Optical properties of bis(cyclopentadienyl)magnesium: excimer-type luminescence of the bis(cyclopentadienyl) ligand frame

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Abstract

The electronic spectra of solid $MgCp_2$ (Cp = cyclopentadienyl) show features which indicate the presence of intramolecular inter-ligand interactions. The fluorescence of $MgCp_2$ (λ_{max} = 363 nm) undergoes a considerable Stokes shift which is apparently caused by a bonding attraction between both Cp rings in the excited state. An additional phosphorescence of the $(Cp^-)_2$ fragment (λ_{max} = 535 nm) appears at 77 K.
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1. Introduction

Excited states which are based on intramolecular interactions between separate ligands of a metal complex have been examined to some extent. These studies have been largely restricted to ligand-to-ligand charge transfer (LLCT) excited states [1,2]. In this case a donor and an acceptor ligand are simultaneously coordinated to a metal which mediates the CT interaction between both ligands. In contrast, very little is known about excited states which are generated by the interaction of identical ligands as they occur in homoleptic complexes. Attractive targets for such an investigation should be metallocenes with a sandwich structure.
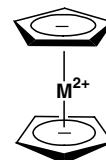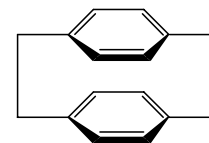
sandwich-type metallocene   [2.2]paracyclophane

The cyclopentadienyl anion $(C_5H_5^- = Cp^-)$ is an aromatic 6π-electron system. The interaction of both Cp^- rings of sandwich-type metallocenes may be compared with that which takes place between benzene rings in simple paracyclophanes [3,4]. Another analogy could be drawn to the electronic interaction in arene excimers [4–6]. They are composed of two parallel arene molecules and exist only in the excited state. Unfortunately, most metallocenes are less appropriate for the examination of interligand excited states because the metal participates in low-energy transitions [7–9]. In particular, metal-centered (MC), ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT) transitions can obscure interligand transitions. This

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problem is encountered, for example, in ferrocene and related metallocenes of transition metals. Accordingly, a suitable metal should not engage in low-energy transitions. We explored this possibility and selected $MgCp_2$ (magnesocene) for the present study. Mg^{2+} does not participate in interfering electronic transitions. Moreover, the Mg^{2+} cation should be sufficiently small ($r \sim 0.65$ Å) to facilitate the interaction of both Cp^- rings.

2. Experimental

2.1. Materials

The compound $MgCp_2$ was commercially available in high purity ("PURATREM") from Strem. It was manipulated and stored under argon in a glove box.

2.2. Instrumentation

Absorption spectra were measured with a Varian Cary 50 or a Kontron Uvikon 860 absorption spectrophotometer. Emission and excitation spectra were recorded on a Hitachi 850 fluorescence spectrometer equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm.

3. Results and discussion

In solution it is difficult to prevent some decomposition of $MgCp_2$ by water and oxygen even when present in traces only. This leads to the generation of impurities which show long-wavelength emissions. Accordingly, the electronic spectra of $MgCp_2$ were only recorded for the solid compound. Fortunately, the solid contains $MgCp_2$ as isolated molecules which are not expected to show a strong intermolecular interaction since the Cp planes of neighbouring molecules have an orthogonal orientation [10]. Indeed, the excitation spectrum of $MgCp_2$ (Fig. 1) which displays shoulders at approximately 240 and 215 nm agrees rather well with the absorption spectrum in solution [11].

$MgCp_2$ is luminescent (Fig. 1). The shorter wavelength emission at $\lambda_{max} = 363$ nm is certainly a fluorescence since it appears at r.t. and overlaps with the excitation spectrum. The fluorescence spectrum exhibits structural features which are probably related to ligand vibrations of $MgCp_2$ [12]. The low-temperature emission spectrum of $MgCp_2$ shows an additional phosphorescence (Fig. 1) at $\lambda_{max} = 535$ nm. Again, the vibronic structure of the phosphorescence band can be clearly recognized. The excitation spectrum (Fig. 1) is the same for the fluorescence and the phosphorescence.

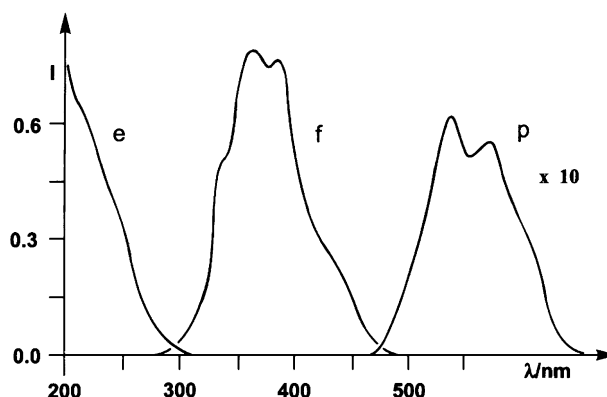The absorption spectrum of Cp^- as it occurs in solutions of LiCp, NaCp and KCp exhibits a shoulder near

Fig. 1. Electronic excitation (e, $\lambda_{em} = 363$ nm), fluorescence (f, $\lambda_{exc} = 280$ nm) and phosphorescence (p, $\lambda_{exc} = 280$ nm) spectra of solid $MpCp_2$ under argon at room temperature (e, f) and at 77 K (p), intensity in arbitrary units.

