Preparation and Study of Some Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and Pb(II) Complexes Containing Heterocyclic Nitrogen Donor Ligands

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Abstract: This paper presents a new mixed-ligand complexes with the general formula $[M(BT)(BI)_2X_2]$ where BT=benzotriazole, BI=benzimidazole, $X=SCN$ and $M=Mn(II)$, $Co(II)$, $Ni(II)$, $Cu(II)$, $Cd(II)$ and $Pb(II)$. The reaction was carried out by using the appropriate molar ratios of metal:ligand (1:1:2:2) (M:BT:BI:X) as required. The resulting products were found to be solids, not soluble in water and in ordinary organic solvents but highly soluble in DMSO. These complexes have been studied by UV-Visible, IR and (1H , ^{13}C) NMR spectra, molar conductivity, elemental analysis of C, H, N, determination of metal and magnetic susceptibility. The result suggests that the benzimidazole as a monodentate was coordinated with the metal ions through the N atom. Nevertheless, the benzotriazole as bidentate was coordinated with the metal ions through the N2 and N3 atoms. SCN was coordinated with the metal ions through the nitrogen atom.

Keywords: Heterocyclic nitrogen donor ligands, Benzotriazole complexes, Benzimidazole complexes, Mixed ligand complexes.

Introduction

Heterocyclic nitrogen play an important role in coordination chemistry^{1,2}. The triazole derivatives have discrete or super molecules in particular, benzotriazole displays remarkable efficiency as a corrosion inhibitor for copper and its alloys, very useful as fungicides and bactericides^{3,4}. Benzotriazole was widely used in the construction of metal-organic frameworks due to the multifunctional linking role, an interesting case of linkage isomerization has been reported for benzotriazole complexes^{5,6}. Furthermore, the reactivity and the properties of transition metal complexes with imidazole derivatives have been studied over the last decades, a few cases involving the interaction of the benzimidazole and benzotriazole ligands with the metal ions complexes are known². Numerous related the heterocyclic ligands have been synthesized that contain other heteroaromatic ring systems⁷. The aim of this paper is to study the coordination chemistry of two ligands that contain benzotriazole and benzimidazole. Each of these ligands is capable of coordinating to the metal ions. Moreover, the benzotriazole have two nitrogen atoms capable of coordination⁷.

Experimental

Metal salts ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, NH_4SCN and KBr) from Riedel dehaen age, ligands (benzotriazole and benzimidazole) from Fluka, ethanol and dimethylsulfoxide were obtained from BDH in high purity.

The IR spectra in the region of $4000\text{--}400\text{ cm}^{-1}$ KBr disc were recorded by using shimadzu FTIR.8400S fourier transform infrared spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded using the JEOL JNM-ECP 400 spectrometer in $\text{DMSO-}d_6$, relative to the internal standard tetramethylsilane (TMS). The UV-Visible were carried out on Shimadzu UV-Visible recorder spectrophotometer UV-160 in DMSO solution 10^{-3} M. Philips PW 9526 digital conductivity meter was used to measure molar conductivity. The magnetic susceptibilities were measured by using balance magnetic susceptibility model MSB. MK1 at 25°C . Elemental analysis C H N was performed by using a Carlo Erba 1106 Elemental Alanyzer and the metal percentage in the complexes was determined following the gravimetric methods. Finally the melting points were recorded by using Stuart melting point apparatus.

Preparation of metal(II) complexes $[\text{M}(\text{BT})(\text{BI})_2\text{X}_2]$

An ethanolic solution of benzotriazole 0.17- 0.34 g (1.42-2.85 mmole) in 15 mL in ethanol and an ethanolic solution of benzimidazole 0.35-0.69 g (2.96- 5.84 mmole) were added respectively to an aqueous solution of the metal salts. The aqueous solution of NH_4SCN 0.22-0.44 g (2.89-5.78 mmole) was added to the mixture with constant stirring. The products were immediately precipitated which were filtered off, washed and recrystallised with 1:1 mixture of water: ethanol and dried in an oven 60°C .

