

SYNTHESIS AND CHARACTERIZATION OF SOME COMPLEXES OF CR(III), CO(II), NI(II), AND CU(II) WITH (1-BENZOYL-3-METHYL-1H-PYRAZOL-5(4H)-ONE

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Abstract

Cr(III), Co(II), Ni(II), and Cu(II) complexes of (1-benzoyl-3-methyl-1H-pyrazol-5(4H)-one have been synthesized and characterized by elemental analysis, FT-IR, UV/ visible spectra, magnetic susceptibility and molar conductivity. All complexes are expected to have an octahedral structure.

Keywords: Cr(III), Co(II), Ni(II), and Cu(II) complexes, Infrared and UV/ visible spectra.

Introduction

Increasing physiological importance of nitrogen donor compounds and active role played by certain metal ions coordinated to them have interested many workers in synthesizing and studying structural aspects of metal complexes with some sulphur and nitrogen donor ligands⁽¹⁻³⁾. Various derivatives of 1,3,4-triazoles, thiadiazoles, and substituted pyrazoles have shown antitubercular⁽⁴⁾, bacteriostatic⁽⁵⁾, antibacterial⁽⁶⁾ antifungal⁽⁷⁾, and anti-inflammatory⁽⁸⁾ activities. The wide range of application of the ligand and its metal complexes interested us to prepare a new series of some of those metal complexes.

Experimental

All chemical used were of reagent grade and used as supplied. The FT-IR spectra in the range (4000–200) cm^{-1} were recorded as cesium iodide disc on FT-IR - 8300 Shimadzu Spectrophotometer. The elemental analysis data of the ligand and complexes were obtained on a Carlo Erba Model EA 1108 (C.H.N.) Elemental Analyzer in (Al-Mustansiriya University. The UV-Visible spectra were measured in ethanol using Shimadzu UV-Vis. 160 A spectrophotometer in the range (200-1000) nm. Magnetic susceptibility measurements for complexes were obtained at room temperature using (Magnetic Susceptibility Balance Model MSB-MKI). Gallen Kamp M.F.B.600 F melting point apparatus was used to measure the melting point for all the prepared compounds.

Synthesis of ethyl benzoate⁽⁹⁾ (Fig. (1)):

Ethyl benzoate was synthesized by the addition of 2.5 ml concentrated sulfuric acid to the solution of (30 gm, 0.246 mole) benzoic acid dissolved in 50 ml ethanol. The resulting solution was refluxed for 4 hrs, of ethyl benzoate (yellowish oil) and was purified by washing it with diethyl ether, yield 75%.

Synthesis of benzohydrazide⁽⁹⁾ (Fig. (2)):

Benzohydrazide was synthesized by the addition of hydrazine hydrate (3.4 ml, 0.069 mole) to (10 ml, 0.069 mole) of ethyl benzoate with stirring then the mixture was refluxed for one hour. Absolute ethanol (50 ml) was added and the mixture was refluxed again until a precipitate is separated out. This was filtered off and recrystallized from ethanol. m.p. 113-116 °C. Yield 70%.

Synthesis of 1-benzoyl-3-methyl-1H-pyrazol-5(4H)-one (Fig. (3)):

Ethylacetoacetate (0.002 mole, 0.26 g) was added to the mixture of 0.002 mole of benzohydrazide in 30ml ethanol and refluxed for (6-8 hours). The solvent was evaporated and the oily product washed with ethanol, yield 45%.

Synthesis of metal complexes:

(1-benzoyl-3-methyl-1H-pyrazol-5(4H)-one) metal complexes were obtained by refluxing the mixture of hydrated metal chlorides, CrCl_3 , CoCl_2 , NiCl_2 , and CuCl_2 (1 mmol) and (2 mmol) of the ligand in 50ml ethanol till the complexes precipitated out. The

colored complexes were filtered, washed with water, ethanol and dried under vacuum.

Results and Discussion

The results obtained from elemental analysis are in satisfactory agreement with the calculated values Table (1).

Infrared Spectroscopy

The IR bands are shown in Table (2).

1. C=O stretching vibration:

The band at 1710 cm^{-1} of the ligand due to C=O stretching lowered to $\approx 1680\text{--}1700\text{ cm}^{-1}$ on complexation.

