Preparation and Spectral Study of New Complexes of Some Metal Ions with 3,5-Dimethyl-1H-Pyrazol-1-yl Phenyl Methanone

*Matheel D. Al-Sabti** *Ahmed A. H. Al-Amiery**
*Amel Ali Hussien Al-Obiady** *Yasmien K. Al-Majedy**

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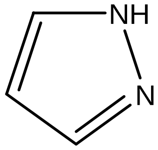
Abstract:

Many complexes of 3,5-dimethyl-1H-pyrazol-1-yl phenyl methanone with Cr(III), Co(II), Ni(II), Cu(II) and Cd(II) were synthesized and characterized by FT-IR, UV/visible spectra, elemental analysis, room temperature magnetic susceptibility and molar conductivity. Cd(II) complex was expected to have tetrahedral structure while all the other complexes were expected to have an octahedral structure.

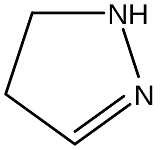
Key words: Pyrazole, Cr(III), Co(II), Ni(II), Cu(II) and Cd(II)

Introduction:

It has been reported that pyrazoles and their derivatives have biological properties, such as medicinal and pesticidal activity [1,2]. Pyrazole refers both to the class of simple aromatic ring organic compounds of the heterocyclic series characterized by a 5-membered ring structure composed of three carbon atoms and two nitrogen atoms in adjacent positions and to the unsubstituted parent compound. Being so composed and having pharmacological effects on humans, they are classified as alkaloids, although they are rare in nature. Pyrazoles are used for their analgesic [3], anti-inflammatory [4], antipyretic, antiarrhythmic, tranquili-zing, muscle relaxing, psychoanaleptic, anticonvul-sant, monoamineoxidase inhibiting, antidiabetic and antibacterial activities [5,6]. Structurally related compounds are pyrazoline and pyrazolidine.

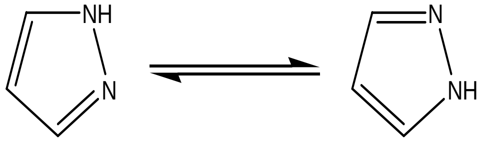


Pyrazole



Pyrazoline

Pyrazole, which is unsubstituted at position-1, exhibits tautomerism, the two tautomeric forms are in rapid equilibrium with each other and the nitrogen atoms are indistinguishable. If pyrazole is tautomeric, then the positions 3 and 5 will be identical. If it is not, then the positions are different [7]. On oxidation both 3-methyl-1-phenyl pyrazole and 5-methyl-1-phenyl pyrazole give the same product viz, methyl pyrazole. Thus, positions 3 and 5 must be equivalent in pyrazole, and this can only be explained by assuming that pyrazole is tautomeric (1-a) and (1-b) [8].



(1-a) **(1-b)**

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.

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*Biochemical division, Department of Applied Sciences, University of Technology

Material and Method:

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. Metal content was measured by atomic absorption (Ibn-Sina company). 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. Conductivity measurements were made in DMF solution using a Jenway Ltd. 4071 digital conductometer.

Preparation of ethyl benzoate [9]:

The mixture of benzoic acid (30 gm, 0.246 mole) with 50 ml absolute ethanol, and 2.5ml concentrated sulfuric acid was refluxed for 4 hrs, yield 75% of ethyl benzoate according to the following reaction:

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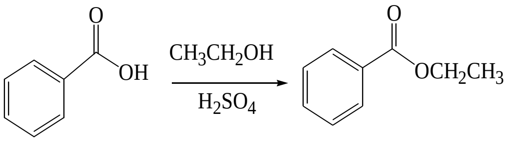
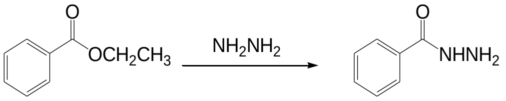


Preparation of benzohydrazide [9]:

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. 113-116C^{o}. Yield 70%.

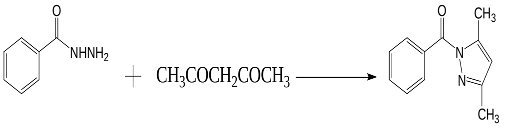
Reaction:



Synthesis of 3,5-dimethyl-1H-pyrazol-1-yl phenyl methanone

Acetylacetone (ACAC) (0.002 mole, 0.2 g) was added to a mixture of (0.002 mole) benzohydrazide in 30 ml ethanol and refluxed for (7-8 hours), then left to cool. The solvent was evaporated and the oily product washed with ethanol, yield 45%.

