SYNTHESIS AND STUDIES OF SOME MIXED–LIGAND METAL COMPLEXES CONTAINING BENZOTRIAZOLE WITH SOME OTHER LIGANDS

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Abstract

This paper presents the synthesis and studying of some mixed–ligands of Benzotriazole, Benzimidazole and thiocyanate ion. The reaction was carried out by using the appropriate molor ratios of Metal: ligand (1:1:2:2) (M: BT: BI: X) as required. The resulting products were found to solids which have been characterized by U.V-visible, I R spectra ,Molar conductivity, thermal stability, Determination of metal and magnetic susceptibility. From the obtained informations the general formula have been given for the prepared Complexes: [M (BT) (BI) X_2]. M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and pb^{2+}

Introduction

Hetrocyclic nitrogens play in turn an important role in coordination chemistry[(1)]. The triazole derivatives have also of discrete or Supermolecules in particular, benzotriazole is largely employed as an efficient corrosion inhibitor for copper and its alloys[(2)]and the benzimidazole derivatives are very useful as fungicides and bacteriacides[(3)]. Although the reactivity and properties of transition metal complexes with imidazole and triazole derivatives have been studied a few cases involving the interaction of benzimidazole and benzotriazole ligands with iron (II, III) and ruthemium (II) (III) complexes[(2)].

Experimental

Materials and Measurements

Metal salts ($MnCl_2$ $4H_2O$,$CoCl_2$ $6H_2O$, $NiCl_26H_2O$,$CuCl_2.2H_2O$,$CdCl_2.H_2O$,$Pb(NO_3)_2$, NH_4SCN and KBr) from Riedeldehaenage, ligands (benzotriazole and benzimidazole) from fluka, (ethanol and dimethyl sulfoxide) was obtained from BDH in high Purity.

The IR spectra in the region (4000 - 400)cm^{-1} (KBrdisc) were recorded by using shimadzu. FTIR.8400S Fourier transform infrared spectrophotometer, the U.V.visible were carried out on shimadzu U.V.visible recorder spectrophotometer U.V-160.in DMSO solution (10^{-3}M) and Philips PW 9526 digital conductivity meter was used to measure Molar Conductivity, magnetic susceptibilities were measured by using Balance Magnetic susceptibility model MSB. MK1 at 25C^o and the metal percentage in the complexes were determined following the gravimetric methods. Finally the melting Points were recorded by using stuart Melting Point Apparatus**.**

General Procedure for the synthesis of the Complexes

To an aqueous solution of metal salts an ethanolic solution of benzotrizole (0.17-0.34 g) (1.42-2.85 m.mole) in 15 ml in ethanol was added follow by the addition of solution of benzimidazole (0.35-0.69 g) (2.96 -5.84 m.mole). The aqeous solution of NH_4SCN (0.22-0.44 g) (2.89-5.78 m.mole) was added to the mixture with constant stirring, the products were precipitated immediately which were filtered off washed with (1:1) mixture of water: ethanol, recrystalized from ethanol ,and dried in an oven (60)C^o .

Results and Discussion:-

All the complexes prepared in this work were insoluble in water and methanol but soluble in dimethyl sulfoxide, the complexes are thermal stable as they decomposed above (300) ^oC (except copper complex which decomposes at (265) ^oC [(4)].

The complexes are nonelctrolytes, the molar conductance are found to be in range

(5.6-8.4) ohm^{-1} $.cm^2$ $.mol^{-1}(10^{-3})$M in DMSO[5-7].

The physical properties are listed on Table (1)

Magnetic Properties

The magnetic moment (μ_{eff}) for the complexes of Mn^{+2} (d^5) ,Ni^{+2} (d^8)were (4.920,2.602) B.M respectively , these values were in agreement with the values expected for spin only [8,9] while the values of μ_{eff} of Co^{+2} (d^7) complex was (4.561) B.M higher than the calculated value may be due to the orbital contribution [10,11], the spin only (μ_{eff}) of Cu^{+2} complex (d^9) was found to be (1.670) B.M within the expected value for one .electron. Finally the complexes of Cd^{+2}, Pb^{+2} were diamagnetic as expected from their electron configuration .All data are included in Table (2).

