

Synthesis and reactivity of coordinated bidentate monothio- β - Diketonate of trivalent transition metal ions

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ABSTRACT

A modified method of synthesizing chelates of tetradentate thio- β -diketonates of Fe(III), Co(III) and Rh(III) have been reported 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 monothio- β -diketonates of metal (III) is compared with that of metal (II). 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: monothio- β -diketonate, trivalent metal ion, α -naphthylisocyanation, halogenations, physic-chemical studies

INTRODUCTION

The coordination of transition metal ions with β -diketonates shows a remarkably different reactivity at γ -CH of the ligand (S.E.Livingstone). The purpose of the present study is to find out various factors that govern the reactivity of coordinated ligands. The reactivity of β -diketonates revealed many salient features that affect the reactivity(A.Yokoyama etal), ligational environment around the metal ion and their oxidation state play a vital part in predicting the reactivity of the coordinated ligands. The substitution of the oxygen atoms with sulphur atom in β -diketone form monothio β -diketonates complexes, which are monomeric, anhydrous and soluble in organic solvents, whereas metal complexes of β -diketonates are solvated, polymeric and insoluble in organic solvents(D.P.Graddon and M.Das). The influence of oxidation state of the metal on reactivity of the complex can be well understood by comparing the reactivity of monothio β -diketonates of Rh(III) are prepared by new synthetic routes and the reactivities are reported with halogenting agents and α -naphthylisocyanate. The reacted products are analysed and reactivities are compared to that of bis(monothioacetylacetonato)metal(II).

EXPERIMENTAL METHODS

Preparation of Monothio β -derivatives of Fe(III), Co(III) and Rh(III):

- Preparation of β -diketone: β -diketone are prepared by claisen condensation of methylketone(RCOCH₃)and ethyl trifluoroacetate(CF₃COOC₂H₅) catalysed by sodium methoxide.
- Preparation of monothio β -diketone: It is prepared by passing a stream of dry HCl gas through a solution of β -diketone and successively passing H₂S gas for about 10 hours at -50°C.
- Preparation of monothioacetylacetonates of M(III): The monothio β -diketonates of Fe(III), Co(III) and Rh(III) were prepared as

Preparation of monothioacetylacetonate of Fe(III): Ferric chloride hexahydrate(0.25g) in alcohol(20ml) was treated with a solution of monothioacetylacetone(0.5g) in alcohol(20ml). To the dark brown solution water(20ml) was added and the mixture was extracted with ligh petroleum. The extract was dried over anhydrous sodium sulphate and after evaporation, the black crystals of the complex were filtered off. The product was recrystallised from acetone.

Preparation of monothioacetylacetonate of Co(III): Cobalt acetate tetrahydrate(0.2g) in 50% aqueous alcohol(20ml) was added to a solution of monothioacetylacetone(0.5g) in alcohol(50ml). The deep brown solution was filtered and air was passed through the solution for about 3 hours. The brown deposit was filtered and washed with ethanol. The product was recrystallised from 80ml petroleum ether.

Preparation of monothioacetylacetonate of Rh(III): Ammonium hexachloro rhodate(III) (0.33g) in water(10ml) was treated with a solution of monothioacetylacetone(0.6g) in acetone(40ml), yielding a white precipitate of ammonium chloride which was removed by filtration. To the deep red filtrate, water(20ml) was added to give a red precipitate which was filtered and recrystallised from acetone to give a bright red crystals of the complex.

