CHEMISTRY

N-ACYLTHIOAMIDE METAL COMPLEXES- II

N-ACETYLTHIOBENZAMIDE COMPLEXES OF MANGANESE (II), IRON (II), COBALT (II), NICKEL (II), COPPER (II) AND ZINC (II) SULPHATES

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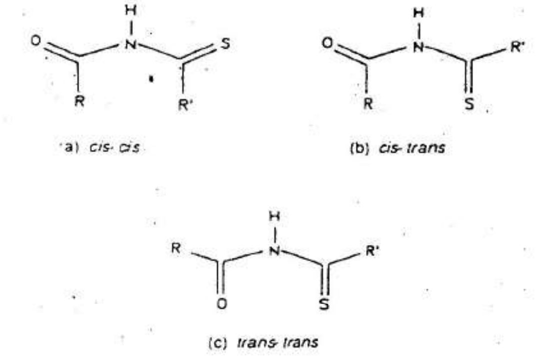
ABSTRACT

The magnetic, electronic (reflectance) and infrared spectral properties of divalent metal complexes, [M(N-ATB)$_3$] SO$_4$ and [Cu(N-ATB)$_2$]SO$_4$ (where M = Mn, Fe, Co, Ni and Zn; N-ATB = N-Acetylthiobenzamide) are reported. Substitution of a methyl group in place of a phenyl one in N-Benzoylthiobenzamide is found to weaken the C=O and C=S; and strengthen the N-H bonds of the metal chelate ring. Out of the two $\pi - \pi^*$ (C=O and C=S) transitions, the thiocarbonyl one shows stronger interaction in the metal complexes. The values of the magnetic moments are similar to those of analogous metal chelates.

Keywords : N-Acetylthiobenzamide, Spectral and Magnetic Properties

INTRODUCTION

Sumarakova et al [1] isolated RCSNHCOR′ (R,R′ = Me, Me; Me, Et; Me, Ph; Ph, Me) respectively for the purposes of studying the various conformers possible. Recently [2], the spectroscopic and magnetic properties of complexes of RCSNHCOR′(R=R′=C_6H_5) with some metal (II) sulphates, isolated through solid-solid interactions, have been reported; where the $C_6H_5CSNHCOC_6H_5$ (N-BTB), was shown from IR data to coordinate to the metal ions in its trans-trans configurational form (fig.1)



(a) *cis-cis*
(b) *cis-trans*
(c) *trans-trans*

Fig. 1: Configurational forms of -CO.NH.CS- group (R = CH_3; C_6H_5-; R' = C_6H_5-)

These studies have been extended to the N-Acetylthiobenzamide (N-ATB) as a ligand, ($C_6H_5CSNHCOCH_3$), complexing with Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) sulphates. It is also of further interest to study the effects of the methyl group substitution in these series compared with the phenyl group in the N-BTB series [2].

DISCUSSIONS

A few selected physical and analytical properties of the ligand N-ATB and its metal complexes are listed in Table 1. As reported earlier [2,3], Cu(II) gave a bis-complex whilst Mn(II), Fe(II), Co(II), Ni(II) and Zn(II) afforded the tris-complexes. All the complexes are stable in air and soluble in acetone, ether, ethanol and chloroform.

Infrared Spectra

The metal-ligand vibrational stretches and the assignment of other important vibrational bands are summarized in Tables 2 and 3. Some

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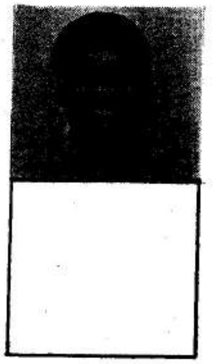