220 nm while the first absorption maximum appears below 200 nm [11,13]. We suggest that the longer-wavelength feature of $MgCp_2$ near 240 nm which is observed in the absorption as well as in the excitation spectrum is associated with the ligand–ligand interaction in $MgCp_2$. A simple MO model for the staggered conformation of both Cp^- rings as it occurs in solid $MgCp_2$ demonstrates that the π-orbital overlap of both Cp^- rings causes a splitting of the π-orbitals which are degenerate for the non-interacting Cp^- rings [14] (Fig. 2). This splitting leads, in turn, to the decrease of the HOMO/LUMO gap and explains the existence of the longer-wavelength feature in the spectrum of $MgCp_2$.
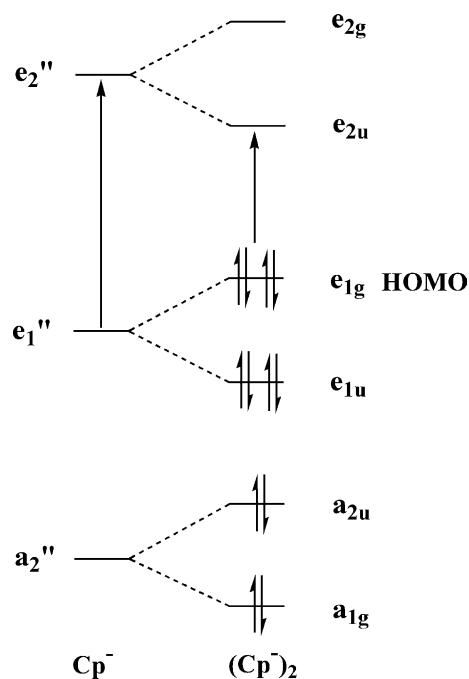

Fig. 2. Qualitative MO scheme for $MgCp_2$ (D_{5d} symmetry) adopted from [14].

A comparison of the electronic spectra of Cp^- and benzene is quite informative since both species have closely related electronic and structural features. The $\pi\pi^*$ transitions of benzene occur at lower energies with the longest-wavelength band at $\lambda_{max} = 255$ nm [15,16] compared to Cp^- which shows its longest-wavelength absorption feature at $\sim$220 nm [11,13]. The ligand–ligand interaction of $MgCp_2$ which causes the red shift of the absorption to 240 nm finds its counterpart in the transannular interaction of [2.2]paracyclophane [3,4]. In this case the ethane bridges enforce a rather strong arene–arene coupling which shifts the longest-wavelength absorption to approximately 315 nm [3,4,17].

The fluorescence of simple arenes undergoes a very moderate Stokes shift since $\pi\pi^*$ excitation in the delocalized aromatic π-electron system is not associated with a large structural rearrangement. For benzene this Stokes shift amounts to approximately 3400 cm^{-1} [16]. For the isolated Cp^- ring this shift is not known but expected to be comparable. However, $MgCp_2$ shows a rather large Stokes shift ($\Delta \sim 14,000$ cm^{-1}). This can be explained on the basis of the ligand–ligand interaction (Fig. 2). Both negatively charged Cp rings repel each other but are forced to stick together by the electrostatic attraction with Mg^{2+}. In the ground state this interaction does not lead to any bonding between both Cp^- rings (nonbonding interaction) [14], but in the lowest-energy excited state a formal bond between both Cp^- rings is formed since an electron is promoted from an antibonding (e_{1g}) to a bonding (e_{2u}) MO with respect to the interligand interaction. As a consequence, both Cp^- rings should come closer together. The large Stokes shift is then explained by a simple potential energy diagram (Fig. 3). Again, this behavior is qualitatively duplicated by [2.2]paracyclophane although this effect is smaller ($\Delta \sim 8000$ cm^{-1}) [18] in this case, probably because the arene–arene interaction is already considerable in the ground state. The excimer formation of arenes is another examp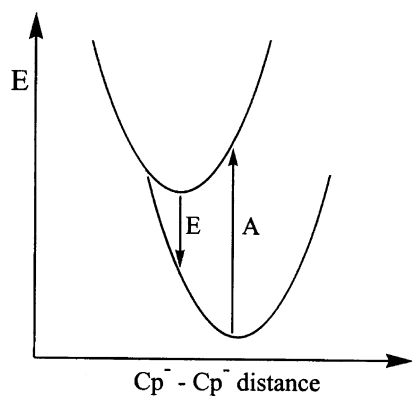le of this type of interaction [4–6]. In the ground state there is no attractive interaction between separate arene molecules. In contrast, in the excited state dimer formation occurs which causes large red shifts from absorption to fluorescence.

The phosphorescence of $MgCp_2$ appears only at low temperatures since spin–orbit coupling is rather weak in such systems. In this context it should be mentioned that in $GdCp_3$ the heavy-atom effect of the central metal induces a r.t. phosphorescence of the ligand system [19]. In this case the ligand–ligand interaction is based on the $(Cp^-)_3$ fragment. Other metallocenes such as $RuCp_2$ [20–25] and $OsCp_2$ [26] exhibit also a phosphorescence. However, this emission originates from dd triplets which are apparently located below the intraligand states.

Finally, it is of interest that the ligand–ligand interaction of $MgCp_2$ resembles in some respect the metal–metal interaction in $[Pt_2^{II}(\mu\text{-}P_2O_5H_2)_4]^{4-}$ [27]. In the ground state both platinum centers are essentially kept together by the bridging ligands. The metal–metal bond order is zero although a small bonding interaction exists. In the lowest excited state an electron is promoted from an antibonding to a bonding MO. A a result a metal–metal bond is formed. The decrease of the metal–metal distance is associated with a large Stokes shift of the luminescence which consists of a fluorescence and a phosphorescence.

Fig. 3. Potential curve diagram for the ground and lowest excited state of $MgCp_2$.

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