19

N-ACYLTHIOAMIDE METAL COMPLEXES-1:

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

A. A. Adimado, BSc PhD CChem MRSC
E. Adei, BSc MPhil

ABSTRACT

Metal (II) complexes of the type $[M(N\text{-}BTB)_3]SO_4$ where N-BTB = $C_6H_5CO.NH.CSC_6H_5$, M=Mn(II), Fe(II), Co(II), Ni(II) and Zn(II); and also $[Cu(N\text{-}BTB)_2]SO_4$, have been synthesized by solid - solid interaction and characterised by means of a number of techniques including elemental analysis, IR spectra, magnetic susceptibility measurements and electronic (reflectance) spectra. All the complexes exhibit octahedral stereochemistry except the Cu(II) complex which is square planar. IR data indicates that the N-Benzoylthiobenzamide coordinates to the metal ions in its trans-trans configurational form.

Keywords: Thioketoiminoketones, N-Benzoylthiobenzamide, Spectral and Magnetic properties

INTRODUCTION

Complexing abilities of acyclic imides containing the -CONHCO - group have received considerable attention over the past few decades [1-4]. However, most of the studies have been concerned with complexes of diacetamide. Although the first systematic study on transition metal complexes of these imides has been reported by Kraihanzel and Grenda [5] very sparse information could be found in the literature concerning the complexing ability of other acyclic imides, especially those containing the -CONHCS- group [6,7].

This paper therefore reports the synthesis of N-Benzoylthiobenzamide (N-BTB), $C_6H_5CONHCSC_6H_5$, by benzoylation of thiobenzamide and the preparation of some metal (II) complexes of this imide by solid-solid interaction [4,8]. The complexes have been studied from their analytical, magnetic, vibrational and electronic (reflectance) spectral data.

DISCUSSIONS

The elemental analysis of these complexes indicates a 1:3 (M:N-BTB) ratio formulation except in the Cu(II) complex where the ratio is 1:2. The melting points are not sharp but all complexes melted with decomposition at the stated temperatures (Table 1).

All complexes are stable in air and quite soluble in acetone, ether, ethanol and chloroform.

Table 1: Physical and Analytical Data* for $[M(N\text{-}BTB)n]SO_4$

Compound	Colour	'Decomp T∘C	%C	%H	%N	%S	%M
$[Mn(N\text{-}BTB)_3]SO_4$ $C_{42}H_{33}MnN_3O_7S_4$	Cream	142	57.60 (57.66)	3.70 (3.80)	4.53 (4.80)	14.82 (14.86)	5.92 (6.28)
$[Fe(N\text{-}BTB)_3]SO_4$ $C_{42}H_{33}FeN_3O_7S_4$	Orange	158	57.60 (57.60)	3.80 (3.80)	4.00 (4.80)	14.80 (14.64)	6.00 (6.38)
$[Co(N\text{-}BTB)_3]SO_4$ $C_{42}H_{33}CoN_3O_7S_4$	dk blue	114	57.00 (57.40)	3.78 (3.78)	4.52 (4.78)	14.20 (14.59)	6.07 (6.71)
$[Ni(N\text{-}BTB)_3]SO_4$ $C_{42}H_{33}N_3NiO_7S_4$	Brownish	156	57.90 (57.41)	3.80 (3.70)	4.03 (4.78)	14.90 (14.59)	6.34 (6.68)
$[Cu(N\text{-}BTB)_2]SO_4$ $C_{28}H_{22}CuN_2O_6S_3$	Coffee	210	52.00 (52.37)	3.40 (3.45)	4.08 (4.36)	15.00 (14.98)	10.20 (9.90)
$[Zn(N\text{-}BTB)_3]SO_4$ $C_{42}H_{33}N_3O_7S_4Zn$	Cream	131	56.90 (56.98)	3.16 (3.76)	4.63 (4.75)	14.48 (14.48)	6.95 (7.38)

