A study of peralkylated derivatives of bis(η^6-benzene)chromium by gas-phase electronic absorption spectroscopy

S. Yu. Ketkov,[a] G. A. Domrachev,[a] and J. C. Green[b]*

[a]G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences, 49 ul. Tropinina, 603600 Nizhny Novgorod, Russian Federation. Fax: (831 2) 66 1497. E-mail: sketkov@imoc.sinn.ru
[b]Inorganic Chemistry Laboratory, University of Oxford, South Rarks Road, Oxford OX1 3QR, Great Britain. Fax: (01865) 27 2690

The gas-phase electronic absorption spectra of $(\eta^6\text{-}C_6R_6)_2Cr$ (R = Me (**1**) and Et (**2**)) reveal Rydberg structures, which disappear on going to the condensed phase. Each spectrum shows a Rydberg series converging to the ionization threshold. The first ionization potential determined as the series convergence limit is 4.662±0.008 eV for **1** and 4.667±0.019 eV for **2**. The Rydberg bands are due to the transitions from the non-bonding MO $3d_{z^2}$ to the *R*4s and *Rn*p (n = 4—10) levels. The influence of methyl and ethyl substituents on the term values of the Rydberg transitions depends on the principal quantum number of the Rydberg MO.

Key words: chromium bisarene complexes, electronic absorption spectra, Rydberg transitions, ionization potential, substituent influence.

Chromium bisarene complexes represent the first class of organometallic compounds, whose gas-phase absorption spectra exhibited the pronounced Rydberg bands.[1—10] The bands are due to electron transitions from the highest occupied MO localized at the chromium atom ($3d_{z^2}$ orbital of a metal) to the Rydberg levels of the sandwich-type molecule. These transitions can be observed only in the gas phase because of large sizes of the electron cloud corresponding to an electron at the Rydberg MO.[11] This specific feature makes the gas-phase electronic absorption spectra of chromium bisarene complexes much more informative than spectra recorded in condensed media.

Series of bands converging to the ionization threshold were found for bis(η^6-benzene)chromium and its derivatives. Frequencies of higher terms of the series are described by the known Rydberg formula

$$\nu_n = I - R/(n - \delta)^2 = I - R/(n^*)^2 = I - T,$$

where I is the ionization threshold (energy of electron detachment from the $3d_{z^2}$ orbital), R is the Rydberg constant (109737 cm^{-1}), n is the principal quantum number, δ is the quantum defect, n^* is the effective principal quantum number, and T is the term value (energy of interaction of the Rydberg electron with the cation core). The presence of the Rydberg series makes it possible to determine with a high accuracy the first ionization potentials (IP) of chromium bisarene complexes.[1—10]

Analysis of parameters of the Rydberg transitions in sandwich-type complexes provides a valuable information on their molecular and electronic structure (geometry of free molecules, degree of delocalization of the d_{z^2} orbital, configuration interactions, *etc.*[1—10,12—15]). Therefore, a study of the influence of the structure of sandwich-type compounds on these parameters seems very significant. We have previously[3,6,7,9] shown that the introduction of alkyl substituents into the benzene ligands $(\eta^6\text{-}C_6H_6)_2Cr$ changes the relative intensities and term values of the Rydberg bands. The complexes studied contained from one to three substituents in the ligand. When examining the influence of alkyl groups, spectra of peralkylated derivatives of bis(η^6-benzene)chromium are of principal interest. On the one hand, the influence of substituents must be most pronounced for these compounds, and on the other hand, side effects related to a decrease in molecular symmetry are reduced to a minimum. In this work, we studied electronic absorption spectra of the complexes $(\eta^6\text{-}C_6Me_6)_2Cr$ (**1**) and $(\eta^6\text{-}C_6Et_6)_2Cr$ (**2**).

