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Ligational Behavior of a Tridentate NOS Donor Ligand Towards Transition Metal Ions

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Abstract. The reaction of a Schiff base (formed by the condensation of S-benzyl dithiocarbazate with benzoin [HBBTC]) with some bivalent metal ions give mono-ligand complexes having general formula M [BBTC]X., nH_2O where [M= Co^{2+}, Cu^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, and Hg^{2+}; X=Ac or Cl and n =0-2]. Elemental analysis, magnetic susceptibility and spectral (Ir, Uv-vis and NMR) measurements have been used to characterize the complexes and suggest their structures. Ir data show that the ligand behaves as mononegative tridentate.

Introduction

Extensive work has been done [1-13] on metal complexes of Schiff bases containing NS, NO and NOS donors. Magnetic and spectroscopic study of Ni^{2+} and Cu^{2+} complexes of Schiff base contain NOS donors *i.e.* (S-benzyl-β-N-[phenyl,phenylhydroxymethyl] methylenedithiocarbazate) are reported [14]. Transition metal complexes of several of these compounds have also been screened for their medicinal properties [15] and possess some degree of cytotoxic activity [16]. In this paper we report the preparation and characterization of some metal complexes derived from Schiff base (formed by the condensation of S-benzyl dithiocarbazate with benzoin [HBBTC] with some transition metal ions.

Experimental

All the chemicals were of A.R. Grade.

Preparation of [HBBTC]

The hydrazine-S-benzyl dithiocarbazate was synthesized according to the general literature [17].

The Schiff base was prepared by heating equimolar amount of the benzoin (21.7 gm , 0.1 mol) and the ester (20 gm, 0.1 mol) in 100 ml absolute ethanol in presence of a few drops of pyridine under reflux for 1/2 hour. The yellow product thus formed

crystallized from benzene and had m.p. 156°C (yield 75%). This Schiff base is lower in melting point by 50°C than reported [14].

Preparation of metal chelates

All complexes were prepared using absolute ethanol or ethanol 90% solution of the hydrated chlorides or acetate salt by mixing equimolar amount of [HBBTC] and the metal salt. The mixture being boiled under reflux for 1/2-2 hours. The resulting solid complexes were filtered hot, washed with hot EtOH followed by ether and dried in vacuum over anhydrous $CaCl_2$. All measurements were carried out as described [13] except that the elemental analysis were performed by the microanalytical unit at King Abdulaziz City for Science and Technology, Riyadh. Molecular weight measurements were made by Rast's method using camphor as solvent.

Results and Discussion

The analytical and physical data for the ligand and its metal complexes are listed in Table 1. The complexes are quite stable in air, insoluble in common organic solvents but are soluble in dimethyl formamide (DMF) and dimethylsulphoxide (DMSO).

The ^{1}H-NMR spectrum of Ligand [HBBTC] in acetone Fig. 1 shows five signals at 2.94, 4.52, 6.53, 6.80-7.89 and 13.04 ppm relative to TMS, which may be assigned to the methylene proton of S-benzyl moiety (-S-CH-Ph), the (-CH-OH-Ph) methine proton, the imino proton, aromatic proton and (-OH) proton respectively. The down field shift of (OH) proton can be related to the presence of an intramolecular equilibrium which suggests that thiol form predominate in solution and also indicates the presence of intramolecular hydrogen bonding. In the ^{13}C-NMR spectrum three signals are observed at δ 150.94, 138.84 and 73.68 which are distributed to the C=S, C=N and C-OH groups respectively.

The principal Ir bands of the ligand [HBBTC] and its metal complexes are listed in Table 2. The Ir spectrum of [HBBTC] (in KBr) shows two bands at 3309 and 3059 cm^{-1} which are assigned to the ν(OH) and ν(NH) [14] groups respectively. The band at 1660 cm^{-1} is assigned to ν(C=N) group vibration [18]. Strong bands at 1240 and 1044 cm^{-1} are the two bands due to ν(C=S) group [19]. A medium band at 956 cm^{-1} is attributed to the ν(N-N) [20]. The broad weak bands in the regions 2360-2340 cm^{-1} and 1950-1920 cm^{-1} are probably due to stretching vibration O...H...N and/or OH...N and may suggest the presence of intramolecular hydrogen bonding [18] as shown in the structure 1. The spectrum does not display ν(SH) at ca. 2570 cm^{-1} indicating that in the solid state [HBBTC] remains in the thion form.

The ligand HBBTC behaves in mononegative tridentate manner coordinating via the azomethine nitrogen, sulphur atom of the thioketo group and the oxygen of hydroxyl group with displacement of hydrogen atom from the latter as shown in structure 2.

