

CHAPTER 7

PHYSICO-CHEMICAL STUDIES OF A FORMALLY NICKEL(IV)

COMPOUND  $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$

ABSTRACT\*

A formally nickel(IV) periodate  $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$  has been investigated. The room temperature magnetic moment of this compound is  $\sim 1$  B.M. Variable temperature EPR spectral measurements have established that the weakly paramagnetic behavior of this compound is due to the presence of  $\text{Ni}^{3+}$  ions which have occupied some nickel(IV) sites in the crystal lattice. Change in spectral pattern from rhombic (77K) to isotropic (300K) is due to dynamic Jahn-Teller effect. Electrical conductivity measurement of this compound at room temperature  $\sigma = 7.5 \times 10^{-12} \Omega^{-1}\text{cm}^{-1}$  has shown it to be a poor semiconductor.  $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$  decomposes exothermally between  $50^\circ$  and  $300^\circ\text{C}$  to a compound which analyzed to have the composition  $\text{K}_2\text{Ni}_2\text{I}_2\text{O}_9$ . This compound is stable in the temperature range 300 to  $400^\circ\text{C}$ . Chemical reactivities and diffuse reflectance spectra of this compound have revealed that  $\text{K}_2\text{Ni}_2\text{I}_2\text{O}_9$  contains bivalent nickel and hexavalent iodates, that is,  $\text{K}_2\text{Ni}^{\text{II}}\text{I}_2^{\text{VI}}\text{O}_9$ .

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## INTRODUCTION

Nickel in + 4 oxidation state has been stabilized by a variety of organic ligands<sup>1</sup>, however, few complexes containing inorganic ions are known. Among the ternary oxides, the best known examples are  $\text{BaNiO}_3$ <sup>2,3</sup> and  $\text{SrNiO}_3$ <sup>2,3</sup>.  $\text{BaNiO}_3$  has hexagonal close packed  $\text{BaO}_3$  layers and trigonally distorted  $\text{NiO}_6$  octahedra. The fluoro complexes  $\text{M}_2\text{NiF}_6$  ( $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) are also structurally well characterized species<sup>4,5</sup>. It is interesting to note that the earliest nickel(IV) species discovered was isolated as the barium salt of 9-molybdonickelate<sup>6</sup>. The corresponding ammonium salt  $(\text{NH}_4)_6\text{NiMo}_9\text{O}_{32} \cdot 5.5\text{H}_2\text{O}$  is also well characterized<sup>7,8</sup>. X-ray crystal structure of the nickel(IV) polyvanadate  $\text{K}_7\text{NiV}_{13}\text{O}_{38} \cdot 16\text{H}_2\text{O}$  has been determined and is known to contain  $\text{NiO}_6$  and thirteen  $\text{VO}_6$  octahedra sharing edges<sup>9</sup>. The heteropolyniobates of nickel(IV) having the compositions  $\text{Na}_{12}\text{NiNb}_{12}\text{O}_{38} \cdot (48-50)\text{H}_2\text{O}$  and  $\text{K}_8\text{Na}_4\text{NiNb}_{12}\text{O}_{38} \cdot 21\text{H}_2\text{O}$  are known<sup>10</sup>. The sodium salt of the nickel(IV) complex is isomorphous with the corresponding manganese(IV) compound, the crystal structure of which revealed<sup>10</sup> that the manganese atom is octahedrally coordinated by oxygen atoms from the two  $\text{Nb}_6\text{O}_{19}$  groups and the Mn-O distances are equal. Nickel(IV) periodates  $\text{MNiO}_6 \cdot x\text{H}_2\text{O}$  ( $\text{M} = \text{Na}, \text{K}$ ) are another series of well known compounds<sup>10</sup>. These consist of

hexagonal sheets of linked  $\text{NiO}_6$  and  $\text{IO}_6$  octahedra with alkali atoms lying in the octahedral holes between the sheets<sup>12,13</sup>.

The nickel(IV) complexes ( $d^6$ ) are invariably spin-paired resulting in diamagnetic or very weakly paramagnetic (temperature independent) behavior. However, we have been intrigued to find that the compound  $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$  has a room temperature magnetic moment of  $\sim 1$  B.M., independent of the source of preparation. This value appears rather high for a nickel(IV) species because at the most it can have a moment of  $\sim 0.6$  B.M. due to temperature independent paramagnetism<sup>14</sup>. We therefore have investigated this compound to find the source of paramagnetism. Among other things, we have examined variable temperature EPR spectra of this compound.

