Journal of Organometallic Chemistry, 429 (1992) C38–C40
Elsevier Sequoia S.A., Lausanne
JOM 22431PC

Preliminary communication

Vapor-phase electronic absorption spectrum of (η^5-cyclopentadienyl)(η^5-cycloheptatrienyl)chromium

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(Received November 11, 1991)

Abstract

The UV and visible absorption spectra of (Cp)(Ch)Cr (Cp = η^5-C_5H_5, Ch = η^7-C_7H_7) vapor show surprisingly well-resolved Rydberg structure. The first ionization potential (5.603 ± 0.007 eV) has been determined as a convergence limit of three Rydberg series. (Cp)(Ch)Cr is the first sandwich complex in which the lowest Rydberg transitions terminating at *ns* and *np*(σ) orbitals have vibrational structure.

Recent studies [1–4] have shown that UV and visible absorption spectra of some transition-metal bisarene complexes and 3*d* metallocenes show narrow bands which disappear on going from the vapor phase to solution. These bands were unambiguously assigned to Rydberg transitions originating at the totally symmetric non-bonding metal *d* orbital. For investigation of the influence of molecular symmetry on the spectra of sandwich organometallics, study of asymmetrical transition-metal complexes containing two different η-bonded ligands seems to be important. The present work presents the first UV and visible absorption spectra of (Cp)(Ch)Cr vapor (Cp)(Ch)Cr being an electronic analog of bis(η^6-benzene)chromium [5]. The title compound was prepared by a previously reported route [6] and purified by repeated vacuum sublimation. The spectroscopic technique has been described previously [1–4].

Very low molecular symmetry of (Cp)(Ch)Cr (C_1 or C_s) can result in mixing between Rydberg and valence-shell states. It may thus be expected that Rydberg transitions in (Cp)(Ch)Cr are broadened as compared with symmetrical bis(η^6-benzene)chromium. However, the vapor-phase spectrum of (Cp)(Ch)Cr (Fig. 1a) shows surprisingly sharp Rydberg structure which is absent in the solution spectrum (Fig. 1b). There are three clearly distinguishable Rydberg series. The frequencies of their members are given by the well-known Rydberg formula $\nu_n = \text{IP} - R/(n-\delta)^2$, where IP is the ionization potential, R is the Rydberg constant, n is

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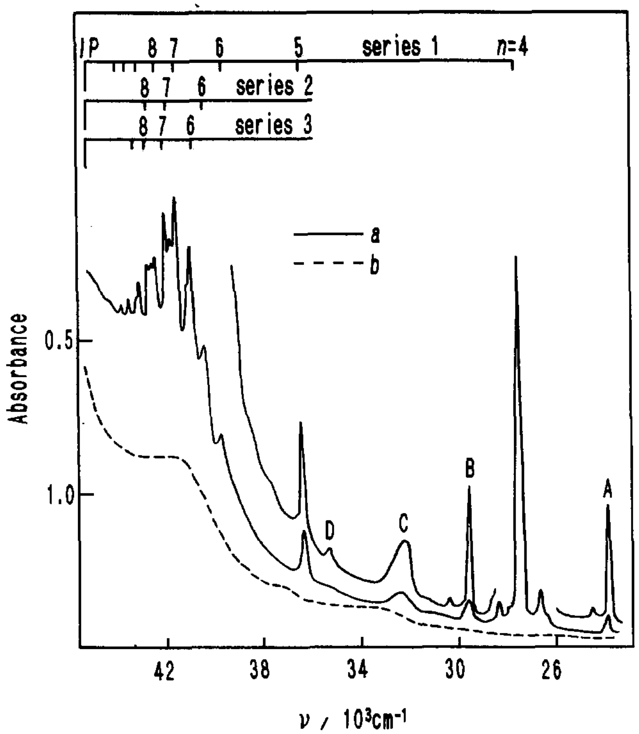

Fig. 1. Electronic absorption spectrum of (Cp)(Ch)Cr in the vapor phase (a) and in pentane solution (b).

the principal quantum number and δ is the quantum defect. The band positions predicted by this formula coincide with those observed for $n > 6$. For lower members of the Rydberg series, the calculated frequencies are somewhat different from the experimental ones; however, this is a typical phenomenon for polyatomic molecules and, in particular, for symmetric sandwich complexes [1–3].

The series are characterized by the following parameters: IP = 45210 cm^{-1}, $n = 4$–12, $\delta = 1.26$ (series 1); IP = 45190 cm^{-1}, $n = 6$–8, $\delta = 1.04$ (series 2); IP = 45170 cm^{-1}, $n = 6$–9, $\delta = 0.82$ (series 3). These data show that all three Rydberg series converge to the same ionization limit. Taking into consideration the error in determining the band positions (20–40 cm^{-1} for narrow peaks), we can accept the average IP value to be 45190 ± 60 cm^{-1} or 5.603 ± 0.007 eV. This magnitude is in excellent agreement with the position of the first band in the photoelectron spectrum of (Cp)(Ch)Cr (5.59 eV [5]; 5.61 eV [6]). Thus, first ionization potential of the sandwich complex has been determined with high accuracy in the present work. The first IP of (Cp)(Ch)Cr corresponds to the ionization from the $3d(\sigma)$ non-bonding molecular orbital (MO) [5,7]. Hence, all three Rydberg series arise from the transitions originating at this MO.