Results and Discussion

All the prepared complexes in this work were insoluble in water and methanol but soluble in dimethylsulfoxide. Thus, the complexes are non-elctrolytes as the molar conductance is found to be in the range of $5.6\text{--}8.4\text{ ohm}^{-1}\text{cm}^2\text{ mol}^{-1}$ in 10^{-3} M in $\text{DMSO}^{8,9,11}$. The physical properties and elemental analysis are listed in Table 1.

Table 1. Physical properties, conductivity and analytical data of the free ligands and its complexes

Compound	Color	M.P °C	Elemental Analysis:				Molar Conductivity Ohm ⁻¹ cm ² mol ⁻¹
			C	H	N	M	
BT	White	98-99	—	—	—	—	9
BI	Brown	172-173	—	—	—	—	7
[Mn(BT)(BI) ₂ X ₂]	Light Brown	>300	50.190 (50.02)	3.251 (3.56)	23.942 (22.91)	10.43 (10.83)	8.4
[Co(BT)(BI) ₂ X ₂]	Dark Green	>300	49.812 (48.71)	3.227 (3.00)	23.762 (23.31)	11.10 (10.78)	6.7
[Ni(BT)(BI) ₂ X ₂]	Gray	>300	49.833 (49.61)	3.228 (2.91)	23.772 (23.26)	11.07 (10.15)	8.2
[Cu(BT)(BI) ₂ X ₂]	Light green	265	49.383 (49.10)	3.199 (2.65)	23.557 (23.11)	11.87 (12.78)	5.6
[Cd(BT)(BI) ₂ X ₂]	White	>300	45.251 (44.82)	2.931 (2.51)	21.586 (20.99)	19.24 (18.46)	6.4
[Pb(BT)(BI) ₂ X ₂]	White	>300	38.930 (38.01)	2.522 (2.77)	18.571 (18.16)	30.52 (30.99)	7.3

Electronic spectral studies

The electronic spectra of the free ligands

The electronic spectrum of the benzotriazole in DMSO shows strong bands at 273 nm and 312 nm due to the electronic transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively. The benzimidazole spectrum exhibited absorption bands at 275 nm which is caused by $\pi \rightarrow \pi^*$ and another bands at 348 nm due to electronic transition of $n \rightarrow \pi^*$ ¹²⁻¹³. Finally, the spectrum of Ammonium thiocyanate shows the electronic transition of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ at 216 and 351 nm respectively.

The electronic spectra of the complexes and Magnetic Moments

[Mn(BT)(BI)₂X₂]

The spectrum of light brown exhibited absorption band at 264 nm which belongs to the ${}^6A_{1g} \rightarrow {}^4T_{1g(G)}$. Another band appeared in the visible region at 634 nm which is assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g(G)}$. The magnetic moment μ_{eff} of the Mn(II) d^5 was 4.920 B.M, this value was in agreement with the expected value for spin only¹⁴. These rules are accepted for Mn⁺² octahedral complexes¹⁵.

[Co(BT)(BI)₂X₂]

The spectrum of dark green complex exhibited band at 272 nm due to the electronic transition ${}^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$ which corresponds to charge transfer C.T. Another band in the visible region at 539 and 760 nm, this may be attributed to the ${}^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$ and ${}^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$ respectively^{15,16}. The value of μ_{eff} of Co(II) d^7 complex was 4.561 B. M higher than the calculated value, this may be attributed to the orbital contribution^{17,18}. All these values confirm that the formed Co(II) complex has octahedral geometry.

