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Preliminary communication

REASSESSMENT OF THE ELECTRONIC ABSORPTION SPECTRA OF $Cr(\eta^6\text{-}C_6H_6)_2$, $Cr(CO)_6$ AND $Cr(\eta^6\text{-}C_6H_6)(CO)_3$

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Summary

The UV absorption bands between approximately 330 and 200 nm have been assigned to Rydberg transitions for the d^6 complexes $Cr(\eta^6\text{-}C_6H_6)_2$, $Cr(CO)_6$ and $Cr(\eta^6\text{-}C_6H_6)(CO)_3$

During a systematic investigation [1] of the electronic spectra of π-arene complexes previously synthesized in this laboratory [2], we observed major absorption bands in regions close to a band of the hexacarbonyl and a band of the dibenzene complex, respectively. This suggested an interpretation in terms of the spectra of these "parent" complexes. A closer look at the published spectra of the latter species and further recordings including a spectrum of $CrBz_2$ in ethanol (not previously published) has led to a reassessment of the bands of $CrBz_2$, $Cr(CO)_6$ and $CrBz(CO)_3$, and this is reported here.

The relevant electronic absorption spectral data from the literature and this work are summarized in Table 1. The solvent effect, which has been previously recognized [3,4], shows up strikingly in the electronic spectrum of $CrBz_2$ in the splitting of the single absorption band at 320 nm in non-polar solvents (dimethylbutane/n-pentane) (Fig. 1), through a band at 312 nm with a shoulder at 285 nm in acetonitrile (Fig. 2), into two quite distinct bands one at 332 nm and the other at 271 nm, with a shoulder at 280 nm, in the more polar ethanol (Fig. 3). This indicates that the solvent has a significant effect on the symmetry of the environment. Such sensitivity of the absorption bands to the solvent

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TABLE 1

ABSORPTION BANDS IN d^6 SYSTEMS: $CrBz_2$, $Cr(CO)_6$ AND $Cr(Bz)(CO)_3$

Compound	Solvent	Bands (nm) (ϵ) [a]	Type of transition	Reference
$CrBz_2$	Cyclohexane	641	d—d	[7]
		417	d—d; CT(M→L)	
		320	d—d; CT(M→L)	
		200	CT(L→M); L→L	
$CrBz_2$	DMB/n-pentane	640 (15)	d—d($^1A_{1g} \rightarrow {}^3T_{1g}$)	This work
		495(sh)	d—d($^1A_{1g} \rightarrow {}^3T_{2g}$)	
		400 (750)	d—d($^1A_{1g} \rightarrow {}^1T_{1g}$)	
		353(sh) (3500)	d—d($^1A_{1g} \rightarrow {}^1T_{2g}$)	
		304 (14500)	Rydberg ($^1A_{1g} \rightarrow {}^1T_{2g}$)	
$CrBz_2$	Acetonitrile	365	d—d($^1A_{1g} \rightarrow {}^1E_{1g}, {}^1B_{1g}$)	This work
		312	Rydberg ($^1A_{1g} \rightarrow {}^1A_{1g}$)	
		285(sh)	Rydberg ($^1A_{1g} \rightarrow {}^1E_{2g}$)	
$CrBz_2$	Ethanol [b] (95%)	332 (9700)	Rydberg ($^1A_{1g} \rightarrow {}^1A_{1g}$)	This work
		280(sh) 271 (9200)	Rydberg ($^1A_{1g} \rightarrow {}^1E_{2g}$)	
$Cr(CO)_6$	Acetonitrile	280 (13100)	CT($^1A_{1g} \rightarrow c\,{}^1T_{1u}$)	[8]
		230 (85100)	CT($^1A_{1g} \rightarrow d\,{}^1T_{1u}$)	
$Cr(CO)_6$	Cyclohexane	280 *(0.27)*	Rydberg ($^1A_{1g} \rightarrow {}^1T_{2g}$)	This work
		229 *(1.35)*	Rydberg ($^1A_{1g} \rightarrow {}^1T_{1u}$)	
$CrBz(CO)_3$	—	320	Cr→ring	[9]
		260	Cr→CO	
		220	Cr→CO Cr and ring→CO	
$CrBz(CO)_3$	Cyclohexane	320 (11100)	Rydberg ($^1A_1 \rightarrow {}^1A_1$)	This work
		265 (8500)	Rydberg ($^1A_1 \rightarrow {}^1E$)	
		220 (26400)	Rydberg ($^1A_1 \rightarrow {}^1A_1$)	

