

Metal Complexes of a Schiff base formed by the Condensation of S-benzyl dithiocarbamate with Furil

MAHMOUD A.S. MONSHI

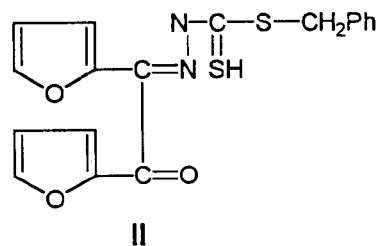
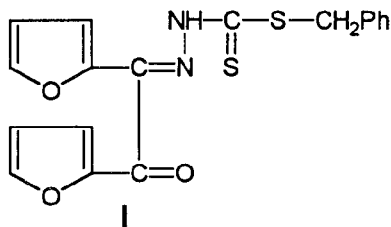
Department of Chemistry, College of Science, King Saud University,
P.O. Box 2455, Riyadh-11451, Saudi Arabia

(Received 13th June, 1997, revised 9th December, 1997)

Summary: New nickel(II), cobalt(II), copper(II) and cadmium(II) complexes of a Schiff base ligand formed by condensation of furil with S-benzylthiocarbamate [HFBT]. These have been synthesised and characterized by element analysis, and spectral [IR, UV-vis, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$] measurements. The spectral data show that the ligand behaves in neutral bidentate or mononegative bidentate manner.

Introduction

In continuation of our previous work [1-5] on a Schiff base ligand containing the S-benzylthiocarbamate moiety, we report here the preparation and characterization of some new metal complexes of a Schiff base formed by condensation of S-benzylthiocarbamate and furil. The transition metal complexes of several of these compounds have also been screened for their medicinal properties [6], possess some degree of cytotoxic activity [7] and their activity against bacteria [2], cancer [8] and fungal [9]. The ligand may possess any one of the structure I-II shown below or they may exist as tautomeric equilibrium mixture of these forms.



Results and Discussion

The analytical and physical data for the metal complexes are listed in Table-1. The $^1\text{H-NMR}$ spectrum of HFBT in [DMSO] shows three signals at 4.54, 7.32 and 8.12 ppm relative to TMS which may be assigned to, methylene protons of the -S-CH₂Ph moiety (S-CH₂Ph), aromatic protons and the imino proton respectively. The signals due to the furan ring protons were observed at 6.61, 6.77, 7.67 and 7.88 ppm. In $^{13}\text{C-NMR}$ spectrum of the ligand, three signals are observed at 199.46, 176.55, and 150.06 which are attributed to the C=S, C=O and C=N

Table-1: Analytical and Physical data for the complexes derived from HFBT

Compound	Empirical Formula	Colour	mp (°C)	Found (Calc.) %			
				C	H	M	Cl
HFBT	C ₁₈ H ₁₄ N ₂ O ₃ S ₂	yellow	122	57.94 (58.37)	3.7 (3.81)	-	-
Co[HFBT]Cl ₂	NiC ₁₈ H ₁₄ N ₂ O ₃ S ₂ Cl ₂	olive	230	43.75 (43.38)	3.05 (2.83)	12.0 (11.64)	13.95 (14.05)
Co[HFBT] ₂ Cl ₂	CoC ₃₆ H ₂₈ N ₄ O ₆ S ₄ Cl ₃	black	170	49.51 (49.77)	3.8 (3.23)	7.02 (6.79)	8.34 (8.18)
Cu[FBT] ₂	CuC ₃₆ H ₂₆ N ₄ O ₆ S ₄	reddish brown	165	53.5 (53.89)	3.48 (3.24)	8.26 (7.92)	-
Ni[HFBT]Ac ₂	NiC ₂₂ H ₂₀ N ₂ O ₇ S ₂	dark green	225	48.70 (48.35)	4.0 (3.69)	10.40 (10.61)	-
Co[HFBT]Ac ₂	CoC ₂₂ H ₂₀ N ₂ O ₇ S ₂	dark gray	177	48.10 (48.26)	3.58 (3.68)	10.82 (10.77)	-
Cu[FBT]Ac	CuC ₂₀ H ₁₆ N ₂ O ₅ S ₂	red	191	48.5 (48.88)	3.5 (3.25)	13.42 (12.93)	-
Cd[FBT] ₂	CdC ₂₀ H ₂₄ N ₂ O ₅ S ₂	orange	104	50.94 (50.37)	3.70 (3.81)	13.92 (13.17)	-

group respectively. The above observation indicate that the ligand actually exists in thione form.

The principle IR bands of HFBT and its metal complexes are listed in Table-2. The IR spectrum of HFBT (in KBr) shows three bands at 3133, 1650 and 1585 cm⁻¹ which may be assigned to $\nu(\text{NH})$, $\nu(\text{CO})$ [10] and $\nu(\text{C}=\text{N})$ [11] stretching vibrations respectively. The double weak bands at 2916 and 2970 cm⁻¹ are attributed to the symmetric and asymmetric stretching vibration of S-CH₂Ph [21,22]. The two bands at 1242 and 931 cm⁻¹ are assigned to $\nu(\text{C}=\text{S})$ and $\nu(\text{N}-\text{N})$ [11] stretching vibrations respectively. The possibility of thione-thiol tautomerism (NH-C=S → N=C-SH) is ruled out, since no band characteristics of thiol group (2500-2650 cm⁻¹) is found in the spectrum of the ligand.