[Ni(BT)(BI)₂X₂]

The spectrum of the gray complex d^8 shows strong band at 271 nm which may be attributed to the transition ${}^3A_{2g(F)} \rightarrow {}^3T_{1g(P)}$ which corresponds to the charge transfer. Another band noticed at 560 nm which is caused by ${}^3A_{2g(F)} \rightarrow {}^3T_{1g(F)}$ transition. The third band was observed at 649 nm due to ${}^3A_{2g(F)} \rightarrow {}^3T_{2g(F)}$ transition^{19,20}. The value μ_{eff} of Ni(II) d^8 was 2.602 B.M, this value was in agreement with the expected value¹⁴. Accordingly to the ligand field splitting energy $10Dq$ was found to be 15408.32 cm^{-1} and the reaction inter electronic repulsion parameter B' was found to be 568.836 cm^{-1} . The ratio of β comes out to be 0.55 and B^0 is equal to 1030 cm^{-1} . These parameter values support an octahedral geometry for the Ni(II) complex^{15,19,20}.

[Cu(BT)(BI)₂X₂]

The octahedral Cu(II) complex was dark green, this color is an effective and shows the absorption bands in the visible region at 507 nm which is assigned to the ${}^2E_{g(D)} \rightarrow {}^2T_{2g(D)}$. This transition is the characteristic for octahedral complex of Cu(II). Furthermore, the spin μ_{eff} of Cu(II) complex d^9 was found to be 1.670 B. M within the expected value for one electron.

The diamagnetic of Cd(II) and Pb(II) complexes have shown absorption bands at 274 and 284 nm respectively. These bands may be attributed to the charge transfer $M \rightarrow L$ because of the electronic configuration of Cd(II) and Pb(II) which is confirmed the absence of any d-d transition. However, their spectrum suffered red shift with Hyper or Hypo chromic effect. The electronic spectral bands and the magnetic moments of the complexes are listed in Table 2.

Table 2. Magnetic susceptibility and electronic spectra of the ligands and its complexes

Compound	μ_{eff} Calc. (Found) B.M	λ_{max} nm	Wave number cm^{-1}	ϵ_{max} $\text{Lmol}^{-1}\text{cm}^{-1}$	Assignment
BT	-	273	36630	2447	$\pi \rightarrow \pi^*$
		312	32051	12	$n \rightarrow \pi^*$
BI	-	275	36363	467	$\pi \rightarrow \pi^*$
		348	28735	38	$n \rightarrow \pi^*$
X ⁻	-	216	46296	109	$\pi \rightarrow \pi^*$
		351	28490	42	$n \rightarrow \pi^*$
[Mn(BT)(BI) ₂ X ₂]	5.916 (4.920)	264 634	37878 15772	488 10	${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{1(\text{P})}$ ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}}(\text{G})$
[Co(BT)(BI) ₂ X ₂]	3.872 (4.561)	272 539	36764 18552	2466 50	${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{A}_{2\text{g}}(\text{F})$ ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})$
		760	13157	43	${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{2\text{g}}(\text{F})$
[Ni(BT)(BI) ₂ X ₂]	2.828 (2.602)	271 560	36900 17857	2252 38	${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{1\text{g}}(\text{P})$ ${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{1\text{g}}(\text{F})$
		649	15408	30	${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{2\text{g}}(\text{F})$
[Cu(BT)(BI) ₂ X ₂]	1.732 (1.670)	270 507	37037 19723	1834 16	Charge transfer (C.T) ${}^2\text{E}_{\text{g}}(\text{D}) \rightarrow {}^2\text{T}_{2\text{g}}(\text{D})$
[Cd(BT)(BI) ₂ X ₂]	diamagnetic	274	36496	1325	C.T (M $\rightarrow$ L)
[Pb(BT)(BI) ₂ X ₂]	diamagnetic	284	35211	2500	C.T (M $\rightarrow$ L)

Infrared spectra studies

Infrared spectra of the free ligands

The spectrum of the benzotriazole shows a weak band at 3247 cm^{-1} which belongs to $\nu(\text{NH})$, another weak band was observed at 3078 cm^{-1} which is attributed to $\nu(\text{C-H})$ aromatic²¹⁻²³. Finally, the strong band belongs to $\nu(\text{N=N})$ was found at 1500 cm^{-1} .