The Electronic Spectra

l Electronic spectra of free ligands:

The electronic spectrum of benzotriazole in DMSO show strong bands at λ_{max} (273) n.m and λ_{max} (312) n.m (32051.282) cm^{-1} due to the electronic transitions ($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) respectively.

The Benzimidazole spectrum exhibited absorption bands at λ_{max} (275) n.m (36363.636) cm^{-1} caused by ($\pi\rightarrow\pi^*$), and another bandsat λ_{max} (348) nm (28735.632) cm^{-1} due to electronic transition of ($n\rightarrow\pi^*$)[12 – 14].

Finally the spectrum of Ammonium thiocyanate shows the electronic transition of ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) at λ_{max} (216) n.m and λ_{max} (351) n.m respectively [15].

The Electronic spectra of Complexes

1. [Mn (BT)$(BI)_2X_2$]

The spectrum of light brown (d^5)complex exhibited absorption band λ_{max} (264) nm (37878. 787)cm^{-1} belong to $^6A_1g\rightarrow{}^4T_1g_{(G)}$ another band appeared at the visible region at λ_{max} (634) n.m (15772 .87) cm^{-1} assigned to $^6A_1g \rightarrow {}^4T_1g_{(G)}$. These rules are accepted for Mn^{+2} Octahedral complexes[16] .

2. [Co(BT)$(BI)_2X_2$]

The spectrum of dark green complex (d^7) exhibited three bands at λ_{max} (272) nm (36764.705) cm^{-1} due to the electronic transition $^4T_1g_{(F)}\rightarrow{}^4A_2g$ $(_F)$ corresponding with charge transfer (C.T) Another bands in the visible region at λ_{max} (539) nm (18553.875) cm^{-1} and λ_{max} (760) nm (13157.894) cm^{-1} attributed to the $^4T_1g_{(F)}\rightarrow{}^4T_1g_{(P)}$ and $^4T_1g_{(F)}\rightarrow{}^4T_2g$ $(_F)$ respectively[16,17].

[Ni (BT) (BI) 2 X2]

The spectrum of the gray complex (d^8) showed strong band at λ_{max} (271) nm (36900.369) cm^{-1}attributed to the transition ^3A_2g $(_F)\rightarrow{}^3T_1g$ $(_P)$ with charge transfer. Another band noticed at λ_{max} (560) nm (17857.142) cm^{-1}caused by $^3A_2g_{(F)} \rightarrow {}^3T_1g$ $(_F)$ transition, the third band at λ_{max} (649) nm (15408.32) cm^{-1} due to^3A_2g $(_F)\rightarrow{}^3T_2g$ $_{(F)}$ transition [18,19].

Accordingly the ligand field splitting energy 10Dq was taken as equal to the electronic transition (u_1) (15408.32) cm^{-1} and the recah inter electronic repulsion parameter (ß¯) found to be (568.836) cm^{-1}. The ratio of $ß = \frac{B'}{B^\circ}$ comes out to be (0.55) (B^o is equal (1030) cm^{-1}) the parameters are show the Ni (II) complex is octahedral [16,18,19].

[Cu (BT) (BI) 2 X2]

The spectrum of light green (d^9) complex exhibited obsorption band at λ_{max} (270) nm (37037.037) cm^{-1}. Another bands in the visible region at λ_{max} (507) nm (19723.865) cm^{-1} assigned to ^2Eg $(_D)\rightarrow{}^2T_2g$ $(_D)$ these transition are characteristic for octahedral complexes of Cu (II)[20,21].

