

Identification of crystal symmetry in Kramers and non-Kramers ions by optical absorption: Divalent copper and nickel ions in diamagnetic lattices

K. Velavan¹, R. V. S. S. N. Ravikumar², R. Venkatesan¹, and P. Sambasiva Rao*¹

¹ Department of Chemistry, Pondicherry University, Pondicherry – 605 014, India.

² Department of Advanced Materials Sciences and Engineering, Yamaguchi University, 2-16-1, Tokiwadai, Ube-755-8611, Japan

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The optical absorption spectra of Ni(II) doped hexaimidazole zinc(II) dichloride tetrahydrate (HZDT) and Cu(II) doped magnesium potassium phosphate hexahydrate (MPPH) have been studied at room temperature. Ni(II)/HZDT spectrum consists of three strong and one weak band. The calculated value of Dq is 1051 cm^{-1} and the interelectron repulsion parameters B and C are 854 and 3626 cm^{-1} respectively. The correlation of optical work with EPR has yielded the spin-orbit interaction parameters λ and ξ as -225 and -450 cm^{-1} respectively. The symmetry around the Ni(II) ion is distorted octahedral, as suggested by EPR results. The estimated percentage covalency of the nickel-nitrogen bond is around 30%. The optical absorption studies of Cu(II)/MPPH show three bands, which are identified as ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions. The octahedral field parameter Dq and the tetragonal field parameters have been evaluated from the observed absorption bands.

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1 Introduction

Many proteins and metal containing enzymes have transition metal ions bound to imidazole and histidine ligand. The diamagnetic host Hexaimidazole zinc(II) dichloride tetrahydrate (abbreviated as HZDT) has six imidazole nitrogen ligands coordinated around the central metal ion in a distorted octahedral environment. Imidazole and histidine ligands are bound to many proteins and metal containing enzymes. The EPR studies of this host lattice (HZDT), when doped with paramagnetic ions such as Cu(II), Cr(III), Fe(III), Mn(II) and Ni(II) [1-5], have given interesting results. Cu(II) has undergone Jahn-Teller distortion, Cr(III) behaves concentration dependent sites with large zero-field splitting (D), Fe(III) under the influence of a strong tetragonal distortion, Mn(II) shows twinning and Ni(II) shows EPR spectrum at room temperature itself with large D . However, the optical studies have not yet reported for these ions. The optical spectra [6] of $K_2Ni[M'(NO_2)_6]$ where M' is divalent cation (lead or barium) shows two low intensity bands before the onset of high-energy band. The two low energy bands are identified as ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}$ and $3T_{1g}(F) \leftarrow {}^3A_{2g}$ and the ground state is ${}^3A_{2g}$. The energy of lowest frequency band gives the $10Dq$ value directly as $13,590\text{ cm}^{-1}$, which is the highest $10Dq$ value reported for nickel(II). In addition, the EPR study of Cu(II) in magnesium potassium phosphate hexahydrate (MPPH) gives very interesting results [7]. The temperature dependence of g and A values have been followed for the polycrystalline sample and the ground state has been unambiguously identified. These EPR results indicate a dynamic Jahn-Teller distortion for Cu(II) ion. The g and A tensor direction cosines are evaluated and

* Corresponding author: e-mail: psr52in@yahoo.co.in

compared with Mg-O directions, which confirms that Cu(II) has entered the lattice substitutionally. Generally a broad adsorption band is seen for divalent copper, which is attributed to ${}^2T_{2g} \leftarrow {}^2E_g$. The asymmetry in band is also seen in some cases, due to low ligand field symmetry. In the present case, we have observed three bands and the results are discussed below in detail.

2 Experimental

2.1 Ni(II) in HZDT

Single crystals of HZDT doped with Ni(II) are grown according to the procedure given in the literature [8]. The method essentially consists of slow evaporation of an aqueous solution of imidazole and zinc chloride in molar concentration of 6:1 and a small amount (about 3%) of nickel chloride is added into the system, adjusting the pH to 6.9 with dil. HCl. The Ni(II) doped crystals are obtained within fifteen days and are collected for further studies, which are flat parallelogram in shape and navy blue in colour. A powder sample of Ni(II)/HZDT is dissolved in ethanol and the optical spectrum has been recorded in Optical Ocean PX-1 spectrophotometer.