The quantum defect of series 1 is typical for Rydberg *np* series in the spectra of vanadium and chromium bisarene complexes [1,2]. The first member of series 1 is responsible for a very intense band at 27610 cm^{-1} (Fig. 1a). The difference between the IP and this frequency (17580 cm^{-1}) is very close to the term values for the first members of the Rydberg $np(\pi)$ series in the spectra of $(Bz)_2M$ (Bz = η^6-

C_6H_6, M = V, Cr, Mo) and $(Cp)_2Fe$ (17200–17500 cm^{-1}) [1–4]. Hence, one can unambiguously assign series 1 to the $3d(\sigma) \rightarrow Rnp(\pi)$ excitations. Series 2 may be formed by transitions terminating at the *Rnd* or *Rnf* orbitals (in the latter case, the $(n-1)$ and (δ-1) values should be used instead of n and δ). Series 3 has the quantum defect appropriate for its assignment as Rydberg *nd* excitations.

In the long-wavelength pattern of the (Cp)(Ch)Cr vapor-phase spectrum there are several low-lying Rydberg transitions (peaks A, B, and D in Fig. 1a) which do not belong to the three series considered above. Their assignment can be made on the basis of the term values (T = IP-ν). Band A at 23800 cm^{-1} has a term value of 21390 cm^{-1}, which is very close to the T magnitudes for the first member of the Rydberg *ns* series in alkylsubstituted derivatives of $(Bz)_2Cr$ [1,2] and $(Bz)_2Mo$ [3]. Hence, peak A arises from the $3d(\sigma) \rightarrow R4s(\sigma)$ transition, which is symmetry-allowed in the $C_{\infty v}$ point group. For unsubstituted complexes $(Bz)_2M$ (point group D_{6h}) and $(Cp)_2Fe$ (point group D_{5h}), this excitation is forbidden and is not observed in the absorption spectra [1–4]. The second member of this series is responsible for weak band D, while the higher members are superimposed on the peaks belonging to series 3. Band B at 29700 cm^{-1} has a term value of 15490 cm^{-1}. This magnitude coincides with the T values for transitions terminating at the non-degenerate component of the $R4p$ MO in $(Bz)_2V$ [2] and $(Cp)_2Fe$ [4]. Peak B must therefore be assigned to the $3d(\sigma) \rightarrow R4p(\sigma)$ excitation.

Narrow bands without labels in the long-wavelength pattern of the vapor-phase spectrum (Fig. 1a) correspond to the vibrational structure of transitions terminating at the $R4s$ and $R4p$ levels. Totally symmetric metal–ligand stretching (ν' = 220 cm^{-1}) and totally symmetric C–H bending (ν' = 830 cm^{-1}) are revealed most clearly. It should be noted that (Cp)(Ch)Cr is the first sandwich complex for which the $3d(\sigma) \rightarrow R4s(\sigma)$ and $3d(\sigma) \rightarrow R4p(\sigma)$ transitions show well-resolved vibrational structure.

Thus, sharp peaks in the electronic absorption spectrum of vaporous (Cp)(Ch)Cr appear to have a Rydberg origin. Only the comparatively broad band C at 32440 cm^{-1} (Fig. 1a) may arise from a valence-shell transition. The narrowness of the Rydberg bands indicates that the $3d(\sigma)$ MO in (Cp)(Ch)Cr is non-bonding despite the very low formal symmetry of the complex. The analysis shows that the Rydberg structure of the spectrum can be described most accurately on the basis of $C_{\infty v}$ symmetry.

Acknowledgments. The author thanks I.L. Fedyushkin for synthesis of (Cp)(Ch)Cr and Professor G.A. Domrachev for helpful discussions.

References

1 S.Yu. Ketkov, G.A. Domrachev and G.A. Razuvaev, Opt. Spectrosc, 63 (1987) 284 (in Russian).
2 S.Yu. Ketkov, G.A. Domrachev and G.A. Razuvaev, J. Mol. Struct., 195 (1989) 175.
3 S.Yu. Ketkov and G.A. Domrachev, J. Organomet. Chem., 389 (1990) 187.
4 S.Yu. Ketkov and G.A. Domrachev, Inorg. Chim. Acta, 178 (1990) 232.
5 S. Evans, J.C. Green, S.E. Jackson and B. Higginson, J. Chem. Soc., Dalton Trans., (1974) 304.
6 H.O. van Oven, C.J. Groenenboom and H.J. de Liefde Meijer, J. Organomet. Chem., 81 (1974) 379.
7 C.E. Davies, I.M. Gardiner, J.C. Green, M.L.H. Green, N.J. Hazel, P.D. Grebenik, V.S. Mtetwa and K. Prout, J. Chem. Soc., Dalton Trans., (1985) 669.