The spectrum of benzimidazole exhibited broad band at 3150 cm^{-1} which is caused by $\nu(\text{NH})$. A weak band noticed at 3040 cm^{-1} which is attributed to $\nu(\text{C-H})$ aromatic, another weak sharp band appeared at 1640 cm^{-1} due to $\nu(\text{C=N})$ ²⁴. The medium band belongs to $\nu(\text{C=C})$ was found at 1605 cm^{-1} . The spectrum of thiocyanate ion shows a strong band at 2053 cm^{-1} which is assigned to $\nu(\text{CN})$ and another band at 740 cm^{-1} was attributed to $\nu(\text{CS})$ ²⁵.

Infrared spectra of complexes

The infrared spectra of the prepared complexes exhibited the following bands: $\nu(\text{C=N})$ in the region of $1620\text{--}1630\text{ cm}^{-1}$ which was shifted to lower frequencies by $20\text{--}10\text{ cm}^{-1}$ compared with benzimidazole spectrum, which indicates that the coordination with metal ions was through nitrogen atom. Thus, the band appeared in the region of $1488\text{--}1496\text{ cm}^{-1}$ belongs to $\nu(\text{N=N})$ in benzotriazole moved to lower frequencies by $12\text{--}4\text{ cm}^{-1}$. Moreover, the spectra of the prepared complexes exhibited weak bands in the region of $550\text{--}570\text{ cm}^{-1}$ which is assigned to $\nu(\text{M-N})$ which indicates that the coordination with metal ions was through the two nitrogen atoms²⁶.

The coordination of SCN^- ion through the nitrogen atom was confirmed by the bands in the region of $2067\text{--}2098\text{ cm}^{-1}$ which is shifted to higher frequencies²⁵ by $14\text{--}45\text{ cm}^{-1}$. Furthermore, the spectra of the complexes shows weak bands between $424\text{--}460\text{ cm}^{-1}$ which is attributed to the $\delta(\text{M-NCS})$. Table 3 gives the diagnostic absorption and their assignments.

Table 3. Fundamental infrared bands (4000-400 cm^{-1}) of the ligands and its complexes

Compound	$\nu(\text{NH})$	$\nu(\text{NCS})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N})$	$\nu(\text{CS})$	$\nu(\text{M}-\text{N})$	$\delta(\text{M}-\text{NCS})$
BT	3247	-	-	1500	-	-	-
BI	3150	-	1640	-	-	-	-
NH_4SCN	-	2053	-	-	-	-	-
$[\text{Mn}(\text{BT})(\text{BI})_2\text{X}_2]$	3333	2075	1620	1488	833	555	432
$[\text{Co}(\text{BT})(\text{BI})_2\text{X}_2]$	3409	2080	1620	1496	748	563	424
$[\text{Ni}(\text{BT})(\text{BI})_2\text{X}_2]$	3394	2090	1620	1496	748	570	460
$[\text{Cu}(\text{BT})(\text{BI})_2\text{X}_2]$	3263	2098	1630	1490	748	570	440
$[\text{Cd}(\text{BT})(\text{BI})_2\text{X}_2]$	3340	2082	1620	1496	750	555	450
$[\text{Pb}(\text{BT})(\text{BI})_2\text{X}_2]$	3456	2067	1627	1490	745	550	447

¹H NMR spectra studies

The ^1H NMR spectrum of the benzotriazole shows singlet signal in 15.3 ppm which is attributed to the NH, this signal was appeared in the Cd(II) and Pb(II) complexes in 10.9 and 11.3 respectively. In addition, the spectrum of the ligand BT shows signals for 4H aromatic proton at: δ 8(H4), 7.59(H7), 7.29(H5) and 7.35(H6). However, these signals were shifted upfield in the complexes by 0.87-0.68 ppm due to the H4 and H7 and by 0.17-0.05 which are attributed to the H5 and H6 respectively²⁷⁻²⁹.

