

Trivalent Chromium, Iron and Cobalt Complexes of Hydrozones Derived from 2,6-Diacetyl pyridine dihydrazide

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In this study, trivalent chromium, iron and cobalt complexes are synthesized by the reaction of 2,6-diacetyl pyridine dihydrazide (DAPD) and diacetyl in the presence of metal ions. The metal complexes having general composition $[M(C_{13}H_{15}N_5)X_2]X$, where $M = Cr(III), Fe(III)$, $X = Cl, Br, NO_3$ or NCS for $Cr(III)$ and $Fe(III)$, $X = OH$, $M = Co(III)$ were characterized by elemental analysis, conductance, magnetic susceptibility, electronic and infrared spectra studies. On the basis of these studies, $Cr(III)$, $Fe(III)$ and $Co(III)$ complexes has assigned trigonal bipyramidal geometry and found to be high spin.

Key Words: 2,6-Diacetyl pyridine dihydrazide, Diacetyl, Trivalent metal complexes.

INTRODUCTION

A large number of complexes of trivalent chromium, manganese, iron and cobalt have been isolated and characterized with the help of magnetic and spectral studies. However, the bulk of work upto date is mainly centered on chromium or cobalt complexes while manganese system has been a subject of scattered reports. During the recent years, there has been an increased interest in the complexes of iron^{1,2} and manganese which confirm to penta coordination. A variety of octahedral, tetrahedral and five coordinate complexes of chromium have been reported and various theories have been put forward to interpret the electronic spectra in cubic and non-cubic fields^{3,4}. Trivalent manganese complexes are susceptible to Jahn-Teller distortion causing them to deviate from idealized symmetry^{5,6} and generally show interesting electronic spectra.

Metal complexes of di or polyamines are known to react with carbonyl compounds to form complexes in which two amine residues are linked by a three carbon atom bridge yielding macrocyclic chelates. The majority of compounds to date have been synthesized from aliphatic or aromatic diamino and aromatic carbonyl compounds in presence of metal ions^{7,8}. However, little is known about the reaction of pyridine based dihydrazide with aliphatic carbonyl compounds.

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In the present paper, trivalent chromium, iron and cobalt complexes are synthesized by the reaction of 2,6-diacetyl pyridine dihydrazide (DAPD) and diacetyl in presence of metal ions. The complexes are characterized by chemical analysis, conductance, molecular weight measurements, electronic and infrared spectra studies.

EXPERIMENTAL

All the chemicals and reagents used were of analytical grades.

Synthesis and isolation of complexes

Chromium and iron complexes: 0.01 mol of 2,6-diacetyl pyridine dihydrazide and 0.01 mol diacetyl in 100 mL methanol were mixed and refluxed for 1 h. 0.01 mol (2.5 g) of chromium(III) chloride or 0.01 mol (2.71 g) of iron(III) chloride dissolved in minimum quantity of methanol (100 mL) was added to the mixture and methanolic KOH solution was added dropwise till the pH of the mixture became 7.5 to 8.0 and refluxing continued for 6 h on a water bath. The coloured solutions were concentrated to half of their volumes. It was cooled and kept in a desiccator for 5 d. The greenish brown (chromium) and reddish brown (iron) crystal were separated which were filtered off, washed with ethanol, acetone, ether and dried *in vacuo* over P_4O_{10} (yield *ca.* 32 %).

The metal bromide and thiocyanate were prepared by adding lithium bromide and ammonium thiocyanate solutions into metal chloride solutions in methanol by continuous stirring and filtering off LiCl and NH_4Cl . From the filtrate the bromo and thiocyanato complexes were synthesized.

The complexes are soluble in dimethyl formamide and insoluble in common organic solvents. They do not decompose upto *ca.* 300 °C.

Cobalt complexes: Cobalt(III) chloride complexes were prepared by refluxing 0.02 mol of 2,6-diacetyl pyridine dihydrazide and 0.02 mol of diacetyl in 100 mL methanol and adding 0.02 mol (3.0 g) of cobalt(II) chloride in 50 mL methanol and by refluxing it, for 3 h. Now the pH was raised to 8.5 by dropwise addition of dilute methanolic solution of KOH. The air was passed through the solution for 24 h. The solution was refluxed for more than 3 h concentrated to half of its volume and left in a desiccator for 3 d. The light brown crystals separated were filtered off, washed with ethanol, acetone and finally with ether and dried *in vacuo* over P_4O_{10} (yield *ca.* 40 %).

The complexes are soluble in dimethyl formamide, dimethyl sulphoxide but are insoluble in common organic solvents. They are thermally stable upto *ca.* 250 °C.

