

## Metal Complexes of a Schiff Base formed by Condensation of *S*-Benzyl-Dithiocarbazate with Benzil monoxime

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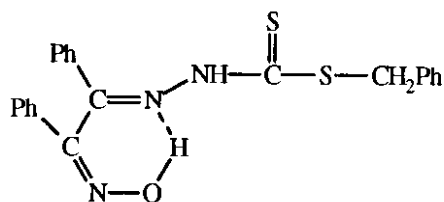
(Received 22nd December, 1993, revised 24th April, 1995)

**Summary:** The synthesis and characterization of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Pd}^{2+}$  and  $\text{Hg}^{2+}$  complexes of benzil monoxime-hydrazine-*S*-benzyl-dithiocarbazate [ $\text{H}_2\text{BzTC}$ ] are reported. Elemental analysis, magnetic moment and spectral [IR, UV-vis,  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR] measurement have been used to characterize the complexes. IR spectra showed that the ligand behaves in a bidentate and/or tridentate manner.

### Introduction

Recently, there has been considerable interest in chemistry of the metal complexes of Schiff bases containing N, S and N, O donors [1-10]. The increased activity in this field may be attributed to the striking structural features and reported carcinostatic and antiviral activity of these donor ligands and the complexes derived from them [1,3,8].

In this paper we reported the preparation and characterization of some new metal complexes derived from benzil monoxime hydrazine-*S* benzyl-dithiocarbazate. The existing literature on the coordination chemistry of this ligand (structure 1) is obscure.



Structure 1

### Results and Discussion

The principal IR bands of  $\text{H}_2\text{BzTC}$  and its metal complexes are listed in Table-2.

The most characteristic feature of the IR spectrum of  $\text{H}_2\text{BzTC}$  has been determined by comparison of the spectra of both  $\text{H}_2\text{BzTC}$  and hydrazine-*S*-benzyl-dithiocarbazate. The  $\text{H}_2\text{BzTC}$

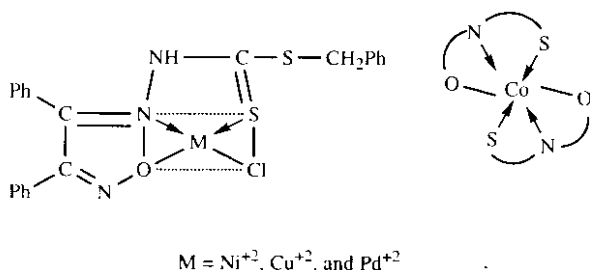
spectrum (in KBr) shows two bands at 1602 and 1464  $\text{cm}^{-1}$  assigned to  $\nu(\text{C}=\text{N})$  imine [11] and  $\nu(\text{C}=\text{N})$  oxime [12] respectively. A strong band at 1010  $\text{cm}^{-1}$  in spectrum of  $\text{H}_2\text{BzTC}$  which is absent in the spectrum of the ester is attributed to the  $\nu(\text{NO})$  vibration. The bands at 934, 962, 1248, 1494 and 1557  $\text{cm}^{-1}$  are attributed to  $(\nu\text{CS} + \nu\text{CN})$ ,  $\nu(\text{N}-\text{N})$ ,  $(\nu\text{CN} + \nu\text{CS})$ ,  $(\nu\text{CN} + \beta\text{NH})$  and  $(\beta\text{NH} + \nu\text{CN})$  respectively. The doublet at 2909 and 2980  $\text{cm}^{-1}$  are attributed to the symmetric and asymmetric stretching vibration of the  $-\text{S}-\text{CH}_2\text{Ph}$  grouping [13, 14], which are reduced to a weak doublet in the IR spectrum of complexes. The two bands at 3302 and 3160  $\text{cm}^{-1}$  are assigned to the oxime NOH and NH respectively. The presence of  $\nu(\text{OH})$  as shoulder at low wave number suggests intramolecular hydrogen bonding. The broad weak bands in the 1808-1963 and 2320-2380  $\text{cm}^{-1}$  regions can be taken as an additional evidence for the presence of intramolecular hydrogen bonding  $[\text{OH} \cdots \text{N}]$  [15] as shown in structure 1. The spectrum does not display  $\nu(\text{SH})$  at ca. 2570  $\text{cm}^{-1}$  indicating that in the solid  $\text{H}_2\text{BzTC}$  remains in the thion form.

The  $^1\text{H}$ -NMR spectrum of  $\text{H}_2\text{BzTC}$  in  $(\text{DCl}_3 + \text{DMSO})$  shows four signals at  $\delta = 4.52$ , 7.33, 9.92 and 11.85 ppm relative to TMS which may be assigned to methylene proton of the *S*-benzyl moiety, aromatic proton, the imino proton and NOH proton respectively. The down field shift of both imino and oxime protons can be related to the presence of intermolecular equilibrium which suggested that the thiol form predominates in

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solution and the presence of intramolecular hydrogen bonding. In the  $^{13}\text{C}$ -NMR spectrum of the ligand, there signal are observed at  $\delta = 153.38$ , 160.52 and 167.8 ppm attributed to the  $\text{C}=\text{NOH}$ ,  $\text{C}=\text{NN}$  and  $\text{C}=\text{S}$  groups respectively.

