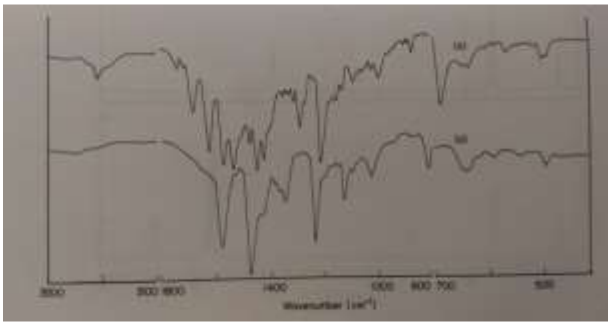
Ther esults of IR, PMR, UV-VisiblestudiesarepresentedinTableswhiletheirrepresentativespectraare shown in Figure.

Results and Discussion

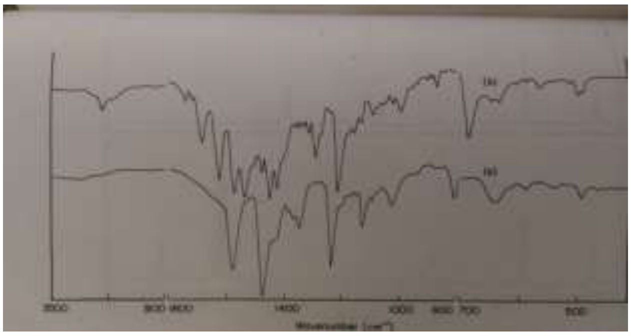
Reactions of complexes of dithioacetylacetonate with α–naphthylisocyanate/halogenating agent in dry benzene produced complexes in the stoichiometric ratios of metal: α–naphthylisocyanate/halogenating agent as 1:3 in the case of tris(dithioacetylacetonate) of Fe(III), Co(III) and Rh(III). A quantitative yield of complexes was formed. All the complexes were well defined crystalline solid with characteristic colour.

Analytical data of the parent and reacted dithio chelates of Metal (III)

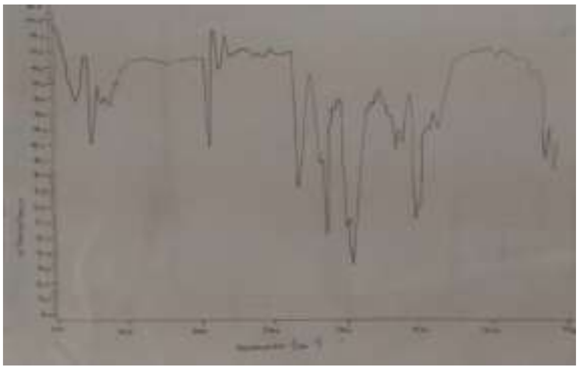
S. No.	Complex	Colour	Melting Point °C	% Analytical data						
				C	H	S	O	Metal	N	X
1	$Fe(S_2AA)_3$	Dark Red	170	40.04 (40.08)	4.68 (4.71)	42.75 (42.79)	-	12.40 (12.42)	-	-
2	$Co(S_2AA)_3$	Dark green	180	39.76 (39.80)	4.65 (4.68)	42.46 (42.50)	-	13.00 (13.02)	-	-
3	$Rh(S_2AA)_3$	Dark red	185	36.24 (36.28)	4.22 (4.26)	38.70 (38.74)	-	20.70 (20.72)	-	-
4	$Fe(S_2AA.\ \alpha\text{-}C_{10}H_7NCO)_3$	Scarlet red	175	60.20 (60.24)	4.40 (4.42)	20.06 (20.10)	5.00 (5.02)	5.80 (5.84)	4.35 (4.39)	-
5	$Co(S_2AA.\ \alpha\ C_{10}H_7NCO)_3$	Green	186	60.00 (60.04)	4.38 (4.41)	20.00 (20.04)	4.95 (4.99)	6.10 (6.14)	4.34 (4.37)	-
6	$Rh(S_2AA.\ \alpha\text{-}C_{10}H_7NCO)_3$	Red	190	57.37 (57.41)	4.20 (4.22)	19.13 (19.16)	4.74 (4.78)	10.21 (10.25)	4.14 (4.18)	-
7	$Fe(S_2AA.Cl)_3$	Red	175	32.54 (32.59)	3.23 (3.28)	34.75 (34.80)	-	10.06 (10.10)	-	19.20 (19.24)
8	$Fe(S_2AA.Br)_3$	Orange Red	180	26.21 (26.25)	2.60 (2.64)	28.00 (28.03)	-	8.10 (8.14)	-	34.90 (34.93)
9	$Fe(S_2AA.I)_3$	Orange Red	183	21.75 (21.78)	2.15 (2.19)	23.22 (23.26)	-	6.70 (6.75)	-	46.00 (46.02)
10	$Co(S_2AA.Cl)_3$	Pale Green	185	32.36 (32.40)	3.21 (3.26)	34.56 (34.60)	-	10.55 (10.60)	-	19.10 (19.13)
11	$Co(S_2AA.Br)_3$	Green	188	26.10 (26.14)	2.60 (2.63)	27.87 (27.91)	-	8.51 (8.55)	-	34.72 (34.77)
12	$Co(S_2AA.I)_3$	Green	193	21.65 (21.70)	2.15 (2.19)	23.14 (23.17)	-	7.06 (7.10)	-	45.82 (45.85)
13	$Rh(S_2AA.Cl)_3$	Red	188	36.45 (36.50)	3.63 (3.68)	38.93 (38.98)	-	20.81 (20.85)	-	21.51 (21.55)
14	$Rh(S_2AA.Br)_3$	Rosy Red	192	24.52 (24.57)	2.42 (2.47)	26.20 (26.24)	-	14.00 (14.30)	-	32.65 (32.69)
15	$Rh(S_2AA.I)_3$	Rosy Red	195	20.57 (20.61)	2.05 (2.08)	21.98 (22.00)	-	11.73 (11.77)	-	43.50 (43.54)



