

Synthesis and characterisation of transition metal complexes of 2,6-diacetylpyridine bis(S-methyl isothiosemicarbazone)

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ABSTRACT

Few complexes of the ligand 2,6-diacetylpyridine bis(S-methyl isothiosemicarbazone DPMITCZ) with metals V(III)&(IV), Mo(V)&(VI), W(VI)&Mn(II)&(III) have been prepared. The complexes have been characterised by elemental analyses, molar conductance, magnetic data, electronic & IR spectra. Based on these studies octahedral geometry has been proposed for all these complexes.

Key words: 2,6-diacetylpyridine bis(S-methyl isothiosemicarbazone) Complexes, octahedral.

INTRODUCTION

Transition metal complexes have been extensively used in organometallic chemistry, biological systems, analytical chemistry, agriculture and anticancer agents¹⁻⁴. The survey of chemical literature reveals the importance of metal complexes of thiosemicarbazone as better anticancer agent⁵⁻⁷. A growing interest is being noticed in biochemistry as well as coordination chemistry of Mn, Co, Ni, Cu, V & Mo due to their biological importance⁸⁻¹⁹.

Keeping these facts in view, an attempt has been made to synthesise and characterise the complexes of metals of bioinorganic importance with the ligand containing thiosemicarbazone moiety.

EXPERIMENTAL

All the chemicals and reagents used were of AR grade or equivalent purity. The ligand as well as its corresponding metal complexes were analysed by standard methods. Conductivity measurements were carried out with Philips conductivity Bridge Model PR 9500 at room temperature and 10^{-3} M dilution. Magnetic susceptibility was determined by Gouy's balance

using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a callibrant. Electronic spectra were recorded by Beckmann DCI-2-spectrophotometer. IR spectra were recorded using Perkin Elmer PC-16F FTIR spectrophotometer by using KBr pellets.

Preparation of the Ligand

2,6-diacetylpyridine was dissolved in double distilled ethanol. Freshly prepared ethanolic solution of S-methylisothiosemicarbazide was then added to the prepared solution. The reaction mixture was refluxed at 40°C for about 3 hour. A creamish white ppt. was formed on cooling in ice bath. It was filtered, washed with methanol. It was recrystallised from ethanol and dried in vacuo over fused calcium chloride.

Preparation of the Complexes

The metal complexes were prepared by adding freshly prepared solution of the ligand in ethanol to the warm solution of the metal salt in 1:1 ratio. The reaction mixture was refluxed for about 8-10 hour with constant stirring. The product so formed was filtered, washed with cold ethanol followed by diethyl ether and dried in vacuo over fused calcium chloride.

RESULTS AND DISCUSSION

The analytical data of the synthesized ligand and the complexes is given in Table 1. The data suggested 1:1(M:L) stoichiometry for all the complexes. The molar conductance values determined at 10^{-3} M dilution and 25°C in both DMF and DMSO suggested 1:2 electrolytic nature for V(III), $\text{WO}_2(\text{VI})$, $\text{MoO}(\text{VI})$, Ni(II) and Mn(II) complexes and 1:3 electrolytic nature for V(IV), $\text{MoO}(\text{V})$, Mn(III) complexes. Room temperature magnetic moment values lie in the range reported for octahedral complexes (Table 1) of the respective metal complexes

The IR spectra of 2,6-diacetylpyridine bis(S-methyl isothiosemicarbazone) was compared with its V(III), V(IV), $\text{WO}_2(\text{VI})$, $\text{MoO}(\text{V})$, $\text{MoO}_2(\text{VI})$, Ni(II), Mn(II) and (III) complexes. The pyridine ring vibrations, most affected by involvement of nitrogen of pyridine in coordination with a metal, are ring deformation, in-plane ring deformation and out-of-plane deformation(II). These vibrations appear at 1580 cm^{-1} , 640 and 410 cm^{-1} respectively in the free ligand. In-plane deformation and out-of-plane deformation bands show an upward shift of $20\text{--}30\text{ cm}^{-1}$ respectively in the IR spectra of the complexes¹². This was further supported by the presence of a new band at $280\text{--}260\text{ cm}^{-1}$ in the IR spectra of the metal complexes, assignable to $\nu(\text{M-Npy})$ vibrations¹³. A medium intensity band at 1610 cm^{-1} assignable to isothiosemicarbazide moieties, showed a downward shift of $10\text{--}20\text{ cm}^{-1}$ due to the involvement of NH_2 group in coordination with the metal¹⁴.

