

LETTERS TO THE EDITOR

SPECTRAL AND MAGNETIC STUDIES OF SOME MIXED LIGAND COMPLEXES OF BIS-(DIMETHYLGLYOXIMATO) COBALT(II)

Bis-(dimethylglyoximato) cobalt(II) resembles very closely the vitamin B₁₂ derivatives¹. Generally, cobalt(II) complexes are susceptible to atmospheric oxidation but *bis*-(dimethylglyoximato) cobalt(II) is found to be quite stable. Hence it was considered worthwhile to study the syntheses, magnetic and spectral behaviour of mixed ligand complexes of diaquo-*bis*-(dimethylglyoximato) cobalt(II) with pyridine, 1, 10, phenanthroline and *a, a'*, dipyridyl.

Experimental

Diaquo *bis*-(dimethylglyoximato) Co(II) was prepared by the literature method². Stoichiometric amount of pyridine (0.02 mol), or 1,10, phenanthroline or *a, a'*, dipyridyl (0.01 mol) in ethanol was added to a solution of diaquo *bis*-(dimethylglyoximato) Co(II) in ethanol. The resulting solution was refluxed for an hour in nitrogen atmosphere. The crystalline solid separated out was filtered, washed with ether in N₂-atmosphere and dried in vacuo. Purity of complexes was established by elemental analyses using standard methods. Electronic spectra were measured on Carl Zeiss VSU-2 Spectrophotometer in ethanol. IR spectra of KBr pellets were recorded on Perkin-Elmer 577 Spectrophotometer. Magnetic measurements were carried out on Gouy magnetic balance at 300° K.

Results and Discussion

In weak field or high-spin Co(II) complexes the experimentally observed spin-allowed transitions in the order of increasing energy, are ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, while in strong field or low-spin Co(II) complexes the increasing energy order is ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$; ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$, and these are denoted as ν_1 , ν_2 and ν_3 respectively^{3,4}. In the present study of low-spin Co(II) complexes the band ν_3 occurs in the region 21978–20618 cm⁻¹ as a shoulder. The band ν_2 occurs in the region 16447–16181 cm⁻¹, while the band ν_1 ranges between the limits 10204–9900 cm⁻¹. The electronic spectral pattern of these complexes have been found to be similar to those of the octahedral hexaquo cobalt(II) ion⁵, suggesting thereby, an octahedral stereochemistry for these low-spin Co(II) complexes. The values for Racah interelectronic repulsion parameter (B) and crystal field splitting energy (10 Dq) have been calculated following strong field coupling

scheme³ (Table I). The lower value for β in mixed ligand complexes as compared to the parent complex, indicates an increase in covalency on complexation.

TABLE I

Calculated values for parameters B and 10 Dq (in cm⁻¹), β and magnetic moment (in B.M.)

Complex	B	10 Dq	β	μ_{eff}
Co(DH) ₂ (H ₂ O) ₂	551.6	11928	0.56	1.74
Co(DH) ₂ (Py) ₂	473.2	10718	0.48	1.71
Co(DH) ₂ (Phen)	478.1	10833	0.49	1.73
Co(DH) ₂ (Dipy)	446.6	10848	0.45	1.72

DH = dimethylglyoxime, Py = pyridine, Phen = 1, 10, phenanthroline and Dipy = *a, a'*, dipyridyl.

The values of magnetic moments (μ_{eff}) for the complexes lie between 1.71–1.74 B.M. (Table I) closer to the spin-only moment value of 1.73 B.M., confirming the stereochemistry as low-spin octahedral having one unpaired electron^{6,7}.