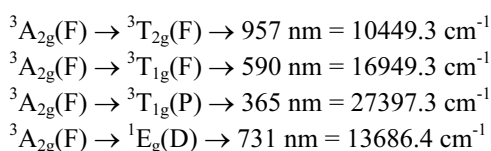
2.2 Cu(II) in MPPH

Single crystal of MPPH [Magnesium Potassium Phosphate Hexahydrate, $MgKPO_4 \cdot 6H_2O$] doped with Cu(II) are grown by slow evaporation of an equimolar solutions of magnesium sulphate and potassium dihydrogenorthophosphate to which about 3% of $CuSO_4$ is added as paramagnetic impurity. Single crystals are obtained within 15 days. The single crystals of Cu(II) doped MPPH are powdered and dissolved in methanol to obtain the optical spectrum with Optical Ocean PX-1 spectrophotometer.

3 Results and discussion

3.1 Ni(II) in HZDT

From the optical spectrum of Ni(II)/HZDT given in Figure 1, one can notice three strong peaks and one weak peak (spin forbidden transition) at 365, 590, 957 and 731 nm respectively. These can be assigned as:



The expected another spin forbidden transition usually seen at lower wavelength region, corresponding to ${}^3A_{2g} \rightarrow {}^1T_{2g}(D)$, is not seen in the present spectrum, which may be buried under the spectrum. From the normal procedure of using Tanabe-Sugano diagram [9], the crystal field splitting value (Dq) and inter electron repulsion parameters B and C (Racah parameters) have been calculated. The final parameters are: Dq = 1051 cm^{-1} and B = 823 cm^{-1} . B for a free Ni(II) ion is 1084 cm^{-1} , which indicates a reduction of about 24% from the free ion value.

The EPR analysis of Ni(II)/HZDT has been reported in an earlier communication [5]. The optical data and EPR data can be correlated to obtain the individual spin-orbital coupling parameter (λ) using the formula

$$g = 2.0023 - 8\lambda/\Delta$$

Here, Δ is the energy of the transition in perfect octahedral case. Using the g value obtained from EPR analysis [5] and Δ from optical data, the value of λ obtained is 225 cm^{-1} . The corresponding value of λ for free Ni(II)

ion is 324 cm^{-1} . This indicates a reduction of 30%, which corresponds to percentage of covalent bonding. This roughly matches with the value obtained from Racah parameter calculations also. The corresponding values found for Cu(II), Cr(III) and Mn(II) are 25, 11 and 14% respectively [1,2,4].

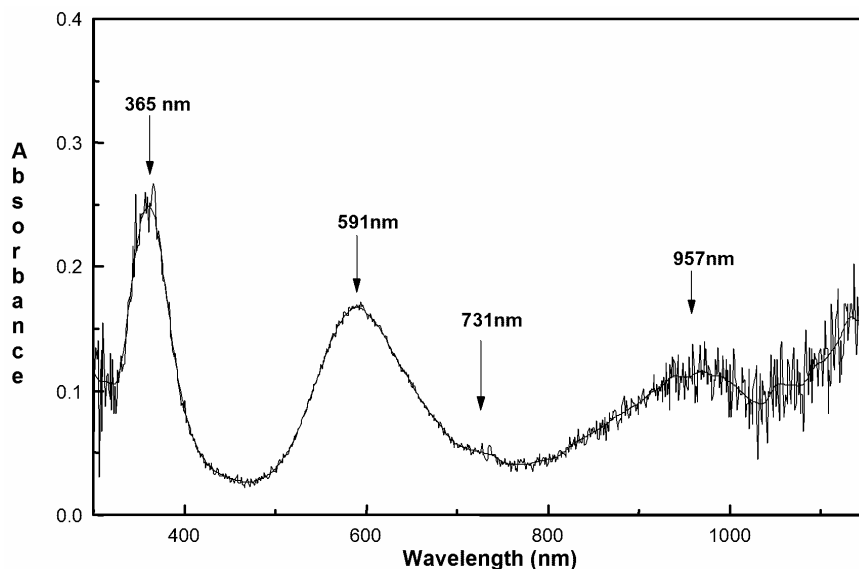


Fig 1 Optical Spectrum of Ni(II)/HZDT recorded at room temperature using methanol as solvent.