The ^1H NMR spectrum of the benzimidazole shows single proton at 12 ppm which is attributed to the NH. This signal was shifted to the up field in both of Cd(II) and Pb(II) complexes by 1.1 and 0.7 ppm respectively. The appearance of NH group in both of the complexes which suggested that the coordination is impossible through the N1. Furthermore, the ligand BI shows signal protons at 7.50, 7.10, 7.24, 7.56 and 7.40 ppm which are attributed to the H4, H5, H6, H7 and H2 respectively. Hence, the distinct signals of H5 and H6 were appeared at high field and the signals of H4 and H7 can be obviously differentiated from H5 and H6. This is caused by the next neighbor of each proton from ^1H - ^1H COSY experiment. Moreover, the signal proton of H2 was desheilded by 0.08-0.18 ppm to the downfield δ in coordination complexes. This fact could be indicated that the benzimidazole was coordinated with the metal ions through the N3 atom³⁰⁻³². The ^1H NMR spectra of the free ligands and their complexes were recorded in DMSO- d_6 and assignments of the peaks are listed in Table 4.

Table 4. ^1H NMR chemical shifts (δ , ppm) of the free ligands and its complexes

Compound	NH	H2	H aromatic proton			
			H4	H5	H6	H7
BT	15.3	-	8	7.29	7.35	7.59
BI	12	7.40	7.50	7.10	7.24	7.56
$[\text{Cd}(\text{BT})(\text{BI})_2\text{X}_2]$	10.9	7.58	7.32	7.26	7.30	7.32
$[\text{Pb}(\text{BT})(\text{BI})_2\text{X}_2]$	11.3	7.48	7.13	7.12	7.11	7.13

¹³C NMR spectra studies

The ^{13}C NMR spectrum of the benzimidazole has shown 136.3, 121.51, 115.84 and 140.3 ppm due to the (C8,9), (C5,6), (C4,7) and C2 respectively. On the complexes, only the signal due to the C2 was desheilded to the downfield by 11.66-11.55 ppm which is adjacent to the coordination site. Thus, the spectrum of the benzotriazole shows three signal protons at 139.80(C8,9), 128.30(C5,6) and 116.25(C4,7), because there are very strong overlap between (C8 and C9); (C5 and C6) and (C4 and C7) peaks. However, there is significant shift

to the up field was observed on Cd(II) and Pb(II) complexes in C8,9 by 7.48-5.1 ppm. These signals support the involvement of N2 and N3 in complexation^{28,29,32}. All the ¹³C NMR chemical shifts (δ , ppm) are listed in Table 5.

Table 5. ¹³C NMR signals of the free ligands and its complexes in DMSO-*d*₆

Compound	C2	C8,9	C5,6	C4,7
BT	-	139.80	128.30	116.25
BI	140.3	136.3	121.51	115.84
[Cd(BT)(BI) ₂ X ₂]	151.85	132.32	121.66	114.41
[Pb(BT)(BI) ₂ X ₂]	151.66	134.7	123.72	114.09

Conclusions

The new mixed ligand complexes of benzotriazole, benzimidazole and thiocyanate with some metal ions like Mn(II), Co(II), Ni(II), Cu(II), Cd(II) and Pb(II) were successfully prepared in this paper. The molar conductance of these complexes was recorded in DMSO 10⁻³ M solution and the result suggested that the products were non-electrolyte. The IR and (¹H, ¹³C) NMR spectra suggested that the benzimidazole as a monodentate which was coordinated with the metal ions through the N3 atom. While the benzotriazole as a bidentate was coordinated with the metal ions through the N2 and N3 atoms. Moreover, the definite geometries of the complexes were improved by the magnetic moment values and their electronic spectra. Thus, from the results presented the metal complexes have octahedral geometry for the Mn(II), Co(II), Ni(II), Cu(II) and Cd(II) complexes as can be seen in Figure. 1 and distorted octahedral for the Pb(II) complex as can be seen in Figure 2.

M=Mn(II), Co(II), Ni(II), Cu(II) and Cd(II)

Figure 1. Octahedral geometry for the [M(BT)(BI)₂X₂] complexes

Figure 2. Distorted octahedral for the [Pb(BT)(BI)₂X₂] complex

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