[a] Values in parentheses which are in italics are the relative absorptivities at an unspecified concentration.
[b] Spectrum recorded at 77 K. All other spectra recorded at 295 K.

has been accepted as evidence for the involvement of Rydberg orbitals in electronic spectral transitions in organic molecules [3] as well as transition metal complexes [5,6]. Thus, in the spectra of certain gold(I) and platinum(II) complexes specific bands have been assigned to Rydberg transitions [5,6]. In the present investigation the evidence points to transitions of a similar nature.

In the non-polar solvent the bands of $CrBz_2$ may be assigned under a pseudo O_h symmetry. The band at 640 nm ($^1A_{1g} \rightarrow {}^3T_{1g}$) and shoulder at 495 nm ($^1A_{1g} \rightarrow {}^3T_{2g}$) are of very low intensity and, together with the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition which occurs at 400 nm, are d—d (LF) bands. The only remaining *d*—*d* band at 353 nm ($^1A_{1g} \rightarrow {}^1T_{2g}$) is intensified and broadened by mixing of terms of identical symmetry. Thus, it follows that the band at 304 nm must be ascribed to $^1A_{1g} \rightarrow {}^1T_{2g}$, resulting from a one-electron transition from the metal t_{2g} orbital to a low-lying Rydberg acceptor orbital (R_1) of a_{1g} symmetry. The higher intensity of this band is accounted for by easing of the

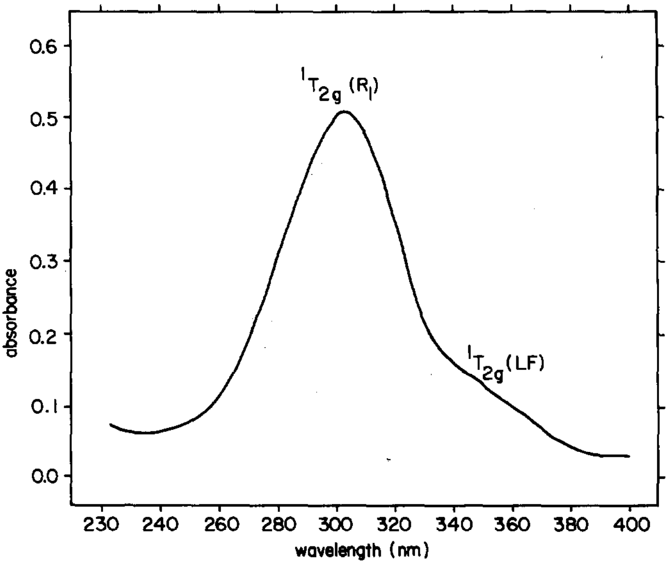

Fig. 1. Electronic absorption spectrum of $CrBz_2$ in dimethylbutane/n-pentane (8/3) at 295 K.

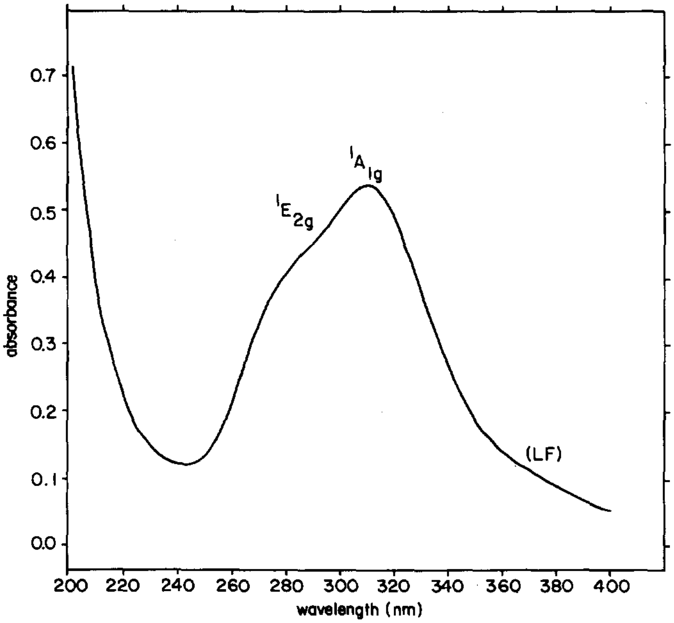

Fig. 2. Electronic absorption spectrum of $CrBz_2$ in the more polar solvent acetonitrile at 295 K (note appearance of shoulder).