Reaction:



Synthesis of metal complexes:

3,5-dimethyl-1H-pyrazol-1-yl phenyl methanone 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 at pH (8-9), till the complexes precipitated out. The colored complexes were filtered, washed with water, ethanol and dried under vacuum (table 1).

Results and Discussion:

Elemental analyses:-

The physical and analytical data of the ligand and its metal complex are given in table (1). The results obtained from elemental analysis are in good agreement with the calculated values. The suggested molecular formula was also supported by spectral measurement as well as magnetic moments.

Infrared Spectroscopy:

The IR bands are shown in (table 2).

1. C=O stretching vibration:

The band at 1720 cm^{-1} of the ligand due to symmetrical C=O stretching shifted to ≈ 1690 – 1700 cm^{-1} on complexation.

2. C=N stretching vibration:

The band at 1583 cm^{-1} in the spectrum of the ligand due to symmetrical ν(C=N) stretching shifted to ≈1579 cm^{-1} or to ≈1590 cm^{-1} on complexation.

The low frequency bands of complexes:

New bands which appeared at low frequencies in the spectra of the synthesized complexes were probably due to (metal–nitrogen) and (metal–oxygen) bond vibrational frequencies.

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

1: The bands at (450–460) cm^{-1} have been assigned to ν(M–N) [10,11].

2: The bands (425 – 440) cm^{-1} have been assigned to ν(M–O) [12-14].

The above evidences are indications of complex formation.

UV/ Visible spectra:

Electronic spectroscopic study:

The ultraviolet spectrum of the synthesized ligand in ethanol showed two absorption bands, the position of the first band at 225 nm which represents the (π – π*) transition, while the position of the second band (which has higher intensity than the first band due to conjugated system) appeared at 285 nm which represents the (n – π*) transition. Generally, the bands of the newly synthesized complexes are either shifted to shorter or longer wavelengths than that of ligands, but the high intensity bands is an indication for complex formation [15-17].

Table (3) shows the electronic absorption peaks for the ligand (L) and its complexes. The peaks are classified into two distinct groups: those that belong to ligand transitions appeared in the UV region while d-d transitions appeared in the visible region; these transitions are assigned in relevance to the structures of complexes.

Cr-complex (C_1):

At room temperature the magnetic susceptibility measurement after diamagnetic corrections yielded a magnetic moment of 3.92 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 showed three bands with the absorbance maxima at 15267 cm^{-1}, 20202 cm^{-1} and 32595 cm^{-1} which were considered as υ_1, υ_2, and υ_3 absorption bands respectively (table 3).

Co-complex (C_2):

The magnetic susceptibility measurement after diamagnetic corrections yielded a magnetic moment of 4.85 BM which is close to that expected for an octahedral Co(II) complexes [15,16]. The electronic absorption spectrum showed two absorption bands (as shown in table (3) at (13513 & 18691) cm^{-1} which is considered as υ_2 and υ_3 respectively. These transitions may be assigned as:

$$\upsilon_2 = {}^4T_{1g(F)} \longrightarrow {}^4A_{2g(F)}$$
$$\upsilon_3 = {}^4T_{1g(F)} \longrightarrow {}^4T_{1g(P)}$$

Experimental υ_2 and υ_3 values have been employed to calculate the position of υ_1: ${}^4T_{1g(F)} \longrightarrow {}^4T_{2g(F)}$ 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 7185 and 830.5 cm^{-1} respectively. The calculated 10 Dq value which is the υ_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 (830.5 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 some kind of bonding between the metal ion and the ligand. The β value which is the ratio of ($B_{complex}$ / B_0) shows a value of 0.9248, 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 (C_3):

Nickel complex is paramagnetic with a room temperature magnetic moment of 2.89 BM which is consistent with the octahedral stereochemistry for the complex. The electronic absorption spectrum showed two absorption bands (as shown in table (3) at (18618 & 29974) cm^{-1} which is considered as υ_2 and υ_3 respectively. These transitions may be assigned as:

$$\upsilon_2 = {}^3\mathbf{A}_{2g(F)} \longrightarrow {}^3\mathbf{T}_{1g(F)}$$
$$\upsilon_3 = {}^3\mathbf{A}_{2g(F)} \longrightarrow {}^3\mathbf{T}_{1g(P)}$$

Experimental υ_2 and υ_3 values have been employed to calculate the position of υ_1: ${}^3\mathbf{A}_{2g(F)} \longrightarrow {}^3\mathbf{T}_{2g(F)}$ 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 11691 and 899.3 cm^{-1} respectively. The calculated 10 Dq value which is the υ_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 (899.3 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 bonding between the metal ion and the ligand. The β value which is the ratio of ($B_{complex}$ / B_0) shows a value of 0.86, 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 (compared with that with cobalt), which in turn suggests sufficient overlapping of the metal orbitals with those of the ligand orbitals.