The total spin-orbital coupling parameter (ξ) is also calculated using the formula $\lambda = \pm \xi/2S$. Here the + sign is required for a shell that is less than half-filled and the – sign for more than half-filled shell. Using a value of $S = 1$ for Ni(II), the obtained ξ value is -450.0 cm^{-1}

The Racah parameters B and C have also been calculated theoretically by using the following equations:

$$\begin{aligned} {}^3A_{2g} (F) & 0 \\ {}^3T_{2g} (F) & 10Dq \\ {}^3T_{1g} (F) & \frac{1}{2} [(15B + 30Dq) - ((9B - 10Dq)^2 + 144B^2)^{1/2}] \\ {}^1E_g (D) & \frac{1}{2} [(17B + 4C + 20Dq) - ((B + 20Dq)^2 + 48B^2)^{1/2}] \\ {}^1T_{2g} (D) & \frac{1}{2} [(17B + 4C + 30Dq) - ((B + 10Dq)^2 + 48B^2)^{1/2}] \\ {}^3T_{1g} (P) & \frac{1}{2} [(15B + 30Dq) + ((9B - 10Dq)^2 + 144B^2)^{1/2}] \end{aligned}$$

The B value obtained from the above equations is 854 cm^{-1} , which is close to the B value calculated from Tanabe-Sugano diagram. Hence, the consistency in the values obtained from different sources. The calculated C value is 3626 cm^{-1} . The B/B' and C/C' values are 0.78 and 0.75 respectively and are very close, which is expected, since the reduction should be the same whether the transition is between states of same spin multiplicity or different multiplicity. Here B' and C' are inter electron repulsion parameters for free Ni(II) ion. A few values obtained from optical data for a few Ni(II) complexes are given in Table 1, for comparison.

Table. 1 Optical data for Ni(II) complexes in related host lattices.

Ni(II)in	Dq (cm^{-1})	B (cm^{-1})	C (cm^{-1})	B/B'	C/C'	ξ (cm^{-1})	Ref.
KMgF ₃	-	955	4234	0.88	0.88	-	[10]
ZnKPO ₄ ·6H ₂ O	900	890	3800	0.82	0.79	600	[11]
Ni ₄ Sb ₄ S ₄	860	840	3350	0.77	0.69	-	[12]
Zn(C ₃ H ₄ N ₂) ₆ Cl ₂ ·4H ₂ O	1051	823	3625	0.78	0.75	450	Present work

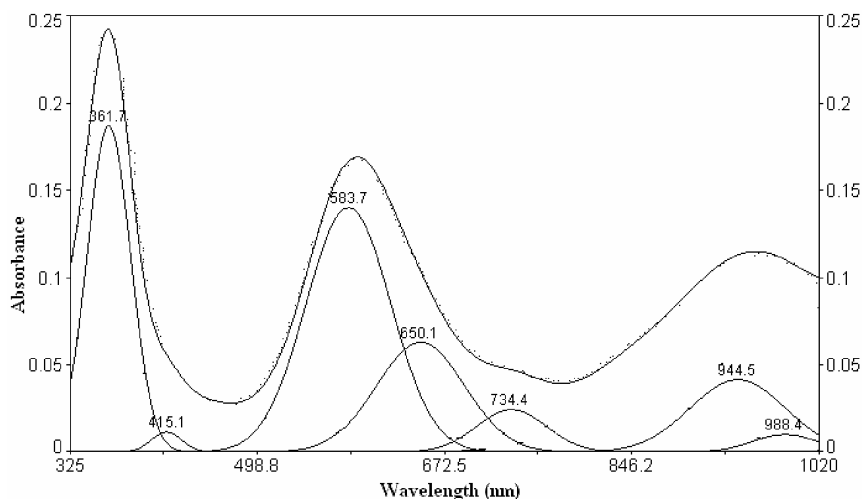


Fig. 2 Deconvoluted optical spectrum of Ni(II)/HZDT recorded at room temperature. (.... observed spectrum; — fitted spectrum).

