Synthesis and Characterization of Co(II) , Ni(II), Cu(II) Zn(II) and Cd(II) mixed complexes of imidazol dithiocarbamate and 1,10-phenanthroline

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Abstract

Co(II) , Ni(II), Cu(II) Zn(II) and Cd(II) metal complexes of new imidazol dithiocarbamate of type $[M(imid.dtc)_2]$ and mixed ligands complexes of the type $[M(imid.dtc)_2.phen]$ (phen=1,10-phenanthroline) have been synthesized and characterized by elemental analysis (atomic absorption) infrared , electronic spectra , molar conductivity measurements and magnetic measurements . It has been found that the imidazol dithiocarbamate behaves as a monodentate ligand in all complexes . The suggest geometry of the four coordinate complexes , appear to be square planer , while octahedral are expected for mixed ligunds.

الخلاصة

تضمن البحث تحضير وتشخيص عدد من معقدات ايونات الكوبلت (II) والنيكل (II) والنحاس (II) والخارصين (II) والكادميوم (II) مع ايميدازول ثنائي- ثايوكارباميت ذات الصيغة $[M(imid.dtc)_2]$ كذلك تم تحضير معقدات مكونة من مزج ليكاندين ذات الصيغة $[M(imid.dtc)_2.phen]$ حيث ان phen=1,10- phenanthroline .

شخصت هذه المعقدات باستخدام تحليل العناصر، الاشعة تحت الحمراء ، الاطياف الالكترونية ، الموصلية الكهربائية والعزم المغناطيسي . وتبين بان الليكاند يسلك احادي السن في جميع المعقدات .كذلك تم اقتراح الشكل الهندسي الرباعي السطوح للمعقدات رباعية التناسق في حين يكون الشكل ثماني السطوح لمعقدات سداسية التناسق في الليكايدين المختلفين .

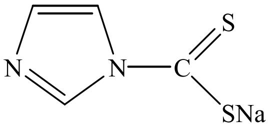
Introduction

Dithiocarbamates (DTC) are product of the reaction between a primary -or secondary amine and carbon disulfide in basic media , the versatility and application was discussed by kitson [1] . They found application as accelerators in vulcanization pesticides , fungicide and as bioactive compounds [2,3] . Most aliphatic and aromatic dithiocarbamate complexes synthesized until now have only the dithio group as ligand , so that they exhibit only uninegative bidentate possibility [4-6] .

Comparatively , the work has been done on the complexes of dithiocarbamate derived from heterocyclic secondary amines. Complexes of nikel (II) , Palladium (II) and platenium (II) with hetrocyclic ligands of tetrahydroquinoline dithiocarbamate were reported . All the complexes have an emperical formula ML_2[7] . Also the behavior of hetrocyclic dithiocarbamate ligands such as 4- Mepipradine , pyrroldine , piperazine and morpholine with different metal ions were prepared [8-11].

Mixed ligand heterocyclic dithiocarbamate complexes so much attention has been attracted to study their interaction with different types of nitrogenous . The mixed complexes of morpholine and piprizine dithiocarbamate with lewis bases , such as glycine , B–alanine were prepared and characterized [9,12] . Mixed ligand complexes can also be of interest from an electrochemical view-powint because of structural and electronic factors might affect the potentials of reaction such as hydrogen evolution and disolution of metal , in acids . Recently , mixed –ligand of Cobalt (III) complexes with macrocyclic amine 1,4,8,11-tetradithiocarbamate were prepared and their electro chemical properties studied by cyclic voltametry[11] .

In this work , we reported the preparation and characterization of some complexes of Co(II) , Ni(II), Cu(II) Zn(II) and Cd(II) ions with mixed ligands of imidazol dithiocarbamet (Na-imid.dte) and 1,10-phenarthroline .



Experimental

Analar grade chemical reagents supplied by B.D.H. and Fluka were used without further purification .

Preparation of Sodium imidazol dithiocarbamate [Na-imid. dtc] :

Amixture of NaOH (4.0g , 0.1 mol) dissolved in the minimum quantity of H_2O and imidazol (6.8 g ,0.1 mol) was refluxed for about three hours . The resulting mixture was cooled to (0-5 ˚C) in an ice bath . To this solution , CS_2 (7.6 g , 0.1 mol) was added in small portions with stirring . The formed oily product was extracted by ether , several times and kept in cool for over night the formed precipitate was filtered off, washed with acetone and dried in over vacuum m. p. 245°c d, yield 70%.

