

Synthesis and Characterization of Some Homobimetallic Mixed Ligands Complexes

Akram A. Mohammed

Department of Chemistry, College of Education, University of Mosul, Mosul, Iraq

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Abstract

Cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) complexes of the type $[M_2LL'(OH)_2(H_2O)_4]$ (where M = Co(II), Ni(II), Cu(II), Zn(II) or Cd(II); L=2, 3 -butanedione; while L' = deprotonated salicylic acid) have been synthesized by 2:1:1 molar reactions of metal chlorides with 2,3-butanedione and salicylic acid. The resulting complexes have been characterized by the metal content measurements, molar conductance measurements, infrared, electronic spectra and magnetic moment measurements. The complexes are non-electrolytes as is evident from low values of their molar conductance. The infrared spectral studies indicate that the two ligands behave as bidentate chelating ligands. Also the IR studies show that the water molecules are coordinated in all the complexes and the metal centres are bridged by OH groups. The different studies reveal dinuclear nature of the complexes and the two metal atoms are hexacoordinated with octahedral geometry.

Introduction

A large number of mixed ligands complexes involving ligands containing functional groups such as sulphur, nitrogen, hydroxyl and carbonyl groups, have been studied for their interesting properties, e.g., their important role in biological processes [1,2], electrochemistry [3], and pharmaceutical synthesis [4]. Also, they are known to possess interesting antimicrobial [5] and antitumour properties [6]. There is growing awareness associated with electrochemical, magnetic and spectroscopic studies of homobimetallic mixed ligands complexes [7,8] due to their biological interest. The synthesis of bimetallic complexes is interesting because they exhibit magnetic exchange between the two metal ions or tendency to undergo multielectron redox reactions [9].

Keeping this in view, it was considered worthwhile to synthesize homobimetallic mixed ligands complexes and the main aim of the present work is to find new homobimetallic mixed ligands complexes by interacting Co(II), Ni(II), Cu(II), Zn(II) or Cd(II) salts with salicylic acid and 2,3-butanedione as bidentate chelating ligands (Figure 1).

Experimental

Materials : Chemicals employed were of analytical grade used without further purification.

Analytical and physical measurements

Metal contents have been determined by applying precipitation methods [10] after the decomposition of the complexes with concentrated nitric acid. Melting points were determined by using electrothermal 9300 digital apparatus. Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using 0.001M of the complexes in dimethylformamide (DMF) solutions at room temperature. IR spectra were recorded on a Bruker tensor 27 spectrophotometer in

the 400-4000 cm^{-1} range using KBr disc. Electronic spectra were recorded on a Shimadzu 1601 spectrophotometer in DMF at 25°C for 0.001M solution of the compounds using a 1 cm quartz cell. Magnetic susceptibilities of the complexes have been measured by Bruker B.M.6.

Synthesis of the homobimetallic mixed ligands complexes

These complexes were synthesized by the reactions of a hot ethanolic solution of (0.02 mol) of metal chloride with a hot solution of (1.38gm, 0.01 mol) of salicylic acid. The pH has been adjusted to 6-8 with NaOH solution (1.25 M). the pH was measured by using of a pH paper. The mixture was refluxed for two hours, then (0.861gm ,0.01 mol) of 2,3-butanedione in the same solvent was added to the mixture and the pH readjusted again. Refluxing was continued for extra five hours. The complexes thus formed were collected and washed with distilled water and ethanol to remove the unreacted starting materials, and then were dried in air.

Results and discussion

All the prepared complexes were as powders, stable in air at room temperature. Their analytical data together with some physical properties are summarized in Table 1. Based on the metal content measurements have been supported the general formulae $[M_2LL'(OH)_2(H_2O)_4]$, which shows that in each complex the ratio of metal : ligand : ligand is 2 : 1:1. The molar conductance of the complexes in DMF are in the range (6-29) $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ (Table 1) indicating a non-electrolytic in nature and that no inorganic anions such as OH^- ions are present in outer sphere coordination [11]. The non-conducting character reveals the presence of (OH) groups and metal ions in the coordination sphere.

Table (1) : Physical and analytical properties of the ligands and their complexes

Compound	Colour	m.p C ^o	Yield %	% Metal Calc. (Found)	Λ_M (DMF) cm ² ohm ⁻¹ mol ⁻¹
Salicylic acid	White	158-160
2,3-Butanedione	Yellow	88(bp*)
[Co ₂ LL' (OH) ₂ (H ₂ O) ₄]	Purple	371 d [#]	61	26.43 (25.89)	18
[Ni ₂ LL' (OH) ₂ (H ₂ O) ₄]	Green	392 d	67	26.36 (26.03)	25
[Cu ₂ LL' (OH) ₂ (H ₂ O) ₄]	Dark Green	340 d	60	27.92 (28.34)	29
[Zn ₂ LL' (OH) ₂ (H ₂ O) ₄]	Brown	249	73	28.49 (27.92)	7
[Cd ₂ LL' (OH) ₂ (H ₂ O) ₄]	White	258	52	40.66 (39.57)	6