Cu-complex (C_4):

The complex has a room temperature magnetic moment of 1.86 BM (one unpaired electron) which corresponds to octahedral structure for the Cu(II) ion [19,20]. The electronic absorption spectrum for Cu(II) complex shows two bands at 24691 and 16260 cm^{-1} which were considered as $({}^2\mathbf{B}_{1g} \longrightarrow {}^2\mathbf{B}_{2g})$ and $({}^2\mathbf{B}_{1g} \longrightarrow {}^2\mathbf{A}_{1g})$ respectively. The expected structure for this complex is distorted octahedral.

Cd-complex (C_5):

The result of magnetic moment measurement of this complex showed that it is diamagnetic. The prepared white Cd(II) complex exhibited a band which appeared at 32258 cm^{-1} which may be related to the ligand (ILCT) transition. The filled d- orbitals show no ligand field transitions. The expected structure for this complex is tetrahedral.

Molar conductivity measurements:

The molar conductance of some complexes in DMF lies in the range (10-20) $\Omega^{-1}\ cm^2\ mol^{-1}$ indicating their nonelectrolytic behavior which may be formulated as $[M(L)_2X_2]$ (where M = Co, Ni, Cu and X = Cl^{-1}), While the other complexes $[Cr(L)_2Cl_2]Cl$ and $[Cd(L)_2]X_2$ showed some conducting behavior (table 3). The proposed structures for the prepared complexes are shown in Figures (1, 2, & 3).

Table (1): Physical data and micro-elemental analysis of the ligand (L) and its metal complexes

Compound	Melting Point C° /color	Elemental analysis (calc.)			
		C%	H%	N%	M%
L: $C_{12}H_{12}N_2O$	Oily	-	-	-	-
C_1: $[Cr(L)_2Cl_2]Cl$	291-292/ dark green	51.1 (51.6)	4.2 (4.3)	10.3 (10.0)	10.1 (9.3)
C_2: $[Co(L)_2Cl_2]$	Over 300/ violet	53.8 (54.3)	4.6 (4.5)	11.2 (10.6)	11.9 (11.1)
C_3: $[Ni(L)_2Cl_2]$	275-279/ dark green	54.7 (54.4)	4.3 (4.5)	10.4 (10.6)	11.8 (11.1)
C_4: $[Cu(L)_2Cl_2]$	253-255/ light green	53.5 (53.9)	4.7 (4.5)	10.8 (10.5)	12.7 (11.9)
C_5: $[Cd(L)_2]Cl_2$	290-293/ white	50.1 (49.4)	3.9 (4.1)	9.9 (9.6)	20.1 (19.3)

Table (2): The most diagnostic FTIR bands of the ligand (L) and its metal complexes

Comp.	υ (C=N)	υ (N–N)	C=O	υ (M–N)	υ (M–O)
L	1625	1050	1720	-	-
C_1	1605	1005	1702	450 s	425 s
C_2	1604	1005	1701	455 s	440 s
C_3	1600	1045	1691	450 s	435 s
C_4	1599	1035	1696	460 s	425 s
C_5	1599	1015	1694	450 s	420 s

Table (3): Electronic spectral data for the ligand (L) and its complexes, the magnetic moments and the molar conductivity (Λ_m) for the complexes in DMF