Table 1. Analytical and physical data for complexes derived from HBBTC

Compound	Emperical Formula	Color	mp°C	Found (calc.) %			
				C	H	M	Cl
HBBTC	$C_{22}H_{20}N_2OS_2$	Yellow	156	68.0 [67.31]	5.0 [5.13]	-	-
Ni[BBTC]Cl	$NiC_{22}H_{19}N_2OS_2Cl$	Green	>300	54.4 [54.1]	3.98 [3.91]		7.0 [7.2]
Ni[BBTC]Ac	$NiC_{24}H_{22}N_2O_3S_2$	Brown	200	56.68 [56.55]	4.07 [4.32	11.81 [11.29]	-
Cu[BBTC]Cl	$CuC_{22}H_{19}N_2OS_2Cl$	Red	187	54.12 [53.87]	3.77 [3.87]	13.36 [12.93]	7.22 7.14)
Cu[BBTC]Ac	$CuC_{24}H_{22}N_2O_3S_2$	Dark green	153	56.25 [56.08]	4.40 [4.28]	12. [12.34]	
Co[BBTC]Cl $2H_2O$	$CoC_{22}H_{23}N_2O_3S_2Cl$	Dark brown	160	50.06 [50.064]	4.14 [4.4]	12. [11.29]	7.2 [6.7]
Co[BBTC]Ac	$CoC_{24}H_{22}N_2O_3S_2$	Black brown	167	57.18 [56.6]	4.23 [4.3]	11.42 [11.56]	
Pd[BBTC]Cl$2H_2O$	$PdC_{22}H_{21}N_2O_2S_2Cl$	Greenish yellow	>300	47.68 [47.91]	3.67 [3.91]	19.95 [19.31]	6.74 6.53)
Pt[BBTC]Cl	$ptC_{22}H_{19}N_2OS_2Cl$	Light green	>300	42.81 [42.49]	2.86 [3.05]	32.1 [31.35]	5.78 [5.62]
Hg[BBTC]Cl H_2O	$HgC_{22}H_{21}N_2O_2S_2Cl$	Light yellow	>300	— [40.94]	— [3.25]	31.59 [31.07]	5.61 [5.42]

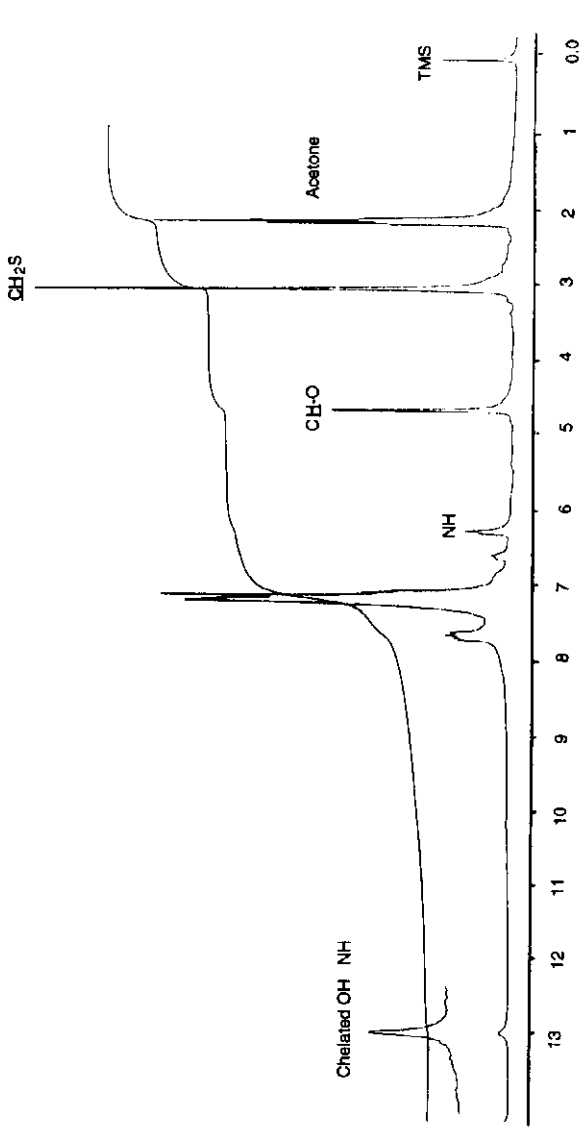
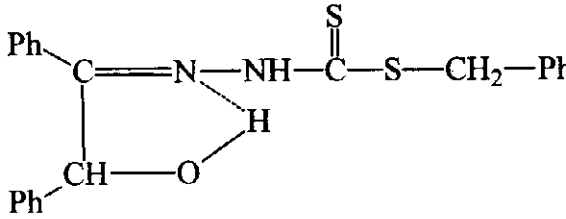