Preparation of mono- α - naphthylamido substituted derivatives of monothioacetylacetonates of M(III):
(SAA)₂(SAA. α -C₁₀H₇NCO)M(III): To the solution of M^{III}(SAA)₃ Where M^{III} = Fe(III),Co(III) and Rh(III) (0.01mole) in dry benzene(50ml) taken in a round bottomed flask, pure α -naphthylisocyanate(0.01mole) was added drop by drop with continuous stirring. The flask was fitted with a condenser and a guard tube. The reaction mixture was refluxed over a boiling water bath for about 2-5 hours. Then the solution was cooled in an ice bath, crystals of α - naphthylamido derivatives were obtained. They were filtered, washed with dry benzene and dried over vacuum over P₂O₅. The yields were roughly about 50-60%

Preparation of di- α - naphthylamido substituted derivatives of monothioacetylacetonates of M(III):

(SAA) (SAA. α -C₁₀H₇NCO) ₂M(III): To the solution of M^{III}(SAA)₃ Where M^{III} = Fe(III),Co(III) and Rh(III) (0.01mole) in dry benzene(50ml) taken in a round bottomed flask, pure α -naphthylisocyanate(0.02mole) was added drop wise with continuous stirring. The mixture was then refluxed in a boiling water bath until the precipitates were formed. The precipitate was filtered and processed further as mentioned in 1.1.2

Preparation of tri- α - naphthylamido substituted derivatives of monothioacetylacetonates of M(III):

(SAA. α -C₁₀H₇NCO) ₃M(III): To the solution of M^{III}(SAA)₃ Where M^{III} = Fe(III),Co(III) and Rh(III) (0.01mole) in dry benzene(50ml) taken in a round bottomed flask, pure α -naphthylisocyanate(0.03mole) was added drop wise with continuous stirring. The mixture was then refluxed in a boiling water bath until the precipitates were formed. The precipitate was filtered and processed further as mentioned in 1.1.2

Preparation of monochloro substituted derivatives of monothioacetylacetonates of M(III):

(SAA)₂(SAA.Cl)M^{III}: To the solution of M^{III}(SAA)₃ Where M^{III} = Fe(III),Co(III) and Rh(III) (0.01mole) in dry benzene(50ml) taken in a round bottomed flask, N-chlorosuccinimide(0.01mole) was added drop by drop with continuous stirring. The flask was fitted with a condenser and a guard tube filled with anhydrous CaCl₂. The reaction mixture was refluxed over a boiling water bath, until the colour of the solution changes. The solution was then cooled, crystals of monochloro derivatives of monothioacetylacetonates were obtained. They were filtered, washed with dry benzene and dried over vacuum over P₂O₅.

Preparation of monobromo substituted derivatives of monothioacetylacetonates of M(III):

(SAA)₂(SAA.Br)M^{III}: Monobromo derivatives of metal(III) monothioacetylacetonate were prepared by the similar procedure as given in 1.1.5, by taking M^{III}(SAA)₃ Where M^{III} = Fe(III),Co(III) and Rh(III) (0.01mole) and dropwise mixing N-bromosuccinimide(0.01mole) in dry benzene. It was recrystallised and separated as detailed in 1.1.5.

Preparation of monoiodo substituted derivatives of monothioacetylacetonates of M(III):

(SAA)₂(SAA.I)M^{III}: Monoiodo derivatives of metal(III) monothioacetylacetonate were prepared by the similar procedure as given in 1.1.5, by taking M^{III}(SAA)₃ Where M^{III} = Fe(III),Co(III) and Rh(III) (0.01mole) and dropwise mixing pyridinium iodide(0.01mole) in dry benzene. It was recrystallised and separated as detailed in 1.1.5.

Preparation of dichloro substituted derivatives of monothioacetylacetonates of M(III):

(SAA)(SAA.Cl)₂M^{III}: Dichloro derivatives of metal(III) monothioacetylacetonate were prepared by the procedure as given in 1.1.5, by taking M^{III}(SAA)₃ Where M^{III} = Fe(III),Co(III) and Rh(III) (0.01mole) and dropwise mixing N-chlorosuccinimide(0.02mole) in dry benzene(50ml). The mixture was refluxed until the precipitates were formed. It was processed further as detailed in 1.1.5.

