Magnesium Cation-perturbed Charge-transfer Interactions

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The biological significance of charge-transfer (CT) interactions between an electron-donor and an electron-acceptor is to date well recognized and established; for instance CT interactions play an important role in the protein–nucleic acid recognition [1], in the primary steps of electron-transfer reactions [2] and in the action mechanism, at molecular level, of particular drugs with natural receptor molecules [3].

In the case of π–π stacking having a partial CT character, a perturbation of the π-electron distribution of one or both of the heteroaromatic interacting molecules is strongly reflected in the CT interaction itself [4, 5]. Among the possible processes polarizing electron-acceptors or -donors having n-binding sites, the direct complexation between bases and metal cations of Groups IA and IIA [6] should be carefully considered.

These interactions have been studied by us [7, 8] through electron absorption spectroscopy, a technique suitable for checking possible perturbations of a π–π CT associate; indeed the so-called CT absorption transitions, which generally are observed in the electronic absorption spectra of a π–π acceptor–donor complex, will be modified if the electron-donor or -acceptor character of the interacting species is altered through an ion-binding process.

Using an appropriate aprotic solvent like acetonitrile (MeCN), some experimental evidence along these lines is reported in the present note.

4-Methoxy-pyridine 1-oxide (**D1**) and 1-methoxy-3-pyridone (**D2**) were selected as π-electron-donors and 2,3,5,6-tetrachloro-*p*-benzoquinone (**A**)** as a π-electron-acceptor. The choice of **A** is connected with its strong π-electron-acceptor [9] and low n-donor character (its electronic absorption spectrum in MeCN is indeed not affected by the presence of Mg(II) up to 1 mol/l). *Vice versa* **D1** and **D2** are good π-electron-donors with respect to **A** and have also a self-evident n-ligand character towards Mg(II) ions[§].

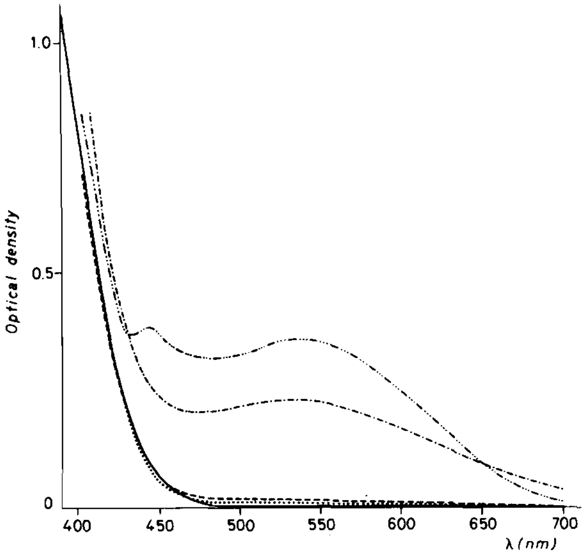

Fig. 1. Ultraviolet absorption spectra in pure acetonitrile of: (——) 2,3,5,6-tetrachlorobenzoquinone (chloranil) 5×10^{-3} M; the spectrum is not modified by the addition of Mg(II) ions (perchlorate) up to 1 M; (· — · — ·) chloranil 5×10^{-3} M + 4-methoxypyridine 1-oxide 10^{-2} M; (······) chloranil 5×10^{-3} M + 4-methoxypyridine 1-oxide 10^{-2} M + $Mg(ClO_4)_2$ 1 M; (··· — ··· —) chloranil 5×10^{-3} M + 1-methoxy-3-pyridone 10^{-2} M; (— — —) chloranil 5×10^{-3} M + 1-methoxy-3-pyridone 10^{-2} M + $Mg(ClO_4)_2$ 1 M. All absorption spectra were recorded at room temperature with a Cary 17 spectrophotometer using 1-cm cells.

As expected for CT complexes, solutions containing a mixture of **A** and **D1** or **A** and **D2** were found to have an intense electronic absorption band in the 400–700 nm region of the spectrum (Fig. 1) where the individual components showed no electronic transitions; the observed maxima positions are consistent with the fact that **D2** is a stronger donor than **D1** [10]. The CT transitions disappear if Mg(II) ions are present in the same solution: the direct interaction between Mg(II) and the bases (through their exocyclic oxygens) influence the donating capabilities of **D1** and **D2** in such a way that they are no longer electron-donors with respect to **A**. As previously described [7], the small amount of water present in the solvent used does not significantly

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**A commercial sample of 2,3,5,6-tetrachloro-*p*-benzoquinone (Fluka) was purified by sublimation. 4-Methoxypyridine 1-oxide and 1-methoxy-3-pyridone were obtained as described in ref. 10.

[§] Addition of $Mg(ClO_4)_2$ (up to 1 M) to the MeCN solutions of **D1** and **D2** gives rise to a blue shift of the observed absorption bands in pure MeCN (from 282 to 255 nm for **D1**; from 355 to 319 nm and from 268 to 250 nm for **D2**, in analogy with the corresponding protonated forms).

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influence the direct ion–ligand interaction; such conclusions also emerge from a recent report [11].

The present findings confirm the important role that alkali and alkaline earth cations play in a non-aqueous environment; they might indeed interact with bases leading to the formation of more or less polarized transients and consequently promote or enhance $\pi-\pi$ stacking associations.

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