Table 1: Physical and Analytical Date* for [MIN-BTB)n]S0$_2$

Compound	Colour	Decomp T°C	%C	%H	%N	%S	%M
[Mn(N-ATB)$_3$]SO$_4$ $C_{27}H_{27}MnN_3O_7S_4$	pale-yellow	118	47.20 (47.09)	3.60 (3.95)	6.29 (6.10)	18.82 (18.62)	7.53 (7.98)
[Fe(N-ATB)$_3$]SO$_4$ $C_{27}H_{27}FeN_3O_7S_4$	Yellow	111	47.00 (47.03)	4.00 (3.95	5.89 (6.09)	18.80 (18.60)	7.98 (8.10)
[Co(N-BTB)$_3$]SO$_4$ $C_{27}H_{27}C_oN_3O_7S_4$	Cream	106	47.10 (46.82)	4.19 (3.93)	6.11 (6.07)	18.76 (18.51)	8.60 (8.51)
[N$_i$(N-ATB)$_3$SO$_4$ $C_{27}H_{27}N_3N_iO_7S_4$	Greenish-Yellow	115	46.94 (46.83)	4.19 (3.93)	6.20 (6.07)	18.33 (18.52)	8.40 (8.48)
[Cu(N-ATB)$_2$]SO$_4$ $C_{18}H_{18}CuN_2O_4O_3$	Golden-yellow	184	41.41 (41.73)	4.04 (4.04)	5.92 (5.41)	18.90 (18.57)	11.72 (12.27)
[Zn(N-ATB)$_3$]SO$_4$ $C_{27}H_{27}N_3O_7S_4Z_n$	Pale-yellow	250	46.52 (46.39)	4.06 (3.89)	6.41 (6.01)	18.65 (18.35)	9.60 (9.35)

* Microanalytical data determined at the University College, Dublin
.Complexes melted with decomposition.

Table 2: IR spectral data (cm^{-1}) as KBr disc

Compound	νN-H	ν C=O	δNH_2 + ν C=O	δNH_2 + νC=S	ν C=S	ν M-Ligand
N-ATB	3291s	1623vs	1594m	1329m	1159w	-
[Mn(N-ATB)$_3$]SO$_4$	3281m	1624vs	1594m	1327m	1134s	420w
[Fe(N-ATB)$_3$]SO$_4$	3284m	1624vs	1594m	1329s	1140s	411w
[Co(N-ATB)$_3$]SO$_4$	3282m	1624vs	1590m	1324m	1135m	400w
[Ni(N-ATB)$_3$]SO$_4$	3280vbr	1620m	1594m	1320m	1130s	400w
[Cu(N-ATB)$_2$]SO$_4$	3265vbr	1624m	1580m	1324m	1139w	403w
[Zn(N-ATB)$_3$]SO$_4$	3284m	1629s	1597s	1324m	1125s	427sh

Table 3: Comparison of C =0, C = S and M-Ligand (cm^{-1})

	Ligand	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
νC=O							
N-ATB	1623	1624	1624	1624	1620	1624	1629
N-BTB	1679	1678	1684	1678	1683	1675	1678
νC=O+δNH							
N-ATB	1594	1594	1594	1590	1594	1580	1597
N-BTB	1629	1632	1624	1631	1624	1620	1631
νC-S+δNH							
N-ATB	1329	1327	1329	1324	1320	1324	1324
N-BTB	1421	1352	1401	1404	1406	1350	1352
νC=S							
N-ATB	1159	1134	1140	1135	1130	1139	1125
N-BTB	1179	1172	1144	1147	1149	1669	1144
νN-H							
N-ATB	3291	3281	3284	3282	3280	3265	3284
N-BTB	3289	3280	3255	3280	3277	3260	3279
νM-Ligand							
N-ATB	-	420	411	400	400	403	427
N-BTB	-	402	413	410	409	402	407

comparisons are drawn between the sensitive IR bands of N-ATB and its complexes on one hand and their corresponding analogues of N-BTB [2] on the other (Table 3). It is observed that, a methyl substitution in place of a phenyl group in N-BTB and the corresponding complexes, shift the C=O and C=S stretches to lower frequencies whilst that of the N-H is shifted to higher frequencies. This could be attributed to the mesomeric interactions of the phenyl group by a methyl (inductive effect) one. In all cases the νC=O: νC=S ratio falls in the range 1.2 - 1.4. The shift in M-Ligand as a result of a methyl substitution is however irregular, as the dominant factor here is the metal-to-ligand (d- π) back bonding which stabilizes the M-S -6 bonding over that of the M-0 one.