A close look at Fig. 1, indicates that the band headed at 16949 cm^{-1} (590 nm) and 10449 cm^{-1} (957 nm) appear to be very broad. Hence the spectrum has been deconvoluted using standard program peak fit v4.11 (SYSTAT Software Inc.) and the deconvoluted spectrum is presented in Fig.2. Here, one could notice a maximum of seven bands at 10117, 10588, 13617, 15382, 17132, 24091 and 27647 cm^{-1} respectively. The spin forbidden transition ${}^3A_{2g} \rightarrow {}^1T_{2g}(D)$ is buried under ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and not seen due to its very low intensity at 415.1 nm (24091 cm^{-1}). The transitions corresponding to ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ are further split into doublets. The all band position which are observed and calculated are given in the Table 2. The optical spectrum of Ni(II)/HZDT is almost invariant in methanol, hexane and dichloromethane solvents.

Table 2 Peak head position of d-d transitions in Ni(II)/HZDT.

Transition from ${}^3A_{2g}(F)$	Band Position				
	Observed (nm)	Observed (cm^{-1})	Deconvoluted (nm)	Deconvoluted (cm^{-1})	Calculated (cm^{-1})
${}^3T_{1g}(P)$	365	27397	361.7	27647	27487
${}^1T_{1g}(D)$	-	-	415.1	24091	23871
${}^3T_{1g}(F)$	591	16949	583.7	17132	16860
${}^1E_g(D)$	731	13686	650.1	15382	16860
${}^1E_g(D)$	731	13686	734.4	13617	13686
${}^3T_{2g}(F)$	957	10449	944.5	10588	10515
			988.5	10117	

In octahedral symmetry associated with spin orbital interaction, ${}^3A_{2g}$ will be transformed as Γ_5 where as ${}^3T_{2g}$ and ${}^3T_{1g}$ split into $\Gamma_3 + \Gamma_4 + \Gamma_5 + \Gamma_2$ and $\Gamma_5 + \Gamma_3 + \Gamma_4 + \Gamma_1$ respectively [13]. Hence the each transition corresponding to $A_{2g} \rightarrow T_{2g}$ and $A_{2g} \rightarrow T_{1g}$ split into four components. In tetragonal distortion, T_{1g} and T_{2g} terms split further into $A_2 + E$ and $B_2 + E$ and in the case of trigonal distortions, each terms namely T_{1g} and T_{2g} are split into further components as $A_2 + E$ and $A_1 + E$; for this reason in both trigonal and tetragonal distortions the transitions correspond to ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ are expected to split into doublets. In the present study, when the spectrum is deconvoluted, one could monitor the transitions corresponding to ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ split into not more than two components respectively. This evidently explains that the spin-orbital interaction can be ignored. Therefore the trigonal (or) tetragonal distortions may rule over the d-d transition, which results in splitting of bands into doublets. When the splitting of terms is governed by tetragonal distortion, the E_g term splits into $A_1 + B$, where as, this is not the case with trigonal distortions. Consequently the transition corresponding to ${}^3A_{2g} \rightarrow {}^1E_g$ will split into two components, if the distortion is

tetragonal. However, in the present investigation, the $^3A_{2g} \rightarrow ^1E_g$ transition remains unsplit. Hence, one can pronounce from the optical studies that the geometry around the Ni(II) ion has undergone trigonal distortion rather tetragonal distortion, as also confirmed by EPR, in which the symmetry is proved to be orthorhombic, as mentioned earlier [5].