Preparation of dibromo substituted derivatives of monothioacetylacetonates of M(III):

(SAA) (SAA.Br) ₂M^{III}: To a solution of the parent complex, M^{III}(SAA)₃ Where M^{III} = Fe(III),Co(III) and Rh(III) (0.01mole) in dry benzene, N-bromosuccinimide(0.02mole) was added dropwise and the dibromo derivatives of metal(III) monothioacetylacetonates were prepared and recrystallised as a pure substance as detailed in 1.1.5.

Preparation of diiodo substituted derivatives of monothioacetylacetonates of M(III):

(SAA) (SAA.I) ₂M^{III}: Diiodo substituted derivatives of monothioacetylacetonates of Fe(III),Co(III) and Rh(III) were prepared as in 1.1.5 by taking the parent complex M^{III}(SAA)₃ (0.01mole) and pyridinium iodide (0.02mole) was added dropwise in dry benzene.

Preparation of trichloro substituted derivatives of monothioacetylacetonates of M(III):

SAA.Cl) ₃M^{III}: Trichloro substituted derivatives of monothioacetylacetonates of Fe(III),Co(III) and Rh(III) were prepared as in 1.1.5 by taking the parent complex M^{III}(SAA)₃ (0.01mole) and N-Chlorosuccinimide(0.03mole) was added dropwise in dry benzene. The mixture was refluxed until the precipitates were formed.

Preparation of tribromo substituted derivatives of monothioacetylacetonates of M(III). $(SAA.Br)_3M^{III}$: To a solution of the parent complex, $M^{III}(SAA)_3$ Where $M^{III} = Fe(III), Co(III)$ and $Rh(III)$ (0.01mole) in dry benzene, N-bromosuccinimide(0.03mole) was added dropwise and the dibromo derivatives of metal(III)monothioacetylacetonates were prepared and recrystallised as a pure substance as detailed in 1.1.5.

Preparation of triiodo substituted derivatives of monothioacetylacetonates of M(III):

$(SAA.I)_3M^{III}$: Triiodo substituted derivatives of monothioacetylacetonates of $Fe(III), Co(III)$ and $Rh(III)$ were prepared as in 1.1.5 by taking the parent complex $M^{III}(SAA)_3$ (0.01mole) and pyridinium iodide (0.0mole) was added dropwise in dry benzene.

ANALYSIS

Carbon, hydrogen, nitrogen, sulphur, halogen and the metal contents in each of the complexes were estimated and listed in table.

Table.1.Analytical data of the parent and reacted monothio chelates of Metal(III)

