Synthesis and characterization of Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with mixed ligands of α-naphthylamine dithiocarbamate and 1,10phenanthroline

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Abstract

Complexes of α -naphthylamine dithiocarbamate of the type $[M(\alpha-naph.dtc)_2]$. Mixed ligands complexes of the type $[M(\alpha -naph.dtc)_2phen]$ (phen = 1,10-phenanathroline), M = Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized and characterized by elemental analysis (atomic absorption, EDTA titration), infrared, electronic spectra, molar conductances and magnetic moments measurements. The results suggest a tetrahedral for all metal ions while Cu⁺² complex has square planer structure and the hexa coordinated complexes have octahedral structure .

Introduction

A large number of transition metals complexes with various aliphatic and aromatic dithiocarbamate ligands, have been reported until now [1-4]. Complexes of dithiocarbamate ligands like dithiocarbamate themselves have practical application in agriculture and for treatment of alcoholism [5,6], recently gold (III) dithiocarbamate complexes have been prepared and used for treatment of human cancer by suppress tumor growth via direct inhibition of the proteasome activity [7].

Complexes of transition metals with mixed ligands, S and N as donor atoms have found great interest among other coordination complexes [8-10].

Complexes of transition metal with heterocyclic dithiocarbamate ligands, such as $[Cu(pyrrol dtc)_2]$ [11] or with mixed ligands such as $[Ni(H_2dtc)(py)_2]$ [12] have been reported.

In the present work, we report the preparation and characterization of some new transition metals complexes (tetrahedral or square planer) of α -naphthylamine dithiocarbamate ligand with of the type, $[M(\alpha$ -naph.dtc)₂], in which the ligand was coordinated as bidentate with metal through both sulphur atoms. The second type was the octahedral complexes prepared by adding N-heterocyclic (1,10-phenanthroline) as mixed ligand. The coordination was occured through two nitrogen donor atoms of the heterocyclic compound as well as with sulphur atoms of dithiocarbamate

Experimental

Materials and methods

All the chemicals and reagents were used as received from commercial sources (BDH, Aldrich and Fluka grade).

Preparation of ligand

The α -naphthylaminedithiocarbamate ligand (α -naph.dtc) was prepared by literature method [11] by adding 0.01 mol. of α -naphthylamine to solution of 0.016 mol. sodium hydroxide in 15 cm³ distilled water with continuous stirring. The mixture was refluxed for about two hours, the resulting mixture was cooled in ice, then 0.01 mol. carbon disulfide was added dropwise with continuous stirring. Formed this oily product was

extracted by ether the formed precipitate, filtered off, washed with acetone and dried in vacuum.

Preparation of complexes [M(α-naph.dtc)₂]

Complexes were prepared by mixing 1:2 molar quantities of the metal salts (dissolved in minimum amount of distilled water) and α -naphthylaminedithiocarbamate (dissolved in ethanol) with continuous stirring until a precipitate was formed . The precipitated complexes were filtered off, washed with equal quantities (1:1) of acetone and water then dried in vacuum .

Preparation of complexes [M(α-naph.dtc)₂.phen]

The complexes were synthesized by mixing a solutions of (α -naph.dtc) and metal salts as in the first step above then an equimolar of (1,10-phenanthroline)(phen) was added with continuous stirring for about three hours. The formed precipitate then filtered off, washed with acetone and dried in vacuum.

Physical and spectral measurements

The ligands and their complexes which characterized by molar conductances were carried out for 10^{-3} M solution in dimethyl formamide (DMF) using an electric conductivity measuring device model LF-42 at 25 °C, Magnetic susceptibility measurements were performed on Bruker BM6 instrument. The infrared absorption spectra were recorded on Pye Unicam SP 1100 Spectrophotometer using KBr pellets within the 400-4000 cm⁻¹ range. The electronic spectra of the complexes in 10^{-3} M solution in DMF solution were recorded on Shimadzu UV-160 Spectrophotometer at 25 °C using a 1 cm quartz cell. Metal analysis were carried out by using an AA240FS VARIAN instrument for atomic absorption and EDTA-titration methods, according to the standard procedures [13].

Results And Discussion

The complexes are stable, non-hydroscopic and coloured solid . Melting points, elemental analysis and molar conductance measurements are listed in Table 1. The values of molar conductance in DMF are within (17-25) ohm⁻¹.cm⁻².mole⁻¹ range, suggesting non-electrolyte behaviour of the prepared complexes [14].