RESULTS AND DISCUSSION

The analytical data of metal, nitrogen, carbon, hydrogen and anions are reported in Table-1. The analytical data indicate that the complexes may be represented by $[M(C_{13}H_{15}N_5)X_2] X$; where M = Cr (III) or Fe(III); X = Cl, Br, NO_3 , NCS while X = OH for Co(III). All the complexes are 1:1 electrolytic nature.

TABLE-1
ANALYTICAL DATA OF TRIVALENT IRON, COBALT AND CHROMIUM COMPLEXES

Complex	Colour	Elemental analysis (%): Found (Calcd.)				
		C	H	N	M	X
[Fe(C ₁₃ H ₁₅ N ₅)(Cl ₂)]Cl	Dark brown	38.62 (38.66)	3.70 (3.72)	17.36 (17.35)	13.90 (13.88)	26.40 (26.39)
[Fe(C ₁₃ H ₁₅ N ₅)(Br ₂)]Br	Brown	29.00 (29.05)	2.76 (2.79)	13.00 (13.04)	10.40 (10.43)	44.72 (44.69)
[Fe(C ₁₃ H ₁₅ N ₅)(NO ₃) ₂]NO ₃	Brown	32.25 (32.30)	3.10 (3.11)	14.65 (14.49)	11.52 (11.59)	38.48 (38.51)
[Fe(C ₁₃ H ₁₅ N ₅)(NCS) ₂]NCS	Brown	33.08 (33.12)	3.16 (3.18)	14.82 (14.86)	11.76 (11.80)	36.90 (36.94)
[Co(C ₁₃ H ₁₅ N ₅)(OH) ₂]OH	Raddish brown	44.38 (44.44)	4.25 (4.27)	19.98 (19.94)	16.83 (16.81)	14.55 (14.53)
[Cr(C ₁₃ H ₁₅ N ₅)(Cl ₂)]Cl	Green	38.99 (39.05)	3.72 (3.75)	17.48 (17.52)	13.00 (13.02)	26.60 (26.60)
[Cr(C ₁₃ H ₁₅ N ₅)(Br ₂)]Br	Brown	30.00 (29.27)	2.80 (2.81)	13.00 (13.13)	9.68 (9.76)	45.00 (45.03)
[Cr(C ₁₃ H ₁₅ N ₅)(NO ₃) ₂]NO ₃	Light green	32.53 (32.57)	3.10 (3.13)	14.58 (14.61)	10.85 (10.86)	38.76 (38.83)
[Cr(C ₁₃ H ₁₅ N ₅)(NCS) ₂]NCS	Light green	33.40 (33.40)	3.20 (3.21)	15.00 (14.99)	11.05 (11.14)	37.20 (37.26)

The infrared spectra of the metal-complexes show various pyridine ring, azomethine and diacetyl moieties vibrations. Several bands found at 1610-1590, 1585-1570, 1490-1650, 1440-1435, 985, 810 and 720 cm⁻¹ are assigned to $\nu(\text{C}=\text{C})$, $\nu(\text{C}=\text{N})$, ring vibrations, respectively. However, the spectra of the complex deviate from the original pattern of pyridine ring vibrations. This deviation may be due to the coordination of pyridine nitrogen to metal atom⁹.

The absorption near 985 cm⁻¹ assignable to the ring breathing mode of vibration is a reliable guide to identify the coordination of the pyridine nitrogen to metal atom. It has been reported^{10,11} that on coordination of pyridine nitrogen, this band increases in energy above 1000 cm⁻¹. In the spectra of the complexes, this band disappears and new bands appear 1020-1010 cm⁻¹. This small shift in the ring breathing mode indicate the coordination of pyridine nitrogen to the metal atom. The various bands observed in the infrared spectra of the complexes show the metal pyridine nitrogen coordination. However, the shifts observed in the vibrations associated with $\nu(\text{C}-\text{C})$, $\nu(\text{C}=\text{N})$ (1580 cm⁻¹) and (C-C) out of plane deformation are comparatively small. These small shifts may be interpreted in terms of weak interactions between metal and pyridine nitrogen. This fact is also supported by the appearance of weak to very weak (M-N) (pyridine) vibrations in the far infrared region. It, therefore, appears that pyridine nitrogen is feebly coordinated to the metal atom.