* bp = boiling point , # d = decomposition

IR spectra :

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. The IR spectrum of the salicylic acid (L'H₂) shows a band at 3518 cm⁻¹, assignable to ν (OH) (phenolic hydrogen). The absence of this band, noted in the spectra of the complexes, indicates the deprotonation of the OH group on complexation. Instead, a band characteristic to ν (OH) of coordinated water was observed in the region (3552-3384) cm⁻¹ [12]. I.R spectrum showed no peaks belong to the ligands in the regions (847-809) and (729-700) cm⁻¹, this was a good confirmation for the presence of coordinated water, assignable to the rocking and wagging modes, respectively. The IR spectrum of 2,3-butanedione(L) shows a band at 1722 cm⁻¹, assignable to ν (C=O) (carbonyl group). In the IR spectra of all the metal complexes, this band is shifted to lower frequencies (1629-1623) cm⁻¹, indicating the involvement of C=O oxygen in coordination with the metal ion [13]. The other coordination site, which can take part in the complexation is the carboxyl group (COOH) of salicylic acid. In this ligand (L'H₂), the asymmetric and symmetric stretching vibration of the carboxylate group, ν as(COO⁻) and ν s(COO⁻) appear

at 1657 and 1444 cm⁻¹, respectively. In the complexes, these bands occur at (1600-1580) and (1399-1361) cm⁻¹, with difference $\Delta\nu$ (COO) of (206-192) cm⁻¹ and indicate the unidenticity of the carboxylate group [14]. Also the bands of the OH of COOH group in the region (2858-2593) cm⁻¹ of the salicylic acid disappeared on coordination with the metal ion [15]. The C-O stretching vibrations appeared at 1325 cm⁻¹ in the spectrum of the salicylic acid. This band is shifted to lower frequencies in the spectra of all complexes (1318-1298) cm⁻¹ (Table 2). This shift confirms the participation of oxygen in the C-O-M bond [16]. Also, the appearance of new bands in all complexes at the region (1249-1234) cm⁻¹ are attributed to the presence of bridged bond (M-OH) [17]. Assignment of the proposed coordination sites is further supported by the appearance of new bands in the region (468-421) cm⁻¹, which could be attributed to the formation of M-O bond (Table 2) [18]. Finally, since M-OH₂ band is located beyond the limits of our instrument (at the far infrared spectra), therefore, the coordination of the water molecules to the metals could not be inferred from the infrared absorption spectra.

Table (2) : Important IR spectral bands of the ligands and the complexes (cm⁻¹)

Compound	ν (OH) H ₂ O	ν (C=O)	ν as (COO)	ν s (COO)	ν (C- O- M)	Bridging (OH)	ν (M- O)	rocking H ₂ O	Wagging H ₂ O
Salicylic acid	-----	-----	1657	1444	1325	-----	-----	-----	-----
2,3-Butanedione	-----	1722	-----	-----	-----	-----	-----	-----	-----
[Co ₂ LL' (OH) ₂ (H ₂ O) ₄]	3552	1624	1600	1399	1305	1234	421	840	729
[Ni ₂ LL' (OH) ₂ (H ₂ O) ₄]	3384	1629	1600	1398	1305	1235	454	829	710
[Cu ₂ LL' (OH) ₂ (H ₂ O) ₄]	3443	1623	Hidden	1361	1318	1247	441	847	Hidden
[Zn ₂ LL' (OH) ₂ (H ₂ O) ₄]	3443	1625	1600	1394	1310	1249	435	812	704
[Cd ₂ LL' (OH) ₂ (H ₂ O) ₄]	3544	Hidden	1580	1388	1298	1247	468	809	700

Electronic absorption spectra and magnetic moments

Electronic absorption spectra of the complexes were recorded in DMF solution (Table 3). The cobalt complex spectrum shows three bands observed at 10352, 15384 and 34246 cm^{-1} , which may be assigned to ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{F})$ (ν_1), ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})$ (ν_2) and to the charge transfer transition, respectively. The UV spectra of Co(II) complex is consistent with the formation of an octahedral geometry [19]. The transition ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})(\nu_3)$ can not be observed, it may be lost in the low energy tail of the charge transfer transition [20,21]. The magnetic moment of 3.51 B.M. per Co atom, indicates that, as expected, magnetic exchange occurs between the two cobalt sites. On the basis of the magnetic data, the cobalt(II) complex has a binuclear structure [22]. The nickel(II) complex shows three absorption bands at 9920, 13550 and 32679 cm^{-1} , which are attributed to the ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})(\nu_1)$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})(\nu_2)$ and the charge transfer transitions, respectively, on the basis of an octahedral geometry [20,21,23]. The complex is