The  $\text{H}_2\text{BzTC}$  behaves as tridentate ligand coordinating via azomethine nitrogen, the CS and deprotonated NOH group as in structure 2. This behaviour is found in  $\text{Ni}[\text{HBzTC}]\text{Cl}$ ,  $\text{Cu}[\text{HBzTC}]\text{Cl}$ ,  $\text{Pd}[\text{HBzTC}]\text{Cl}$  and  $\text{Co}[\text{HBzTC}]_2$ . This mode of complexation is supported by the following observation, the disappearance of  $\nu(\text{OH})$ , the shift to lower wave number  $\nu(\text{CN})$  together with the shift to higher wave number of  $\nu(\text{N}-\text{N})$  and  $\nu(\text{NO})$ .



In addition the  $\text{H}_2\text{BzTC}$  may behave in a tridentate way coordinating via the imine nitrogen, the deprotonated NOH and the CS in the thiol form with displacement of hydrogen atom from the latter group. This behaviour is found in  $\text{Ni}[\text{BzTC}]\text{H}_2\text{O}$ ,  $\text{Cu}[\text{BzTC}]\text{H}_2\text{O}$ ,  $\text{Cd}[\text{BzTC}]\text{H}_2\text{O}$  complexes that were prepared from their acetate salt.

The  $\text{H}_2\text{BzTC}$ , on the other hand, may act as bidentate ligand coordinating via imine nitrogen and the thiol sulphur atom with replacement of hydrogen atom from the latter group. This behaviour is found in  $\text{Cd}[\text{HBzTC}]\text{Cl} \cdot 2\text{H}_2\text{O}$ . This is also confirmed by IR spectrum which shows a strong band at  $3345\text{ cm}^{-1}$  due to  $\nu(\text{OH})$  oxime indicating that this does not participate in the complexation.

The NMR spectrum of this diamagnetic complex in  $(\text{DCl}_3 + \text{DMSO})$  exhibits signals at  $\delta = 7.29 - 7.95$  and  $4.5$  ppm due to aromatic and the  $-\text{S}-\text{CH}_2\text{Ph}$  proton respectively. The imino proton and the oxime proton have disappeared from the

down field indicating the deprotonation in the presence of metal ion. By comparing the signal integration of aromatic group before and after addition of  $\text{D}_2\text{O}$ , it is found that the integration decreases by percentage corresponding to a replaceable one proton. This proton may be due to the  $(\text{OH})$  of the oxime that is shifted to the higher field region as a result of cleavage of the hydrogen bond after participation of imine group in the complexation. The observed new bands in the complex at  $528-490$ ,  $470-380$ ,  $350-320$  and  $310-280$  are tentatively assigned to  $\nu(\text{M}-\text{O})$  [16],  $\nu(\text{M}-\text{N})$  [17],  $\nu(\text{M}-\text{S})$  [14] and  $\nu(\text{M}-\text{Cl})$  [18] respectively. The water of crystalline was determined from the mass loss observed upon heating the complex in an oven at  $120^\circ\text{C}$  for 4 hours.

### Magnetic and spectral studies

The electronic spectrum of  $\text{Co}^{2+}$ , complex  $\text{Co}[\text{HBzTC}]_2$  in DMF shows two bands at  $16722$  and  $26881\text{ cm}^{-1}$  attributed to the  ${}^4\text{T}_{1g} \leftarrow {}^4\text{A}_{2g}$  and charge transfer transition, respectively, in an octahedral structure [19]. The electronic spectrum together with the value of magnetic susceptibility at room temperature ( $5.04\text{ BM}$ ) supports the octahedral geometry [20] of  $\text{Co}[\text{HBzTC}]_2$  complex.

The  $\text{Ni}^{2+}$  complex  $\text{Ni}[\text{HBzTC}]\text{Cl}$  is found to be diamagnetic that suggests a square planar structure. The electronic spectrum of this complex in DMF shows bands at  $18115$  and  $27137\text{ cm}^{-1}$  assigned to the  ${}^1\text{A}_{2g} \leftarrow {}^1\text{A}_{1g}$  and  ${}^1\text{B}_{1g} \leftarrow {}^1\text{A}_{1g}$  transition respectively [21]. The fact that no band is observed below  $1000\text{ cm}^{-1}$  indicates square planar structure for this complex [22] that may also be deduced from their brown colour. Square planar  $\text{Ni}^{2+}$  complex with sulphur ligand generally exhibits an additional well-defined band around  $11000\text{ cm}^{-1}$  referred to as  $\nu_1$  but in present complex this band is absent. while, the  $\text{Ni}^{2+}$  complex  $[\text{Ni}(\text{BzCT})\text{H}_2\text{O}]$  shows band at  $25641\text{ cm}^{-1}$  due to tetrahedral complex [23]. Also, the value of magnetic moment ( $3.61\text{ BM}$ ) is in good agreement with those reported for tetrahedral geometry [23].

