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Intraligand Charge Transfer Spectrum of Biacetyl-bis-(mercaptoethylimine)-nickel(II)

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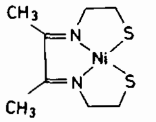
Electronic transitions of coordination compounds are classified according to the origin of the orbitals involved in these transitions. Dependent on the metal, its oxidation state, and the nature of the ligands ligand-field (LF), metal–to-ligand-charge-tranfer (MLCT), ligand–to-metal-charge-transfer (LMCT), and intraligand (IL) transitions may occur in mononuclear complexes. In mixed-ligand complexes ligand–to-ligand-charge-tranfer (LLCT) transitions from one ligand to another are possible [1]. We report here our observation on a related but new type of electronic transition: intraligand-charge-transfer (ILCT), which is mediated by the central metal.

The complex biacetyl-bis(mercaptoethylimine)-nickel(II) (NiBE)



was prepared by Thompson and Busch in 1962 [2]. They also reported the impressive solvochromic behavior of this compound but without an explanation. During our recent work on LLCT spectra [1] we realized that the electronic structure of NiBE is related to that of M(II)(diimine)(1,2-dithiolate) with M = Ni [3] and Pt [1]. These complexes are also strongly solvochromic.

We suggest that the intense visible absorption band of NiBE (Fig. 1) which is responsible for the solvochromic behavior belongs to a sulfur-to-diimine ILCT transition within the tetradentate ligand, mediated by the nickel ion. Although attempts to prepare the free ligand BEH_2 were not successful [2], the non-coordinated BEH_2 is not expected to show the ILCT absorption since the sulfur atoms and the diimine unit are separated by electronically insulating $-CH_2-CH_2-$ groups. Only the metal mediates then the ILCT interaction.

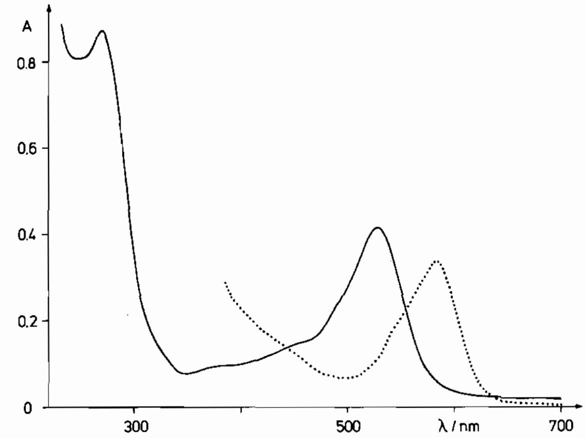


Fig. 1. Absorption spectrum of 2.73×10^{-4} *M* NiBE in CH_3CN (solid line) and of 6.75×10^{-5} *M* in CCl_4 (dotted line); 1 cm cell.

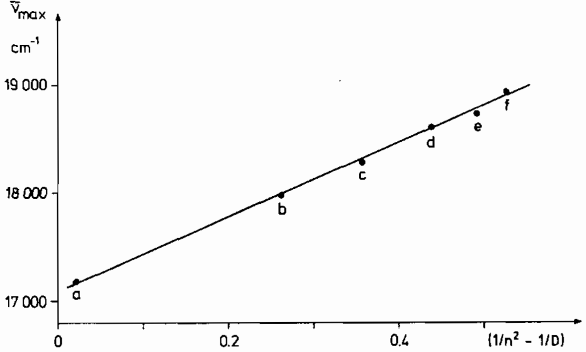


Fig. 2. Solvent dependence for the ILCT band of NiBE; a: Carbontetrachloride, b: Chlorobenzene, c: Pyridine, d: Dimethylsulfoxide, e: Acetone, f: Acetonitrile.

The solvent dependence of the ILCT band of NiBE is in accordance with an equation derived by Hush for intervalence transitions [4]. The energy at the band maximum $\tilde{\nu}_{max}$ is proportional to $(1/n^2) - (1/D)$ where n^2 and D are the optical and static dielectric constants of the solvent (Fig. 2).

A MLCT transition from Ni(II) to the diimine component of BE^{2-} as origin of the solvochromic behavior can be excluded. Such an absorption band should occur at much higher energies due to the resistance of Ni(II) towards oxidation. Accordingly, diiminenickel(II) complexes as [Ni(II)(biacetyl-

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bisanil)$_2$]$^{2+}$ [5] do not display long-wavelength MLCT bands in their absorption spectra.

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