Complex	Colour	Melting Point	C	H	S	O	Metal	N	X
$Fe(SAA)_3$	Black	168	44.85 (44.89)	5.22 (5.27)	23.94 (23.95)	11.92 (11.96)	13.86 (13.91)	-	-
$Co(SAA)_3$	Brown	175	44.49 (44.54)	5.20 (5.23)	23.74 (23.78)	11.85 (11.87)	14.52 (14.57)	-	-
$Rh(SAA)_3$	Bright red	180	40.12 (40.17)	4.65 (4.72)	21.41 (21.45)	10.67 (10.70)	22.90 (22.95)	-	-
$Fe(SAA.\alpha-C_{10}H_7NCO)_3$	Dark Brown	172	63.35 (63.43)	4.60 (4.66)	10.54 (10.58)	10.53 (10.56)	6.10 (1.14)	4.60 (4.62)	-
$Co(SAA.\alpha-C_{10}H_7NCO)_3$	Chocolate Brown	185	63.15 (63.22)	4.60 (4.64)	10.50 (10.55)	10.50 (10.52)	6.40 (6.46)	4.55 (4.61)	-
$Rh(SAA.\alpha-C_{10}H_7NCO)_3$	Red	190	60.25 (60.31)	4.40 (4.43)	10.00 (10.06)	10.00 (10.04)	10.70 (10.76)	4.35 (4.39)	-
$Fe(SAA.Cl)_3$	Chocolate Brown	170	35.62 (35.69)	3.52 (3.59)	19.01 (19.06)	9.50 (9.51)	11.01 (11.07)	-	21.05 (21.07)
$Fe(SAA.Br)_3$	Reddish Brown	175	28.18 (28.23)	2.80 (2.84)	15.02 (15.08)	7.50 (7.52)	8.70 (8.75)	-	37.55 (37.57)
$Fe(SAA.I)_3$	Light brown	178	23.08 (23.12)	2.33 (2.33)	12.30 (12.35)	6.15 (6.18)	7.12 (7.17)	-	48.83 (48.87)
$Co(SAA.Cl)_3$	Brown	179	25.44 (35.48)	3.52 (3.57)	18.90 (18.94)	9.40 (9.45)	11.55 (11.61)	-	20.90 (20.95)
$Co(SAA.Br)_3$	Reddish Brown	185	28.06 (28.10)	2.80 (2.83)	14.95 (15.00)	7.42 (7.49)	9.16 (9.19)	-	37.34 (37.39)
$Co(SAA.I)_3$	Orange brown	190	23.00 (23.04)	2.25 (2.32)	12.25 (12.30)	6.10 (6.14)	7.50 (7.53)	-	48.64 (48.63)
$Rh(SAA.Cl)_3$	Orange red	185	32.61 (32.65)	3.22 (3.29)	17.40 (17.44)	8.65 (8.70)	18.60 (18.65)	-	19.24 (19.28)
$Rh(SAA.Br)_3$	Yellowish red	190	26.25 (26.30)	2.60 (2.65)	14.00 (14.04)	7.00 (7.01)	15.00 (15.02)	-	34.96 (35.00)
$Rh(SAA.I)_3$	Orange red	194	21.75 (21.81)	2.15 (2.20)	11.60 (11.64)	5.76 (5.81)	12.40 (12.45)	-	46.02 (46.08)

PHYSICO-CHEMICAL TECHNIQUES

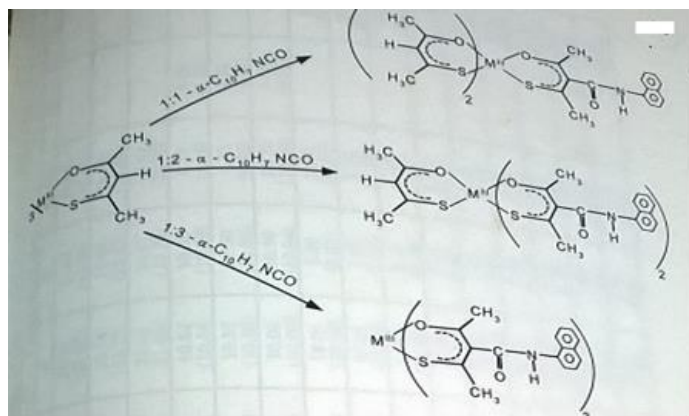
The results of IR, PMR, UV-Visible studies are presented in Tables while their representative spectra are shown in Figure

RESULTS AND DISCUSSION

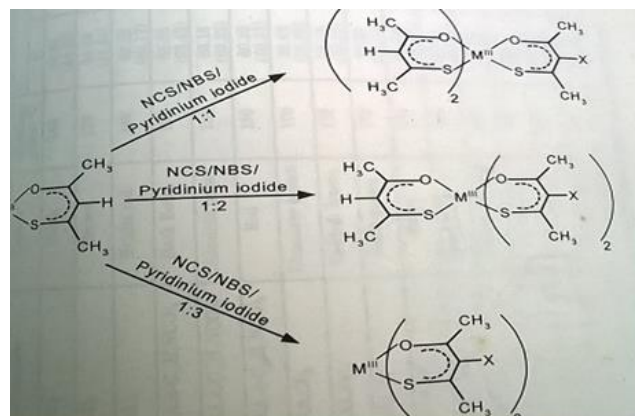
Nature of bonding and structure of α -naphthylamido substituted monothio- β -diketonates of M(III), Where M(III) = Fe(III), Co(III) and Rh(III)