The electronic spectra of  $\text{Cu}^{2+}$  complexes  $\text{Cu}[\text{HBzTC}]\text{Cl}$  and  $\text{Cu}[\text{BzTC}]\text{H}_2\text{O}$  in DMF show band at  $27650$  and  $17420\text{ cm}^{-1}$  assigned to charge transfer [24] and  ${}^2\text{E}_g \leftarrow {}^2\text{T}_{2g}$  transition, respectively. The band positions are in agreement

with those generally observed for square planar  $\text{Cu}^{2+}$  complexes [22,24,25]. The magnetic moment of  $\text{Cu}[\text{HBzTC}]\text{Cl}$  complex at room temperature is (1.68 BM) and (1.01 BM) for  $\text{Cu}[\text{BzTC}]\text{H}_2\text{O}$  complex. For the  $\text{Cu}^{2+}$  complex,  $\text{Cu}[\text{HBzTC}]\text{Cl}$  magnetic values lie near the spin only value of (1.73 BM) which excluded a polymeric structure [26], while the value of the magnetic moment (1.01 BM) for the complex  $\text{Cu}[\text{BzTC}]\text{H}_2\text{O}$  may be explained on the basis of the existence of a polymeric structure including copper-copper interaction or due to the covalent nature of the metal sulphur bond. However, the diamagnetic nature of palladium(II) complex reveals the square planar arrangement around the palladium(II) ion. This is expected for  $d^8$  metal ions [27]. Further the electronic spectrum of the palladium(II) complex shows band at  $18518\text{ cm}^{-1}$  due to  ${}^1\text{B}_{1g} \leftarrow {}^1\text{A}_{1g}$  transition in the planar configuration [28].

## Experimental

All chemicals used were of analar grade.

### Synthesis of $[\text{H}_2\text{BzTC}]$

The hydrazine-S-benzylthiocarbamate was synthesis according to the general literature [18]. The benzil monoxime was prepared according to procedures given [29]. The Schiff base was prepared by heating equimolar amount of benzil monoxime (22.5 g, 0.1 mol) in 100 mL ethanol in presence of few drops of glacial acetic acid, under

reflux for 4 hours. The solution was cooled, then vigorously stirred for 0.5 hour, yielded yellow precipitate which separated and crystallized from benzene and had m.p.,  $180^\circ\text{C}$  [found: C, 65.4, H, 4.4, N, 10.7, calc. for  $\text{C}_{22}\text{H}_{19}\text{N}_3\text{OS}_2$ : C, 65.1, H, 4.7, NH, 10.3%].

### Synthesis of metal chelates

The metal chelates were prepared by refluxing equimolar amounts of the ligand (0.01 mol) in absolute ethanol (50 mL) and hydrated metal chloride (0.01 mol) in 20 mL absolute ethanol or metal acetate (0.01 mol) in 25 mL double distilled water from 0.5 to 4 hours. The product was filtered off, washed with hot ethanol, then diethyl ether and finally dried in vacuum desiccator over anhydrous calcium chloride.

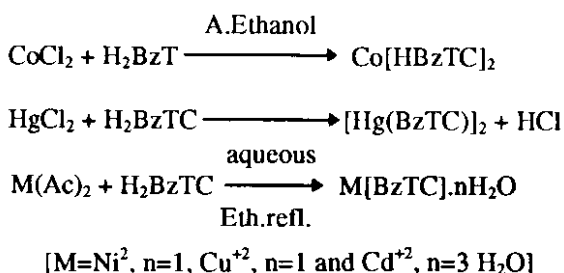
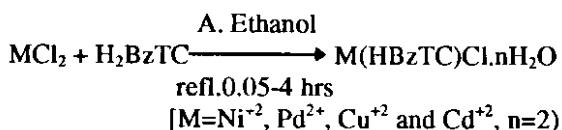


Table-1: Analytical and physical data for the complexes derived from  $\text{H}_2\text{BzTC}$