#### EXPERIMENTAL SECTION

##### Preparation of $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$ .

This compound was prepared according to the method described in literature<sup>15</sup>. A mixture of  $\text{Ni}(\text{SO}_4)_2 \cdot 7\text{H}_2\text{O}$  (7 mmol) and  $\text{KIO}_4$  (13 mmol) was dissolved in hot water (450 mL). The solution was heated to boiling and  $\text{K}_2\text{S}_2\text{O}_8$  (15 mmol) was added in small portions with stirring. The dark red, almost black crystals that deposited were collected

on a sintered glass crucible and washed several times with boiling water. The compound was dried over  $\text{CaCl}_2$ .

### Analysis

Nickel was estimated as the dimethyl glyoximate after decomposing the compound with  $\text{HCl}$  and  $\text{SO}_2$ . From the filtrate potassium was estimated gravimetrically as  $\text{K}_2\text{SO}_4$ . Iodine was determined as  $\text{AgI}$  after reducing the compound with  $\text{SO}_2$  in dilute  $\text{H}_2\text{SO}_4$  solution. Oxidation states of iodine in  $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$  and  $\text{K}_2\text{Ni}_2\text{I}_2\text{O}_9$  were determined by measuring the quantity of iodine liberated from  $\text{KI}$  in acidic solution.

### Physical measurements.

Magnetic moments were measured in a PAR vibrating sample magnetometer as described in Chapter 4. EPR spectra of polycrystalline materials were recorded in a Varian 4 X-band spectrometer in the temperature range 77-300K. 1,1-diphenyl-2-picryl hydrazil was used as the marker. Thermal analysis was carried out in a MOM Derivatograph. Diffuse reflectance spectra were recorded in a Cary 17D spectrophotometer. The sample was diluted with  $\text{BaSO}_4$ . Electrical conductivity of pelletized specimen was measured by four-probe method as detailed out in Chapter 4.

### RESULTS AND DISCUSSION

The room temperature magnetic moments of several specimens of  $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$  prepared were found to lie in the close range 1.05-1.10 B.M. We suspected this could be due to the presence of some nickel(II) or nickel(III) impurity. While the analytical data were consistent with the composition  $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$  it was felt that the concentration of such impurity is very low. Thus the paramagnetic impurity resides in magnetically dilute form in the diamagnetic host, that is,  $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$ . It was expected therefore that well resolved EPR spectra should be obtained.

For genuine low-spin nickel(III) ( $d^7$ ) in a tetragonal ligand field, the ground state is usually  $(d_{xz}, d_{yz})^4 (d_{xy})^2 (d_z^2)^1 (d_{x^2-y^2})^0$  which is often simply stated as  $(d_z^2)^1$ . In the more general case of rhombic symmetry ( $d_{xz}, d_{yz}$  not degenerate) the EPR  $g$ -tensors can be written as

$$g_{xx} = 2 - 6 \lambda / \epsilon_1 \quad \dots (7.1)$$

$$g_{yy} = 2 - 6 \lambda / \epsilon_2 \quad \dots (7.2)$$

$$g_{zz} = 2$$

where  $\lambda$  is the spin-orbit coupling constant ( $-715 \text{ cm}^{-1}$ , in the

free ion) and  $\epsilon_1$  and  $\epsilon_2$  are respectively the energy gaps  $d_{z^2} - d_{yz}$  and  $d_{z^2} - d_{xz}$ . In tetragonal symmetry these gaps are equal ( $\epsilon_1 = \epsilon_2 = \epsilon$ ) and