In comparison with the non-substituted parent monothio- β -diketonate metal complexes which are reported to display bands in the region $1468-1455\text{cm}^{-1}$ (ν_{C-O} coordinated) $510-485\text{cm}^{-1}$ (ν_{M-O}), $815-718\text{cm}^{-1}$ (ν_{C-S}) $855-810\text{cm}^{-1}$ (π_{C-H}), out of plane bending C—H and $1432-1423\text{cm}^{-1}$ (δ_{C-H}) inplane bending C—H mode (R.K.Y.Ho,etal,A.Yokoyama etal,Akira Ouchi etal,S.E. Livingstone and M.Cox etal) respectively. All the mono aith non substituted complexes may be assignable to the free amido CONd di γ -CH substituted α -naphthylamido derivatives of monothio- β -diketonates of $Fe(III), Co(III)$ and $Rh(III)$ exhibit two additional bands in the region $1690-1670\text{cm}^{-1}$ and $3380-3340\text{cm}^{-1}$ (R.P. Eckberg etal,and V. Balasubramanian etal). These two

additional bands in comparison with non substituted complexes may be assignable to the free amido CO ($1690 - 1670 \text{ cm}^{-1}$) and amido N-H ($3380 - 3340 \text{ cm}^{-1}$)^{10,17,18} respectively. As in the case of monothio- β -diketonates of metal(II), α -naphthylisocyanate adds on to γ -CH and after prototropic rearrangements forms α -naphthylamido substituents. The mechanism is the same as suggested for divalent β -diketonates to metal(III) monothio- β -diketonates. As expected, stepwise addition of α -naphthylisocyanate gives expected mono- α -naphthylamido, di- α -naphthylamido and tri- α -naphthylamido substituted complexes. The intensity of bands due to π_{CH} and δ_{CH} also corresponds to stepwise addition of α -naphthylisocyanate. The tri- α -naphthyl derivative of metal(III) exhibit complete absence of bands due to π_{CH} and $\delta_{\text{C-H}}$ thereby confirming completion of the substitution. Therefore the structure and reaction of the complex may be tentatively proposed as follows.



Naphthylisocyanation reaction of monothioacetylacetonate of metal(III)



Halogenation reaction of monothioacetylacetonate of metal (III)

PMR spectra of Co(III) and Rh(III) exhibit characteristic methane proton signals at δ 6.7 – 6.3 (R.K.Y.Ho,etal, A.Yokoyama etal, Akira Ouchi etal, S.E. Livingstone and M.Cox etal) . The stepwise addition of α -naphthylisocyanate is confirmed by the reduced integrated intensity of γ_{CH} proton signals in their respective substituted derivatives. Tri- α -naphthylamido substituted derivatives show the disappearance of γ_{CH} signals confirming complete substitution. Further the new signals that appear in the register δ 7.3 – 7.5 and δ 8.9 – 9.1 are assignable to protons of α -naphthyl and NH group respectively. Hence, comparing IR and PMR data, it is clear that α -naphthylisocyanate adds on γ_{CH} proton of the chelate and after prototropic rearrangement forms mono- α -naphthylamido, di- α -naphthylamido and tri- α -naphthylamido substituted complexes.

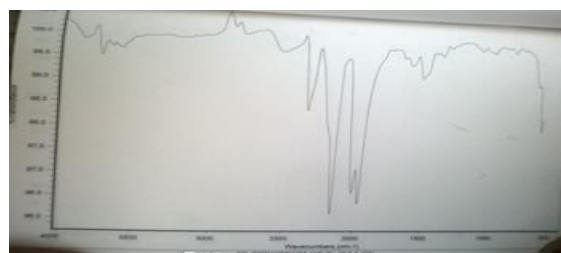
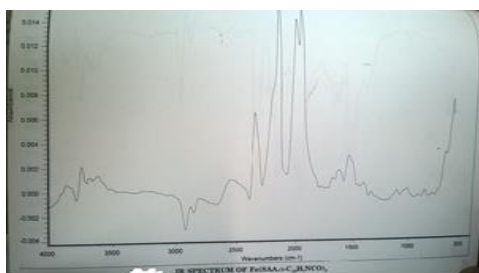
Characteristic PMR data of the parentand reacted monothio chelates of Metal(III)

