Synthesis and characterization of some transition Metal homo binuclear complexes

Maher A. M. Al-Ta'yy[1] **, Maha L. J. Al-Samarie**[2]

[1] Dept . of Chem. , College of Education for Girls , Univ. of Mosul , Mosul , Iraq

[2] Dept. of Chem. , College of Science , Univ. of Tikrit , Tikrit , Iraq

(**Received:** 1 / 11 / 2009 ---- **Accepted:** 14 / 2 / 2010)

Abstract

Benzilidenedi(benzoylhydrazine) ($BDBH_2$)prepared form benzil and benzoylhydrazine, has been isolated and reacted with some transition metal Fe(II), Co(II), Ni(II) and Cu(II) in both neutral and basic media the reactions have shown to yield complexes of the general formulae [$M_2(BDBH_2)_2X_2$]X_2 and [$M_2(BDB)_2$] (where $BDBH_2$ and BDB^{2-} are the neutral and dibasic forms of the ligand, $X = Cl^-$ or NO_3^-) the complexes are characterized by analytical ,physical and spectral methods .

These measurements have shown that the ligand acts as neutral tetradentated in neutral medium, while in the basic medium, the ligand behave as dibasic tetradentated giving binuclear complexes with the most probable octahedral structure.

Introduction

In acid hydrazides, the presence of two nitrogen atoms in addition to the carbonyl group makes it possible for such compounds to act as ligands(1,2). The coordination chemistry of acid hydrazides and their Schiff bases with aldehydes and ketoses are of special interest in a variety of ways in which theses species could be bonded with the metal ions(3,4). their reaction in neutral and basic media gives different types of metal complexes. Also, they can coordinate with more than one donor atom, act as multidentate ligands and formation of oxygen bridged bi-and tri-nuclear complexes have been reported(5-8). In addition to their ability to act as complexing agents, these ligands play an important role in biological systems and they have proved to be antitumour and numerous activities(9-11).

The present work describes the preparation and characterization of homo binuclear complexes of Fe(II), Co(II), Ni(II) and Cu(II) formed with benzilidenedi (benzoylhydrazine) in neutral and basic media.

Experimental

All chemicals are of analytical grade and used as supply without further purification. Infrared spectra are recorded on a Shimadzu FTIR -8400S spectrophotometer at a range of 400-4000 cm^{-1} by using KBr discs. Electronic spectra of the complexes are studied by using a Shimadzu UV-160 UV-Visible spectrophotometer for 10^{-3} M solution of the compounds in DMF at 25°C, and by using 1cm quartz cell. Elemental analysis are carried out by using spectroscopic method on PYEUNICAM SP-9 Atomic absorption spectrophotometer (Phillips) and reasonable results were obtained as given in (Table-1).

Magnetic susceptibility measurements are made at 25°C by using the Faraday method on the solid in a pyrex tube using BM6 instrument.

Conductivity measurements are made on 10^{-3} M solutions of the complexes in DMF at 25°C by using conductivity measuring apparatus model LF-42.

The ligand benzilidenedi (benzoylhydrazine) ($BDBH_2$) is synthesized by the condensation of 1:2 molar of benzil and benzoylhydrazine.

A solution (0.01 mol) of benzil in ($15cm^3$) ethanol is added slowly to an ethanolic solution containing (0.02mol) of benzoylhydrazine in ethanol ($15cm^3$). The mixture is boiled under refluxed for 3 hours, and then cooled. The Precipitated ligand is filtered off ,washed with cold ethanol and then recrystallized form ethanol.

Preparation of the Complexes:

All the complexes were prepared by the same procedure as follows:

An ethanolic solution of the metal salt (0.01mol) in ethanol ($15cm^3$) was added to hot stirred solution of the ligand (0.01 mol) in ethanol ($15cm^3$). The solution so obtained was subsequently treated in two different ways. In the first method, it was refluxed for ca 30 minutes with occasional shaking and on cooling, colored crystals were separated out. In the second method, 1N KOH solution was added slowly to the mixture until complete precipitation was occurred at pH 9-10. The mixture was digested on a water bath for about 1 hour and then cooled. The separated complexes in both methods were filtered off, washed several times with cold ethanol and dried in a vacuum desiccators.