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

Infrared spectra

Comparison of the IR spectra of the ligand with those of the complexes (Table 2) reveal a shift in most of the important bands. The free N-H band in the ligand as a result of a trans-trans configuration (Fig. 1) of N-benzoylthiobenzamide, appears to have shifted to lower frequencies in the metal complexes, possibly attributable to an >N-H...OSO_3 hydrogen bonding. The sulphate anion being outside the co-ordination sphere, is involved

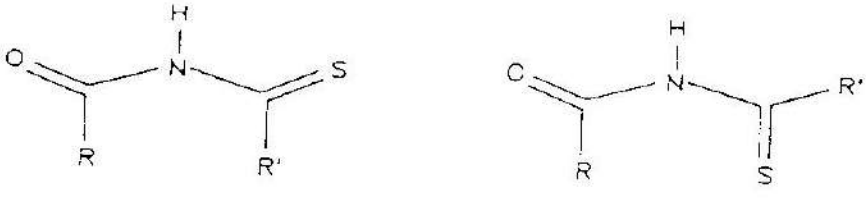
Dr. A. A. Adimado
Dept. of Chemistry
USt, Kumasi, Ghana

E. Adei
Dept. of Chemistry
UST, Kumasi,Ghana

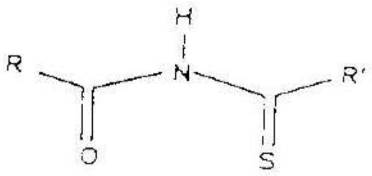
Table 2: IR spectral data (cm^{-1}) as KBr disc

Compound	N-H	νC=O	δNH + νC=O	δNH + νC=S	νC=S	M-Ligand
N-BTB	3289m	1679vs	1629vs	1421m	1179m	-
$[Mn(N\text{-}BTB)_3]SO_4$	3280s	1678s	1632vs	1352m	1172vs	402w
$[Fe(N\text{-}BTB)_3]SO_4$	3255vbr	1684s	1624m	1401s	1144vs	413w
$[Co(N\text{-}BTB)_3SO_4$	3280s	1678s	1631s	1404w	1147vs	410w
$[Ni(N\text{-}BTB)_3]SO_4$	3277w	1683s	1624m	1406m	1149vs	409w
$[Cu(N\text{-}BTB)_3]SO_4$	3260vbr	1675m	1620m	1350m	1169vs	402w
$[Zn(N\text{-}BTB)_3]SO_4$	3279s	1678vs	1631vs	1352w	1144vs	407w

vs-very strong; s-strong; m-medium; w-weak; br-broad



(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-)

in such a hydrogen bonding to the imide hydrogen in the complexes. This is confirmed by a single broad band at 980cm^{-1} characteristic of uncoordinated sulphate ion [9].

In the complexes the thiopeptide linkage, -CONHCS- does not bite the metals in the same fashion as does monothio-ß - diketones [10], as is evidenced by IR findings. The imide bands in the 1700-1100cm^{-1} region are not vibrationally pure. these bands are mainly due to the νCO + δ NH; νCS + δNH and also the C-N-C skeletal vibrations. The maximum shift in the pure ν C=O band in the complexes is 5cm^{-1} whilst that for νC=S is 35cm^{-1} relative to the ligand. These marked unequal shifts in the carbonyl and thiocarbonyl modes suggest unequal biting of the metal by the -CONHCS- group, compared with that of -$COCH_2CS$- group in the monothio-ß-diketone complexes [10]. The greater shift in C=S over that in C-O to lower frequencies in the complexes could be a result of metal-to-ligand (d-π) back bonding thereby stabilizing the sulphur-metal σ bonding. Thus the (d-π) back bonding stabilizes the oxygen-metal - bonding to a much lesser extent. The bands between 300-450 cm^{-1} have been assigned to the M-Ligand vibrations.