paramagnetic with a low μ_{eff} value (2.60 B.M. per nickel). This may be caused by a strong nickel-nickel interaction. The electronic spectrum of the copper(II) complex shows bands at 13477 and 27472 cm^{-1} due to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition and charge transfer, respectively, suggesting a distorted octahedral structure [23]. The magnetic moment per Cu(II) ion, 1.44 B.M., is well below the calculated value, 1.73 B.M., indicating spin-exchange interaction between the copper(II) ions [24]. Since the zinc and cadmium ions have d^{10} configuration, the absorption at 33112 cm^{-1} for the zinc complex and at 32894 cm^{-1} for the cadmium complex could be assigned to a charge transfer transition [25]. Zn(II) and Cd(II) complexes are diamagnetic as expected for the d^{10} configuration. However, taking into account the spectra and other physicochemical evidences, hexa-coordinated octahedral geometry is suggested for Zn(II) and Cd(II) complexes[23].

Table (3) : Electronic spectral bands and the magnetic moments of the complexes

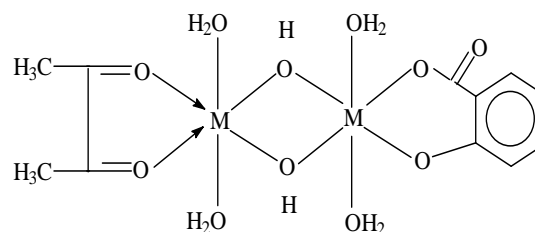
Complexes	Band (nm)	Position (cm^{-1})	Assignments	μ_{eff} (B.M.)
[Co ₂ LL' (OH) ₂ (H ₂ O) ₄]	292	34246	Charge transfer	3.51
	650	15384	${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}(\text{F})$	
	966	10352	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{F})$	
[Ni ₂ LL' (OH) ₂ (H ₂ O) ₄]	306	32679	Charge transfer	2.60
	738	13550	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$	
	1008	9920	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$	
[Cu ₂ LL' (OH) ₂ (H ₂ O) ₄]	364	27472	Charge transfer	1.44
	742	13477	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$	
[Zn ₂ LL' (OH) ₂ (H ₂ O) ₄]	302	33112	Charge transfer	Dia*
[Cd ₂ LL' (OH) ₂ (H ₂ O) ₄]	304	32894	Charge transfer	Dia*

* Dia = Diamagnetic

Conclusions

From the above discussion, and from the data given in Tables 1,2 and 3, it is concluded that the both ligands in these complexes coordinated as bidentate chelating ligands. Further coordination at the metal ion was occurred with two molecules of water on the Z axes (axial ligand) to each metal. Also additional coordination of the hydroxyl groups was observed for metal complexes, in which the metal centre are bridged by OH moieties, giving hexacoordinated metal ions.

Based on these data, an octahedral geometry has been assigned for all the binuclear complexes (Figure 1).



M = Co(II), Ni(II), Cu(II), Zn(II) or Cd(II)

Figure (1) : The proposed structure of the complexes

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تحضير وتشخيص بعض معقدات ثنائية النوى المتجانسة لمزيج من الليكاندات

أكرم عبد القادر محمد

قسم الكيمياء ، كلية التربية ، جامعة الموصل ، الموصل ، العراق

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الملخص

تم تحضير معقدات الكوبلت ، النيكل ، النحاس ، الخارصين ، والكادميوم الثنائية الموجبة حيث اقترحت الصيغة $[M_2L(OH)_2(H_2O)_4]$ (M) تمثل ايون الكوبلت (II) ، النيكل (II) ، النحاس (II) ، الخارصين (II) او الكادميوم (II) و = حامض السلسليك المزال منه بروتونين بينما $L=$ ٢، ٣-بيوتان دايون).

حضرت هذه المعقدات بنسبة مولارية ٢ : ١ : ١ (فلز : ليكاند : ليكاند).

شخصت المعقدات من خلال التحليل الدقيق للفلز ، قياسات التوصيلية المولارية ، الاشعة تحت الحمراء ، الطيف الالكتروني والقياسات المغناطيسية. دلت القيم الواطنة للتوصيلية الكهربائية لهذه المعقدات بانها ذي طبيعة متعادلة. اوضحت اطياف الاشعة تحت الحمراء بان كلا الليكاندين يعملان بشكل ثنائي السن مخلبي. كذلك اظهرت دراسات الاشعة تحت الحمراء اتصال جزيئات الماء بالفلز لجميع المعقدات وكذلك وجود مجموعتي هيدروكسيل جسرية. اعتمادا على هذه الدراسات المختلفة، دلت القياسات كون هذه المعقدات ثنائية النوى وان كل فلز في المعقد يكون سداسي التناسق وذو بنية ثمانية السطوح.