$$g_{\perp} = 2 - 6\lambda/\epsilon \quad \dots (7.3)$$

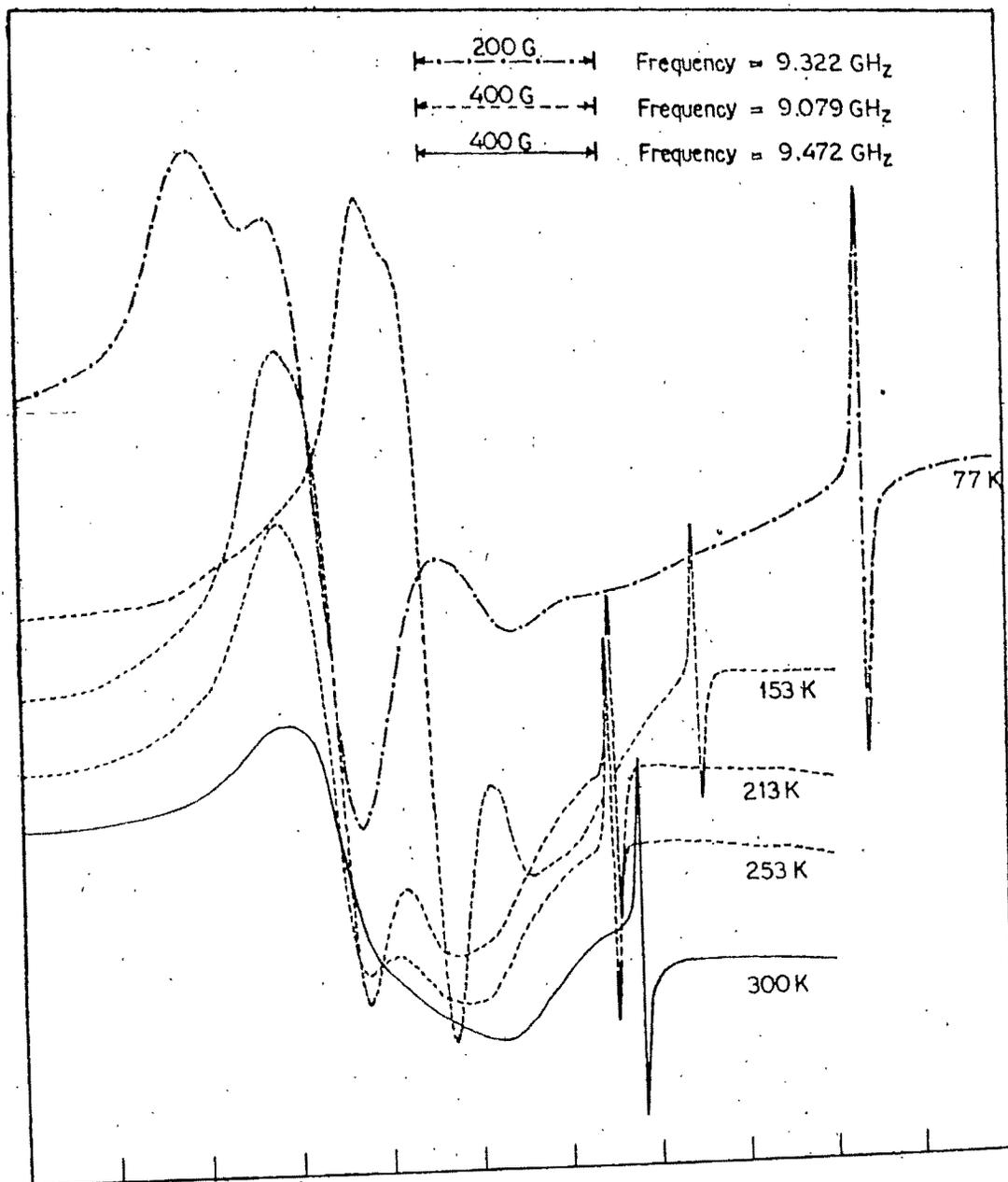
$$g_{\parallel} = 2 \quad \dots (7.4)$$

that is  $g_{\perp} > g_{\parallel}$ .

It should be noted that a  $\text{Ni}^{3+}$  ion can not remain in a perfect octahedral field due to Jahn-Teller distortion. According to the Jahn-Teller theorem, if the ground state of an ion in a crystal is orbitally degenerate, with no other perturbation present, the crystal will distort to one of lower symmetry in order to remove the degeneracy<sup>16</sup>. In nickel(III)  $t_{2g}^6 e_g^1$ , the electronic state of the ion is a degenerate  $E_g$  state. The distortion preserves the center of gravity of the  $e_g$  level of the cation, and hence there can be distortion, for example, in tetragonal symmetry with  $c/a > 1$  or  $< 1$ . The system can resonate between the two stable configurations unless one gets stabilized due to some other effect. This can happen in the case of dynamic Jahn-Teller effect through coupling between lattice vibration and low-frequency electronic motion<sup>17</sup>.