2. C=N stretching vibration:

The band at 1625 cm^{-1} in the spectrum of the ligand due to symmetrical $\nu(\text{C}=\text{N})$ stretching decreased to $\approx 1600\text{ cm}^{-1}$ in the complex, while the band at 1610 cm^{-1} was assigned to $\nu(\text{C}=\text{N})$ frequency shifted to the lower frequency at 1587 cm^{-1} in the complex.

The low frequency bands of complexes:

New bands which appeared at low frequencies in the spectra of the synthesized complexes were probably due to (M–N) and (M–O) bond vibration frequencies.

The facts are further supported by newly formed low frequency bands:

- 1- The band at $(450\text{--}560)\text{ cm}^{-1}$ have been assigned to $\nu(\text{M}–\text{N})$ ^(10,11).
- 2- The bands at $(430\text{--}440)\text{ cm}^{-1}$ have been assigned to $\nu(\text{M}–\text{O})$ ⁽¹²⁻¹⁴⁾.

On the basis of the above evidence is an indication of complex formation.

UV/ visible spectra:

The ultraviolet spectrum of the synthesized ligand in DMF showed two absorption bands, the position of the first band at 220 nm which represents the $(\pi \rightarrow \pi^*)$ transition while the position of the second band (which has higher intensity than the first band due to conjugated system) appeared at 295 nm which represents the $(n \rightarrow \pi^*)$ transition⁽¹⁵⁻¹⁷⁾. Generally, the bands of the newly synthesized complexes are either shifted to shorter or longer wavelengths than that of ligands, but the high intensity of the bands is an indication for complex formation. The peaks observed in the electronic spectra are reported in Table (3). The origin of the band observed at about 700

nm in the electronic spectra of complexes has been identified as d-d transition. In these complexes the bands observed at 300-400 nm could be assigned to nitrogen-metal charge transfer absorption.

Cr-complex (C₁):

At room temperature the magnetic susceptibility measurement after diamagnetic corrections yielded a magnetic moment of 3.65 BM which is close to that expected for an octahedral Cr(III) complexes^(15,16).

The UV-visible spectrum of the dark green solution of chromium the Cr(III) complex recorded in DMF showed three bands with the absorbance maxima at 16267 cm^{-1} , 20202 cm^{-1} and 31920 cm^{-1} which were considered as ν_1 , ν_2 , and ν_3 absorption bands respectively (Table 3).

Co-complex (C₂):

The magnetic susceptibility measurement after diamagnetic corrections yielded a magnetic moment of 4.7BM which is close to that expected for an octahedral Co(II) complexes^(15,16,17).

The electronic absorption spectrum showed two absorption bands (as shown in table (III)) at $(16267\text{ \& } 18202)\text{ cm}^{-1}$ ν_2 and ν_3 respectively (Table 3). Experimental ν_2 and ν_3 values have been employed to calculate the position of ν_1 band from Lever tables⁽¹⁸⁾. Also these tables have been used to calculate the ligand field parameters, 10 Dq and B which were found to be 8813 and 766 cm^{-1} respectively. The calculated 10 Dq value which is the ν_1 transition is found to be in the near infrared region which is out of the range of our absorption apparatus. The calculated B value (766 cm^{-1}) for the complex is lower than the respective B_0 value of (971 cm^{-1}) for the free cobalt ion, indicating the presence of covalent bonding between the metal ion and the ligand. The β value which is the ratio of $(B_{\text{complex}} / B_0)$ shows a value of 0.79, and this reduction in the B_0 value indicates that ligand non-bonding orbitals have been used to delocalize the metal d-electrons i.e, increasing back donation from cobalt to the ligand.

Ni-complex (C₃):

Nickel complex is paramagnetic with a room temperature magnetic moment of 3.28 B.M. which is consistent with an octahedral field.

The electronic absorption spectrum showed two absorption bands (as shown in table (III)) at (18018 & 29850) cm^{-1} ν_2 and ν_3 respectively Table (3). Experimental ν_2 and ν_3 values have been employed to calculate the position of ν_1 band from Lever tables⁽¹⁸⁾. Also these tables have been used to calculate the ligand field parameters, 10 Dq and B which were found to be 11114 and 966 cm^{-1} respectively. The calculated 10 Dq value which is the ν_1 transition is found to be in the near infrared region which is out of the range of our absorption apparatus. The calculated B value (966 cm^{-1}) for the complex is lower than the respective B_0 value of (1041 cm^{-1}) for the free nickel ion, indicating the presence of covalent bonding between the metal ion and the ligand. The β value which is the ratio of (B_{complex} / B_0) shows a value of 0.93, and this reduction in the B_0 value indicates that ligand non-bonding orbitals have been used to delocalize the metal d-electrons i.e, increasing back donation from nickel to the ligand. On the basis of spectral bands, an octahedral geometry is therefore proposed for the Ni(II) complex. The values of ligand field parameters reflect that the M-L bond is quite strong, which in turn suggests sufficient overlapping of the metal orbitals with those of the ligand orbitals.