The HFBT behaves as neutral bidentate ligand coordinating via the azomethine nitrogen and the ketone oxygen atom. This behaviour is found in Ni[HFBT]Cl₂, Ni[HFBT]Ac₂, Co[HFBT]₂Cl₂ and Co[HFBT]Ac₂. This mode of complexation is supported by the shift in $\nu(\text{C}=\text{N})$ to and to higher frequency in lower $\nu(\text{N}-\text{N})$ indicating coordination through the azomethine group [23]. Also the shift in $\nu(\text{C}=\text{O})$ to lower energy indicating that the coordination is through oxygen atom. The $\nu(\text{C}=\text{S})$ band remain at the same position for the free ligand indicating that this does not participate in the complexation.

The HFBT, on the other hand, may act as mononegative bidentate ligand coordinating via the

azomethine nitrogen and CS in the thiol form, with the displacement of hydrogen atom from the latter group. This behaviour is found in Cu[FBT]₂, Cu[FBT]Ac and Cd[FEFT]₂ complexes. The $\nu(\text{C}=\text{N})$ band shifts to lower wavenumber confirming the participation of azomethine nitrogen in coordination. Also the disappearance of $\nu(\text{C}=\text{S})$ and $\nu(\text{NH})$ band with the appearance of new bands in the region 1616-1620 and 617-620 cm⁻¹ assigned to $\nu(\text{N}=\text{C}-\text{S})$ and $\nu(\text{C}-\text{S})$ respectively [12], indicate the involvement of this sulphur in bonding to the metal ion. The observed new bands in the complexes between 532-545, 470-485, 378-390, and 305-320 cm⁻¹ are tentatively assigned to (M-O) [13], (M-N) [14], (M-S) [12], and $\nu(\text{M}-\text{Cl})$ [12] respectively.

Spectral studies

The electronic spectra of cobalt complex Co[HFBT]Cl₂ and Co[HFBT]Ac₂ in CHCl₃ showed two bands in the region 2000-20080 and 25380-26178 cm⁻¹ which are assigned to ${}^4\text{A}_{2g} \leftarrow {}^4\text{T}_{2g}(\text{F}) \nu_2$ and ${}^4\text{T}_{1g} \leftarrow {}^4\text{T}_{1g}(\text{P}) \nu_3$ [24] transition respectively in an octahedral geometry. The calculated ν_1 , Δq , B and ν_2/ν_1 values for Co[HFBT]₂Cl₂, are 9289 cm⁻¹, 1070 cm⁻¹, 1220 cm⁻¹, 1.26 and 2.153 respectively, and for Co[HFBT]Ac₂, are 9340 cm⁻¹, 1073 cm⁻¹, 1162 cm⁻¹, 1.19 and 2.149 respectively. The values ν_2/ν_1 suggest octahedral geometry for both cobalt complexes [15].

The electronic spectra of nickel complexes Ni[HFBT]Cl₂ and Ni[HFBT]Ac₂ in CHCl₃ show bands in the region 18868-21739 and 25906-26178 cm⁻¹ which are assigned to the ${}^1\text{A}_{2g} \leftarrow {}^1\text{A}_{1g}$ and ${}^1\text{B}_{2g}$

Table-2: IR spectral bands of HBATC and its metal complexes

Compound	$\nu(\text{NH})$	$\nu(\text{C-O})$	$\nu(\text{C=N})$	$\nu(\text{N-N})$	$\nu(\text{C-S})$	$\nu(\text{N=C-S})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{M-S})$	$\nu(\text{M-Cl})$
HFBT	3133	1650	1585	938	-	-	-	-	-	-
Ni[HFBT]Cl ₂	3131	1572	1558	989	-	-	540	470	-	320
Co[HFBT] ₂ Cl ₂	3137	1563	1547	994	-	-	532	471	-	305
Cu[FBT] ₂	-	1660	1572	995	620	1616	-	471	390	-
Ni[HFBT]Ac ₂	3131	1571	1545	988	-	-	545	473	-	-
Co[HFBT]Ac ₂	3134	1567	1557	986	-	-	542	477	-	-
Cu[FBT]Ac	-	1663	1567	963	618	1620	-	485	384	-
Cd[FBT] ₂	-	1657	1565	970	622	1618	-	480	378	-

$\leftarrow {}^1A_{1g}$ transition in square planar geometry for these complexes [16]. The ¹H-NMR spectra for these complexes show the presence of signal for imino proton with shift to higher field by (1.28-1.34 ppm) indicate that the both complexes remain in the thione form. Also, the signals for aromatic protons and the methylene proton are shifted to lower field by (0.2 ppm) and (0.12-0.14 ppm) respectively, while the signals due to the furan rings appeared at 6.15, 6.49, 6.81 and 8.01 ppm. Thus, the nickel complexes have diamagnetic properties and square-planar structure.