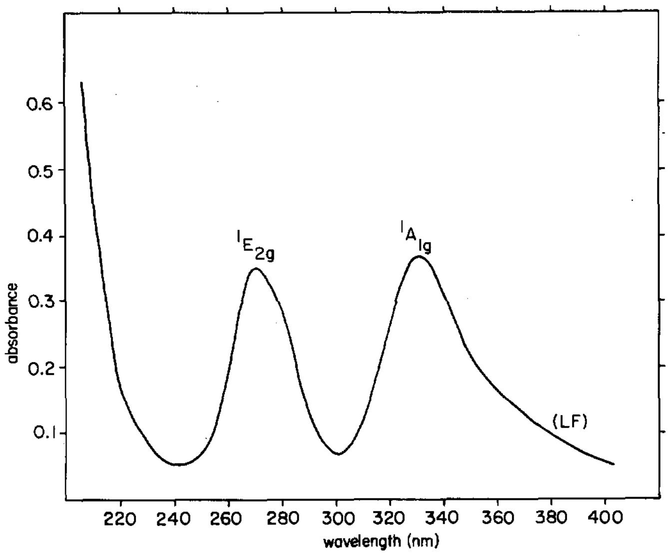

Fig. 3. Electronic absorption spectrum of $CrBz_2$ in the highly polar solvent ethanol (95%) at 77 K. (Note the emergence of two distinct bands. The asymmetry of the second band indicates splitting of the metal e level.)

Laporte rule. This would be expected on the grounds that the centre of symmetry of the central atom and ligands do not generally coincide, and furthermore because Rydberg orbitals are strongly perturbed under environmental influences and thus show irregularities in their electron density distributions [3].

In acetonitrile D_{6h} symmetry is evident in the splitting of the t_{2g} into a_{1g} and e_{2g} orbitals. This gives rise to the transition $^1A_{1g} \rightarrow {}^1A_{1g}$ ($a_{1g} \rightarrow R_1$) for the band at 312 nm and $^1A_{1g} \rightarrow {}^1E_{2g}$ ($e_{2g} \rightarrow R_1$) for the shoulder at 285 nm. In ethanol this splitting of the above-mentioned Rydberg transitions is increased, leading to two distinct bands; at low temperatures the first band is not split, confirming the $a_{1g}(d_{z^2}) \rightarrow R_1$ assignment. The second band, however, is asymmetric, which reveals the partial removal of the degeneracy through spin-orbital coupling in the $e_{2g}(d_{x^2-y^2}, d_{xy}) \rightarrow R_1$ transition.

$Cr(CO)_6$ shows two spin-allowed bands of extremely disparate intensity. These can be readily explained on the basis of Rydberg transitions of the type d^6 (Cr) $\rightarrow R_1, R_2$. There is only one transition to R_1 (a_{1g} in octahedral symmetry), namely $^1A_{1g} \rightarrow {}^1T_{2g}$ (i.e. $t_{2g} \rightarrow a_{1g}$). From symmetry considerations R_2 must be a t_{1u} acceptor orbital. This results in the fully allowed transition $^1A_{1g} \rightarrow {}^1T_{1u}$ in agreement with the observed intensity of the main UV absorption band at approximately 230 nm.

In the electronic spectrum of $CrBz(CO)_3$ the first two absorption bands can be assigned under C_{3v} symmetry to the $d_{z^2} \rightarrow R_1$ (a_1) and $d_{x^2-y^2}, d_{xy} \rightarrow R_1$ (a_1) transitions, whereas the more intense absorption band at higher energy is attributed to the transition $d_{z^2} \rightarrow R_2$ (a_1). The nature of these Rydberg orbitals is considered at greater length in a systematic study of π-arene type d^6 complexes to be published [1].

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