The EPR spectrum of  $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$  at 77K is shown in Figure 7.1. Variable temperature EPR spectra of this compound are shown in Figure 7.2. The spectral feature remains broad isotropic from 300 to 260 K. At 253K the spectrum is slightly splitted (Figure 7.2) and the extent of splitting goes on increasing as the temperature is lowered. A clear rhombic spectrum results at 77K (Figure 7.1) which has the following g- values:  $g_1 = 2.130$ ,  $g_2 = 2.212$ ,  $g_3 = 2.261$ ,  $\langle g \rangle = 2.201$ . For the isotropic spectrum,  $g = 2.205$ . The nature of these spectra can be readily explained by assuming  $s = \frac{1}{2}$  which clearly means the presence of  $\text{Ni}^{3+}$  ion in the crystal lattices of  $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$ . The  $\langle g \rangle$  value also indicates that the unpaired electron resides mainly in the metal ion orbital. The variation of EPR spectral characteristics as a function of temperature is clearly due to dynamic Jahn-Teller effect of nickel(III).

X-ray crystallographic studies of  $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$  have revealed the presence of hexagonal sheets of linked  $\text{NiO}_6$  and  $\text{IO}_6$  octahedra with the alkali metal ions lying in the octahedral holes between the sheets. Thus during formation some of the interstitial sites in the crystal lattice are occupied by  $\text{Ni}^{3+}$  ions. Obviously the concentration of  $\text{Ni}^{3+}$  ions is very low as the chemical composition indicates. Although quantitative determination of  $\text{Ni}^{3+}$  ion concentration was not

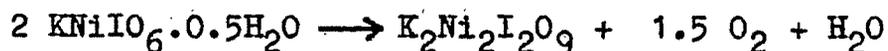


EPR spectra of  $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$  at different temperature  
 Figure 7.2

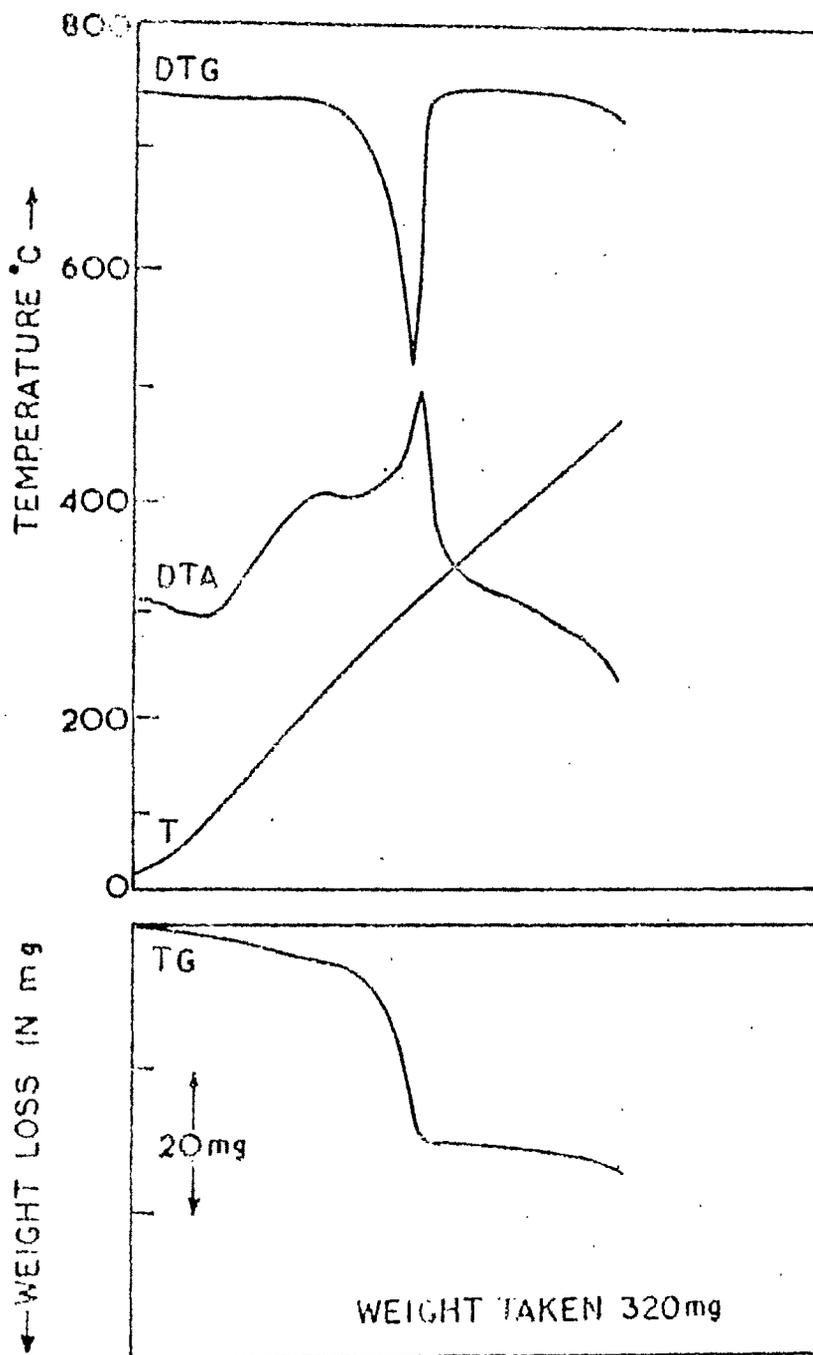
made by EPR method, however, we considered that the compound will act as a poor extrinsic semiconductor.