Results and discussion:

The reaction of the metal salts with the ligand is carried out in both neutral and basic media and it may be depicted as follows:

$$2MX_2.nH_2O + 2BDBH_2 \rightarrow [M_2(BDBH_2)_2]X_2 + 2nH_2O \cdots \quad (1)$$

$$2MX_2.nH_2O + 2BDBH_2 + 4KOH \rightarrow [M_2(BDB)_2] + 4KX + (2n+4)H_2O \quad \ldots(2)$$

Where $M = Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$; n = 2,3,4,6

As indicated by the above equations, binuclear complexes are separated out from neutral and basic media reactions.

The analytical data of the complexes (Table-1) are reasonable and agree well with the given formulations.

The complexes are stable in air at room temperature and have good keeping qualities. They are insoluble in water methanol , ethanol but soluble in dimethylformamide (DMF). The molar conductivities measured in DMF for 10^{-3} M solutions at 25^{o}C (Table-1) suggest that 1:2 and non-electrolytes for complexes(12) are prepared in neutral and basic medium, respectively. These results are consistent with the given formulations.

The infrared absorption spectra of the prepared ligand and their complexes were recorded and the data are given in (Table-2). Different perturbations which are observed in the spectra of the complexes are compared to these of the free ligand spectrum. In the $\left[M_2(BDB)_2\right]$ complexes, the υC=N stretch which was also shifted to a lower frequency by 35-50cm^{-1} suggesting involvement of the azomethine nitrogen in coordination with the metal ions, similar to the ionic complexes(14).

For the $\left[M_2(BBH_2)_2X_2\right]X_2$ complexes, the υC=O stretch is shifted by about 20-50 cm^{-1} this suggests a coordination of the carbonyl oxygen atom, similar to that observed for hydrazide complexes. The C=N stretching mode shows a negative shift 25-60cm^{-1}, this indicates a coordination of the nitrogen atom of the azomethine group.(13,15,16)

Another important observation is the absence of υ(NH) and υ(C=O) which was attributed to the enol tautomer(17). Instead, new bands as appeared at 1572-1580cm^{-1} are assigned to υ(O-C=N+υC=N) combination and υ(C=N-N=C) (azine chromophor) respectively(18,19). The presence of these bands is a strong evidence for enolization and deprotonation in basic medium. In these complexes, new stretching bands which appear in the regions 765-775cm^{-1} are attributed to M-O-M bridge and not observed for neutral complexes(14,20). Such bridges occur more readily via enolic oxygen atom.

In the far infrared region, other new bands for both types of complexes are found at 420-425 and 460-480cm^{-1} and assigned to M-N and M-O stretching vibration, respectively(21,22). In the infrared spectra, the M-Cl stretching band of the complexes formed in neutral solution. The band located at about 540-575cm^{-1} is assigned to ionic chloride(20,23). The bands are due to coordinate chloride ion in complexes formed with metal chloride were fall below the limits of our i.r spectrophotometer and could not be observed.

The complexes which are prepared in neutral medium and containing nitrate group form three bands at 1000-1525cm^{-1} regions. Because the difference among high frequency bands υ$_1$-υ$_5$ is more than 190cm^{-1}, the coordination of bidentated nitrate ion with one of the two oxygen atoms is enhanced. This becomes consistent with the molar conductivity measurements of these complexes. No bands are observed for the complexes prepared in basic medium and this is an evidence that nitrate group is not found in these complexes.