The electronic spectra of copper complexes Cu[FBT]₂ and Cu[FBT]Ac in CHCl₃ show bands in the 18382-19920 and 25906-26595 cm⁻¹ region the first band was assigned to ²E_g \leftarrow ²T_{2g} transition, the position for square-planar copper (II) complexes and the second band as ligand-metal charge transfer transition [17].

Experimental

All chemicals used were of analar grade.

Synthesis of [HFBT]

The hydrazine-S-benzylthiocarbamate was synthesized according to the general literature [18]. The furil was prepared according to the reported procedure [19]. The Schiff base was prepared by heating equimolar amount of furil (9.5 g, 0.05 mol) and the ester (10 g, 0.05 mol) in methanol (100 mL) in presence of few drops of pyridine and refluxed for 3 hours. The brownish yellow crystals (m.p. 122°C) appeared which were separated and crystallized from absolute ethanol.

Preparation of metal chelates

All complexes were prepared by mixing equimolar quantities of metal halide or acetate and the Schiff base HFBT in absolute ethanol. The

mixture was refluxed from 10 to 50 minutes depending on the salt used. The resulting solid complexes were filtered off hot, washed with hot ethanol, then diethyl ether and dried in a vacuum desiccator over anhydrous calcium chloride. The metal halide were determined by standard methanol [20]. All measurements were carried out as described earlier [1].

References

1. M.A.S. Monshi and N.M. Abd El-Salam, *J. Chem. Soc. Pak.*, **18**(2), 155 (1996).
2. M.A.S. Monshi, N.M. Abd El-Salam and A.A. Salamah, *J. Chem. Soc. Pak.*, **18**(3), 214 (1996).
3. M.A.S. Monshi and N.M. Abd El-Salam, *J. King Saud Univ.*, **8**, Science (2), (1996).
4. M.A. S. Monshi, *J. King Saud Univ.*, **9**, Science (2), (1996).
5. M.A. S. Monshi, *Egypt J. Chem.*, (in print).
6. K.C. Staphaty and H.P. Mishra, *Ind. J. Chem. Sect. A*, **20A**, 1035 (1981).
7. M. Das and S.E. Livingston, *Inorg. Chim. Acta*, **19**(1), 5-10 (1976).
8. M.M. Rahman and M.A. Ali, *Transition Met. Chem.*, **18**(4), 396 (1993).
9. D. Sen, A.K. Panda, B. Bqnerjee and S.S. Sen, *Ind. J. Chem.*, **21A**, 1096 (1982).
10. M.A. Ali and S.G. Teoh, *J. Inorg. Nucl. Chem.*, **40**, 451 (1978).
11. A. Braibanti, F. Delvalla, M.A. Pellinghelli and E. Leoparati, *Inorg. Chem.*, **7**, 1430 (1968).
12. G.M. Abdu El-Reash, F.I. Taha, A.M. Shallaby and O.A. El100 mL-Gamal, *Synth. React Inorg. Met-Org. Chem.*, **20**(7), 887 (1990).
13. B.B. Kaul and K.B. Pandeya, *J. Inorg. Nucl. Chem.*, **40**, 1035 (1977).
14. M.P. Teotia, D.K. Rastogi and W.U. Malik, *Inorg. Chim. Acta*, **7**, 339 (1973).
15. K.M. Ibrahim and M.M. Bekheit, *Transition Met. Chem.*, **13**, 230 (1988).
16. A.B.P. Lever, "Inorganic Electronic

- Spectroscopy", Elsevier, Amsterdam, (1968).
17. M. Paulaniandavar and C. Natarajan, *Aust. J. Chem.*, **33**, 737 (1980).
 18. M.A. Ali and S.G. Teah, *J. Inorg. Nucl. Chem.*, **41**, 809 (1979).
 19. A.I. Vogel, "Text Book of Practical Organic Chemistry" 3rd Ed., Longman, London, P. 835 (1956).
 20. A.I. Vogel, "Quantitative Inorganic Chemistry", Longman, London, (1956).
 21. A. El-Dissouki, G.B. Mohamad and A.Z. El-Sonbati, *Inorg. Chim. Acta*, **74**, 279 (1983).
 22. M.M. Abou-Sekkina, A. El-Dissouki and A.Z. El-Sonbati, *Acta. Chim. Hung.*, **114**, 29 (1983).
 23. A.A. El-Asmy and T.Y. El-Ansi, *Synth. React. Inorg. Met-org. Chem.*, **19**(4), 309 (1989).
 24. C.K. Jorgenson, *J. Inorg. Nucl. Chem.*, **24**, 1521 (1967).