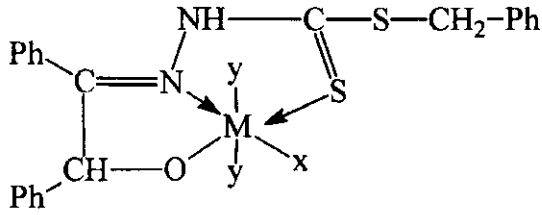
Fig. 1. ^{1}H-NMR spectrum of the ligand in Acetone

Table 2. Ir spectral data of [HBBTC] and its metal complexes

Compouns	υ(OH)	υ(NH)	υ(C=N)	υ(C=S)	υ(N-N)	υ(M-O)	υ(M-N)	υ(M-S)	υ(M-Cl)
HBBTC	3309	3059	1660	1240, 1044	956	—	—	—	—
Ni[BBTC]Cl	—	3060	1634	1200, 1032	1000	564	468	392	286, 330
Cu[BBTC]Cl	—	3059	1650	1223, 1036	994	528	478	401	286
Co[BBTC]Cl.2H_2O	—	3056	1645	1238, 1028	998	514	457	388	276, 330
Pd[BBTC]Cl.H_2O	—	3056	1650	1229, 1028	995	564	470	401	284. 328
Pt[BBTC]Cl.	—	3056	1650	1227, 1028	998	564	469	380	281, 304
Hg[BBTC]Cl.H_2O	—	—	1638	1238, 1028	1001	562	468	353	283, 330
Ni[HBBTC]Ac	—	3059	1650	1236, 1022	984	535	476	398	—
Cu[BBTC]Ac	—	3059	1646	1223, 1027	976	527	475	400, 344	—
Co[BBTc]Ac		3058	1639	1231, 1013	964	562	470	400	—



Structure 1



M = Co^{2+}, Cu^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, and Hg^{2+}
x = Cl^- or Ac^-
y = $2H_2O$ for Co, $1H_2O$ for Pd and Hg

Structure 2

This behavior is found in all complexes and is evident from Ir spectra by the disappearance of ν(OH) band, the ν(C=N) band shift to lower wave number by about (10-26 cm^{-1}) confirming the coordination of azomethine nitrogen which is consistent with nitrogen bonding ν(N-N) shift to higher frequency by (40-45 cm^{-1}) as expected. A shift in the two characteristic bands of ν(C=S) to lower energy in the spectra of all complexes is a result of coordination through sulphur atom. The observed new bands in the complexes at 564-514, 476-457, 400-353 and 286-250 cm^{-1} are tentatively assigned to ν(M-O) [21] ν(M-N) [22], ν(M-S) [21], and ν(M-Cl) [23]. The water of crystallization was determined from the mass loss observed upon heating the complex in an oven at 120°C for 4 hours.

Magnetic and Spectral Studies

The band position and magnetic moment are given in Table 3. The magnetic moment value (5.05 BM) for Co[HBBTC] Cl.$2H_2O$ falls in the range reported for a high spin octahedral complexes (4.7-5.2 BM) [24]. The spectrum in DMF shows two bands in 20,080 and 25,125 cm^{-1} assigned to the $^2Tlg \rightarrow {}^2A2g(F)\ \nu_2$, and $^4Tlg \rightarrow {}^4Tlg(P)\ \nu_3$ [25]

Table 3. Magnetic moment, electronic bands and ligand field parameters

Compound	Band Position cm^{-1}	Dq	ß	υ_2/υ_1	μ_{eff} (BM)
Ni[BBTC]Cl	17730, 24875	956	1195	2.15	3.4
Ni[BBTC]Ac	13698, 25906, 26737	—	—	—	Diam
Cu[BBTC]Cl	19841, 31446	—	—	—	2.1
Cu[BBTC]Ac	1529, 31055	—	—	—	1.86
Co[BBTC]Cl.2H_2O	20080; 25125; 27973-28488	1082	1139	2.13	5.05
Co[BBTC]Ac	13550, 19011-20833, 25646	—	—	—	3.16
Pd[BBTC]Cl.H_2O	24038, 25510	—	—	—	Diam
Pt[BBTC]Cl	17421 — 18115	—	—	—	Diam

transitions. The lowest band ν_1 could not be observed in our instrument and is calculated to be at 9427 cm^{-1} and so the value ν_2/ν_1 is 2.14 indicating the octahedral structure. The Dq and β values are 1082 and 1139 cm^{-1} respectively. The broad band in region 27,973-28,248 and cm^{-1} is assigned to charge transfer, probably HBBTC → Co.

