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Synthesis and Characterization of Metal Complexes with a Schiff Base Formed by Condensation of S-Benzyldithiocarbazate with Furoin

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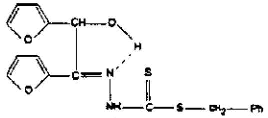
Abstract. New nickel (II), cobalt (II), copper (II), cadmium (II), and palladium (II) complexes of a Schif base ligand formed by condensation of furoin with S-benzyl-dithiocarbazate [H_2FC]. These have been synthesised and characterized by elemental analysis, magnetic moment, and spectral [IR, Uv-vis and NMR] measurements. The special data show that the ligand behaves in a bidentate and/or tridentate manner.

Introduction

Metal complexes of dithiocarbazate have recently drawn special attention due to their activity against cancer [1,2] tumor, tuberculosis [3], bacteria [4,5], fungus [6] and as antipyretic [7] agents. The antifungal activity of these compounds is due to the presence of the toxophorically important (-N-C=S) moiety [8]. The dithiocarbazate and its derivatives are amongst the widely studied nitrogen and sulphur donors [9]. The nickel II and copper complexation with Schiff bases derived from condensation S-benzyldithiocarbazate with furfural were reported elsewhere [10]. We have previously [11] investigated the complexes derived from Schiff base (formed by the condensation of S-benzyldithiocarbazate with benzoin) with transition metal ion. In this work the results of the synthesis and characterization of cobalt (II), nickel (II), copper (II), cadmium (II), and palladium (II) complexes with S-benzyl-β-N-[furfuryl, furfuryl hydroxymethyl] methylene dithiocarbazate are described. The structure of the ligand is shown below:



Structure -I

S-benzyl-β-N-[furfuryl, furfuryl hydroxymethyl] methylene dithiocarbazate

Experimental

All the chemicals used in the present investigation were of A.R. Grade.

Preparation of [H_2FC]

The hydrazine-S-benzyldithiocarbazate was synthesized according to the authors reported in literature [12]. The Schiff base was prepared by heating equimolar amount of the furoin (19.2 g, 0.1 mol) and the ester (20 g, 0.1 mol) in 300 mL absolute ethanol in the presence of a few drops of glacial acetic acid under reflux for 2 hours. It was then evaporated to about 100 mL at a temperature 100°C and left overnight to form the shining yellow crystals which were separated from absolute ethanol and their m.p. has found to be 114°C.

Preparation of complexes

Using EtOH (80%) solution of the hydrated metal (II) salts, all complexes were prepared by mixing equimolar amounts of [H_2FC] and the metal salt, the mixture was boiled at a temperature 100°C under reflux for 1-2 hours. The resulting solid complexes appearing after evaporation to 50%, were filtered, washed with EtOH followed by Et_2O. The complexes were finally dried in vacuum over anhydrous $CaCl_2$. All measurements were carried out as described in an earlier publication [13]. Molecular weight measurements were made by using Rast's method with camphor as a solvent.

Results and Discussion

Table 1 shows an analytical and physical data for complexes derived from H_2FC. Figure 1 shows the ^{1}HNMR spectrum of the ligand [H_2FC] in chloroform. It is observed that the signals at 12.17, 7.37, 4.58 and 1.67 ppm relative to TMS, corresponding to the hydroxyl (OH^-), phenyl, methylene (-CH2-Ph-), and methine (-CH-) protons respectively [14]. The signals due to furan rings protons observed at 6.65, 7.61 and 7.76 ppm. In the ^{13}CNMR spectrum (Fig. 2) five signals are observed at δ 149.42, 145.02, 95.3, 52.9 and 39.69 which attributed to the (C=S), (C=N), (CH-O), (C-N) and (CH_2-S) groups respectively. Also, three signals are observed at δ 78.43, 77.14 and 75.85 corresponding to (C-O) and chloroform.

The principle IR bands of [H_2FC] and its metal complexes are listed in Table 1. The absence of band around 2570 cm^{-1} which would be indicative of SH [15], indicate that in the solid state the molecule remains in the thione form.