Compound	Empirical formula	colour	mp $^\circ\text{C}$	Found (Calc.) %			
				C	H	M	Cl
$\text{H}_2\text{BzTC}$	$\text{C}_{22}\text{H}_{19}\text{N}_3\text{OS}_2$	yellow	180	65.4 (65.1)	4.4 (4.7)	-	-
$\text{Ni}[\text{HBzTC}]\text{Cl}$	$\text{NiC}_{22}\text{H}_{18}\text{N}_3\text{OS}_2\text{Cl}$	light brown	205	53.1 (52.9)	3.8 (3.6)	11.8 (11.7)	7.3 (7.1)
$\text{Ni}[\text{BzTC}] \cdot \text{H}_2\text{O}$	$\text{NiC}_{22}\text{H}_{19}\text{N}_3\text{O}_2\text{S}_2$	red	320	55.7 (55.0)	3.5 (3.9)	12.5 (12.2)	-
$\text{Cu}[\text{HBzTC}]\text{Cl}$	$\text{CuC}_{22}\text{H}_{18}\text{N}_3\text{OS}_2\text{Cl}$	green	174	52.7 (52.4)	3.7 (3.5)	12.9 (12.6)	7.5 (7.0)
$\text{Cu}[\text{BzTC}] \cdot \text{H}_2\text{O}$	$\text{CuC}_{22}\text{H}_{19}\text{N}_3\text{O}_2\text{S}_2$	brown	167	51.1 (50.6)	4.1 (3.8)	12.8 (12.1)	-
$\text{Cd}[\text{HBzTC}]\text{Cl} \cdot 2\text{H}_2\text{O}$	$\text{CdC}_{22}\text{H}_{22}\text{N}_3\text{O}_5\text{S}_2\text{Cl}$	yellow	>350	45.2 (44.9)	3.2 (3.3)	20.6 (20.1)	6.3 (6.0)
$\text{Cd}[\text{BzTC}] \cdot 3\text{H}_2\text{O}$	$\text{CdC}_{22}\text{H}_{23}\text{N}_3\text{O}_4\text{S}_2$	beige	>350	50.0 (49.5)	3.6 (3.3)	20.7 (21.0)	-
$\text{Co}[\text{HBzTC}]_2$	$\text{CoC}_{44}\text{H}_{36}\text{N}_6\text{O}_2\text{S}_4$	brown	233	60.9 (60.8)	4.3 (4.1)	6.9 (6.7)	-
$\text{Pd}[\text{HBzTC}]\text{Cl}$	$\text{PdC}_{22}\text{H}_{18}\text{N}_3\text{OS}_2\text{Cl}$	brick red	221	48.8 (48.3)	3.6 (3.3)	19.0 (19.4)	6.8 (6.4)
$[\text{Hg}(\text{BzTC})]_2$	$\text{Hg}_2\text{C}_{44}\text{H}_{34}\text{N}_6\text{O}_2\text{S}_4$	yellow	>350	- (43.7)	- (2.8)	34.0 (33.9)	-

Table-2: IR spectra bands of H<sub>2</sub>BzTC and its metal complexes (cm<sup>-1</sup>)

Compound	$\nu$ (C=N) imine	$\nu$ (C=N) oxime	$\nu$ (OH)	$\nu$ (CS)	$\nu$ (NO)	$\nu$ (N-N)	$\nu$ (S-C=N)	$\nu$ (C-S)
H <sub>2</sub> BzTC	1602	1464	3302	934	1010	962	-	-
Ni(HBzTC)Cl	1575	1454	-	881	1028	994	-	-
Ni(BzTC).H <sub>2</sub> O	1562	1442	-	-	1031	1002	1620	760
Cu(HBzTC)Cl	1575	1451	-	882	1027	990	-	-
Cu(BzTC).H <sub>2</sub> O	1560	1447	-	-	1028	1000	1640	660
Cd(HBzTC)Cl.2H <sub>2</sub> O	1580	1470	3545	-	1000	995	1620	670
Cd(BzTC).3H <sub>2</sub> O	1568	1442	-	-	1028	975	1630	680
Co(HBzTC) <sub>2</sub>	1575	1450	-	888	1025	982	-	-
Pd(HBzTC)Cl	1595	1452	-	879	1028	985	-	-
[Hg(BzTC)] <sub>2</sub>	1567	1452	-	-	1031	1003	1614	663

The analytical and physical data for the metal complexes are listed in Table-1. The solid complexes isolated are quite stable in air and insoluble in common organic solvent but soluble in dimethyl formamid [DMF] and dimethyl sulphoxide [DMSO]. Elemental analyses were performed by the Micro analytical unit at Cairo University. The metal halide contents were determined by standard [30]. The infrared spectra were recorded on Perkin Elmer 883 spectrophotometer (4000-200 cm<sup>-1</sup>) using KBr discs. Electronic spectra [DMF] were recorded using a Beckman Du 70 spectrophotometer.

Magnetic measurements were made on solid specimens by Gouy method at Mansoura university using Hg [Co(SCN)<sub>4</sub>] as a calibrant.

The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were carried out on Jeol FX-100, FT-NMR.

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