The spectrum of the ligand showed a band at 1640 cm^{-1} assignable to azomethine linkage of the isothiosemicarbazide, $-\text{N}=\text{C}(\text{SCH}_3)\text{NH}_2$, and the isothiosemicarbazide linkage, $\text{C}_5\text{H}_3\text{N}(\text{CH}_3)_3\text{C}=\text{N}$ ^{15,16}. Band due to isothiosemicarbazide fragment remained at same position but the $\text{C}_5\text{H}_3\text{N}(\text{CH}_3)_3\text{C}=\text{N}$ linkage were lowered by $15\text{--}20\text{ cm}^{-1}$ in the spectra of the complexes. This suggested the involvement of azomethine group in coordination. It was further supported by the appearance of a non-ligand band in the IR spectra of the complexes in the range of $360\text{--}380\text{ cm}^{-1}$ assignable to $\nu(\text{M-N})$ vibrations. The new band appearing in the range of $315\text{--}335\text{ cm}^{-1}$ in the spectra of the some complexes

may be assigned to $\nu(\text{M-Cl})$. Thus the ligand is behaving in neutral quinque-dentate manner with N5 type coordination.

In the case of Mn(II), Mn(III) and Ni(II) complexes the sixth position is occupied by the water molecule. This was indicated by appearance of 2 non-ligand bands in their IR spectra in the range of $3310\text{--}3400\text{ cm}^{-1}$ to $\nu(\text{OH})$ group of coordinated water molecule¹⁷ and $850\text{--}865\text{ cm}^{-1}$ assignable to wagging mode of coordinated water molecule¹⁷. The electronic spectrum of V(III) complex exhibited a band at 16000 cm^{-1} with a shoulder at $20,500\text{ cm}^{-1}$. The low energy band has been assigned to ${}^3\text{T}_{1g} \rightarrow {}^3\text{T}_{2g}$ and the high energy band to ${}^2\text{T}_{1g} \rightarrow {}^3\text{T}_{1g}$ (P) transitions respectively. These bands are characteristic of octahedral geometry¹⁸. The electronic spectrum of V(IV) complex exhibited a single band at 12820 cm^{-1} . In the absence of finely resolved spectra, it was therefore, not appropriate to judge the geometry of the complex as regular octahedral¹⁹.

The electronic spectrum of dioxotungsten(VI) complex showed a band due to ligand to metal charge transfer transition. However, no absorption occurs in the range of $25000\text{--}12500\text{ cm}^{-1}$ which suggested the metal ion in $(n-1)d^0ns^0$ electronic configuration²⁰. The electronic spectrum of oxomolybdenum(V) complex suggested that the complex may be considered as octahedral with a strong tetragonal distortion resulting from $\text{Mo}=\text{O}$ bond²¹. The spectrum exhibited 3 distinct absorption bands in the ligand field region. The low intensity band at 13000 cm^{-1} in the long wavelength region is possibly due to first crystal field transition ${}^2\text{B}_2 \rightarrow {}^2\text{E}(\text{dxy}, \text{dyz}, \text{dxz})$. The second crystal field transition at 19000 cm^{-1} is assignable to ${}^2\text{B}_2 \rightarrow \text{B}_1(\text{dxy} \rightarrow \text{dx}^2 - \text{y}^2)$. The third peak was observed at $30,000$ assignable to ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1(\text{dxy} - \text{dz}^2)$. The electronic spectrum of $\text{MoO}_2(\text{VI})$ complex has a single band due to charge transfer transition.

The electronic spectrum of Ni(II) complex showed bands at 11700 , 17500 and $26,800\text{ cm}^{-1}$ assignable to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (P) transitions respectively which are characteristic of octahedral geometry²². The electronic spectrum of Mn(III) complex exhibited a band at 25000 cm^{-1} (charge transfer) and a spin allowed d-d

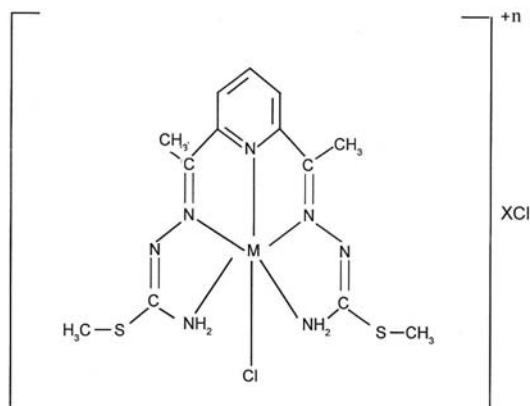
Table1 : Analytical & Physical data of the Complexes