In the Co[HBBTC]Ac the μ_{eff} value (3.16 BM) is lower than those observed for high spin tetrahedral or octahedral complexes. This lowering may arise on account of **1)** the presence of Co^{III} species, **2)** the covalent nature of the metal-ligand bond, **3)** the presence of the low symmetry components and 4) equilibrium between high spin and low spin state ($^4A_2 \leftarrow {}^2T_2$) state [26]. The spectrum of the complex shows a characteristic band at 13,550 cm^{-1} for the tetrahedral structure and other bands in region 19,011-20,833 and at 25,641 cm^{-1} indicating the presence of Co^{III} species in this complex which also absorbs in this region due to $^1A_1 \rightarrow {}^1T_{1g}$ and $^1A_1 \rightarrow {}^1T_2g$ transition [27]. In view of the uncertain nature of the complex no attempt has been made to calculate ligand field parameters.

The magnetic moment value (3.4 BM) for Ni[BBTC] Cl complex lies in the range of tetrahedral structure (3.4-4 B.M) [27]. Also the spectrum show two bands at 17,730 and 24,875 cm^{-1} due to $^3T_1(f) \rightarrow {}^3A_2(f)$ and $^3T_1(f) \rightarrow {}^3T_1(p)$ transition evidence that the tetrahedral configuration [28].

The Ni[BBTC]Ac complex was found to be diamagnetic which suggests a square-planar 4-coordinate structure. The electronic spectrum of these complexes show bands at 13,698 and 25,908 cm^{-1} assigned to $^1A_1g \rightarrow {}^1B_{1g}$ and $^1A_1g \rightarrow {}^1A_2g$ transitions respectively [28]. The broad band that appears in the region 26,737 →30,487 cm^{-1} is assigned to charge transfer probably HBBTC →Ni.

The spectra of Cu[BBTC]Cl and Cu[BBTC]Ac complexes exhibit bands at 15,290 and 19,841 cm^{-1} respectively, which may be assigned to the $^2T_2g \rightarrow {}^2Eg$, transitions. There are also bands at 31,446 cm^{-1} which may be to a ligand metal charge transfer [29; 30]. Strong evidence for the square-planar structure for the Cu complex is the values of the magnetic moment (2.1 and 1.86 BM) respectively which lies within the range reported and implies no copper-copper interaction having monomeric structure [31].

The spectrum of palladiumII complex which was found diamagnetic shows two bands at 13,550 and 24,030-25,510 cm^{-1} due to $^1E' \rightarrow {}^1A'_1$ and $^1E'' \rightarrow {}^1A'_1$ transition in low spin trigonal bipyramidal five coordinate structure [28]. The diamagnetic nature of Platinum ^{II} complex indicate square-planar geometry as expected for d^8 metal ion [32]. Further, the electronic spectrum shows broad band in the region 17,421-18,115 cm^{-1} assigned to $^1A_1g \rightarrow {}^1B_1g$ transition suggests square-plannar structure [28].

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السلوك الارتباطي للمجموعات الثلاثية المانحة N, O, S تجاه أيونات العناصر الانتقالية

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(سُلِّم في ١٩ شوال ١٤١٥هـ؛ وقُبل للنشر في ١٨ جمادى الآخرة ١٤١٦هـ)

ملخص البحث. أعطت تفاعلات قواعد شيف (بواسطة تكثيف S-benzyldithiocarbazate اس - بنزيل داي ثيوكربزات مع bezoin البنزوين [HBBTC]) مع بعض أيونات الفلزات ثنائية التكافؤ معقّدات أحادية لها الصيغة العامة M [BBTC] x.nH$_2$O حيث إن:

[M = Co^{2+}, Cu^{2+}, Ni^{2+}, Pd^{2+}, and Hg^{2+}; x = Ac^- or Cl^- and n = 0 - 2]

تمّ استخدام كل من تحليل العناصر، وأطياف الأشعة تحت الحمراء والمرئية وفوق البنفسجية والطنين النووي المغناطيسي والاستجابة المغناطيسية لإثبات التركيب البنائي للمعقّدات. أوضح طيف الأشعة تحت الحمراء أن المجموعة تتصرف كمجموعة ثلاثية ذات شحنة سالبة أحادية.