Magnetic and Electronic Spectral studies

The magnetic and electronic spectral properties of the metal complexes are given in Tables 3 and 4 respectively along with the probable assignments for the electronic transitions based on available literature data [5,11,12]. The electronic spectra in the UV region generally show bands characteristic of $\pi \rightarrow \pi^*$ transitions and charge transfer bands. For the titled compounds, these are due to the $\pi \rightarrow \pi^*(C=O)$ and π-$\pi^*(C=S)$ transitions. These occur at 40.36 and 32.86kK respectively in the ligand and have been observed to shift to lower frequencies (Table 3) in the metal complexes, an evidence of metal to ligand (d-π) back bonding. The zinc (II) complex shows bands due mainly to the ligand except that compared to those of the ligand, there is a general bathochromic shift. Magnetic data confirm a diamagnetic character for $[Zn(N\text{-}BTB)_3SO_4$ and no d-d bands were observed as expected.

Table 3: Reflectance Spectra of N-BTB and its metal (II) complexes (lkK = 1000cm^{-1})

Compd	maxkK	Probable assignment
N-BTB	40.36	$\pi - \pi^*$(C=O)
	32.86	$\pi - \pi^*$(C=S)
	26.08	C.T.
Mn(N-BTB)$_3$SO$_4$	35.03	$\pi - \pi^*$(C=O)
	31.54	$\pi - \pi^*$(C=S)
	25.27	${}^6A_{1g}(S) \rightarrow {}^4Eg, {}^4A2g$ (G)
	19.46	${}^6A_{1g}(S) \rightarrow {}^4T2g$ (G)
	17.10	${}^6A_{1g}(S) \rightarrow {}^4T1g$(G)
Fe (N-BTB) $_3$SO$_4$	39.51	$\pi - \pi^*$(C=O)
	30.12	$\pi - \pi^*$(C=O)
	25.31	MLCT
	11.49	${}^5T_{2g} \rightarrow {}^5E_g$
Co(N-BTB)$_3$SO$_4$	39.37	$\pi - \pi^*$(C=O)
	31.45	$\pi - \pi^*$(C=S)
	24.77	MLCT
	19.46	${}^4T_{1g}$ (F)$\rightarrow {}^4T_{1g}$(P)
	16.87	${}^4T_{1g}$ (F)$\rightarrow {}^4A_{2g}$(F)
	12.60	${}^4T_{1g}$ (F)$\rightarrow {}^4T_{2g}$(F)
Ni(N-BTB)$_3$SO$_4$	39.51	$\pi - \pi^*$(C=O)
	30.12	$\pi - \pi^*$(C=S)
	25.31	${}^3T_{2g}$(F)$\rightarrow {}^3T_{1g}$(P)
	18.62	${}^3T_{2g}$(F)$\rightarrow {}^3T_{1g}$(F)
	13.77	${}^3T_{2g}$(F)$\rightarrow {}^3T_{2g}$(F)
Cu(N-BTB)$_3$SO$_4$	37.06	$\pi - \pi^*$(C=O)
	30.69	$\pi - \pi^*$(C=S)
	24.30	MLCT
	15.43	${}^2E_g \rightarrow {}^2B_{1g}$
	11.84	${}^2E_g \rightarrow {}^2B_{1g}$
Zn(N-BTB)$_3$SO$_4$	37.76	$\pi - \pi^*$(C=O)
	31.69	$\pi - \pi^*$(C=S)
	24.98	MLCT

MLCT: Metal-Ligand Charge Transfer.

Table 4: Magnetic properties at 283k

Compd	Susceptibility X_M X 10^6 c.g.s.u.	μobs.B.M. ±0.06 c.g.s.u.
Mn(N-BTB)$_3$ SO4	15239	5.98
Fe(N-BTB)$_3$ SO4	13363	5.60
Co(N-BTB)$_3$ SO4	11171	5.12
Ni(N-BTB)$_3$ SO4	4984	3.42
Cu(N-BTB)$_3$ SO4	1522	1.89
Zn(N-BTB)$_3$ SO4	Diamagnetic	Diamagnetic