Preparation of Complexes [M(imid-dtc)$_2$] :

To a solution containing 0.001 mole of the required salt ($CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$ and $Cd(NO_3)_2.4H_2O$) in a small amount of water-ethanol 1:1 (v:v), 0.002 mole of the Na-imid.dtc was added . The mixture was stirred for about one hour , then the precipitate complexes were filtered off , washed several times with equal quantities (1:1) of acetone and water and finally air dried. Other complexes were prepared by the same procedure.

Preparation of mixed ligand Complexes [M(imid-dtc)$_2$-phen] :

Into a solution containing 0.02 mole (3.32 g) of (Na-imid-dtc) ligand dissolved in 10 cm^3 of water-ethanol mixture 1:1 , (v:v) , and 0.01 mole (1.98 g) of 1,10-phenanthroline in 5 cm^3 of water , the metal salts were added . The mixture was continuously stirred for 15 min . at 90 ˚C , cooled to room temperature and finally filtered of , washed with acetone and dried .

Instruments

The metal determined by atomic absorption using a (pye Unicom Spg atomic absorption spectrophotometer) .

Conductivity measurements for the complexes were carried out for 10^{-3} M solution in dimethylsulfoxide (DMSO) using LF-42 digital conductivity metar at 25˚C . Infrared absorption spectra recorded on pye- Unicam-Sp 1100 spectrophotometer in the range 400-4000 cm^{-} using KBr – pellets. The UV-spectra were recorded on Shimaddzu UV-160 spectrophotometer in dimethylsulfoxide (DMSO) at 25˚C using a 1 cm quartz cell. Magnetic succeptilities were determined at 25˚C using Braker BM6 instrument .

Results and Discussion

The complexes are solid , stable in atmospheric condtions and non-hydroscopic . All these complexes are insoluble in common organic solvents only very poor solubility in DMSO .

The melting point , metal analyses , the conductance measurements are listed in Table (1) . The values of molar conductance in DMSO are in the range (0.1-3.3) Λ^{-1} cm^2 mol^{-1} , indicates a non electrolyte behavior [12].

The mixed ligand complexes were prepared according to the bellow reaction .

$$MX_n + 2Na - imid\text{-}dtc + 1\ phen \longrightarrow [M(imid\text{-}dtc)_2.phen] + nNaX$$

Table (1) : Analytical and some physical properties of complexes

No.	Compound	M.P (˚C)	Colour	Yield %	Λ ohm^{-}.cm^{2} mol^{-1}	M% calculated (found)
1.	Na-imid.dtc	245 d	---	70	---	---
2.	[Co(imid.dtc)$_2$]	>300 d	Pink	80	3.3	---
3.	[Ni(imid.dtc)$_2$]	>300 d	green	85	0.1	17.02 (16.88)
4.	[Cu(imid.dtc)$_2$]	290	Pale green	78	0.4	18.2 (17.8)
5.	[Zn(imid.dtc)$_2$]	340 d	white	90	0.3	18.62 (18.23)
6.	[Cd(imid.dtc)$_2$]	350 d	white	88	0.7	28.38 (27.92)
7.	[Co(imid.dtc)$_2$ .phen]	350 d	Pink	87	0.1	---
8.	[Ni(imid.dtc)$_2$ .phen]	325 d	Pale green	79	0.1	10.8 (9.45)
9.	[Cu(imid.dtc)$_2$ .phen]	300	Green	80	0.1	11.61 (10.1)
10.	[Zn(imid.dtc)$_2$ .phen]	360 d	white	80	0.1	11.91 (11.45)
11.	[Cd(imid.dtc)$_2$ .phen]	> 350 d	white	85	0.1	18.85 (17.95)

I.R. Spectroscopy

The assignment of the infrared spectra bands of ligand and their complexes are listed in Table (2) . The ligand and complexes show a sharp bands between 1418 and 1498 cm^{-} which attributed to the $\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{N}$ streching vibration [13] .An increase in double band character of $\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{N}$ band results in higher frequency for this vibration .This fact can be attributed to the electron releasing ability of hetrocyclic group which forces high electron density towards the sulphur atoms , *Via* the π system , producing a greater double band character in $\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{N}$ band . All complexes show $\upsilon(\mathrm{C}\overset{\text{- - -}}{\text{—}}\mathrm{N})$ bands in the range (1416-1498) cm^{-} which is lie between $\upsilon(\mathrm{C{=}N})$ and $\upsilon(\mathrm{C{-}N})$ in the 1640-1690 and 1250-1350 cm^{-1} ranges respectively [9] .