The room temperature electrical conductivity of this compound has been measured. Indeed the specific conductivity is very low,  $\sigma = 7.5 \times 10^{-12} \Omega^{-1} \text{cm}^{-1}$  showing it to be a poor semiconductor. Higher temperature measurements were intended but could not be carried out as the compound begins to decompose slightly above room temperature.

Thermal analysis of  $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$  has established that the compound undergoes exothermic decomposition between  $50^\circ$  and  $300^\circ\text{C}$  (Figure 7.3). A light green product is obtained which is stable from  $300$ – $400^\circ\text{C}$ . The observed weight loss 9.6% agrees satisfactorily with the calculated value 10.0% for the reaction

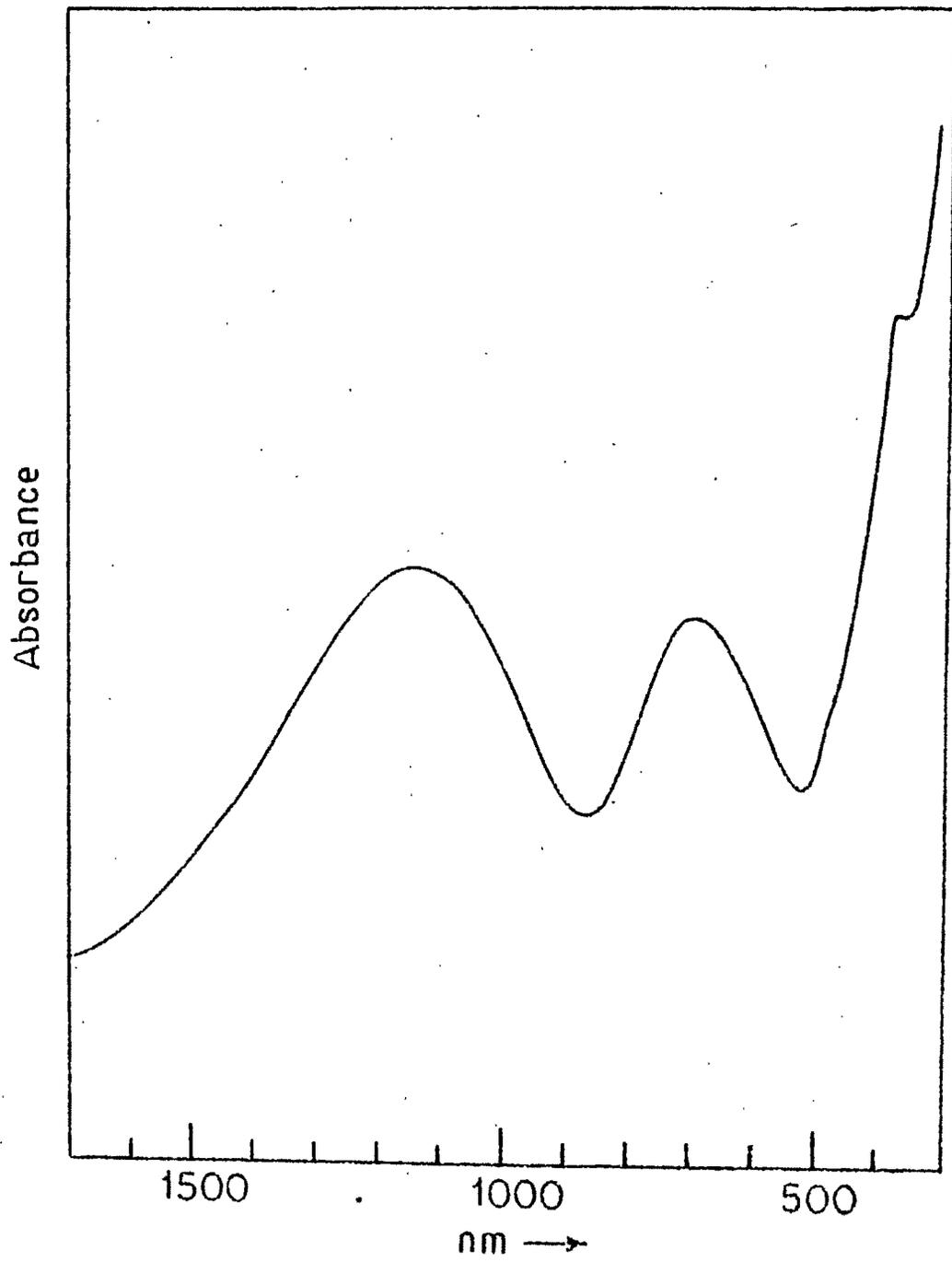


The analytical data of the thermolysis product agrees with the composition  $\text{K}_2\text{Ni}_2\text{I}_2\text{O}_9$  (found: Ni = 19.6%, I = 42.3%; calcd: Ni = 19.8%, I = 42.8%). Redox titration has shown that either nickel(III) or iodine(VI) is present in  $\text{K}_2\text{Ni}_2\text{I}_2\text{O}_9$ . The compound is insoluble in water and the aqueous solution did not respond to the presence of free  $\text{KIO}_3$  thus precluding the composition of  $\text{K}_2\text{Ni}_2\text{I}_2\text{O}_9$  as  $2 \text{KIO}_3 + \text{Ni}_2\text{O}_3$ . However, the