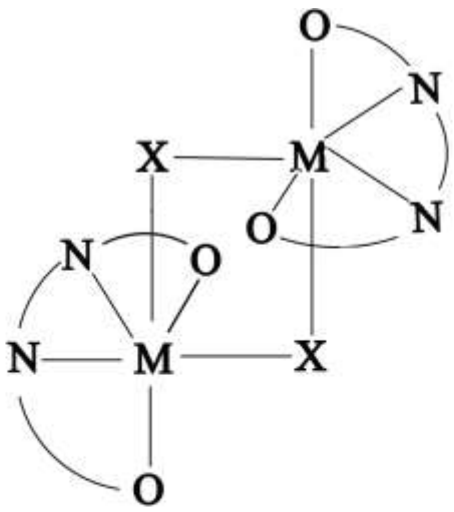
The electronic spectra of the complexes in DMF as a solvent are recorded (Table -3). The spectra of iron(II) complexes show only one band assigned to $^5T_2g(D)\rightarrow{}^5E_2g$ transition is broadened or split. Besides stereo chemical distortion , spin-orbital coupling and a Jahn-Teller effect in the excited configuration(2).

Cobalt(II) complexes exhibit three bands due to the spin-allowed transitions $^4T_1g(F)\rightarrow{}^4T_2g(F)\upsilon_1$, $^4T_1g(F)\rightarrow{}^4A_2g(F)\upsilon_2$ and $^4T_1g(F)\rightarrow{}^4T_1g(p)\upsilon_3$. The electronic spectra of nickel(II) complexes show three bands attributed to υ$_1$, υ$_2$ and υ$_3$ corresponding to $^3A_2g(F)\rightarrow{}^3T_2g(F)$, $^3A_2g(F)\rightarrow{}^3T_1g(F)$ and $^3A_2g(F)\rightarrow{}^3T_1g(p)$ transitions, respectively. The number and positions of these bands corresponding to octahedral structure for both cobalt and nickel complexes are formed in neutral and basic media.

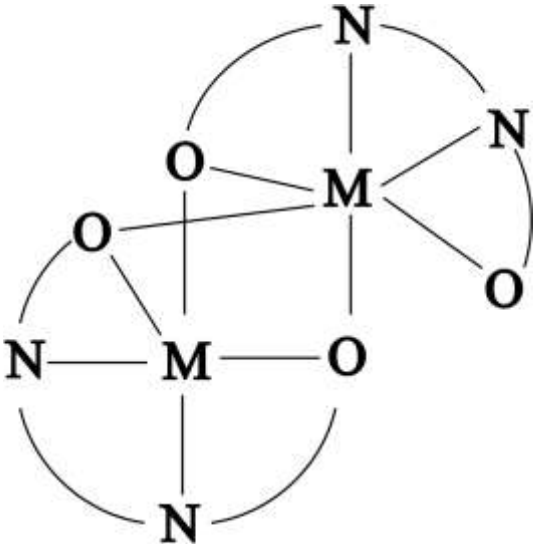
The electronic spectra of copper (II) complexes, show one broad band assigned to the three combined transitions $^2B_1g\rightarrow{}^2A_1g$, $^2B_1g\rightarrow{}^2B_2g$, and $^2B_1g\rightarrow Eg$, suggesting a distorted octahedral geometry with D$_4$h symmetry in terms of Jahn-Teller effect for the complexes(5,18,24).

The values of the effective magnetic moments for all complexes (Table-1) are due to paramagnetic behavior and corresponding to unpaired electrons of the metal ion complexes. The effective magnetic moments calculated per metal atom in the complexes which are less than the expected spin-only values (Table-1), suggesting that these complexes are binuclear. Oxygen bridging of the metal center which permits some kind of super-exchange, leading to partial quenching of the magnetic moment of the coupled unpaired electrons(25,26).

From the different physiochemical studies and various spectral measurements, it is concluded that the ligand, which gives very stable complexes with the various metal ions used in this work, acts as neutral tetradentated in neutral medium, coordinating through both azomethine nitrogen, and both carbonyl oxygen atoms and acts dibasic tetradentated in basic medium forming oxygen – bridged binuclear complexes. In both types of complexes, hexacoordinated metal ions with octahedral structure is suggested ,as shown in Fig.1.