IR spectra of (a) $Co(S_2AA)_3$



IR spectra of (a) $Rh(S_2AA)_3$



(b) $Co(S_2AA.$ α $C_{10}H_7NCO)_3$

(b) $Rh(S_2AA.$ α $C_{10}H_7NCO$

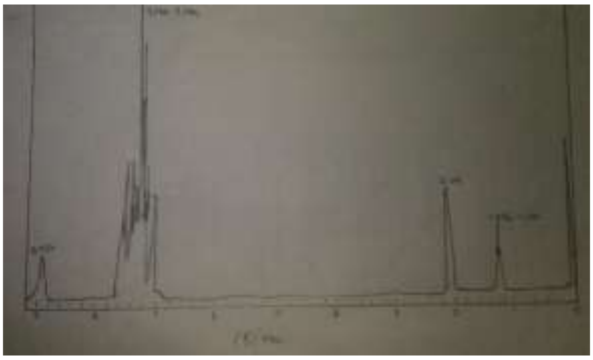
IR spectrum of $Fe(S_2AA.$ α-$C_{10}H_7NCO)_3$IR spectrum of $Rh(S_2AA.Cl)_3$

The quasiaromatic character of thio-β-diketonate ring and the effect of the ligational sulphur environment were proved by the α–naphthylisocyanation and halogenations reaction of the complexes of Fe(III), Co(III) and Rh(III). Between the transition metal ion and the oxygen donor in the case of β-diketonates,[10] the π-bonding is hardly expected, because of the absence of vacant d-orbital in oxygen for the backbonding of electrons from the metal ions.[11]

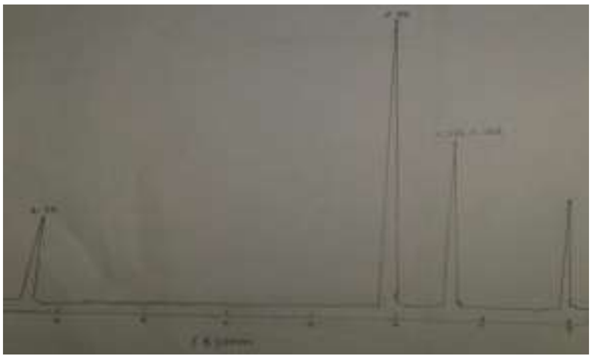
Characteristic IR spectra (in cm^{-1}) of the parent and reacted dithio chelates of metal (III)