Cu-complex (C₄):

The complex has a room temperature magnetic moment of 1.58 B.M. which corresponds to octahedral structure for the Cu(II) ion⁽¹⁹⁾. A broad low intensity band appeared at 14798 cm^{-1} which is attributed to the d-d transition of the Cu(II) ion, this band is of low molar absorptivity being Laporte forbidden and could be assigned to 2E_g ${}^2T_{2g}$ transition. The absorption band at 32268 cm^{-1} may be due to ligand to metal charge transfer (LMCT) which is a characteristic of copper(II) complexes with nitrogen donors. In order to determine if the Cu(II) complex undergoes solvatochromic shifts in different solvents, the complex was dissolved in a variety of polar solvents, such as DMSO, DMF, and THF and their UV-Vis spectra were recorded. Since the spectra do not exhibit any variation in the absorption pattern as a function of solvent, it is suggested that binding of solvent to the Cu(II) ion does not occur which means that geometry of the Cu(II) ion does not change in solution.

Molar conductivity measurements:

From Table (3), it is show that all the complexes are none conducting in solution accept Cr-complex (C₁).

The proposed structures for the prepared complexes are shown in Figs. (4 & 5).

Table (1)
Physical properties and micro-elemental analysis of the prepared compounds.

Compound	Melting Point C° /color	Elemental analysis (calc.)			
		C%	H%	N%	M%
L: C ₁₁ H ₁₀ N ₂ O ₂	Oily	65.01 (65.35)	5.32 (4.95)	13.93 (13.86)	
C ₁ : [Cr L ₂ Cl ₂]Cl	oily/dark green	-	-	-	-
C ₂ : [Co L ₂ Cl ₂]	260-263/ blue	50.43 (49.46)	4.04 (3.77)	11.46 (10.49)	11.22 (11.03)
C ₃ : [Ni L ₂ Cl ₂]	288-291/ green	50.26 (49.48)	4.42 (3.77)	11.67 (10.49)	11.84 (10.99)
C ₄ : [Cu L ₂ Cl ₂]	241-245/ green	50.11 (49.04)	4.12 (3.74)	11.00 (10.40)	12.01 (11.79)

Table (2)
Selected IR bands in cm^{-1} for the ligand and its complexes.

Compound	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\text{C}=\text{O}$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{O})$
L	1625	1055	1710	-	-
C ₁	1593	1043	1685	444 s	437 s
C ₂	1600	1035	1705	450 s	441 s
C ₃	1598	1035	1681	445 s	431 s
C ₄	1587	1030	1699	445 s	433 s

s: small

Table (3)
Electronic spectra for ligand and complexes in DMF & the molar conductivity Λ_m .

compound	Absorption Bands	Assigned transition	Λ_m ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)
L	220 nm, 45454 cm^{-1}	$\pi \rightarrow \pi^*$	-
	295 nm, 33898 cm^{-1}	$n \rightarrow \pi^*$	
C ₁	230 nm, 43478 cm^{-1}	$\pi \rightarrow \pi^*$	110
	615 nm, 16267 cm^{-1}	${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$	
	495 nm, 20202 cm^{-1}	${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$	
	313 nm, 31920 cm^{-1}	${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	
C ₂	225 nm, 44444 cm^{-1}	$\pi \rightarrow \pi^*$	1.39
	113 nm, 8813 cm^{-1} (calc.)	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$	
	615 nm, 16267 cm^{-1}	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$	
	549 nm, 18202 cm^{-1}	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$	
C ₃	215 nm, 46512 cm^{-1}	$\pi \rightarrow \pi^*$	1.23
	899 nm, 11114 cm^{-1} (calc.)	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$	
	555 nm, 18018 cm^{-1}	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$	
	335 nm, 29850 cm^{-1}	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$	
C ₄	215 nm, 46511 cm^{-1}	$\pi \rightarrow \pi^*$	0.19
	675 nm, 14798 cm^{-1}	$n \rightarrow \pi^*$	
	310 nm, 32268 cm^{-1}	${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$	

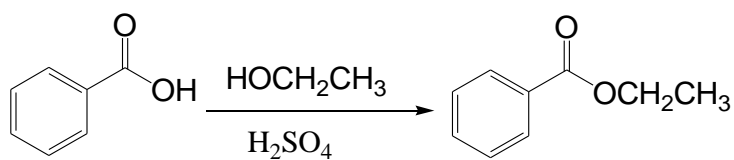


Fig.(1): Synthesis of ethyl benzoate.