$BDBH_2$ Complexes



BDB^{2-} Complexes

M= Fe(II), Co(II), Ni (II), Cu (II);

$X=Cl^-$, NO_3

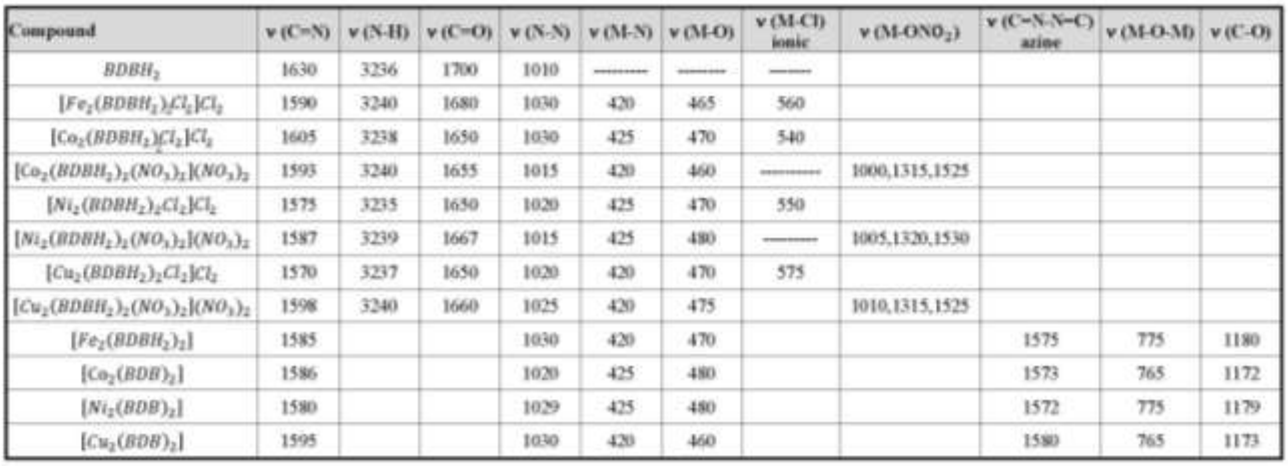
Fig. 1: The Suggested Structures for $BDBH_2$ Complexes

Table-1 Analytical and some physical properties of the ligand and its complexes

Compound	Colour	$m.p\ ^{\circ}c$	Λ_M in DMF ($cm^2ohm^{-1}mol^{-1}$)	Analysis% Found (calculated)	μ_{eff} (BM)
$BDBH_2$	White	١٨٦	–		
$[Fe_2(BDBH_2)_2Cl_2]Cl_2$	Pale brown	٢٨٣	١٥٨	(10.10)(9.75)	4.32
$[Co_2(BDBH_2)_2Cl_2]Cl_2$	Pale orange	٢١٢	١٦٧		3.47
$[Co_2(BDBH_2)_2(NO_3)_2](NO_3)_2$	Beige-yellow	٢٣٤	١٦١		3.43
$[Ni_2(BDBH_2)_2Cl_2]Cl_2$	Pale yellow	٢٥٢	١٣٨	11.34(10.85)	2.66
$[Ni_2(BDBH_2)_2(NO_3)_2](NO_3)_2$	Yellow	٢١٨	١٦٩	11.10(11.18)	2.71
$[Cu_2(BDBH_2)_2Cl_2]Cl_2$	Gray	٢٦٨	١٥٤	10.34(10.94)	1.49
$[Cu_2(BDBH_2)_2(NO_3)_2](NO_3)_2$	Pale gray	٢٧١	١٤٧	11.35(11.11)	1.48
$[Fe_2(BDBH_2)_2]$	Beige	٣٠٩	١٩	12.02(11.17)	4.71
$[Co_2(BDB)_2]$*	Dark green	٣١٧	١٠		3.33
$[Ni_2(BDB)_2]$*	Very pale green	٢٢٦	١٧	11.43(11.67)	2.84
$[Cu_2(BDB)_2]$*	Pale green	٢٥٠	٢٣	12.85(13.59)	1.72

(*) The same complexes was obtained by using different metal salts in alkaline medium.