Thermal analysis of  $\text{KNiIO}_6 \cdot 0.5\text{H}_2\text{O}$

Figure 7.3



Reflectance spectrum of  $K_2Ni_2I_2O_9$

Figure 7.4

compound liberates oxygen in the presence of dilute mineral acids. On the basis of these observations  $K_2Ni_2I_2O_9$  may be considered either as  $K_2Ni_2^{III}I_2^{VI}O_9$  or  $K_2Ni_2^{II}I_2^{VI}O_9$ . The room temperature magnetic moment is 4.7 B.M./nickel and iodine atoms. Definitive information about the oxidation state of nickel was obtained from diffuse reflectance spectra of this compound (Figure 7.4). The spectrum shows the presence of three bands which are clearly due to  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  (26,300  $cm^{-1}$ ),  ${}^3A_{2g} \rightarrow {}^3T_{1g}$  (14,300  $cm^{-1}$ ) and  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  (8,850  $cm^{-1}$ ) transitions of nickel(II) in an octahedral ligand field. The ligand field stabilization energy  $10 Dq$  as determined from Tanabe-Sugano diagram<sup>16</sup> is 8,500  $cm^{-1}$  which is typical of  $NiO_6$  chromophore. Thus  $K_2Ni_2I_2O_9$  is a compound that contains bivalent nickel and hexavalent iodine,  $K_2Ni_2^{II}I_2^{VI}O_9$ . It may be pointed out that hexavalent iodates of the alkaline earths ( $MIO_4$ ) were obtained by the thermolysis of their corresponding dimeso periodates,  $M_2I_2O_9 \cdot nH_2O$ <sup>18</sup>.

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