Optical outer-sphere ligand to metal charge transfer in bis(*N*-ethylsalicylaldiminato)nickel(II)/tris(oxalato)ferrate(III)

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Abstract

A mixture of [Ni(Et-sal)$_2$] (=bis(*N*-ethylsalicylaldiminato)nickel(II)) and [Fe(Ox)$_3$]$^{3-}$ (tris(oxalato)ferrate(III) ion) displays longwavelength absorption at $\lambda_{max}=472$ nm. This new absorption band is assigned to an outer-sphere LMCT transition from the coordinated ethylsalicylaldimine of [Ni(Et-sal)$_2$] to Fe(III) of [Fe(Ox)$_3$]$^{3-}$. Mixing free ethylsalicyldimine or [M(Et-sal)$_2$] (where M=Co(II), Cu(II) or Zn(II)) and [Fe(Ox)$_3$]$^{3-}$ also shows the same phenomenon; the maximum of the new absorption band is independent on the nature of the metal.

Introduction

Optical electron transfer between electronically weakly coupled redox metal complexes is of particular interest with regard to photoredox processes [1–3]. It may take place from the ligand to the metal (LMCT) [4], from the metal to the ligand (MLCT) [2, 3], from one metal to another metal (MMCT) [5] or from one ligand to another ligand (LLCT) [6–8]. Independently of the above classification, optical charge transfer (CT) transitions between a reducing and an oxidizing metal center can be observed, either if both metals are bonded via bridging ligands in a dinuclear complex (inner sphere) [9], or are in close contact in separated metal complexes (outer sphere) [10, 11]. The latter CT transitions are commonly observed in ion pairs. The present study gives evidence for the occurrence of an optical outer-sphere LMCT in a non-ion pair system. However, a neutral complex [Ni(Et-sal)$_2$] (=bis(*N*-ethylsalicylaldiminato)nickel(II)) and an anionic complex [Fe(Ox)$_3$]$^{3-}$ (=tris(oxalato)ferrate(III) ion) were selected.

Experimental

The complexes [M(Et-sal)$_2$] where M=Co(II), Ni(II), Cu(II) and Zn(II), [Fe(Et-sal)$_3$] [12] and K$_3$[Fe(Ox)]$_3$] [13] were prepared by literature procedures and their purities were checked by elemental analyses and spectral data. Spectrophotometric measurements were recorded on a Shimadzu UV-200 S double beam spectrophotometer, using a rectangular cell of 1 cm pathlength against solvent as the blank.

Resuls and discussion

Upon mixing alcoholic [Ni(Et-sal)$_2$] (yellow) and aqueous [Fe(Ox)$_3$]$^{3-}$ (slightly greenish yellow), the solution turned reddish immediately. This red colour is caused by a new absorption with a maximum at 472 nm (Fig. 1), which is not due to a chemical reaction but originates from the interaction between the two complexes. At a fairly high equimolar concentration of both complexes ($>5\times10^{-4}$ M), this absorption follows the Lambert-Beer law with $\epsilon=920$ at the 472 nm maximum. It is suggested that this new absorption is assigned to an outer-sphere LMCT transition from the coordinated ethylsalicylaldimine of [Ni(Et-sal)$_2$] to Fe(III) of [Fe(Ox)$_3$]$^{3-}$. This assignment is based on the following considerations. The mixtures [M(Et-sal)$_2$]/[Fe(Ox)$_3$]$^{3-}$ where M=Co(II), Cu(II) or Zn(II), also exhibit the same behaviour; the maximum of the new absorption was independent of the nature of the metal (Table 1). This indicates that the new absorption is certainly due to the transition from coordinated ethylsalicylaldimine of [M(Et-sal)$_2$] to Fe(III) of [Fe(Ox)$_3$]$^{3-}$.

The spectrum of a 50% ethanolic solution of the free ethylsalicylaldimine/[Fe(Ox)$_3$]$^{3-}$ equimolar mixture also displays the ethylsalicylaldimine to Fe(III) of [Fe(Ox)$_3$]$^{3-}$ CT absorption at $\lambda_{max}=488$ nm,

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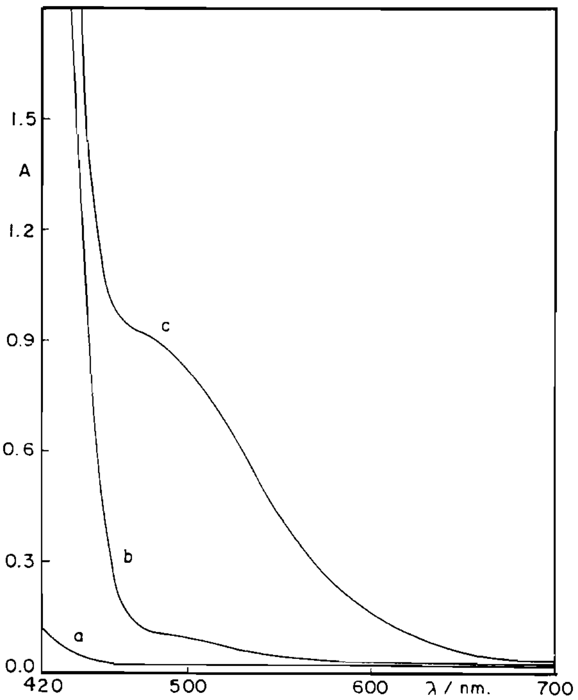