Table 4: Reflectance Spectra of N-ATB and its metal (II) complexes (lkK = 1000cm^{-1})

Compd	$\bar{\nu}$maxkK	Probable assignment
N-ATB	36.22	$\pi - \pi^*$(C=O)
	27.71	$\pi - \pi^*$(C=S)
Mn(N-ATB)$_3$SO$_4$	38.18	$\pi - \pi^*$(C=O)
	30.05	$\pi - \pi^*$(C=S)
	26.31	d-d/MLCT
Fe (N-ATB)$_3$SO$_4$	38.18	$\pi - \pi^*$(C=O)
	30.05	$\pi - \pi^*$(C=S)
	28.06	
	25.77	$T_g \rightarrow {}^5E_g$
Co(N-ATB)$_3$SO$_4$	36.13	$\pi - \pi^*$(C=O)
	30.86	$\pi - \pi^*$(C=S)
	26.36	MLCT
	25.83	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
	20.09	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
	15.63	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
Ni(N-ATB)$_3$SO$_4$	38.31	$\pi - \pi^*$(C=O)
	29.74	$\pi - \pi^*$(C=S)
	26.36	MLCT
	17.34	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
	15.44	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
	13.92	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
Cu(N-ATB)$_2$SO$_4$	37.88	$\pi - \pi^*$(C=O)
	29.85	$\pi - \pi^*$(C=S)
	23.28	MLCT
	13.40	${}^2Eg \rightarrow 2B_{1g}$ (dxz, dyz-dx^2y^2)
Zn(N-ATB)$_3$SO$_4$	32.42	$\pi - \pi^*$(C=O)
	25.90	$\pi - \pi^*$(C=S)

Table 5: Magnetic Properties at 293K

Compd	Susceptibility $X_M \times 10^6$ c.g.s.u	μobsB.M $\pm$0.06
Mn(N-ATB)$_3$SO$_4$	14683	5.87
Fe(N-ATB)$_3$SO$_4$	12426	5.40
Co(N-ATB)$_3$SO$_4$	10867	5.05
Ni(N-ATB)$_3$SO$_4$	4754	3.34
Cu(N-ATB)$_2$SO$_4$	1603	1.94
Zn(N-ATB)$_3$SO$_4$	diamagnetic	diamagnetic

Electronic and Magnetic Properties

The electronic spectral and magnetic data for the N-ATB series of complexes and their assignments are summarised in Tables 4 and 5. The band positions are very similar to those reported for the N-BTB series [2] except that the $\pi - \pi^*$ (C=O) and $\pi - \pi^*$ (C=S) of the N-ATB series occur at 36.22 and 27.71kK respectively. Out of the two $\pi - \pi^*$ transitions, the thiocarbonyl (C=S) one showed stronger interaction in the metal complexes when compared with the ligand; and on complexation, both shift to higher frequencies. The probable assignments have been based on previous work and related complexes [2 - 5]. These assignments reveal a close similarity in structural properties between the N-ATB and the N-BTB series.

The magnetic data reveal no irregularity in the moment values; and are all within the ranges commonly observed for high spin octahedral complexes [6]. That for the copper (II) complex supported by the d-d bands suggest a square planar configuration for $[Cu(N\text{-}ATB)_2]SO_4$.

EXPERIMENTAL

The ligand, N-Acetylthiobenzamide was prepared by a method reported [2] in an earlier paper except that, the acid chloride used in this case is acetylchloride instead of benzoylchoride.

N-Acetylthiobenzamide (N-ATB), C_9H_9NOS, Deep yellow m.p 105-107°C; (lit.[1,7] m.p105°C).

(Found:C,60:58;H,5.06;N,8.21;S,18.10 Calc. for C_9H_9NOS, C,60.31;H,5.06;N,7.81;S,17.87).

The complexes $[M(N\text{-}ATB)_3SO_4$ (M=Mn(II), Fe,(II), Co(II), Ni(II) and Zn(II) and $[Cu(N\text{-}ATB)_2]SO_4$ were prepared using similar methods described [2] for $[M(N\text{-}BTB)_3]SO_4$ and $[Cu(N\text{-}BTB)_2]SO_4$. The analytical and physical data of the complexes are presented in Table 1.

The spectroscopic and magnetic methods used have also been described elsewhere [2].

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