Infrared spectrum of the parent complex Co(DH)₂(H₂O)₂ has confirmed the presence of coordinated water molecules by a moderately intense band at 3440 cm⁻¹. I.R. spectra of mixed ligand complexes derived from it do not show absorption in this region, showing these to be anhydrous. The vibrations due to coordinated dimethylglyoxime⁸ are ν (C–N), ν (N–O) and ν (M–N) and have been found to occur in the region 1555–1540 cm⁻¹, 1080–1055 cm⁻¹ and 515–505 cm⁻¹ respectively. Since both the coordinated ligands, viz., dimethylglyoxime and second ligand (pyridine, 1, 10, phenanthroline and *a, a'*, dipyridyl) show absorption in the same region, it is difficult to assign particular absorption bands in detail. However, it is observed that the bands of both the ligands of complex are modified on complexation showing their coordination to the metal atom.

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VARIATION IN MAJOR LIPID COMPONENTS IN THE INTESTINE OF *ANTHERAEA MYLITTA* DURING LARVAL DEVELOPMENT AND SPINNING PERIOD

Introduction

In insects, haemolymph is the link between intestine and the fat body, the major site for storage of lipids, the composition whereof resembles that of dietary lipids¹. Hence the analysis of intestinal lipids was considered pertinent to provide information regarding their digestion, absorption and resynthesis in the intestine and their transport to other tissues. The study was also anticipated to throw light on the utilization of lipids as a potential energy source for maintenance of the structural and physiological integrity of cellular organelles.

Materials and Methods

Larvae of *A. mylitta* were procured from Tasar Field Research Station, Jagadapur (M.P.). Larvae were dissected and lipids extracted and fractionated as described earlier^{2,3}.

All assays were carried out in duplicates in three separate pools of intestines from 10 insects each, as well as from a grand pool of the three pools and average values were employed for calculations.

Results and Discussion

In *A. mylitta* larva, intestinal (Table I) total lipids (TL) vary between 15.3-16.9, 16.9-24.0 and 11.4-

23.1% respectively during 3rd, 4th and 5th instar stages. This indicates that the intestinal lipids are of dietary origin and their significant fluctuations observed, during development in the intestine itself, is suggestive of the transport of dietary lipids to the storage site, the fat body. This is substantiated by the concurrent increase in the fat body lipid and the maintenance of very low level thereof, in the haemolymph during fifth instar^{4,5}.

Neutral lipids (NL) vary more or less in the same manner as the total lipids (TL) and constitute the major lipid fraction all through larval development and spinning period except at 48 h. This suggests their role as the main energy supplier⁶ during period of high energy requirement like growth, development and silk synthesis. Reciprocal relationship between NL and free fatty acids (FFA) as observed during 3rd instar stage is indicative of the interconversion of the two (NL and FFA) when the *de novo* synthesized FFA get incorporated into the triglyceride reserve⁷. The high level of NL could also be attributed to its synthesis from non-lipoidal substrate⁸.

While in *Melanoplus*, only 30% of FFA exists as NL and the remaining 70% as FFA², in *A. mylitta* the former (FFA) stands at a lower concentration than either NL or phospholipids (PL) during larval development till 24 h to the commencement of spinning. It is noteworthy that during spinning, except at 48 h PL and NL reveal a decreasing trend, while FFA do not depict any significant variation. This is suggestive of the conversion of NL to FFA earmarked for utilization during pupal development and for high energy demanding processes.

The proportion of PL in the insects, although is usually low in comparison in some insect tissues (intestine and wing buds), sometimes even as high as 50% of TL has been reported⁹. Kulkarni *et al.*¹⁰ based on similar observations in *Mimodesma sexta* termed this as one of the biochemical characteristics of lepidopteran larva. The same appears to hold good for *A. mylitta* in the present investigation.

PL in the 3rd instar larva depicts initially a steady increase followed by a decline (Table I). The initial accumulation of about 38.8% (day 3) indicates that the PL are of dietary origin since TL, NL and FFA do not show regular decline during the same period.

Intestine of 4th instar larva accumulates 8.1% (Table I) of PL on day 3 with simultaneous sharp decline in other components. This is indicative of the synthesis of PL from other components.

On the eve of spinning, the intestine does not reveal variation in TL concentration, suggesting the storage of lipids for utilization during silk synthesis and prepupal development. At the same time PL depicts a declining trend till 48 h prior to the spinning period while the position is reverse for other compo-