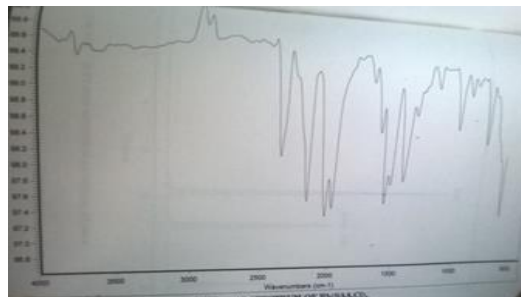
COMPLEX	CH ₃ CS CH ₃ CO	$\gamma_{\text{C-H}}$	Naphthyl	NH
Co(SAA) ₃	^a 2.26-2.35	6.39 (s,3)	-	-
Co(SAA) ₂ (SAA. α -C ₁₀ H ₇ NCO)	^a 2.26-2.35	6.39 (s,2)	7.3 (m)	8.9 (b,1)
Co(SAA)(SAA. α -C ₁₀ H ₇ NCO) ₂	^a 2.26-2.42	6.39 (s,1)	7.3 (m)	8.9 (b,2)
Co(SAA. α -C ₁₀ H ₇ NCO) ₃	^a 2.26-2.49	-	7.3(m)	8.9 (b,3)
Co(SAA) ₂ (SAA.Cl)	^a 2.26-2.35	6.37 (s,2)	-	-
Co(SAA)(SAA.Cl) ₂	^a 2.26-2.40	6.37 (s,1)	-	-
Co(SAA.Cl) ₃	^a 2.25-2.50	-	-	-
Co(SAA) ₂ (SAA.Br)	^a 2.25-2.40	6.40 (s,2)	-	-
Co(SAA)(SAA.Br) ₂	^a 2.25-2.42	6.40 (s,1)	-	-
Co(SAA.Br) ₃	^a 2.26-2.50	-	-	-
Co(SAA) ₂ (SAA.I)	^a 2.26-2.35	6.42 (S,2)	-	-
Co(SAA)(SAA.I) ₂	^a 2.25-2.45	6.42 (S,1)	-	-
Co(SAA.I) ₃	^a 2.25-2.50	-	-	-
Rh(SAA) ₃	^a 2.3-2.45	6.5 (S,3)	-	-
Rh(SAA) ₂ (SAA. α -C ₁₀ H ₇ NCO)	^a 2.3-2.48	6.5 (S,2)	7.5 (m)	9.1 (b,1)
Rh(SAA)(SAA. α -C ₁₀ H ₇ NCO) ₂	^a 2.3-2.50	6.5 (S,1)	7.5 (m)	9.1 (b,2)
Rh(SAA. α -C ₁₀ H ₇ NCO) ₃	^a 2.3-2.55	-	7.5 (m)	9.1 (b,3)
Rh(SAA) ₂ (SAA.Cl)	^a 2.3-2.43	6.4 (S,2)	-	-
Rh(SAA)(SAA.Cl) ₂	^a 2.3-2.45	6.4 (S,2)	-	-
Rh(SAA.Cl) ₃	^a 2.3-2.48	-	-	-
Rh(SAA) ₂ (SAA.Br)	^a 2.3-2.45	6.5 (S,2)	-	-
Rh(SAA)(SAA.Br) ₂	^a 2.3-2.48	6.5 (S,2)	-	-
Rh(SAA.Br) ₃	^a 2.3-2.52	-	-	-
Rh(SAA) ₂ (SAA.I)	^a 2.3-2.48	6.7 (S,2)	-	-
Rh(SAA)(SAA.I) ₂	^a 2.3-2.50	6.7 (S,2)	-	-
Rh(SAA.I) ₃	^a 2.3-2.55	-	-	-