The complexes of [Cd(BT) $(BI)_2X_2$], [Pb(BT) $(BI)_2X_2$] showed sbsorption bands at λ max (274) nm and λ_{max} (284) nm respectively attributed to charge transfer (M→L) because the electronic configuration of Cd^{+2} and Pb^{+2} which confirm absence of any (d-d) transition [22]. But their spectrum suffered red shift with Hyper or Hypo chromic effect this absorption has been fully assigned in Table (3).

Infrared Spectra

The spectrum of benzotriazole showed a weak band at (3247) cm^{-1} which belongs to stretching vibration ν (NH), another weak band at (3078) cm^{-1} attributed to ν (C-H) aromatic [23 -25], finally the strong band belong to str.Vib *n* (N=N) was found at (1500) cm^{-1}.

The spectrum of benzimidazole exhibited broad band at (3150) cm^{-1} caused by str.vib *n* (NH), a weak band noticed at (3040) cm^{-1} attributed to *n* (C-H) aromatic ,another weak sharp band appeared at (1640) cm^{-1} to *n* (C= N) [26]. The medium band belong to str.vib of *n* (C=C) was found at (1605)cm^{-1}.

The spectrum of thiocyanate ion showed a strong band at (2053) cm^{-1} assigned to *n* (CN) and another band at (740) cm^{-1} was attributed ע (CS) [27].

Infrared Spectra of Complexes

The infrared spectra of the prepared complexes exhibited the following bands:

n (C= N) in the region (1620-1630) cm^{-1} which was shifted to lower frequencies by (20-10) cm^{-1} in comparison with benzimid-azole spectrum indicates coordination with metal ions through nitrogen atom and the bands appeared in the region (1488-1496) cm^{-1} belong to *n* (N=N) in benzotriazole moved to lower frequencies by (12-4) cm^{-1} which indicated coordination with metal ions through the two nitrogen atoms.

The coordination of $(SCN)^-$ ion through the nitrogen atom was comfired by the bands in the region (2067–2098)cm^{-1} shifted to higher frequencies by (14-45) cm^{-1} [27] .

M–Ligand bonds

The spectra of prepared complexes exhibited weak bands in the region (550-570) cm^{-1} and (424-460) cm^{-1} assigned to *n* (M–N) and bending vibration of s(M–NCS) respectively.

Table (4) gives the diagnostic absorption and their assignments.

The proposed geometrical structures:-

From all above studies the probable structure has been suggested:-

a. Octahedral geometry for the complexes of **Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2} and Cd^{+2}.**

Distorted Octahedral geometry for the Pb^{+2} complex [14, 20, 28].

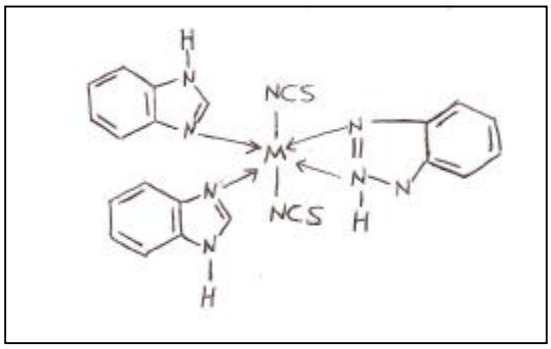

Fig. (1) : M = Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2} ,Cd^{+2}.

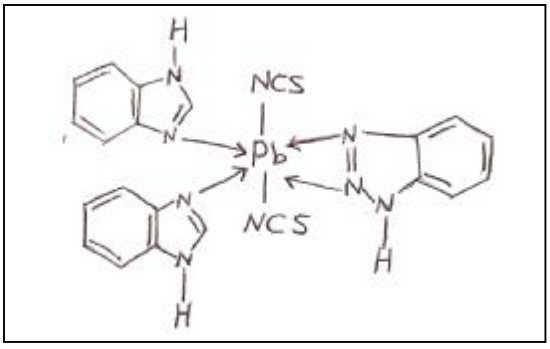

Fig. (2).

