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The Electronic and Magnetic Properties of the Ni(II)–Nucleotide Complex NiIMP·$7H_2O$

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Metal ions have been implicated in a wide variety of biological processes. Their interactions with nucleic acids and their constituents have been reviewed [1–3], and their role in the replication, translation, and transcription of nucleic acids is well documented [4]. Although the isolation and structural characterization of metal–nucleotide complexes has developed into an active area of research [5], no attempt to elucidate and systematically study the spectral and magnetic properties of these complexes has been undertaken until very recently when Nelson and Villa reported [6] a spectroscopic study on three novel Cu(II) nucleotide complexes.

In an effort to elucidate the chemical properties of transition metal–nucleotide complexes containing various transition metal ions with pyrimidine and purine nucleotides, the 1:1 complex of Ni(II) with inosine-5′-monophosphate (NiIMP·$7H_2O$) was synthesized and its spectral and magnetic properties measured. This represents the first report on the chemical characterization of any Ni(II) coordination compound containing a pyrimidine or purine nucleic acid base.

Light green crystals of $C_{10}H_{11}O_8N_4P_1Ni\cdot 7H_2O$ (m.p. 153–156 °C(d)) were prepared by adding $Ni(NO_3)_2\cdot 6H_2O$ to an aqueous solution of NaIMP in an equivalent mol ratio, adjusting to pH 6 with dilute nitric acid, followed by slow evaporation at room temperature. The stoichiometry of the complex was determined by elemental analysis.

The IR spectra of the free and coordinated ligand were obtained as KBr pellets. The loss of ring vibrations in the area 1300–1550 cm^{-1}, and the presence of stretching vibrations attributable to the ribose sugar and phosphate groups in the areas 950–1250 cm^{-1} strongly support exclusive ring coordination to the metal. The severe broadening noted in both these regions, however, undoubtedly results from the extensive hydrogen bonding of the coordinated water molecules to the oxygen atoms of the carbonyl, ribose sugar, and phosphate groups. Recent structural data on this complex, Figure 1, confirm these hydrogen bonding interactions and N(7) coordination to the metal ion [7].

The solid state visible absorption spectra (Nujol mull) exhibits three spin allowed transitions (cm^{-1}) at: 25800 ($^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$), ν_3; 13950 ($^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$), ν_2; and 8390 ($^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)$), ν_1, yielding internally consistent values of 10Dq and B of 8390 and 960 cm^{-1}, respectively. The small reduction in the value of the Racah parameter B from the free ion value of 1040 cm^{-1} ($\beta = 0.92$) points to a small degree of covalent character in the bonds attached to Ni(II). A high energy peak on the second transition at 15190 cm^{-1} results from the splitting of this band due to spin–orbit coupling which mixes the $^3T_{1g}(F)$ and ^1E_g states [8] which are very close in energy at the values of 10Dq produced by $5H_2O$ and 1N. The values of Dq, B, and ν_2/ν_1 observed here are in the range of those found for similar octahedral systems [9].

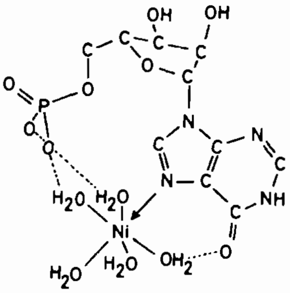

Fig. 1. Schematic of NiIMP·$7H_2O$ molecule. Ring coordination through N(7) of purine; hydrogen bonding to ribose sugar hydroxyl groups not shown.

The variable temperature magnetic susceptibility data (298–77 °K) conform to the Curie–Weiss Law, $\chi = C/(T - \theta)$, with Curie and Weiss constants of $C = 1.264$ cgs units and $\theta = -8$ °K, respectively. A temperature independent paramagnetism (TIP) correction of 248×10^{-6} cgs units ($= 8N\beta^2/10Dq$) for Ni(II) [9], and a diamagnetic correction for the complex of -246×10^{-6} cgs units obtained from Pascal's constants [11] were used in the calculations. The effective magnetic moment of 3.13 BM at room temperature is consistent for an octahedrally coordinated Ni(II) system [8]. The decrease in the room temperature moment to 3.05 BM at 77 °K, as well as the negative Weiss constant, suggest a small degree of antiferromagnetic interactions which can be attributed to lattice effects throughout the crystallites. Variable temperature magnetic susceptibility measurements down to 12 °K are in progress in an effort to measure and characterize these interactions further.

Despite X-band EPR scans (0–12000 G) run at various power levels at room and liquid nitrogen temperatures, no signals originating from a high-spin d^8 (S = 1) configuration were observed. Presumably the degeneracy of the three spin levels in the $^3A_{2g}$ ground term has been lifted in the absence of a magnetic field by the presence of a low symmetry ligand field component (*i.e.*, a tetragonal distortion, possibly with a trigonal component) which splits the triplet (S = 1) spin state into a singlet level ($M_s = 0$) and a higher lying doublet level ($M_s = \pm 1$) [10] with a separation between the two levels given by D, the zero field splitting parameter. If the |D| is larger than the microwave radiation employed at X-band (~ 9 GHz), resonance absorptions will not in general be observed unless large fields are attainable. Although a g-value of 2.30 can be calculated from the relation $g = 2.00 (1 - 4\lambda/10Dq)$ [9] with $\lambda = -315$ cm^{-1} and $10Dq = 8390$ cm^{-1}, verification of this value will have to await the results of high-field X-band and Q-band (~ 35 GHz) EPR studies.

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