Nature of bonding mode of halogenated derivatives: All parent monothioacetyl-acetonates of metal(III) chelates exhibit the characteristic frequencies around the region $510 - 485\text{cm}^{-1}$, $815 - 718\text{cm}^{-1}$, $855 - 810\text{cm}^{-1}$, $1432 - 1423\text{cm}^{-1}$ and $1468 - 1455\text{cm}^{-1}$ are assignable to $\gamma_{\text{M-O}}$, $\gamma_{\text{C-S}}$, $\pi_{\text{C-H}}$, out of plane bending C-H, $\delta_{\text{C-H}}$, in plane bending C-H mode and $^1\text{C-O}$ respectively. The stepwise addition of halogenating agents show expected frequencies with reduced intensities of the bands due to π_{CH} and δ_{CH} . All trihalogenated derivatives show complete absence of bands due to π_{CH} and δ_{CH} . All trihalogenated derivatives show complete absence of bands due to π_{CH} and δ_{CH} . Hence like α -naphthylisocyanationm halogenations also takes place in a stepwise manner. The above result is further substantiated by complexes undergo expected reduced integrated intensities and for trihalogenated derivatives of Co(III) and Rh(III) show the disappearance of signals due to γ_{CH} . Hence considering IR, PMR and analytical data available, confirms regulated α -naphthylisocyanation and halogenations reactions.

Characteristic IR spectra (in cm^{-1}) of parent and reacted monothio chelates of Metal(III)