S. No.	Complex	ν_{M-S}	ν_{C-S}	π_{C-H}	δ_{C-H}	Amide	
						ν_{CO}	ν_{NH}
1	$Fe(S_2AA)_3$	400w	865s	841w	1295w	-	-
2	$Fe(S_2AA.$ α- $C_{10}H_7NCO)_3$	410w	870s	-	-	1670-1650s	3451-3340(m,b)
3	$Fe(S_2AA.Cl)_3$	405w	860s	-	-	-	-
4	$Fe(S_2AA.Br)_3$	405w	860s	-	-	-	-
5	$Fe(S_2AA.I)_3$	405w	860s	-	-	-	-
6	$Co(S_2AA)_3$	405w	810s	700w	1425w	-	-
7	$Co(S_2AA.$ α $C_{10}H_7NCO)_3$	415w	820s	-	-	1680s	3400-3300(m,b)
8	$Co(S_2AA.Cl)_3$	410w	815s	-	-	-	-
9	$Co(S_2AA.Br)_3$	410w	815s	-	-	-	-
10	$Co(S_2AA.I)_3$	410w	815s	-	-	-	-
11	$Rh(S_2AA)_3$	400w	830s	830w	1180w	-	-
12	$Rh(S_2AA.$ α-$C_{10}H_7NCO)_3$	410w	840s	-	-	1670s	3410-3330(m,b)
13	$Rh(S_2AA.Cl)_3$	405w	835s	-	-	-	-
14	$Rh(S_2AA.Br)_3$	405w	835s	-	-	-	-
15	$Rh(S_2AA.I)_3$	405w	835s	-	-	-	-

The spectral data confirms that the α–naphthylisocyanation and halogenations reaction on dithiochelates of M(III) were successful. The stability of the chelate rings was confirmed by the characteristic frequencies responsible for νM-O andνC-S in all α–naphthylamido substituted derivatives. The complete substitution of γ-CHhydrogen of the chelate ring is indicated by the disappearance of bands due to πC-HandδC-H in the diamagnetic chelates of Co(III) and Rh(III). Two new bands free amidoC=O(1670-1650cm^{-1}) and freeamidoNH(3415-3340cm^{-1}) also appears with the non-substituted complexes. The substituted complexes of M(III) shows the disappearance of methine proton γ-CH signals and appearance of signal due to NH around the region 8.2-8.9δ andα-naphthylproton signal appear in the region 7.5-7.8δ. The analytical techniques confirm the presence of halogen in the halogenated complexes of Fe(III), Co(III) and Rh(III) with significant disappearance of the IR bands due to πC-HandδC-H and disappearance of γ-CH NMR signal.



^{1}H FT NMR spectrum of $Co(S_2AA.\ \alpha\ C_{10}H_7NCO)_3$



^{1}H FT NMR spectrum of $Co(S_2AA)_3$ in $CDCl_3$

Characteristic PMR data of the parent and reacted dithio chelates of Metal (III)

S. No.	COMPLEX	CH_3CS	$\gamma_{C\text{-}H}$	Naphthyl	NH
1	$Co(S_2AA)_3$	2.63 (s,18)	7.4 (s,3)	-	-
2	$Co(S_2AA.\ \alpha\ C_{10}H_7NCO)_3$	2.65 (s,18)	-	7.5(m,21)	8.7 (b,3)
3	$Co(S_2AA.Cl)_3$	2.60 (s,18)	-	-	-
4	$Co(S_2AA.Br)_3$	2.61 (s,18)	-	-	-
5	$Co(S_2AA.I)_3$	2.64 (s,18)	-	-	-
6	$Rh(S_2AA)_3$	2.72 (s,18)	7.4 (s,3)	-	-
7	$Rh(S_2AA.\ \alpha\text{-}C_{10}H_7NCO)_3$	2.75 (s,18)	-	7.6 (m,21)	8.8(b,3)S
8	$Rh(S_2AA.Cl)_3$	2.70 (s,18)	-	-	-
9	$Rh(S_2AA.Br)_3$	2.72 (s,18)	-	-	-
10	$Rh(S_2AA.I)_3$	2.73 (s,18)	-	-	-

Though higher reactivity was expected due to complete sulphurligational environment, the spectral results clearly indicates less quasiaromatic character of dithio-β-diketonate moiety. On comparison of the reactivity of M(II) with M(III)dithio-β-diketonates,[16] it is found that dithioacetylacetonates of M(II) react faster than M(III) dithio-β-diketonates. The effect of ligational environment on the coordinated ligand was confirmed by the reactivity of monothioanalogue in comparison with dithio analogue.[17]Dithio-β-diketonates react slower than their monothio-β-diketonates. Hence the effect of oxidation state and number on d^n electrons present in the metal ion on the reactivity of coordinated ligand is confirmed by the relative rate of α–naphthylisocyanation and halogenations reaction being qualitatively decreasing in the order as Rh(III) < Co(III) < Fe(III). The decreasing ring current / quasiaromaticityare also confirmed.

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