The magnetic properties of these complexes in the solid state at 293K are given in Table 4. There is no irregularity in the magnetic moments as the values for the Mn(II), Fe(II), Co(II) and Ni(II) complexes are all within the ranges commonly observed for high spin octahedral complexes [13]. The magnetic moment for the Cu(II) complex is reasonable and supports the bands observed in the visible region for square planar copper(II) complexes. Simple Cu(II) complexes, those lacking Cu-Cu interactions, are generally in the range 1.75-2.20 B.M.[14]. A magnetic moment value of 1.89B.M recorded for the Cu(II) complex coupled with the d-d bands at 15.43 and 11.84kK, which have been assigned to ${}^2Eg \rightarrow {}^2B_{1g}(d_{xy},d_{yz} \rightarrow d_{x^2-y^2})$, and ${}^2A_{1g} \rightarrow {}^2B_{1g}$ ($d_{z^2} \rightarrow d_{x^2-y^2}$) respectively, are indicative of a square planar formulation for the [Cu(N-BTB)$_2$] SO$_4$ complex. The third and lowest band, ${}^2B_{2g} \rightarrow {}^2B_{1g}$ ($dxy \rightarrow dx^2\text{-}y^2$), was not observed in the reflectance spectra.

The d-d bands in the electronic spectra of the Mn(II) complex occur around 17.10, 19.46 and 25.27kK which have been assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$(G), ${}^6A_{1g} \rightarrow {}^4T_{2g}$(G) and ${}^6A_{1g} \rightarrow {}^4E_g$, ${}^4A_{2g}$ (G) respectively. The magnetic moment of 5.98 B.M. confirms that the Mn (II) is in high spin with a ground term of ${}^6A_{1g}$. The three bands therefore support the octahedral configuration.

The observed magnetic moment for the Fe(II) complex, with some orbital contribution, is 5.60B.M., and supports an octahedral stereochemistry. The electronic spectra gives a broad band around 11.49kK assignable to ${}^5T_{2g} \rightarrow {}^5Eg$ transition. Magnetic moment value of 5.12 B.M reported for the Co(II) complex is characteristic of high-spin d^7 octahedral Co(II) system. The electronic spectra gives three bands at 12.60, 16.87 and 19.46kK which have been assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively.

With a $t_{2g}^6e_g^2$ configuration having a ground term of ${}^3A_{2g}$, the Ni(II) complex shows three bands around 13.77, 18.02 and 25.31kK assignable to ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_2g \rightarrow {}^3T_{1g}(P)$ transitions respectively; and a magnetic moment of 3.42 B.M. at 293K confirms the presence of two unpaired electrons typical of octahedral Ni(II) complexes.

EXPERIMENTAL

N-Benzoylthiobenzamide (N-BTB) was obtained by adding 0.10 mole of benzoylchloride slowly with stirring to an ice-cold solution of 0.10 mole of thiobenzamide dissolved in 50cm^3 pyridine. The mixture was stirred for 5 - 6 hr and poured slowly with stirring into ice-cold 10% sulphuric acid thus leading to the precipitation of N-BTB. The product was recrystallized from toluene and then stored in a desiccator over drierite. N-Benzolythiobenzamide (N-BTB), $C_{14}H_{11}NOS$, red garnets: m.p 119-120°C; (lit m.p. 119°C) [15]. (Found : C,69.21; H,4.08; N,5.12; S,12.92. Calc for $C_{14}H_{11}NOS$: C,69.68; H,4.59; N,5.81; S,13.29)

Preparation of Metal chelates.

The imide chelates were prepared by solid-solid interactions. Stoichiometric quantities of the imide (N-BTB) and anhydrous metal (II) sulphate in a 3:1 stoichiometric ratio were ground in a mortar; alternate 15 min period of grinding and vacuum drying were continued until infrared data indicated that the reaction was complete. the products were washed thoroughly with anhydrous ether to remove unreacted imide and dried in vacuo for 10 min. The physical data of these chelates are presented in Table 1.