Experimental

The complexes were synthesized, isolated, and purified in a standard Schlenk apparatus under dry nitrogen or in evacuated ampules. Complexes **1** and **2** were synthesized using a known procedure[16] by the reduction of anhydrous $CrCl_3$ with powdered aluminum in the presence of $AlCl_3$ and a benzene derivative at 140 °C; C_6Et_6 was prepared by the complete ethylation of PhEt with ethyl chloride in the presence of $AlCl_3$; other reagents were commercially available (Aldrich, Merck). After the end of the reaction, the mixture was hydrolyzed with an aqueous solution of MeOH, and the reaction product was

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reduced with aluminum in an alkaline medium (aqueous solution of NaOH) and dissolved in toluene.

The oxidation—reduction cycle was additionally performed to remove an excess of solid organic compounds. After the complexes were oxidized with air oxygen in the presence of water, organic admixtures were extracted with diethyl ether. Then cations were again reduced to neutral compounds, which were dissolved in toluene. After the solvent was removed, the complexes were sublimed *in vacuo*. Compound **1** was additionally recrystallized from toluene at −80 °C, and complex **2** was repeatedly sublimed.

The use of completely substituted arenes in the preparation of bisarene derivatives by the above method excludes side transalkylation processes, which are observed for partially alkylated arenes.[17] The individual character of the synthesized compounds was confirmed by the data of ^{1}H NMR spectroscopy and fragment analysis (only the corresponding arenes were found in the products of complex decomposition with a dilute solution of HCl).

Electronic absorption spectra of complexes **1** and **2** in the gas phase were recorded on a Specord UV Vis spectrometer (Carl Zeiss, Jena) using an evacuated heated quartz cell at 140—180 °C. The accuracy of determination of maxima positions was 40—60 cm^{-1} for narrow peaks and 100—150 cm^{-1} for broad bands and shoulders. For comparison, the absorption spectra of solutions of compounds **1** and **2** in *n*-heptane were recorded at ~20 °C on the same instrument in an evacuated quartz cell. Parameters of the Rydberg series were determined by nonlinear regression analysis.[18,19]

Results and Discussion

The spectra of gaseous complexes **1** and **2** distinctly exhibit comparatively narrow Rydberg bands, which disappear on going to the condensed phase (Figs. 1 and 2). Analysis of the band frequencies allows, in each case, the separation of one series, which is well described by the Rydberg formula for $n > 5$. The frequencies of terms of the series and parameters obtained by nonlinear regression analysis are presented in Table 1. Below we present the ionization threshold (I), quantum

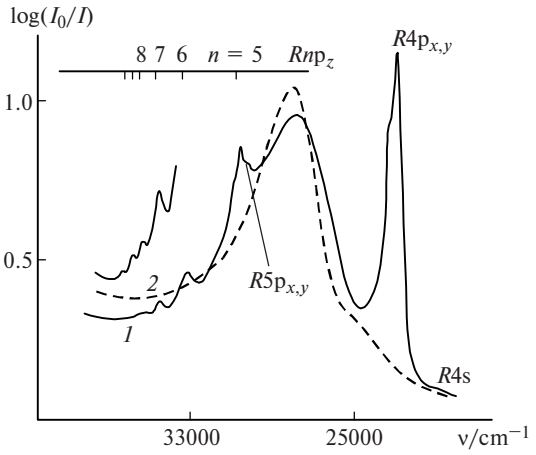

Fig. 1. Electronic absorption spectrum of the $(\eta^6\text{-}C_6Me_6)_2Cr$ complex (**1**) in the gas phase (*1*) and in *n*-heptane (*2*): δ = 0.95.

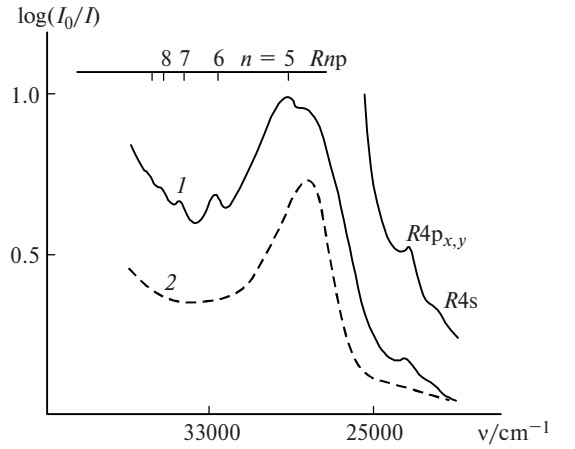

Fig. 2. Electronic absorption spectrum of the $(\eta^6\text{-}C_6Et_6)_2Cr$ complex (**2**) in the gas phase (*1*) and in *n*-heptane (*2*): δ = 1.28.

defect (δ), correlation coefficient (r), and standard deviation (s).

