# AN EPR STUDY OF ELECTRONIC STRUCTURE AND SYMMETRY OF SOME MOLECULAR PARAMAGNETIC SPECIES IN ALKALI HALIDE CRYSTALS

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# PREFACE

EPR studies on some paramagnetic ($d^7$ or $d^9$) cyanide complexes of Ni, Co and Fe, stabilized in NaCl and/or KCl lattices, and on $BO_2$ radical ions in KCl, KBr, KI and NaCl lattices, are reported in this thesis. The studies were mostly carried out at 93K and at X-band microwave frequencies. All the paramagnetic species investigated were produced in suitably doped crystals, by a combination of irradiation and heat treatment. The identification of the species thus produced is based on the g factors and the hfs in the EPR spectrum.

Transition metal cyanide complexes are of special interest because the $CN^-$ ligand has a $\pi$-orbital system. In these complexes, $\pi^*$ orbitals on the $CN^-$ ligand also participate in the metal-ligand bonding. Paramagnetic transition metal complexes with the metal ion configuration $d^n$ for $n > 6$ are generally unstable, but could be stabilized by producing these complexes in a suitable diamagnetic host lattice. In the present work, low spin $d^7$ Ni, Co and Fe complexes of type $[M(CN)_4 . Cl_2]^{x-}$ have been successfully produced and stabilized in KCl and/or NaCl. This was achieved, as mentioned above, by a suitable combination of irradiation and heat treatment of the crystals doped with stable diamagnetic $Ni(CN)_4^{2-}$, $Co(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ complexes. $[Fe(CN)_4.(CN)Cl]^{5-}$ and $[Fe(CN)_4.(NC)Cl]^{5-}$ complexes have also been identified in NaCl and KCl, respectively. The unpaired electron in all these complexes is in the $d_{z^2}$ ($a_{1g}^*$) orbital, and the spin Hamiltonian parameters show systematic variations. These are discussed in terms of changes in the nature of bonding in these complexes in relation to the charge state of the metal ion, the host lattice spacings and the nature of the axial ligands. The above discussion also covers the available data on similar low spin $d^7$ complexes of the type $[M(CN)_4.XY]^{x-}$, where M is $Co^{2+}$, $Rh^{2+}$ or $Fe^+$, the axial ligands X, Y being $NC^-$, $CN^-$ or $Cl^-$. In addition to showing that $CN^-$ and $NC^-$ are much stronger ligands than $Cl^-$, this study also points out the importance of back-bonding in the case of $CN^-$ and $NC^-$ ligands.

The $Ni^+(d^9)$ complex $[Ni(CN)_4.Cl_2]^{5-}$ has been identified in X or $\gamma$ irradiated $NaCl:Ni(CN)_4^{2-}$ crystals. The stabilization of this complex, with the unpaired electron in the highly destabilized $d_{x^2-y^2}$ $(b_{1g}^*)$ orbital, is presumably due to a distortion of the $(CN^-)_4$ plane, the symmetry changing from $D_{4h}$ to $D_{2d}$. This leads to the lowering of the $d_{x^2-y^2}$ orbital, resulting in the observed smaller $(x^2-y^2)$ - xy separation of 11400 $cm^{-1}$. The distortion of the $(CN^-)_4$ plane necessarily brings in strong coupling of the complex to the lattice, which is reflected in (a) spin-lattice relaxation broadening of the EPR lines at RT, which is uncommon for a highly covalent complex, and (b) the strong temperature dependence of the g factors (the reduction in $\Delta g$ from RT to 93K is 24%, the largest ever observed for a $d^9$ complex).

Anomalous intensity distribution is observed in the EPR spectra of $[Ni(CN)_4.Cl_2]^{3-}$ and $[Ni(CN)_4.Cl_2]^{5-}$ complexes in NaCl.

Also, the intensity distribution does not reflect the cubic symmetry of the host lattice. This shows that the planar $Ni(CN)_4^{2-}$ complex ions are unequally distributed in the three equivalent $\{100\}$ planes of the NaCl lattice. A systematic study revealed that the planar $Ni(CN)_4^{2-}$ complex enters the lattice preferentially, with the $(CN^-)_4$ plane parallel to the growth plane of the crystal which is a $\{100\}$ plane.

The complex $[Ni(CN)_4 \cdot Cl_2]^{3-} + \boxplus$ is formed in $NaCl{:}Ni(CN)_4^{2-}$ crystals on X irradiation at LAT. This complex converts to $[Ni(CN)_4 \cdot Cl_2]^{3-} + 2\ \boxplus$ complex on warming the crystals to RT, by capturing a cation vacancy. This made possible a determination of the energy of migration of cation vacancies in NaCl lattice, using the EPR technique.

$BO_2$ molecular ions are identified in quenched alkali halide crystals doped with boric acid or borax. These ions undergo free rotation in the lattice at RT. The motion freezes gradually, as the temperature is lowered. Temperatures lower than 93K are required to completely freeze the motion of the radicals. It was noted during this study that in addition to $BO_2$ and possibly $BO_3^{2-}$, some other boron-oxygen radicals also show $^{11}B$ hf splitting of about 12 gauss. An identification of the radiation damage centers in borate glasses on the basis of the $^{11}B$ hfs alone, is therefore likely to lead to erroneous conclusion.

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