Physical Measurements

The IR spectra (4000-299cm^{-1}) as KBr discs were recorded using a Perkin Elmer 283B IR spectrophotometer whilst the Diffuse Reflectance spectra were recorded in the 40,000-10,000cm^{-1} range at room temperature on a Perkin Elmer UV 552 spectrophotometer equipped with a reflectance attachment, using $BaCO_3$ as reference. Peak positions were read off on a Perkin Elmer IR Data Station equipped with a UV Programme IF552 Disc, hooked through a Perkin Elmer 283 on-line communication accessory. Magnetic measurements were made by the Gouy method at 293K using Hg $[Co(SCN)_4]$ as a calibrant. All samples were measured as powdered solids.

ACKNOWLEDGEMENT

One of us (A.A.A) is grateful to the University College, Dublin for allowing the use of laboratory facilities. Travel grant by UNESCO and Irish Science Foundation to (A.A.A) is gratefully acknowledge.

REFERENCES

1. ***T. Uno, K. Machida and I. Hamanaka,*** *"Infrared Spectra of Acyclic Imides (IV). Effects of Alkali halides on the Infrared Spectra of Diacetamide" Bull. Chem. Soc. Japan., 34, 1448, (1961).*
2. ***T. Uno and K. Machida,*** *"Infrared Spectra of Acyclic Imides (I)", Bull. Chem. Soc. Japan., 34, 545 (1961).*
3. ***I. Lindquist,*** *"Inorganic Adduct Molecule of Oxo-compounds", Academic Press, New York, p17, (1963).*
4. ***P.S. Gentile and T.A. Shankoff,*** *"Solid-Solid Interaction. III. Complexes of Acetamide and Alkali and Alkaline Earth Metal Salts." J. Inorg. Nucl. Chem., 27, 2301, (1965).*
5. ***C.S. Kraihanzel and S.C. Grenda,*** *"Acyclic Imides as Ligands I Diacetamide complexes of Manganese (II), Iron(II), Cobalt(II), Nickel(II), Copper(II) and Zinc (II) Perchlorates". Inorg. Chem., 4, 1037, (1965).*
6. ***T.N. Sumarakova, R.A. Slavinskaya, V.A. Solomin and T.A. Tember-Kovaleva,*** *"Physicochemical Properties and Structures of Acyclic N-Acyl substituted Thioamides" Akad. Nauk. Kaz SSR, Ser Khim, 28, 28, (1978).*
7. ***E.M. Vorobeva, I.G. Litvik, T.N. Sumarakova, M.F. Vereshak and A.K. Guembaev,*** *"Coordinate compounds of Fe(II) with N-Acylamides," Zh. Obshch. Khim., 51, 2773, (1981).*
8. ***P.S. Gentile and T.A. Shankoff,*** *"So[illegible]-Solid Interaction of Mixed Halo Com[illegible]exes of Copper (II) and Cobalt (II)", J. Inorg. Nucl. Chem., 29, 1393, (1967).*
9. ***L.J. Bellamy,*** *"The Infrared Spectra of Complex Molecules", John Wiley and Sons Inc. (New York), p205, (1958).*
10. ***M.Cox, J. Darken, B.W. Fitzsimmons, A.W. Smith, L.F. Larkworthy and K.A. Rogers,*** *"Spin isomerism in tris (monothio-β-diketonato) iron (III) complexes", J. Chem. Soc (Dalton), 1192, (1972).*
11. ***F.A. Cotton,*** *"Ligand Field Theory", J. Chem. Educ. 41, 466 (1964). 1192.*
12. ***T. Shankoff,*** *"Diacetamide as a Ligand", PhD Dissertation, Department of Chemistry, Fordham Univ. (Univ.) (USA), (1966).*
13. ***F.E. Mabbs and D. Machin,*** *"Magnetism and Transition Metal Complexes", Chapman and Hall. London. (1973). 2, 124.*
14. ***B.J. Hathaway,*** *"Stereochemistry and electronic properties of Copper (II) ion". Academic Press London. Essays in Chemistry, 2, 61, (1971).*
15. ***J. Geordeler and K. Studelbauer,*** *"N-Acylthioamides". Chem. Ber., 98, 1556, (1965).*