Complex	I/cm^{-1}	δ	r	s/cm^{-1}
1	37590[a]	0.96[a]	0.99964[a]	9[a]
	37594.8[b]	0.9554[b]	1.00000[b]	0[b]
2	37640[a]	1.28[a]	0.99985[a]	28[a]
	37639.7[b]	1.2817[b]	1.00000[b]	0[b]

[a] The values correspond to the approximation of experimental data by the Rydberg formula. [b] Nonrounded I and δ values for the calculation of ν_{theor} and the corresponding regression parameters r and s.

The found ionization thresholds I in these columns were rounded to 10 cm^{-1}, and the quantum defect values δ were rounded to 0.01.

The high correlation coefficient r and low standard deviation s corresponding to the experimental frequencies were obtained for both compounds. Note a good correspondence between the ν_{theor} and ν_{exp} values.

Variation of the experimental frequencies of terms of the series within the measurement error changes the I values by 60 cm^{-1} for **1** and by 150 cm^{-1} for **2**. The ionization threshold of the Rydberg series in the spectra of $(\eta^6\text{-}C_6R_6)_2Cr$ corresponds to the detachment of a

Table 1. Experimental (ν_{exp}) and calculated (ν_{theor}) frequencies of terms of the Rydberg series in spectra of complexes **1** and **2**

n	$(\eta^6\text{-}C_6Me_6)_2Cr$ (**1**)		$(\eta^6\text{-}C_6Et_6)_2Cr$ (**2**)	
	ν_{exp}	ν_{theor}	ν_{exp}	ν_{theor}
	cm^{-1}			
6	33280	33282.6	32700	32710.4
7	34600	34591.4	34300	34283.7
8	35380	35383.5	35230	35208.4
9	35890	35899.1	35770	35797.6
10	36260	36253.4	—	36196.0

$3d_{z^2}$ electron.[1—9] Thus, analysis of the Rydberg frequencies gives the first IP equal to 37590±60 cm^{-1} (4.662±0.008 eV) for complex **1** and 37640±150 cm^{-1} (4.667±0.019 eV) for **2**. The value obtained for compound **1** agrees well with the data of photoelectron spectroscopy (4.68 eV).[20] It is lower than the first IP for such derivatives as $(\eta^5\text{-}C_5Me_5)_2Co$ (4.70 eV)[21] and $(\eta^8\text{-}C_8H_8)(\eta^5\text{-}C_5Me_5)Zr$ (4.70 eV),[22] which were considered for a long time to the lowest values for stable organometallic compounds.

It is of interest that on going from $(\eta^6\text{-}C_6H_6)_2Cr$ to $(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2Cr$ the ionization potential decreases by 0.46 eV,[3,6—9] and on going from $(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2Cr$ to complex **1** it decreases by 0.34 eV. This implies that the introduction of many Me groups into the benzene ligands $(\eta^6\text{-}C_6H_6)_2Cr$ results in deviation from the linear correlation between the IP and number of methyl substituents, which has previously been found[7] for the chromium complexes with benzene, toluene, xylenes, and mesitylene. This deviation indicates an increasing mutual influence of the methyl groups in molecule **1**, which results in a decrease in the effect induced by each substituent.

An increase in the size of alkyl groups on going to complex **2** should enhance the mutual effect of substituents. Indeed, the appearance of one ethyl group in each $(\eta^6\text{-}C_6H_6)_2Cr$ ligand results in a strong drop of the IP than that induced by the introduction of one methyl substituent (the first IP of compounds $(\eta^6\text{-}C_6H_5Et)_2Cr$ and $(\eta^6\text{-}C_6H_5Me)_2Cr$ are 5.25 and 5.29 eV, respectively[7]). For the complete alkylation of the cycle, the changes in IP for Et and Me become almost equal (see Table 1).