Complex	$\nu_{\text{M-O}}$	$\nu_{\text{C-S}}$	$\pi_{\text{C-H}}$	$\delta_{\text{C-H}}$	$\nu_{\text{M-O}}$	Amide	
						ν_{CO}	ν_{NH}
Fe(SAA) ₃	490(w)	725(s)	810 (w)	1425 (w)	1468 (s)	-	-
Fe(SAA) ₂ (SAA. α -C ₁₀ H ₇ NCO)	490(w)	725 (s)	810 (w)	1425 (w)	1468 (s)	1680	3380(m,b)
Fe(SAA)(SAA. α -C ₁₀ H ₇ NCO) ₂	490(w)	725 (s)	810 (w)	1425 (vw)	1467 (s)	1680	3380(m,b)
Fe(SAA. α -C ₁₀ H ₇ NCO) ₃	490(w)	725 (s)	-	-	1468 (s)	1680	3380(m,b)
Fe(SAA) ₂ (SAA.Cl)	487(w)	721 (s)	815 (w)	1423 (w)	1468 (s)	-	-
Fe(SAA)(SAA.Cl) ₂	487(w)	721 (s)	815 (w)	1423 (vw)	1468 (s)	-	-
Fe(SAA.Cl) ₃	487(w)	721 (s)	-	-	1468 (s)	-	-
Fe(SAA) ₂ (SAA.Br)	489(w)	724 (s)	815 (w)	1425 (w)	1468 (s)	-	-
Fe(SAA)(SAA.Br) ₂	490(w)	724 (s)	815 (w)	1425 (vw)	1466 (s)	-	-
Fe(SAA.Br) ₃	490(w)	725 (s)	-	-	1466 (s)	-	-
Fe(SAA) ₂ (SAA.I)	495(w)	725 (s)	-	1428 (w)	1468 (s)	-	-
Fe(SAA)(SAA.I) ₂	495(w)	725 (s)	815 (vw)	1428 (vw)	1468 (s)	-	-
Fe(SAA.I) ₃	495(w)	725 (s)	-	-	1468 (s)	-	-
Co(SAA) ₃	497(w)	720 (s)	820 (w)	1425 (m)	1465 (s)	-	-
Co(SAA) ₂ (SAA. α -C ₁₀ H ₇ NCO)	497(w)	720 (s)	820 (w)	1425 (m)	1465 (s)	1670	3340(m,b)
Co(SAA)(SAA. α -C ₁₀ H ₇ NCO) ₂	497(w)	720 (s)	820 (vw)	1425 (m)	1465 (s)	1670	3340(m,b)
Co(SAA. α -C ₁₀ H ₇ NCO) ₃	497(w)	720 (s)	-	-	1465 (s)	1670	3340(m,b)
Co(SAA) ₂ (SAA.Cl)	495(w)	718 (s)	825 (w)	1423 (m)	1464 (s)	-	-
Co(SAA)(SAA.Cl) ₂	495(w)	718(s)	825 (vw)	1423 (m)	1464 (s)	-	-
Co(SAA.Cl) ₃	495(w)	718(s)	-	-	1464 (s)	-	-
Co(SAA) ₂ (SAA.Br)	497(w)	720 (s)	825 (w)	1425 (m)	1465 (s)	-	-
Co(SAA)(SAA.Br) ₂	497(w)	720 (s)	825 (vw)	1425 (m)	1465 (s)	-	-
Co(SAA.Br) ₃	497(w)	720 (s)	-	-	1465 (s)	-	-
Co(SAA) ₂ (SAA.I)	500(w)	722 (s)	825 (w)	1428 (m)	1465 (s)	-	-
Co(SAA)(SAA.I) ₂	500(w)	722(s)	825 (w)	1428 (m)	1465 (s)	-	-
Co(SAA.I) ₃	500(w)	722(s)	-	-	1465 (s)	-	-
Rh(SAA) ₃	505(w)	790(s)	850 (w)	1430 (m)	1458 (s)	-	-
Rh(SAA) ₂ (SAA. α -C ₁₀ H ₇ NCO)	505(w)	790(s)	850 (w)	1430 (m)	1458 (s)	1690	3365(m,b)
Rh(SAA)(SAA. α -C ₁₀ H ₇ NCO) ₂	505(w)	790(s)	850 (w)	1430 (vw)	1458 (s)	1690	3365(m,b)
Rh(SAA. α -C ₁₀ H ₇ NCO) ₃	505(w)	790(s)	-	-	1458(s)	1690	3365(m,b)
Rh(SAA) ₂ (SAA.Cl)	503(w)	785 (s)	845 (w)	1428 (w)	1455 (s)	-	-
Rh(SAA)(SAA.Cl) ₂	503(w)	785(s)	845 (w)	1428 (vw)	1455 (s)	-	-
Rh(SAA.Cl) ₃	503(w)	785(s)	-	-	1455 (s)	-	-
Rh(SAA) ₂ (SAA.Br)	505(w)	790(s)	850 (w)	1430 (w)	1458(s)	-	-
Rh(SAA)(SAA.Br) ₂	505(w)	790(s)	850 (vw)	1430 (vw)	1458 (s)	-	-
Rh(SAA.Br) ₃	505(w)	790(s)	-	-	1458 (s)	-	-
Rh(SAA) ₂ (SAA.I)	510(w)	795(s)	855 (w)	1432 (w)	1460 (s)	-	-
Rh(SAA)(SAA.I) ₂	510(w)	795(s)	855 (vw)	1432 (vw)	1460 (s)	-	-
Rh(SAA.I) ₃	510(w)	795(s)	-	-	1460 (s)	-	-





CRITICAL REVIEW

Comparing the qualitative rates of formation of α -naphthylamido substituted derivatives and halogenated derivatives and α -naphthylisocyanation undergo faster than halogenations.

Comparing with metal(II)monothioacetylacetonates, metal(III)monothioacetylacetonates undergo reaction slowly. Among metal(III)monothio- β -diketonates, the reaction rate of α -naphthylisocyanation qualitatively decreases as Rhodium(III) < cobalt(III) < iron(III). Hence decreasing order may be due to the decreasing ring current/quasiaromaticity.

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