3.2 Cu(II) in MPPH

For the ions with d^9 configuration, all the broad spin absorption bands are related to the transitions between the levels derived from $^2D \rightarrow ^2E_g + ^2T_{2g}$. The ground state 2E_g is often found to split under Jahn-Teller effect, which causes distortion in the octahedral symmetry. In a tetragonally distorted octahedral symmetry (C_{4v}), 2E_g splits into $^2B_{1g}$ (corresponds to $d_{x^2-y^2}$ orbital) and $^2A_{1g}$ (corresponds to d_z^2 orbital) while the $^2T_{2g}$ splits into $^2B_{2g}$ (corresponds to d_{xy} orbital) and 2E_g (corresponds to d_{yz} and d_{xz} orbital levels). The energy values of different terms in tetragonal field are given in the literature [14] and therefore, three bands are expected for a copper(II) complex [15,16]. The optical absorption spectrum of the Cu(II)/MPPH sample is shown in Fig.3. Since the spectrum consists of three bands, the site symmetry of Cu(II) is presumed to be D_{4h} . The three bands observed at 9506, 10661 and 12562 cm^{-1} .

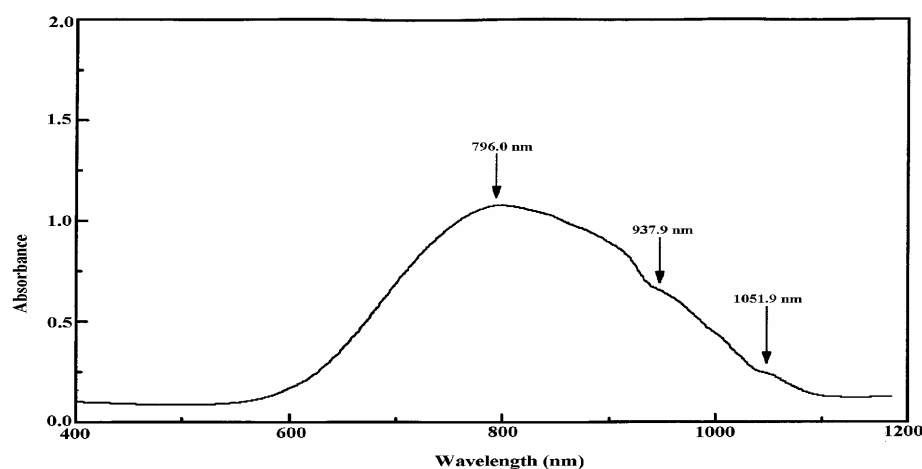


Fig. 3 Optical spectrum of Cu(II)/MPPH at room temperature in methanol solvent.

Table 3 Comparison of crystal field parameters (cm^{-1}) for a few copper(II) complexes.

Compound	Dq	Ds	Dt	Ref.
Cu(HCO ₂) ₂ ·4H ₂ O	1120	1600	560	[17]
Cu ²⁺ :CaC ₄ H ₄ O ₆ ·4H ₂ O	1000	1540	470	[18]
Cu ₈ (Si ₄ O ₁₁) ₄ ·OH ₄	1070	1674	327	[19]
Cu ₅ (SiO ₃) ₄ ·OH ₂	1333	1565	380	[20]
ZnCu(CO ₃) ₂ ·(OH) ₂	1250	1600	520	[20]
Cu ²⁺ :MgKPO ₄ ·6H ₂ O	1066	1630	597	Present work

The bands in the range 5000-15000 cm^{-1} are characteristic of d-d transitions in Cu(II) systems. The broad band at 12562 cm^{-1} is characteristic of octahedral Cu(II). Based on these assignments and as mentioned above, octahedral field parameter Dq and tetragonal field parameter Ds and Dt are evaluated from the observed absorption bands. The values of the parameters are found to be 1066, 1630 and 597 cm^{-1} respectively. In tetragonal field, the values of Dt and Dq will have same sign if there is an axial elongation and will have opposite sign if the complex has axial compression [21]. In the present case, the values of Dt and Dq are found to have the same sign. This confirms the lowering of octahedral symmetry to an axially elongated tetragonal of

Cu(II) ion MPPH. A few copper systems having related crystal field parameters are given in Table 3, for comparison. Single crystal EPR studies of Cu(II)/MPPH indicates orthorhombic symmetry for the Cu(II) ion [7]. A close look at the three g values (2.307, 2.277 and 2.094) indicates that two of the three g values, i.e., 2.307 and 2.277 are close and hence, one can say that the copper complex is having axially elongated tetragonal symmetry. Hence, the optical studies confirm the EPR results. The complex is insoluble in other solvents.