S. No	Ligand complex (colour)	M:L ratio	M:P (°C)	Elemental Analyses% found(calculated)						µeff.	Electrolytic nature
				C	H	N	S	Cl	M		
	2,6- diacetylpyridine bis(S-methyl isothiosemicarbazone)[DPMITCZ] (Creamish)	-	139	45.87 (46.0)	5.22 (5.4)	28.69 (28.9)	18.41 (18.60)	-	-	-	-
1	[V(DPMITCZ)Cl]Cl ₂ (yellow)	1:1	175	31.32 (31.57)	4.71 (4.84)	19.69 (19.83)	12.73 (12.95)	21.10 (21.45)	10.11 (10.32)	2.92	1:2
2	[V(DPMITCZ)Cl]Cl ₃ (light yellow)	1:1	182	27.49 (27.78)	3.29 (3.36)	17.10 (17.34)	11.21 (11.32)	24.90 (25.13)	9.00 (9.02)	1.69	1:3
3	[W ₂ (DPMITCZ)]Cl ₂ (white)	1:1	210	29.3 (29.48)	5.02 (5.12)	15.61 (15.70)	10.12 (10.24)	11.29 (11.37)	29.11 (29.48)	Diam agnetic	1:2
4	[MoO(DPMITCZ)]Cl ₃ (violet)	1:1	195	27.98 (28.10)	3.59 (3.65)	17.59 (17.65)	11.42 (11.53)	18.96 (19.09)	17.10 (17.29)	1.76	1:3
5	[MoO ₂ (DPMITCZ)]Cl ₂ (violet)	1:1	198	28.99 (29.10)	3.51 (3.54)	18.11 (18.28)	11.89 (11.94)	13.18 (13.24)	17.82 (17.91)	Diam agnetic	1:2
6	[Ni(DPMITCZ)H ₂ O]2CH ₃ COO (green)	1:1	165	31.82 (31.95)	4.98 (5.07)	18.14 (18.42)	11.89 (12.03)	-	17.98 (18.43)	2.75	1:2
7	[Mn(DPMITCZ)H ₂ O] 3 CH ₃ COO (brown)	1:1	175	32.15 (32.36)	4.99 (5.11)	16.48 (16.69)	10.81 (10.90)	-	9.18 (9.36)	4.95	1:3
8	[Mn(DPMITCZ)H ₂ O]2 CH ₃ COO (light brown)	1:1	170	31.98 (32.19)	4.89 (5.11)	18.13 (18.56)	11.96 (12.12)	-	10.21 (10.41)	5.92	1:2

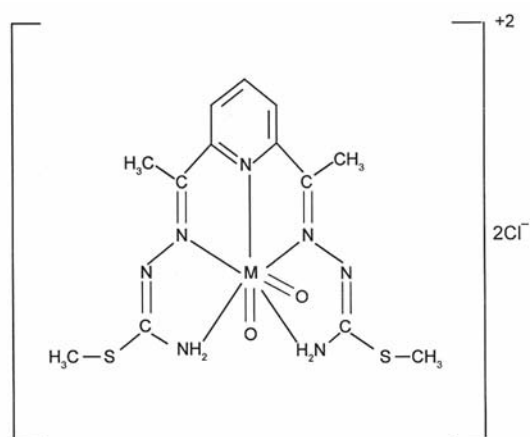
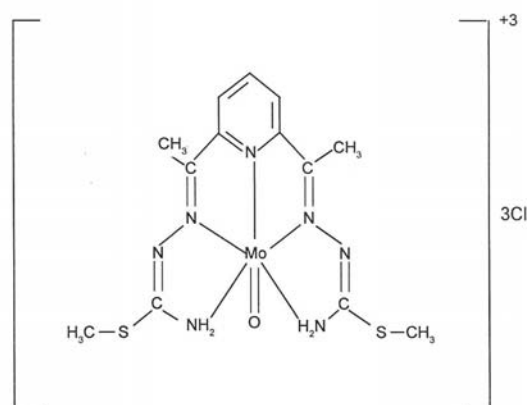
Note-The figures given in brackets are calculated values.

transition band $SEg \rightarrow ST_{2g}^{23}$, characteristic of octahedral geometry. The octahedral Mn(II) complex shows bands at 8330, 15625, 25000 and 295000 cm^{-1} which are of not much help in deciding the transition²⁴.

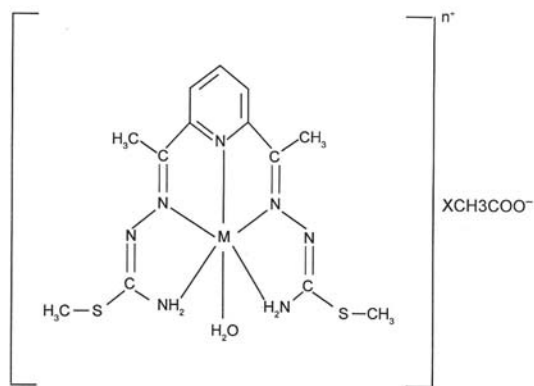
The aforesaid physicochemical evidences suggested octahedral geometry for all the reported complexes with possible distortion in case of MoO(V), MoO₂(VI) and WO₂(VI) complexes.



M = V(III), V(IV) X=2 or 3, n = 2/3



M = W or Mo



M = Mn²⁺, Mn³⁺ or Ni²⁺, n=2 or 3, X = 2 or 3

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