It has been shown that two vibrations 16b (an out of plane deformation) and 6a (in-plane ring deformation) show an upward trend on coordination of the pyridine nitrogen. The magnitude of the shift has proved to be of diagnostic value in assigning the stereochemistry of tetrahedral and octahedral molecules. But in the present complexes these bands shift towards higher frequencies; chromium (675 and 430 cm^{-1}), iron (670 and 425 cm^{-1}) and cobalt (685 and 440 cm^{-1}). The higher frequencies of 16b and 6a vibrations clearly indicate the coordination of pyridine-nitrogen to the metal atom¹².

The vibrations assignable to NH_2 group are not observed in the infrared spectra of these complexes, however, various new bands observed at *ca.* 2910, 1350, 1270, 1180, 690 cm^{-1} and may be assignable to $\nu(\text{CH}_3)$, $\nu(\text{C-C})$, $\nu_{\text{sym}}(\text{CH}_3)$, $\nu(\text{C-CH}_3)$, $\delta(\text{C-H})$ and $\nu(\text{C-CH}_3 + \text{ring deformation})$ of diacetyl moiety¹³, respectively. The presence of these vibrations indicate that the diacetyl moiety has considered with two amino groups of 2,6-diacetyl pyridine dihydrazide¹⁴.

Strong bands appearing in the spectra of all the complexes in 1615-1590 cm^{-1} may be assigned to $\nu(\text{C-N})$ vibrations and these bands also indicate the presence of coordinated azomethine group¹⁵.

The nitrate complexes of all the metals exhibit bands in the region at *ca.* 1270 (ν_2), 1020 (ν_3) and 810 cm^{-1} (ν_4) assignable to symmetric NO_2 stretching and non-polar deformation vibrations, respectively and are consistent with monodentate nature of nitrate group. The meaningful evidence for monodentate coordinated nitrate group comes from the appearance of two strong bands 1770 and 1750 cm^{-1} due to ($\nu_1 + \nu_4$) combination vibrations, respectively.

In the spectra of complexes involving thiocyanato group, generally three vibrations originating from (C-N) stretching (ν_2), N-C-S bonding (ν_4) and C-S stretching (ν_3) are observed and are utilized to differentiate the modes bonding of this group¹⁶. Except the complex of cobalt, the spectra of all the complexes exhibit bands ~2100 (ν_1), 490 (ν_2) and 830 cm^{-1} (ν_3) and may be assignable to $\nu(\text{CN})$, (NCS) bending and $\nu(\text{CS})$ of NCS group, respectively and are in accordance with N-bonded thiocyanato group¹⁶.

In cobalt(III) complex new bands are observed 3600-3500 cm^{-1} which may be assigned to $\nu(\text{OH})$ of hydroxyl group and a distinct medium band at *ca.* 535 cm^{-1} in the far IR spectra is due to $\nu(\text{CO-OH})$ and thus indicate that hydroxyl group is coordinated in this complex.

Chromium(III) complexes: The magnetic moments of chromium(III) complexes observed at room temperature (300 K) are found to lie in the range 4.25-4.40 BM. The value is quite close to the value of 4.24 BM reported for d^3 systems¹⁷. However, magnetic moments do not provide any direct evidence of coordination number but the value reported for the present Cr(III) complexes are consistent with the values reported earlier for penta-coordinate species¹⁸.

The electronic spectra of chromium(III) complex are very similar to each other and show various bands 9900-9800, 12900-12800, 18100-18000 and 35360 cm^{-1} ,

respectively. The four spectral bands can not be interpreted in terms of 4 or 6 coordinate environment around the metal atom. However, the spectra resemble to those reported to be penta-coordinate and whose structures have been established by X-ray measurements¹⁷. The tridentate nature of the ligand molecule and formation of the natural complexes at comparatively higher pH incorporating two anions in the coordination sphere indicate that these complexes may be penta-coordinated.

It is, however, difficult to distinguish between square pyramidal and trigonal bipyramidal structures but the presence of a spectral band at *ca.* 18000 cm⁻¹ in the electronic spectra of chromium(III) complexes can be considered as an indication for the trigonal bipyramidal geometry¹⁸.

The molecule however, can not conform to an idealized D_{3h} symmetry due to the presence of donor atoms of unequal strength and hence the effective symmetry of the complexes may be C_{3v}. Thus, various bands can be assigned to 4_E→4_E' (*ca.* 9850 cm⁻¹), 4_E→4A₁' (*ca.* 12850 cm⁻¹) and 4_E→4A₂' (*ca.* 18050 cm⁻¹), respectively. The band *ca.* 35000 cm⁻¹ may be charge transfer. Thus, keeping in view in the sterical requirement of the ligand it appears that the ligand occupies the trigonal plane and two anions are present on axial positions making the structure of the complexes to be trigonal bipyramidal.