Table 1. Analytical and physical data for complexes derived from [H_2FC]

Compound	Empirical	Color	m.p.	Found (calc.) %			
				C	H	M	Cl
H_2FC	$C_{18}H_{16}N_2O_3S_2$	Shining yellow	144	58.90	4.0	-	-
				(58.56)	(4.33)	-	-
Ni[HFC]$_2$	$NiC_{36}H_{30}N_4O_3S_4$	Brownish black	222	54.42	4.11	6.97	-
				(54.0)	(3.78)	(7.24)	-
Cu[FC]H_2O	$CuC_{18}H_{16}N_2O_4S_2$	Deep red	137	48.27	3.05	14.19	-
				(47.90)	(3.58)	(13.95)	-
Cd[HFC]$_2$	$CdC_{36}H_{30}N_4O_6S_4$	Olive	>300	51.03	3.08	14.02	-
				(50.47)	(3.53)	(13.31)	-
Pd[HFC]Cl	$PdC_{18}H_{15}N_2O_3S_2Cl$	Peige	165	42.70	2.52	21.13	7.22
				(42.19)	(2.95)	(20.69)	(6.83)
Ni[HFC]Ac	$NiC_{20}H_{13}N_2O_5S_2$	Greenish black	163	49.89	3.11	12.05	–
				(49.18)	(3.72)	(11.87)	–
Co[HFC]Ac.2H_2O	$CoC_{20}H_{22}N_2O_7S_2$	Grey	200	46.12	3.77	11.78	-
				(45.71)	(4.22)	(11.22)	-
Cu[HFC]Ac.2H_2O	$CuC_{20}H_{22}N_2O_7S_2$	Brown	190	45.70	3.84	12.38	-
				(45.37)	(4.19)	(11.90)	-
Cd[HFC]$_2$	$CdC_{36}H_{30}N_4O_3S_4$	Orange	105	50.77	2.96	13.66	-
				(50.47)	(3.53)	(13.31)	-

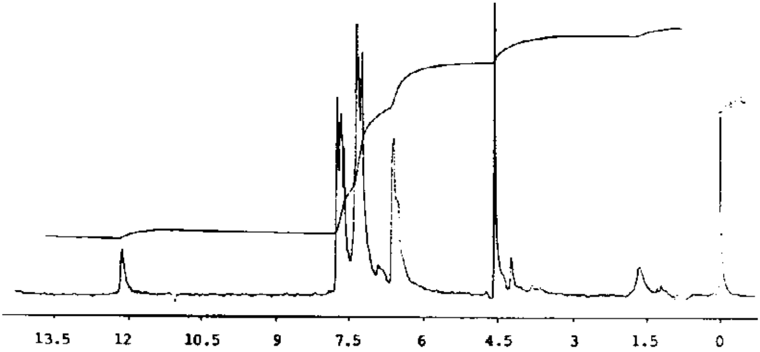


Fig. 1. ^1H **NMR spectra of the ligand in chloroform.**

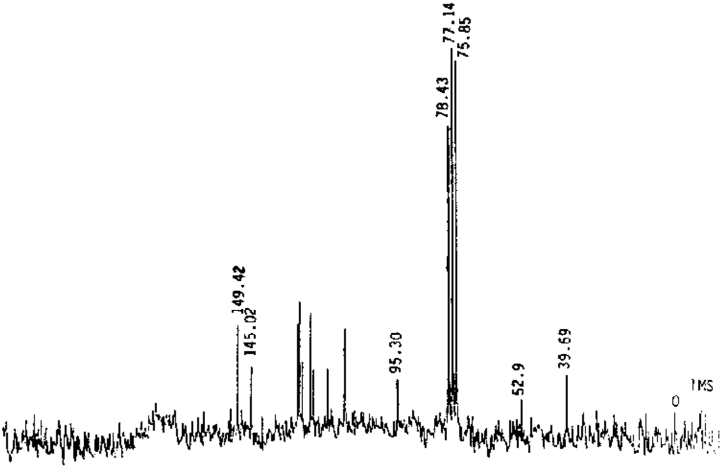


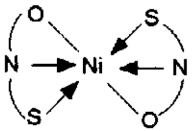
Fig. 2. ^{13}C **NMR spectra of the ligand in chloroform.**

The Schiff base [H_2FC] acts as a tridentate ligand coordinating the metal ion via the β-nitrogen, thioketo sulphur and oxygen of the hydroxyl group (structure 2,3) as evident from IR spectral data. This behavior is found in Ni[HFC]$_2$, Ni[HFC]Ac,

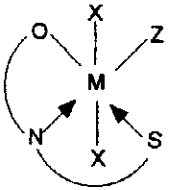
Table 2. IR spectral data of [H_2FC] and its metal complexes