4 Conclusion

The optical studies for Ni(II)/HZDT indicate three spin allowed and one spin forbidden transitions for Ni(II) ion. The various optical parameters have been calculated using the optical and EPR data and the values are found to be well in agreement with the reported values. The reduction in spin orbit coupling is around 30% indicating a slightly higher covalency for the Ni(II)-imidazole bond, compared to other transition metal ion-imidazole bonds found in this host lattice. The symmetry around the metal ion is distorted octahedron. The optical study of Cu(II) doped magnesium potassium phosphate hexahydrate shows that Cu(II) ion has tetragonal symmetry with axial elongated local symmetry whereas the EPR study shows the electrostatic field around the Cu(II) ion is orthorhombic. The octahedral field parameter Dq , the tetragonal field parameter Ds and Dt are evaluated.

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References

- [1] P. Sambasiva Rao and S. Subramanian, *J. Mag. Reson.* **22**, 191 (1975).
- [2] P. Sambasiva Rao and S. Subramanian, *Mol. Phys.* **39**, 935 (1980).
- [3] P. Sambasiva Rao and S. Subramanian, *Mol. Phys.* **54**, 415 (1985).
- [4] P. Sambasiva Rao and S. Subramanian, *Mol. Phys.* **54**, 429 (1985).
- [5] K. Velavan, T. M. Rajendiran, R. Venkatesan, and P. Sambasiva Rao, *Solid State Commun.* **122**, 15 (2002).
- [6] H. Elliott, B. J. Hathaway, and R. C. Slade, *Inorg. Chem.* **669** (1966).
- [7] P. Prabukanthan, K. Velavan, R. Venkatesan, and P. Sambasiva Rao, *Solid State Commun.*, **136**, 285 (2003).
- [8] C. Sandmark and C. I. Branden, *Acta. Chem. Scand.* **21**, 993 (1967).
- [9] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan* **9**, 753 (1954).
- [10] J. Owen and J. H. M. Thronley, *Rep. Prog. Phys.* **29**, 675 (1966).
- [11] N. Madhu, R. V. S. S. Ravikumar, A. V. Chandrasekhar, B. J. Reddy, and Y. P. Reddy, *Physica Scripta* **58**, 345 (1998).
- [12] S. N. Reddy, R. V. S. S. N. Ravikumar, B. J. Reddy, and Y. P. Reddy, *Indian J. Eng. Mater. Sci.* **7**, 459 (2000).
- [13] S. N. Rao, S. Vadanad, R. Ravikumar, R. V. S. S. N. Ravikumar, and Y. P. Reddy, *Solid state Commun.* **92**, 815 (1994).
- [14] A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 19 (1984).
- [15] M. A. Hitchman and P. J. Cassidy, *Inorg.Chem.* **18**, 1745 (1975).
- [16] M. A. Hitchman, *Trans.Met.Chem.* **9**, 1 (1985).
- [17] D. E. Billing and B. J. Hathway, *J. Chem.Soc. (A)* 1516 (1968).
- [18] Y. K. R. Swamy, Y. P. Reddy, and B. Reddy, *J. Physica* **B89**, 202 (1980).
- [19] P. Sreeramulu, K. M. Reddy, A. S. Jacob, B. J. Reddy, and Y. P. J. Reddy, *Cryst. Spet. Res.* **20**, 93 (1990).
- [20] S. Vedanand, B. Madhu Sudhna, B. J. Reddy, and P. S. Rao, *Bull Mater. Sci.* **19**, 1089 (1996).
- [21] J. Ferguson, T. E. Wood, and H. Guggenheim, *J. Inorg.Chem.* **14**, 177 (1975).