Table (1)
The physical prosperities of the free ligands and their complexes.

Compound	Colour	M.P.(C^o)	Dec (C^o)	Elemental Analysis %M Calc.(found)	Molar Conductivity Λ ($ohm^{-1}.cm^2.mol^{-1}$) 10^{-3} M in DMSO
BT	white	98	—	—	9
BI	Brown	172	240	—	7
NH_4SCN	white	149	—	—	26
[Mn(BT) $(BI)_2$ X_2] (C_{22} $H_{17}N_9$ S_2) Mn	Light Brown	—	>300	10.43 (10.83)	8.4
[Co(BT) $(BI)_2$ X_2] (C_{22} $H_{17}N_9$ S_2) Co	Dark Green	—	>300	11.10 (10.78)	6.7
[Ni(BT) $(BI)_2$ X_2] (C_{22} $H_{17}N_9$ S_2) Ni	Gray	—	>300	11.07 (10.15)	8.2
[Cu(BT) $(BI)_2$ X_2] (C_{22} $H_{17}N_9$ S_2) Cu	Light green	185	265	11.87 (12.78)	5.6
[Cd(BT) $(BI)_2$ X_2] (C_{22} $H_{17}N_9$ S_2) Cd	white	—	>300	19.24 (18.46)	6.4
[Pb (BT) (BI)2 X2] (C22 H17N9 S2) Pb	white	—	>300	30.52 (30.99)	7.3

*** Calc % (found %)**

Table (2)
The magnetic susceptibilities for the complexes.

Complexes	d^n	Electron configuration	Term Symbole	Ground State	m eff		Orbital Contribution in Octahedral
					Found	Calc.	
[Mn(BT) $(BI)_2$ X_2]	d^5	$t_2g^3eg^2$	^6S	^6A_1g	4.920	5.916	No
[Co(BT) $(BI)_2$ X_2]	d^7	$t_2g^5eg^2$	^4F	^4T_1g	4.561	3.872	Yes
[Ni(BT) $(BI)_2$ X_2]	d^8	$t_2g^6eg^2$	^3F	^3A_2g	2.602	2.828	NO
[Cu(BT) $(BI)_2$ X_2]	d^9	$t_2g^6eg^3$	^2D	^2Eg	1.670	1.732	NO
[Cd(BT) $(BI)_2$ X_2]	d^{10}	$t_2g^6eg^4$	^1S	—	Zero	Zero	—
[Pb (BT) $(BI)_2$ X_2]	—	—	^1S	—	Zero	Zero	—

Table (3)
The electronic spectra of free ligands and their complexes.

Compound	Imax n.m	ABS	Wave number Cm^{-1}	Emax	Transitions	Remarks
BT	273	2.447	36630.036	2447	$p \rightarrow p^*$	—
	312	0.012	32051.282	12	$n \rightarrow p^*$	—
BI	275	0.467	36363.636	467	$p \rightarrow p^*$	
	348	0.038	28735.632	38	$n \rightarrow p^*$	
X^-	216	0.109	46296.296	109	$p \rightarrow p^*$	
	351	0.042	28490.028	42	$n \rightarrow p^*$	
[Mn (BT) $(BI)_2$ X_2]	264	0.488	37878.787	488	$^6A_1g \rightarrow {}^4T_{1g}(P)$	—
	634	0.010	15772.87	10	$^6A_1g \rightarrow {}^4T_{1g(G)}$	—
[Co(BT)$(BI)_2$ X_2]	272	2.466	36764.705	2466	$^4T_1g_{(F)} \rightarrow {}^4A_{2g(F)}$ (n_2)	Corresponding with charge Transfer(C.T)
	539	0.050	18552.875	50	$^4T_1g_{(F)} \rightarrow {}^4T_{1g(P)}$ (n_3)	New band
	760	0.043	13157.894	43	$^4T_1g_{(F)} \rightarrow {}^4T_{2g}(F)$ (n_1)	New band
[Ni(BT) $(BI)_2$ X_2]	271	2.252	36900.369	2252	$^3A_2g_{(F)} \rightarrow {}^3T_{1g}(P)$ (n_3)	Corresponding with(C.T)
	560	0.038	17857.142	38	$^3A_2g_{(F)} \rightarrow {}^3T_{1g(F)}$ (n_2)	New band
	649	0.030	15408.32	30	$^3A_2g_{(F)} \rightarrow {}^3T_{2g(F)}$ (n_1)	New band
[Cu(BT) $(BI)_2$ X_2]	270	1.834	37037.037	1834	(C.T)	Blue shift
	507	0.016	19723.865	16	$^2Eg_{(D)} \rightarrow {}^2T_{2g(D)}$	-
[Cd(BT) $(BI)_2$ X_2]	274	1.325	36496.35	1325	(C.T) (M → L)	-
[Pb (BT) $(BI)_2$ X_2]	284	2.500	35211.267	2500	(C.T) (M → L)	-