No.	Compound	m.p. (°C)	Colour		μ _{eff} B.M. (25°C)	% Metal Found (calcul.)
L	Lα-naph.dtc	193-194	Dark pink	-	-	-
1	$[Fe(\alpha-naph.dtc)_2]$	230d	Deep pink	17	Dia	10.9 ^a (11.3)
2	$[Co(\alpha-naph.dtc)_2]$	232d	Deep pink	20	4.78	-
3	$[Ni(\alpha-naph.dtc)_2]$	200d	Pale pink	22	3.12	11.2 ^a (11.8)
4	$[Cu(\alpha-naph.dtc)_2]$	210d	Brown	23	2.02	11.5 ^b (12.6)
5	$[Zn(\alpha-naph.dtc)_2]$	212d	Pale brown	18	Dia	-
6	[Fe(α -naph.dtc) ₂ phen]	212d	Violet	22	4.62	-
7	$[Co(\alpha-naph.dtc)_2phen]$	230-231	Brown	19	3.80	8.1 ^a (8.6)
8	[Ni(\alpha-naph.dtc)2phen]	234-236	Deep violet	27	2.91	-
9	$[Cu(\alpha-naph.dtc)_2phen]$	187-188	Violet	20	2.00	8.9 ^b (9.1)
10	$[Zn(\alpha-naph.dtc)_2phen]$	181-182	Violet	25	Dia	9.0 ^a (9.4)

Table 1: Analytical and some physical properties of the prepared complexes

 $(\alpha$ -naph.dtc) = L α -naphthylamine dithiocarbamate

phen = 1,10-phenanthroline

d = decomposed, a = elemental analysis using EDTA titration method

b = elemental analysis using atomic absorption method

Dia = Diamagnetic

Infrared spectra measurements

The C^{...}S stretching frequency of the α -naphthylamine dithiocarbamate ligand recorded 796-1000 cm⁻¹ range indicates that the ligands act as a bidentate, the value of this absorption was shifted to a higher frequencies in the spectra of the complexes and appeared in the range 1010-1115 cm⁻¹ Table 2 this is in agreement with other published work [15-17].

The N (C····N) stretching vibration of the free ligand Table 2 appeared at 1492 cm⁻¹ that while of the complexes are shifted to a higher frequency 1512-1526 cm⁻¹ for all complexes this is in a good agreement with the published work [18-20].

The coordination of metals with 1,10-phenanthroline through nitrogen atoms were proved by the appearance of the bands in the 464-475 cm⁻¹ region in the IR spectra of the complexes [21].

UV-Visible spectroscopy

The UV spectra of the ligand showed two absorption bands assigned to the transition $n \rightarrow \pi^*$ of azomethine group at 23923 cm⁻¹ and $\pi \rightarrow \pi^*$ transition of aromatic ring at 24752cm⁻¹.

The electronic spectra for the prepared complexes were recorded in the range 200-1100 nm using dimethyl formamide (DMF) as a solvent.

In the present work, four coordinated iron (II) complexes show d-d absorption band, as indicate in Table 2, is similar to reported spectra for square planar iron (II) complexes [22] at 13192 and at 29940 cm⁻¹ due to charge transfer (C.T).

The electric spectra of four coordinated Co (II) complexes exhibited two absorption bands 15970 and

32894 cm⁻¹ due to ${}^{4}A_{2}g(F) \rightarrow {}^{4}T_{g}(P)(v_{3})$ and to charge transfer respectively indicated tetrahedral geometry as reported before but $(v_{2}){}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(F)$ and (N_{1}) ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{2}(F)$ could not observed due to the sensitivity of the instrument used [23,24].

The electronic spectra of four coordinated tetrahedral nickel (II) complexes [22,25] exhibited 15822 cm⁻¹ which correspond to ${}^{3}T_{1}(F) \rightarrow {}^{3}T_{1}(P)$ (v₃) while the other

bands $v_1 \xrightarrow{3} T_1(F) \rightarrow \xrightarrow{3} T_2(F)$ and $v_2 \xrightarrow{T_1(F)} \xrightarrow{3} A_2(F)$ did not appear due to the sensitivity of the instrument used but the band at 30487 cm⁻¹ due to charge transfer.

The electric spectra of four coordinated Cu (II) complexes Table (2) exhibited a strong absorption band at 20833 cm⁻¹ which assigned to combined transition ${}^{2}B_{1}g \rightarrow {}^{2}Eg$ and ${}^{2}B_{1}g \rightarrow {}^{2}A_{1}g$, which supports square planar geometry [26]. Since the zinc ion has d¹⁰ configuration the absorption at 34965 cm⁻¹ and 34488 cm⁻¹ for the zinc complexes are assigned to charge transfer transition [27,28].

The electronic spectra of cobalt (II) six coordinated complexes with ligands Table (2) showed an absorption in the region 14535, 16480, 19623 and 34846 cm⁻¹. These bands assigned to the transitions : ${}^{4}T_{1}g(F) \rightarrow {}^{4}T_{2}g(F)(v_{1}), {}^{4}T_{1}g(v_{2}) \rightarrow {}^{4}A_{2}g(v_{2})$ and

 ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)(v_{3})$ receptivity. The fourth band may be assigned to a charge transfer transition. This is typical for octahedral structure, these values are in agreement with the described values for cobalt (II) complexes [22].