Compound	υ(OH)	υ(C=N)	υ(C=S)	υ(N-N)	υ(S-C=N)	υ(C-S)	υ(M-O)	υ(M-N)	υ(M-S)	υ(M-Cl)
H_2FC	3300	1583	1249	942	-	-	-	-	-	-
Ni[HFC]$_2$	-	1571	1230	989	-	-	541	471	389	-
Cu[FC].H_2O	-	1569	-	1000	1666	631	565	473	366	-
Cd[FC]$_2$	3299	1556	-	1001	1616	690	-	464	409	-
Pd[HFC]Cl	-	1566	1229	950	-	-	553	476	377	329-282
Ni[HFC]Ac	-	1570	1230	989	-	-	540	471	388-371	-
Co[HFC]Ac.2H_2O	-	1571	1231	986	-	-	539	471	387	-
Cu[HFC]Ac.2H_2O	-	1566	1250	961	-	-	563	487	-	-
Cd[HFC]$_2$	-	1566	1250	973	-	-	541	479	-	-

$Co[HFC]Ac.2H_2O$ and Pd[HFC]Cl complexes and supported by the following observation : the disappearance of $\nu(OH^-)$ observed in the free ligand at (3300 cm^{-1}) [16], clearly indicates the loss the proton from OH on coordination and formation of a new bond between metal and oxygen. The ν(C=N) shifted to lower wave number, while the ν(N-N) shifted to higher wave number, this lowering in (C=N) stretching mod on complexation may tentatively be attributed to lowering of the C=N bond order as a result of M-N bond formation [17]. The shift of ν(C=S) towards the lower frequency region may be taken as an indication of coordination by the thioketo sulphur. The α-nitrogen atom is not bonded with metal as ν(NH) band (3136 cm^{-1}) of free ligand does not suffer any shifting in the complexes.



Structure 2

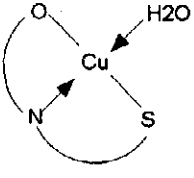


Structure 3

$M = Co^{2+}, Ni^{2}, Ni^{2+}$ and Pd^{2+}

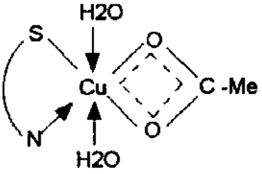
$Z = Ac^-$ or Cl^- $X = H_2O$ for Co^{2+}

On the other hand, the $[H_2FC]$ may acts as a binegative tridentate ligand coordinating via azomethine nitrogen, deprotonated (OH^-) and the CS in thiol form with displacement of a hydrogen atom from the latter group (structure 4). This behavior is found in $Cu[FC].H^2O$ complex and evidence by the following observation : the disappearance of $\nu(OH^-)$, the ν(C=N) shift to lower wave number and the disappearance (C=S) observed in the free ligand at (1249 and 755 cm^{-1}) with appearance of new bands at 1660 and 631 cm^{-1} assignable to ν(S-C=N) and ν(C-S), respectively.

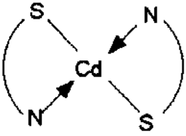


Structure 4

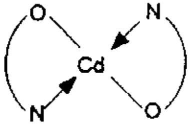
In addition, the [H_2FC] acts as mononegative bidentate ligand via azomethine nitrogen and deprotonated (OH^-) group (structure 4,5). This behavior is found in Cu[HFC]Ac.2H_2O and Cd[HFC]$_2$ complexes which were prepared from their acetate salts. This confirmed by IR spectra which shows the disappearance of $\nu(OH^-)$ band, the shift of ν(C=N) to lower wavenumber and the two characteristic bands for ν(C=S) remain at the same position indicate that the sulphur atom does not participate in coordination.



Structure 5



Structure 6



Structure 7

Also, the ligand may act as a mononegative bidentate via azommethine nitrogen and the C=S in thiol form with lost hydrogen proton from the latter group (structure 7). This behavior is found in Cd[HFC]$_2$ complex and supported by the following observation the $\nu(OH^-)$ appear at ν(3299 cm^-) as that of the free ligand, the ν(C=N) shift to lower frequency and the disappearance of ν(C=S) with appearance of new bands at 1616 and 690 cm^{-1} assignable to ν(S-C=S) and ν(C-N) respectively, this indicate the coordination by the thiol sulphur. Also, the observation of new bands in the regions 565-539, 487-464, 409-366 and 329 cm^{-1} attributed to ν[M-O] [18,] ν[M-N] [19], ν[M-S] [18], ν[M-C1] [20], respectively.