Table-2: Important IR, spectral bands (cm^{-1}) for $BDBH_2$ and its complexes



Compound	ν (C=N)	ν (N-H)	ν (C=O)	ν (N-N)	ν (M-N)	ν (M-O)	ν (M-Cl) ionic	ν (M-ONO$_2$)	ν (C=N-N=C) azine	ν (M-O-M)	ν (C-O)
$BDBH_2$	1630	3236	1700	1010	---------	--------	------				
$[Fe_2(BDBH_2)_2Cl_2]Cl_2$	1590	3240	1680	1030	420	465	560				
$[Co_2(BDBH_2)_2Cl_2]Cl_2$	1605	3238	1650	1030	425	470	540				
$[Co_2(BDBH_2)_2(NO_3)_2](NO_3)_2$	1593	3240	1655	1015	420	460	----------	1000,1315,1525			
$[Ni_2(BDBH_2)_2Cl_2]Cl_2$	1575	3235	1650	1020	425	470	550				
$[Ni_2(BDBH_2)_2(NO_3)_2](NO_3)_2$	1587	3239	1667	1015	425	480	---------	1005,1320,1530			
$[Cu_2(BDBH_2)_2Cl_2]Cl_2$	1570	3237	1650	1020	420	470	575				
$[Cu_2(BDBH_2)_2(NO_3)_2](NO_3)_2$	1598	3240	1660	1025	420	475		1010,1315,1525			
$[Fe_2(BDBH_2)_2]$	1585			1030	420	470			1575	775	1180
$[Co_2(BDB)_2]$	1586			1020	425	480			1573	765	1172
$[Ni_2(BDB)_2]$	1580			1029	425	480			1572	775	1179
$[Cu_2(BDB)_2]$	1595			1030	420	460			1580	765	1173

Tabl-3: Electronic spectral data (cm^{-1}) of the complexes

Complex	ν_1	ν_2	ν_3	CT*
$[Fe_2(BDBH_2)Cl_2]Cl_2$	10230,10755,11345			٢٦٣٨٧
$[Fe_2(BDBH_2)]$	10157,10517,11211			٢٦٢١١
$[Co_2(BDBH_2)Cl_2]Cl_2$	10244	١٥١٢٨	٢١٨٨١	٢٩٤٩٨
$[Co_2(BDB)_2]$	٩٨٩٦	١٤٦٥٨	٢١٤١٣	٣٠٣٩٥
$[Ni_2(BDBH_2)_2Cl_2]Cl_2$	١١٥٦٢	١٤٥٦٥	٢٤٦٥٢	٣٠١٣٠
$[Ni_2(BDBH_2)_2(NO_3)_2](NO_3)_2$	١٠٥١١	١٥٧٥٤	٢٥٧٧٣	٣٠٣٩٥
$[Ni_2(BDB)_2]$	١٠٢٦٧	١٤٧١٣	٢٥٠٦٢	٢٩٥١١
$[Cu_2(BDBH_2)_2(NO_3)_2](NO_3)_2$	١٢٤٣٠			٢٨٧٦٥
$[Cu_2(BDB)_2]$	١٣٥١٣			٢٦٣١٥

(*) Charge Transfer

References

1- W. Kutzelingy And R. Mecke, Spectrochim Acta, 18, 549, (1962).

2- G. A. Wilkinson, R. D. Gillard, and J. A. McCleverty, "Comprehensive Coordination Chemistry", 1st edn., Pergamon Press, Oxford, England, Vol. 2, (1987).

3- J. Chakraarty and B. Sahoo, Indian, J. Chem., 20A, 432, (1981).

4- D. K. Rastogi, S. K. Dua, V. B. Rana and S. K. Sahir, J. Coord. Chem., 8, 97, (1979).

5- S. Padbye and G. B. Kauffman, Coord. Rev. , 63, 127, (1985).

6- T. A. K. Al. Allaf and A. Z. M Sheet, Polyhedron, 14, (1995).

7- A. A. Maihub, M. Mel-Ajaily And S. S. Hudere, Asian J. Chem 19, 1, (2007).

8- H. B. Hassib and K. Fariba, Inorg. Chim. Acta, 75, 3, 950, (2007).