Fig. 1. Electronic absorption spectra of aqueous 1×10^{-3} M $K_3[Fe(Ox)_3]$ (a), ethanolic 1×10^{-3} M $[Ni(Et\text{-}sal)_2]$ (b) and 50% ethanolic solution containing 1×10^{-3} M $K_3[Fe(Ox)_3]$ and 1×10^{-3} M $Ni(Et\text{-}sal)_2$ (c); 298 K, 1 cm cell.

TABLE 1. LMCT absorption of 50% ethanolic solution of $[M(El\text{-}sal)_2]/[Fe(Ox)_3]^{3-}$ equimolar mixture

M	λ_{max} (nm)	ϵ (cm^{-1} mol^{-1} l)
Co	470	890
Ni	472	920
Cu	472	980
Zn	471	820

$\epsilon = 440$ (Fig. 2). The blue shift of this CT absorption which takes place when free ethylsalicylaldimine is replaced by the coordinated one of $[Ni(Et\text{-}sal)_2]$ may be related to the stabilization of the occupied ligand orbitals which takes place upon coordination. Other observations also support the LMCT assignment of the new absorption of $[Ni(Et\text{-}sal)_2]/Fe(Ox)_3]^{3-}$; the longwavelength absorption of $[Fe^{III}(Et\text{-}sal)_3]$ at $\lambda_{max} = 490$ nm is clearly assigned to an inner-sphere LMCT transition from the coordinated ethylsalicylaldimine to Fe(III) [12]. It is then interesting to compare the energy of the ethylsalicylaldimine to Fe(III) LMCT transition of $[Fe^{III}(Et\text{-}sal)_3]$ (inner sphere) and $[Ni(Et\text{-}sal)_2]/[Fe(Ox)_3]^{3-}$ (outer sphere). The increase of the energy of this transition in $[Ni(Et\text{-}sal)_2]/[Fe(Ox)_3]^{3-}$ is certainly due to a distance effect.

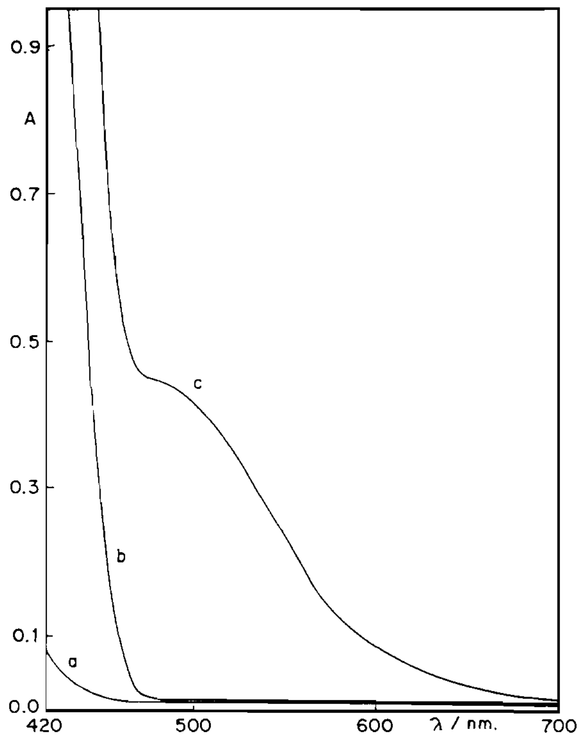

Fig. 2. Electronic absorption spectra of aqueous 1×10^{-3} M $K_3[Fe(Ox)_3]$ (a), ethanolic 1×10^{-3} M ethylsalicylaldimine (b) and 50% ethanolic solution containing 1×10^{-3} M $K_3[Fe(Ox)_3]$ and 1×10^{-3} M ethylsalicylaldimine (c); 298 K, 1 cm cell.

A CT transition requires larger energies if the distance between an electron donor and acceptor increases [5, 14]. The distance between (Et-sal) and Fe(III) is doubtless larger in the $[Ni(Et\text{-}sal)_2]/[Fe(Ox)_3]^{3-}$ mixture when compared with $[Fe(Et\text{-}sal)_3]$.

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