No.	Compound	vC-S	vC-N	vM-N	d-d and $\operatorname{cm}^{-1}(\operatorname{cm}^{-1})$
L	α-naph.dtc	1000 796	1492	-	23923 , 24752
1	$[Fe(\alpha-naph.dtc)_2]$	1108	1512	-	13192 , 29940
2	$[Co(\alpha-naph.dtc)_2]$	1011	1524	-	15970 , 32894
3	[Ni(α -naph.dtc) ₂]	1013	1525	-	15822 , 30487
4	$[Cu(\alpha-naph.dtc)_2]$	1113.	1520	-	20833
5	$[Zn(\alpha-naph.dtc)_2]$	1115.	1513	-	34965
6	[Fe(α -naph.dtc) ₂ phen]	1014	1526	466	10910, 31645
7	[Co(α -naph.dtc) ₂ phen]	1010	1516	464	14535, 16480, 19623, 34846
8	[Ni(α -naph.dtc) ₂ phen]	1013	1516	465	10700, 13820, 24750, 32150
9	[Cu(α -naph.dtc) ₂ phen]	1108	1525	470	12953
10	$[Zn(\alpha-naph.dtc)_2phen]$	1107	1519	475	34488

Table 2: Selected IR bands (cm⁻¹) and electronic spectral data of the ligand and prepared complexes

Magnetic susceptibility studies Four coordinated complexes

Fe(II) complex: The magnetic moment value of the Fe(II) complex (μ_{eff} = Dia BM) Table 1 suggest a square planer stereochemistry of the compound [31].

Co(II) complex: The complex has magnetic moment value of 4.78 BM Table 1 corresponding to three unpaired electrons which were higher than the spin only value may be one to orbital contribution [31].

Ni(II) complex: The magnetic moment value of 3.12 BM at 25° C for the complex suggest the presence of two unpaired electrons which reveals the spin free nature of the complex, so the complex may have tetrahedral stereochemistry [32].

Cu(II) complex: The magnetic moment for the complex has been found to be 2.02 BM Table 1. This value corresponds to the presence of one unpaired electron in the complex which suggest a square planer stereochemistry of the compound [32].

Six coordinated complexes

The room temperature 25° C magnetic moment 4.62 B.M Table 1 corresponds to an octahedral geometry of iron (II) [29]. The magnetic moment value for the hexa coordinate cobalt (II) complex Table 1 is 3.80 BM which is typical of high spin octahedral cobalt (II) complexes [33]. The Ni(II) complex shows a magnetic moment 2.91 B.M Table 1 at room temperature, this value is shows the presence of an octahedral environment around Ni(II) ion in the complex [34]. The Cu(II) complex has magnetic moment 2.00 B.M Table 1 shows a distorted octahedral structure around Cu(II) [35].

As the spectrum of Zn(II) complexe was not well resolved . It was not interpreted but has μ_{eff} value indicated that is diamagnetic as expected.

On the basis of the above discussions we propose the following structures which indicates four coordinate of metal ions with bidentate ligand (α -naph.dtc) through two sulphur atoms (Fig. 1). With the most expected tetrahedral structure except Cu⁺² complex which suggested square planet geometry .



Fig.1: Suggested structure for four coordinate complexes (where M: Fe(II), Co(II), Ni(II), Cu(II) and Zn(II))

While the six coordinate complexes indicates the coordination via four sulphur atoms of α -

naphthyldithiocarbamate and two nitrogen atoms of 1,10phenanthroline to metal (II) ions proposing the following structure: octahedral.



Fig. 2: Suggested structure for the six coordinate complexes (where M: Fe(II), Co(II), Ni(II), Cu(II) and Zn(II))

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تحضير وتشخيص عدد من معقدات الحديد (II) والكويلت (II) والنيكل (II) والنحاس (II) والخارصين (II) مع ليكاندات مختلطة من الفا – نفثيل امين ثنائي ثايوكارباميت و ١٠،١-فينانثرولين

امال يونس العساف و جاسم محمد الياس و عبير سالم محمد قسم الكيمياء ، كلية التربية ، جامعة الموصل ، الموصل ، العراق (تاريخ الاستلام: 1 / ٤ /2008 ، تاريخ القبول: ١ / ٩ / ٢٠٠٨)

الملخص

يتضمن هذا البحث تحضير وتشخيص عدد من معقدات الفا- نفثيل امين ثنائي- ثايوكارباميت ذات الصيغة [M(α-naph.dtc)₂] [M = [I] و Fe(II) = [M(α-naph.dtc)₂] و Ni(II) و Ni(II) و Cu(II) و Ni(II) و Cu(II) و Cu(II) و Ni(II) و Cu(II) و Cu(

شخصت هذه المعقدات المحضرة باستخدام تحليل العناصر ، واطياف الاشعة تحت الحمراء والاطياف الالكترونية والموصلية الكهربائية والعزوم المغناطيسية. وتبين بانها معقدات رباعية النتاسق رباعية السطوح لجميع الايونات ماعدا النحاس كان بترتيب المربع المستوي اما المعقدات سداسية النتاسق كانت بترتيب ثماني السطوح الاكثر احتمالاً .