A second region between 1055-1090 cm^{-1} associated with the $\upsilon(\mathrm{CSS})$ vibration and has been effectively used in differentiating between monodentate and bidentate Rdtc ligands [13-15] . The presence of only one strong band supports bidentate coordination of the dithiocarbamat ligands , where's a doublet is expected in the case of monodentate coordination [13,16] . The presence of single $\mathrm{N(C}\overset{\text{- - -}}{\text{—}}\mathrm{S)}$ around 1000 cm^{-1} in this work indicates that the ligand present as a bidentate behavior in all complexes and this is in agreement with previous published literature for dithiocarbamat complexes [9,17,18].

The new band a pear in spectra of mixed ligand complexes at 413-482 cm^{-1} due to M-N streching mode [19] .

Table (2) : Selected I.R. bands cm^{-1} and Electronic data of the ligand and complexes

No.	Compound	υ(C ═ S)	υ(C ═ N)	υ(M–N)
1.	Na-imid.dtc	1055	1448	---
2.	[Co(imid.dtc)$_2$]	1069	1460	---
3.	[Ni(imid.dtc)$_2$]	1069	1458	---
4.	[Cu(imid.dtc)$_2$]	1084	1470	---
5.	[Zn(imid.dtc)$_2$]	1090	1448	---
6.	[Cd(imid.dtc)$_2$]	1071	1416	---
7.	[Co(imid.dtc)$_2$ .phen]	1083	1488	482
8.	[Ni(imid.dtc)$_2$ .phen]	1088	1458	482
9.	[Cu(imid.dtc)$_2$ .phen]	1085	1456	422
10	[Zn(imid.dtc)$_2$ .phen]	1089	1480	413
11	[Cd(imid.dtc)$_2$ .phen]	1075	1420	418

Electronic Spectra and magnetic moment

The electronic spectra of the ligand and complexes display the absorption bands listed in Table (3) . The ligand show bands between 9852 cm^{-1} and 33557 cm^{-1} due to intraligand arised from $\pi \longrightarrow \pi^*$ and

$n \longrightarrow \pi^*$ transitions located on sulfur atoms [20-22]

Four coordinated complexes

The electronic spectra of cobalt (II) complexes exhibits low intensity band (due to very low solubility in all common organic solvents) at 15197 cm^{-1} which may be assigned to $^2A_1g \longrightarrow {}^2Eg$ transition in square planer field for Co(II) complexes [23 , 24]. The magnetic moment values for Co(II) complexes is (1.93 B.M.) , This low value of the magnetic moment have been reported to be as a typical characteristics of cobalt having low-spin square planar configuration [23,25] . Electron pairing happen as a result of stereo strain caused by the ligand owing to the formation of strong covalent band using one of 3d orbitals of cabalt (II) atom and $4s^2 4p^2$ square planer , the orbital contribution increase the value of μeff in excess of the spin only value for one unpaired electron (1.73 B.M) for this type of complexes [26] .

The electronic spectra and Nickel(II) show absorption band at 18519 cm^{-1} which is assigned to $^1A_1g \longrightarrow {}^1A_2g$

(Ni) ,while present of some bands in the region 9000-11000 cm^{-1} , indicate that the complexes consist square plane with little distorted to tetrahedral geometry . The magnetic moment value (1.5 B.M.) confirming this distortion [24,27-29].

The electronic spectra of copper(II) complex exhibits absorption band at 14286 cm^{-1} and have room temperature magnetic moment value of 1.937 B.M. It can be suggest that copper (II) is constrained in square planer arrangement , as the maxima band observed can be to combination of transition ($^2B_1g \longrightarrow {}^2A_1g$) and ($^2B_1g \longrightarrow {}^2Eg$) [30,31].