Table (4)
The characteristics infrared absorption free ligands and their complexes.

Compound	*n* (NH)	*n* (C-H) aromatic	*n* (NCS)	*n* (C=N–)	*n* (N=N)	*n* (CS)	*n* (M-N)	δ (M-NCS)
BT	3247.90 W.b	3078.18 v.w	–	—	1500 w	–	—	
BI	3150 b	3040 v.w	–	1640 w.sh	–	–	—	
NH_4SCN	–	–	2053	–	–	–	–	
[Mn(BT) $(BI)_2$ X_2]	3333.06 v.w	3078.18 v.w	2075.26 v.s	1620.09 v.w	1488.94 w	833 v.s	555.46	432.03
[Co(BT)(BI) X_2]	3409.91 v.w	3109.04 v.w	2080 v.s	1620 w	1496.66 w.sh	748.33 v.s	563.18 w	424.31 w
[Ni(BT) $(BI)_2$ X_2]	3394.48 W.b	3139.90 V.W	2090 V.S	1620.09 S	1496.66 W.sh	748.33 V.S	570 W	460 M
[Cu(BT) $(BI)_2$ X_2]	3263.33 w.b	3147.61 sho	2098.41 v.s	1630 w	1490.37	748 S	570.89 w	440 w
[Cd(BT) $(BI)_2$ X_2]	3340.48 v.w	3070.46 sho	2082.98 S	1620 m	1496 w.sh	750 v.s	555.46 w	450 m
[Pb (BT) $(BI)_2$ X_2]	3456.20 v.w	3016.46 v.w	2067.55 v.s	1627.81 w	1490 v.w	745.61 S.b	550 sho	447.45 m.sh

*** S = strong, m = medium ,W = weak , sho =shoulder ,b = broad , v = very**

References

[1] Reedijk, J. In ,Wilkinson, G., Gillard, R. DMc cleverty, J.A. "Comprehensive Coordination chemistry" 1987.

[2] Reginaldo C.Rocha, Francisco N.Rein and Henrigue E.Tama."Ruthenium and Iron Complexes with Benzotriazole and Benzimidazole Derivatives as simple Models for proton–Couplred Electron transfer systems "Journal" .Braz.chem. Soc.,12 (2),2001,pp. 234 -242.

[3] Marion H.O Leary," Contemporary Organic chemistry", 1976.

[4] Pederson, C. J., J. Am. chem. Soc., 89 (20), 1967, pp.7024.

[5] Kettle,S.F.A."Coordination Compounds" Thomas nelson and Sons, London, 1975, pp.165.

[6] Sutton, D. "Electronic spectra of transition metal complexes" 1968, Mc. Graw. Hill Publishing Company lited.

[7] Burger, K. "Coordination Chemistry Experimental Methods", 1973, London Bult / worths and Co (Publishers) Ltd.