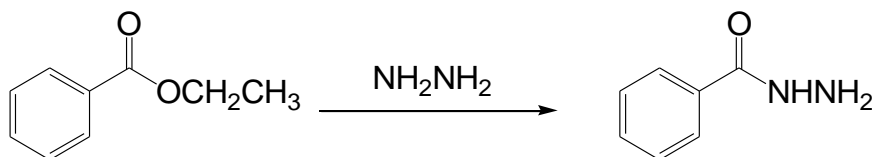


Fig. (2) : Synthesis of benzohydrazide.

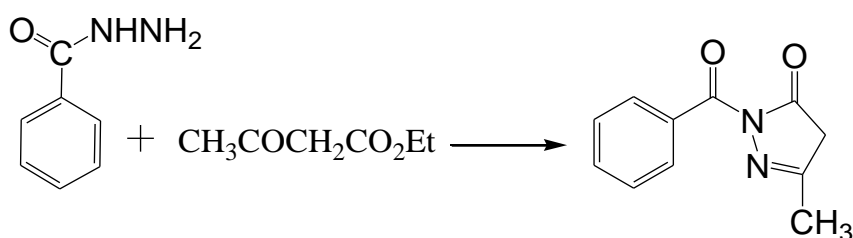


Fig.(3) : Synthesis of 1-benzoyl-3-methyl-1H-pyrazol-5(4H)-one.

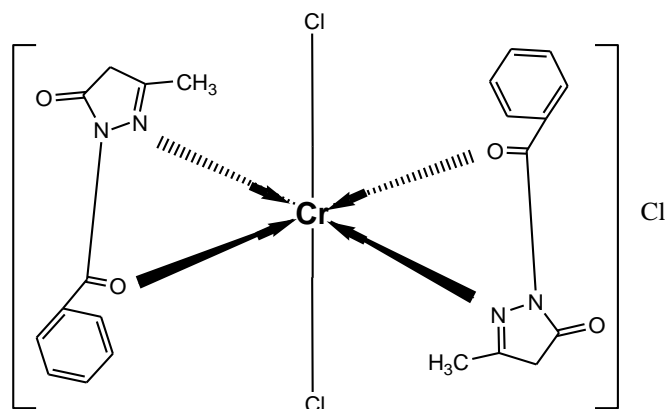


Fig.(4) : The proposed structures for Cr complex.

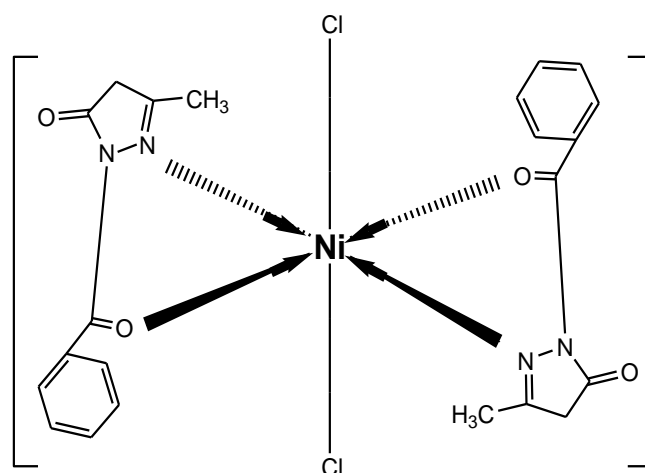


Fig. (5) : The proposed structure for Co, Ni and Cu complexes.

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الخلاصة

تم تحضير وتشخيص بعض معقدات أيونات [الكروم الثلاثي والكوبلت والنيكل والنحاس الثنائية مع الليكاند 1-3-بنزويل-3-مثيل-1-هيدرو-بايروزول-5(4-هيدرو)-ون .
بوساطة التحليل الدقيق للعناصر ومطيافية الأشعة تحت الحمراء والأطياف الإلكترونية والخاصية المغناطيسية والتوصيلية المولارية. تم اقتراح الشكل ثماني السطوح لجميع المعقدات المحضرة.