Iron(III) complexes: The magnetic moment of iron (III) complexes lie in 5.80-5.86 BM range at room temperature. The values are slightly lower than expected for high spin iron(III) complexes. These values indicate that there is no significant magnetic interaction in the molecules and suggest penta coordinate spin free nature of these complexes¹⁹.

The electronic spectra of iron complexes show various spectral bands in the region 8000-7500, 10000-9800, 15600-15400 and 2700 cm⁻¹. These bands do not indicate octahedral or tetrahedral environment around the metal atom since the bands of octahedral lie in the range *ca.* 13000, 17000 and 23000 cm⁻¹ and those for tetrahedral *ca.* 15000, 16500 and 20000 cm⁻¹, respectively. However, these bands are well within the range reported for penta-coordinated complexes²⁰. It can therefore, be concluded that these complexes are also penta-coordinated trigonal bipyramidal. Any attempt to make assignments is, however, difficult due to the likelihood of interaction of metal ligand system lifting the degeneracy of the d_{xz}, d_{yz} pair. Further interpretations and calculations of any parameter is not possible since correct energy level sequence and equations are not available for high spin trigonal bipyramidal iron complexes²¹.

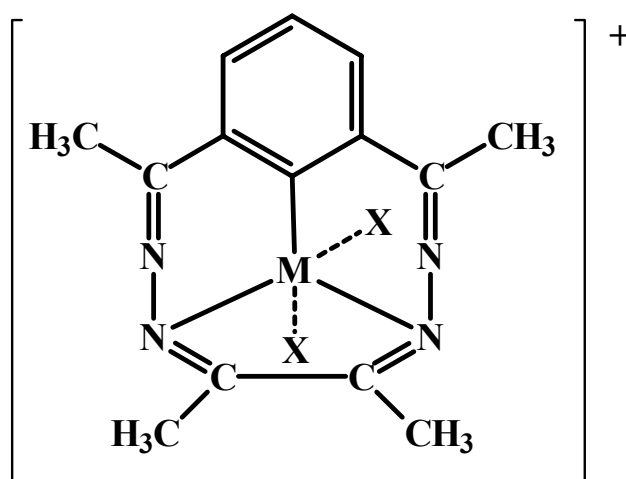
Cobalt(III) complexes: The magnetic measurement of dihydroxy cobalt(III) shows that this complexes is diamagnetic in nature. The electronic spectra of cobalt(III) complex exhibit bands at *ca.* 15850, 18250 cm⁻¹, respectively. The spectra are not consistent with hexa-coordinated geometry of the molecule as its characteristic bands at *ca.* 21000 and 25000 cm⁻¹ are not observed in the spectra. The isomorphism of this complex with those the chromium and tridentate nature of the ligand and coordination of the two hydroxyl groups to the metal atom suggest a trigonal

bipyramidal geometry of the complex. The band *ca.* 18250 cm^{-1} may also be taken as an evidence for such a structure.

Far Infrared spectra: Various bands are observed in this region. The far infrared spectra of these complexes exhibit a series of medium to strong bands in the region emerging from bending, deformation modes of vibrations. A number of important bands appear near 270-240 cm^{-1} . The various bands fall in this region are 245-240, 255-250 and 270 cm^{-1} and may be assigned to $\nu(\text{Cr-N})$, $\nu(\text{Fe-N})$ and $\nu(\text{Co-N})$ vibrational modes, respectively. Metal nitrogen stretching vibrations may be assigned by comparing the spectra of complexes and in turn with those of metal amines and related ligands. Lever²¹ have suggested a method which has been used for these assignments. The spectra show a number of bands near at *ca.* 390 cm^{-1} which have originated from metal nitrogen stretching modes.

The far infrared spectra of metal halides of the complexes of pyridine and related ligands have been systematically reviewed by Clark and Williams²². According to Basolo²³ in penta-coordinated complexes the (Ni-X) (where X-halides, NO_3 and NCS) stretching vibrations should occur between those reported for coordination numbers 4 and 6 complexes, which has actually been observed in practice. However, no reports are available for distinguishing between the square pyramidal and trigonal bipyramidal geometries of penta-coordinated complexes on the basis of infrared spectra thus it may be conclude on the basis of IR spectral studies (conventional and far infrared) that 2 amino groups of 2,6-diacetyl pyridine dihydrazide are condensed with the carbonyl group of the diacetyl molecule and metal is coordinated through the pyridine nitrogen, azomethine nitrogen to form a ring giving rise to a 12-membered macrocyclic system.

Thus, based on various physicochemical studies the following structure confirm for the complexes:



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