Compound	Absorption Bands (cm^{-1})	Assigned transition	Magnetic moment (B.M.)	Λ_m ($\Omega^{-1}cm^2mol^{-1}$)	Dq/B	β
L_1	44444	$\pi \longrightarrow \pi^*$	-	-		
	35088	$n \longrightarrow \pi^*$				
C_1	15267	$^4A_{2g(F)} \longrightarrow {}^4T_{2g(F)}$	3.92	143	3.24	0.513
	20202	$^4A_{2g(F)} \longrightarrow {}^4T_{1g(F)}$				
	32595	$^4A_{2g(F)} \longrightarrow {}^4T_{1g(P)}$				
C_2	7185 (calc.)	$^4T_{1g(F)} \longrightarrow {}^4T_{2g(F)}$	4.85	13.3	1.01	0.9248
	13513	$^4T_{1g(F)} \longrightarrow {}^4A_{2g(F)}$				
	18691	$^4T_{1g(F)} \longrightarrow {}^4T_{1g(P)}$				
C_3	11691 (calc.)	$^3A_{2g} \longrightarrow {}^3T_{2g(F)}$	2.89	13.6	1.3	0.86
	18618	$^3A_{2g} \longrightarrow {}^3T_{1g(F)}$				
	29974	$^3A_{2g} \longrightarrow {}^3T_{1g(P)}$				
C_4	24691	$^2B_{1g} \longrightarrow {}^2B_{2g}$	1.86	18.5	-	-
	16260	$^2B_{1g} \longrightarrow {}^2A_{1g}$				
C_5	32258	ILCT	-	154	-	-

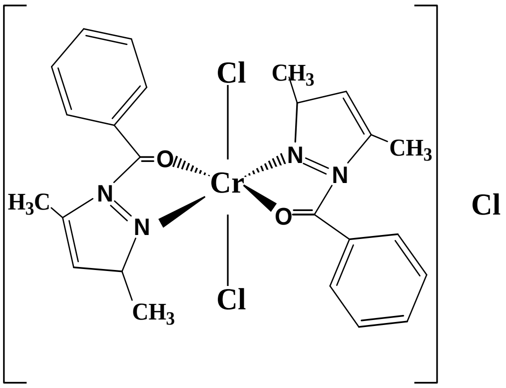


Fig. (1): The proposed structure for Cr(III) complex

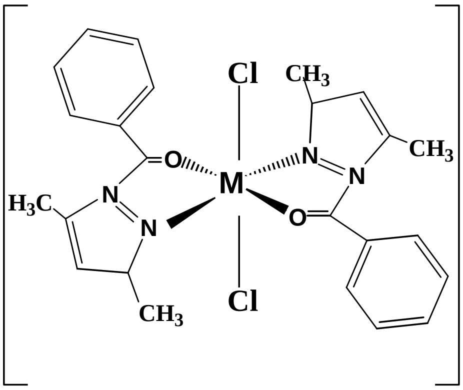


Fig. (2): The proposed structures for Co(II), Ni(II) and Cu(II) complexes

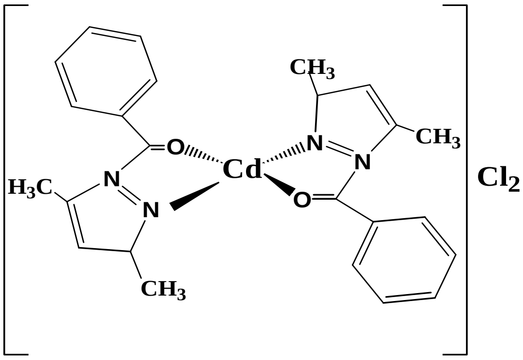


Fig. (3): The proposed structure for Cd(II) complex

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تحضير ودراسة طيفية لمعقدات جديدة مشتقة من 5,3-ثنائي المثيل-1-هيدرو-بايروزول-1-يل فنيل ميثانون

مثيل ضايف السبتي* ***احمد عبدالامير حسين العامري**** ***امل علي حسين العبيدي****
ياسمين كاظم الماجدي*

*فرع التقانات الكيميائية الاحيائية, قسم العلوم التطبيقية, الجامعة التكنولوجية

الخلاصة:

تم تحضير معقدات كيليتيه لبعض العناصر الانتقالية [Cr(III)، Co(II)، Ni(II), Cu(II), Cd(II)] لليكاند 5,3-ثنائي المثيل-1-هيدرو-بايروزول-1-يل فنيل ميثانون. تم تشخيص المعقدات بوساطة طيف الأشعة تحت الحمراء F.T.I.R، الأطياف الإليكترونية، التحليل الدقيق للعناصر، التوصيلية الكهربائية إضافة الى الحساسية المغناطيسية. تم اقتراح الشكل ثماني السطوح لجميع المعقدات عدا معقد الكادميوم فهو هرم رباعي السطوح.