[8] Nicholls, D. "Cpmplexes and first Row Transition Elements", 1984, Translated by

Dr.Wissam Ibrahim Azeez, Mousel University.

[9] د.احسان عبد الغني مصطفى ،د. سعد عز الدين المختار،" الكيمياء اللاعضوية والتناسقية ",1988, وزارة التعليم العالي والبحث العلمي ، جامعة الموصل.

[10] Day,M.C and Selbin, J. " theoretical Inorganic chemistry Transition Elements", 1933, Translated by Dr. Issam, Mousl University .

[11] Cotton,F.A and Wilkinson,G. "Advanced Inorganic chemistry", 1998,wily inter Science ,New York.

[12] Al. Hashim ,S.Al Noor ,T. and Alazawi ,S. " Synthesis and Characterization of som mixed–Ligand Complexes with some Metal ions " Iraqi Journal of chemistry, 29(1), 2003,pp. 105 -113.

[13] Timothy, G. Ernest, E. Karsten Krogh. Jesperson and Harvey ., J. Am. chem. Soc., 102, 1980, pp.2600.2604.

[14] Roger, L. Dekock, Harry, B. Gray. "Chemical structure and bonding", 1980, translated by Dr.Mahdi Naji Zakom, 1983,Basrah University.

[15] Alazawi, S. "Sythesis and study of some mixed Ligand complexes of Coffeine, 8. picoline and thiocyanate ion with some metal ions" Journal of Um. Salama for science, 3(2), 2006,314-320.

[16] Lever, A.B.P. "Inorganic electronic spectroscopy",1968.

[17] speca, A. N. Miklski, C. M. Iaconianni ,L.L.Pytlewski and Karayannis, N.M. "Purine complexes with Divalent 3d Metal perchlorates" Inorg. Chem. 19 (11), 1980, pp.3491 -3495.

[18] Dunn,T.M." The visible and Ultraviolet spectra of complexes compounds in modern Coordination chemistry", 1960, New York.Inter Science.

[19] Duward, F.S and Atkins, P.W. "Inorganic chemistry ",1990, oxford University press.

[20] Huheey, J. E. "Inorganic chemistry principles of structure and reactivity", 1972.

[21] Alazawi, S. A. 2004, Ph.D, University of Baghdad.

[22] Al.Janabi ,M.Y. " The physical Methods in Inogranic chemistry ",1983.

[23] Cross, A. D. Alan Jones, R. "Antroducion to partical Infrared spectroscopy", 1969, Third edition.

[24] John ,R.Dyer. "Application of Absorption spectro scopy of organic Compounds", 1965.

[25] William and Fleming ."spectroscopic methods in Organic chemistry", 1973, second edition.

[26] Socrates, G. "Infrared characteristic group frequencies", 1980.

[27] Nakamoto, Kazuo. " Infrared and Raman spectra of Inorganic and coordination compounds ",1997,part B.5th edition.

[28] السعدي ،د. باسم محمد. **" الكيمياء اللاعضوية العصرية** ",1988, الجزء الثاني، جامعة بغداد.

الخلاصة

تم تحضير و معقدات فلزية ذات لكاندات مختلفة من البنزوترايازول (BT) والبنزايمدازول(BI) وايون الثايوسيانات (X^-) مع الايونات الفلزية المنغنيز(II) والرصاص (II) وبالنسبة المولية (2:2:1:1) شخصت المعقدات المحضرة على تقدير النسبة المئوية للفلز أطياف الأشعة فوق البنفسجية المرئية واطياف الاشعة تحت الحمراء بالاضافة الى قياسات التوصلية المولارية وقياسات الحساسية المغناطيسية وبناءً على ما تم استنتاجه فقد اقترحت الصيغة العامة للمعقدات المحضرة وكما يأتي :

$[M (BT) (BI)_2 X_2]$

M=Mn^{2+} ، Co^{2+} ، Ni^{2+} ، Cu^{2+} ، Cd^{2+} ، Pb^{2+}.