Magnetic and Spectral Studies

The electronic spectrum of Co[HFC]Ac.2H_2O shows two bands at 15105 and 26737 cm^{-1} which are referred to $^4T_{1g} \rightarrow {}^4T_{1g}$ (F) ν_2 and $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) ν_3 transition [20], respectively. The calculated values of (Dq = 816 cm^{-1}, B=1401 cm^{-1}, ν_1 = 6939 cm^{-1}, β=1.44 and ν_1/ν_2 = 2.17) lie in the range reported for an octahedral structure. The magnetic moment (4.9 BM) can be taken as additional evidence for an octahedral configuration.

The electronic spectrum in (DMF) of Ni[HFC]$_2$ shows two bands at 15060 and 25641 cm^{-1} attributable to $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transition [21] respectively. The calculated values of Dq, B, β, ν_1 and ν_1/ν_2 are 977 cm^{-1}, 758 cm^{-1}, 0.72, 9770 cm^{-1} and 1.54 respectively, indicating an octahedral structure around the NiII ion. Also, value of the magnetic moment (3.13 BM) is additional evidence for an octahedral structure.

The electronic spectrum of the diamagnetic Ni[HFC]Ac exhibits two band at 20325 and 26455 cm^{-1} assignable to $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$ transition in a square-planar geometry.

The electronic spectrum of the Cu[FC].H_2O complex show a broad band centred at 18315 cm^{-1} is due to combination of transition $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ in a square-planar configuration [22]. The band centred at 31446 cm^{-1}' is probably due to d-π^* charge transfer. Strong evidence for the planar structure for Cu II complex is the value of the magnetic moment (1.8 BM) which lie within the range reported and implies no copper-copper interaction.

The magnetic moment value of Cu[HFC]Ac.$2H_2O$ complex is (1.92 BM), lie in the range of high spin copper II complex having monomeric structure. The electronic spectrum exhibit a weak intensity band at 11876 cm^{-1}. The position and the shape indicate distorted octahedral environment [23].

The palladium II complex Pd[HFC]Cl is diamagnetic and electronic spectrum of this complex show broad band at 27027 cm^{-1} assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ transition, which suggest square-planar geometry for this complex.

Conclusion

1) The molecule remains in the thion form in the solid state.
2) The present Schiff base acts as a tridentate ligand coordinating the metal ion via β-nitrogen, thioketon sulphur and oxygen of the hydroxyl group.
3) The [H_2FC] may act as a binegative tridentate ligand coordinating through azomethine nitrogen, deprotonated (OH^-) and the CS in thiol form.
4) Also, the [H_2FC] may act as mononegative bidentate coordinating through azomethine nitrogen and deprotonated (OH^-) or through azomethine nitrogen and CS in thiol form.
5) Magnetic and electronic spectra reveal that the complexes of this ligand can exist in either octahedral geometry as for Co^{2+}, Ni^{2+} or in square-planar as for Ni^{2+}, Cu^{2+} and Pd^{2+}.

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تحضير وتحديد خواص معقّدات المعادن مع قاعدة شيف المتكونة من تكثيف إس بتريل داي ثيو كربازيت مع الفيروين

محمود أحمد. س. منشي

قسم الكيمياء، كلية العلوم، جامعة الملك سعود، ص.ب. ٢٤٥٥،
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(استلم في ٢٧/ ١٢/ ١٤١٦هـ، وقبل للنشر في ٢١/ ٧/ ١٤١٧هـ)

ملخص البحث. تمّ تحضير معقّدات جديدة لكل من عناصر النيكل، الكوبالت، النحاس، الكادميوم والبلاديوم الثنائية مع قاعدة شيف المتكونة من تكثيف إس بنزيل داي ثيو كربازيت مع الفيروين. تمّ تحديد خواصها بتحليل العناصر والخواص المغناطيسية وكذلك أطياف الأشعة تحت الحمراء وفوق البنفسجية والمرئية بالإضافة إلى الرنين النووي المغناطيسي حيث تبين أن القاعدة تعمل كمجموعة ثنائية وثلاثية المخلبية.