Six coordinated Complexes

The electronic spectra of Co (II) complex show a band at 13793 cm^- which is generally considered to correspond to the ($^2E_2g \longrightarrow {}^2T_2g$) transition which is consistent with octahedral low spin geometry (t_2g^6 eg^1) , while the low value of magnetic moment (1.83 B.M.) confirming this geometry [32].

For the nickel (II) complexes , the magnetic moment (3.13 B.M.) and d-d spectrum show bands at 11236 and 18518 cm^- which can suggesting the existence of $^3A_2g \longrightarrow {}^3T_1g(F)(\upsilon_2)$ and $^3A_2g \longrightarrow {}^3T_1g(P)(\upsilon_3)$ transitions for octahedral spatial configuration [33,34].

The electronic spectrum of Cu (II) complex shows a band at 14771 cm^-, The band in this position typically is expected for an octahedral configuration , corresponding to the transition ^2Eg ^2T_2g [35] . Also the the magnetic moment value was 2.00 B.M. corresponding to one unpair electron [36] .

Finally complexes of Zinc (II) and Cd(II) are diamagnetic and do not display any d-d transition .

Table (3): Magnetic moment and Electronic spectra of the ligand and complexes

No.	Compound	μ B.M.	υ (cm^{-1})
1.	Na-imid.dtc	---	9852,10173,33557
2.	$[Co(imid.dtc)_2]$	1.93	9756,10111,15197,37037
3.	$[Ni(imid.dtc)_2]$	1.5	9862,10111,18519,36496
4.	$[Cu(imid.dtc)_2]$	1.937	11641,14286,35211
5.	$[Zn(imid.dtc)_2]$	Dia	9862,10151,35587
6.	$[Cd(imid.dtc)_2]$	Dia	10183,35461
7.	$[Co(imid.dtc)_2 .phen]$	1.83	9862,10163,13793,33445
8.	$[Ni(imid.dtc)_2 .phen]$	3.13	9862,10163,11587,18518,33445
9.	$[Cu(imid.dtc)_2 .phen]$	2.0	10184 , 14771 , 32788
10.	$[Zn(imid.dtc)_2 .phen]$	Dia	9862 ,10163 ,33445
11.	$[Cd(imid.dtc)_2 .phen]$	Dia	9852 ,10173 ,33557

On the basis of the above physical and spectral data the structure formula of four and six coordinated complexes may be proposed as shown in Figures 1 and 2

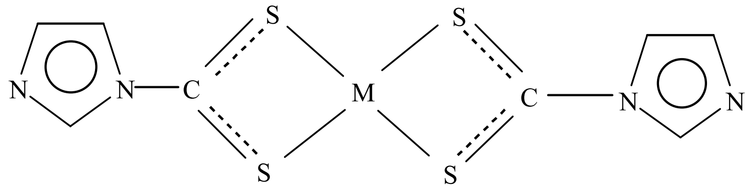


Fig 1 , The proposed structural formula of the four coordinate metal complexes , M=(Co(II) , Ni(II) , Cu(II) , Zn(II) and Cd(II)) .

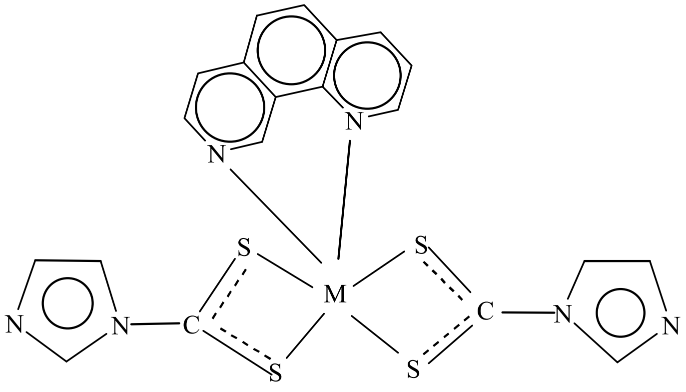


Fig 2 , The proposed structural formula of the six coordinate metal complexes , M=(Co(II) , Ni(II) , Cu(II) , Zn(II) and Cd(II)) .

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