9- L. T. Yidirim, A. D, Azaz and O. Atakol, Polyhedron, 26, 4187, (2007).

10- A. Gyolcu, H. Demirelli and R. A. Wheatly, Inorg. Chim Acta, 358, 6, 1785, (2005).

11- B. Dash, M. Patra And P. K. Mahapatra, J. Indian Chem. Soc., 60, (1983).

12- W. J. Geary, Coord. Chem. Rev., 7, 81, (1971).

13- S. Mayandavi and K. K, Mohamed Synth. React. Inorg. Met-Org. Chem., 47, 319, (1997).

14- M. A. Al- Tayy, Tikrit J. Pure Sci. , 11, 2, (2006).

15- D. K. Dwived, B. V. Agarwala And A. K. Dey, J. Indian Chem. Sic., 65, 461, (1988).

16- S. Dayagi and Y. Degani, "The Chemistry Of Carbon-Nitrogen Double Bound", Ed. Sparai, Wikey-Interscience, New York, (1970).

17- N. S. Biradar and N. H. Kullari, Inorg. Nucl, Chem., 33, 2451, (1971).

18- R. R. Jha And P. Mukarjee, Asian J. Chem. 19, 1, (2007).

19-M. A. Ali, S. E. Livingston And D. J. Phillips, J. Inorg. Chem. Acta, 7, 179, (1973).

20- K. Nakamoto, Infrared Spectra And Coordination Compounds, 5thedn., Wiley Inter science, New York, (1998).

21-Y. M. Issa, A. L. El-Ansary, O. E. Sherif And M. M. El-Ajaily, Transition Met. Chem., 22, 441, (1997).

22- J. R. Ferraro, Low Frequency Vibrations of Inorganic and Coordination Compounds, Plenum, New York, (1971).

23- C. C. Addison and B. N. Gatehouse, J. Chem. Soc., (1960).

24- M. Gerloch, Coord. Chem. Rev., 99, 117, (1990).

25- R. L. Dutta and A. Syamal, Elements of Magnetochemistry 2nd Edn., Elsevier, New Delhi, (1992).

26- H. C. Rai, R. U. Sharmaq and R. S. Thakur, J. Indian Chem. Soc., 63, 495, (1986).

تحضير وتشخيص عدد من معقدات العناصر الانتقالية ثنائية النوى المتجانسة

ماهر عبد الرزاق محمد الطائي[١] ، مها لطيف جاسم السامرائي[٢]

[١] قسم الكيمياء ، كلية التربية للبنات ، جامعة الموصل ، الموصل ، العراق

[٢] قسم الكيمياء ، كلية العلوم ، جامعة تكريت ، تكريت ، العراق

(**تاريخ الاستلام:** 1 / 11 / 2009 ---- **تاريخ القبول:** 14 / 2 / 2010)

الملخص

يتضمن البحث تحضير الليكاند بنزيليدين ثنائي بنزويل هيدرازين ($BDBH_2$) وذلك من تكثيف البنزيل مع بنزويل هيدرازين. بعد ذلك اجري تحضير معقدات هذا الليكاند بتفاعله مع عدد من أملاح الحديد (II) والكوبلت (II) والنيكل (II) والنحاس (II) في الوسطين المتعادل والقاعدي والتي لها الصيغة العامة $[M_2(BDBH_2)_2X_2]X_2$ و $[M_2(BDB)_2]$ (حيث يمثل $BDBH_2$ و BDB^{2-} الشكل المتعادل وثنائي القاعدة لليكاند و $X = Cl^-$ أو NO_3^-)، تم تشخيص المعقدات الناتجة بالطرق التحليلية والفيزيائية والطيفية، وقد أظهرت هذه الدراسات الحصول على معقدات ثنائية النواة ففي الوسط المتعادل يسلك الليكاند بشكل متعادل رباعي السن أما في الوسط القاعدي يعمل الليكاند بشكل ايون سالب ثنائي القاعدية رباعي السن وأشارت هذه الدراسات أيضا إلى أن المعقدات ذات استقرار عالي ولها بنية ثماني السطوح.