The Rydberg series in the spectra of **1** and **2** should be attributed to the $3d_{z^2}\rightarrow Rnp$ transitions by analogy to the previously studied chromium bisarene complexes.[1—9] Note that the quantum defects for compounds **1** and **2** differ substantially. The series in the spectra of compounds $(\eta^6\text{-}C_6H_5Et)_2Cr$ and $(\eta^6\text{-}C_6H_5Me)_2Cr$ are characterized by very close δ values.[7] Two series due to the transitions of the $3d_{z^2}$ electron to the Rydberg $p_{x,y}$ and p_z orbitals were observed for the chromium bisarene complexes.[3,6—9] The quantum defect of the long-wave series $p_{x,y}$ was 1.40—1.56, and that of the short-wave p_z series was 1.16—1.28.

The low δ value for the series in the spectrum of **1** allows us to assign it to p_z transitions. Higher $p_{x,y}$ transitions are absent from this spectrum, which can be explained by their very low intensity. This assumption is confirmed by the analysis of the Rydberg bands in the region of $n = 5$ (see Fig. 1). This region contains an intense peak at 30640 cm^{-1} ($R5p_z$). The calculated frequency of the $R5p_z$ transition is 30890 cm^{-1}. A slight bathochromic shift of the band relatively to the theoretical position indicates a stronger (compared to the higher terms of the series) penetration of the Rydberg orbital into the electron shell of the core or the configuration interaction of the Rydberg state with the higher electron-excited state. The long-wave shoulder at 30400 cm^{-1} is adjacent to the peak at 30640 cm^{-1}. This shoulder has a relative intensity, which is too low for the 0_0^0 transition to the $R5p_z$ level but sufficiently high to exclude the possibility of its assignment to the "hot" vibronic component due to the transition from the excited vibrational level of the ground electron state. Therefore, the shoulder at 30400 cm^{-1} appears upon electron excitation involving another Rydberg MO. Of symmetry-allowed transitions, only the $3d_{z^2}\rightarrow R5p_{x,y}$ transition can lie in this region. A similar ratio of intensities of the $R5p_z$ and $R5p_{x,y}$ bands was observed for the $(\eta^6\text{-}1,4\text{-}C_6H_4Me_2)_2Cr$ molecule.[9]

In the case of complex **2**, the assignment of the Rydberg series is not so unambiguous. It can correspond to both the Rnp_z and $Rnp_{x,y}$ orbitals. On the one hand, an increased $\delta(p_z)$ (compared to that of compound **1**) can be related to an increase in the size and enhancement of the polarizability of the molecular core when Me is replaced by Et. On the other hand, we cannot exclude the assignment of this series to $p_{x,y}$ transitions because the complete alkylation of cycles can result in a decrease in the quantum defect due to the inductive effect of substituents (for example, for the $R5p_{x,y}$ transition in molecule **1** δ = 1.09). Unlike complex **1**, the spectrum of compound **2** in the region of $n = 5$ contains only one Rydberg band at 29200 cm^{-1} broadened due to configuration interactions. The relatively high value of quantum defect (δ = 1.39) allows us to assign it to the transition to the $p_{x,y}$ level.

The determination of the first IP of complexes **1** and **2** by the convergence limit of the Rydberg series makes it possible to calculate the term values T and effective principal quantum numbers n^* for all observed Rydberg series (Table 2). Note that the values of parameters δ, T, and n^* corresponding to the Rydberg MO with $n > 4$ in molecule **1** are substantially lower than similar characteristics for other studied methyl-substituted derivatives

Table 2. Frequencies (ν), term values (T), effective principal quantum numbers (n^*), and assignments of the Rydberg bands in spectra of complexes **1** and **2**

$(\eta^6\text{-}C_6Me_6)_2Cr$ (**1**)			$(\eta^6\text{-}C_6Et_6)_2Cr$ (**2**)			Rydberg orbital
ν	T	n^*	ν	T	n^*	
cm^{-1}			cm^{-1}			
21500[a]	16090	2.61	22000[a]	15640	2.65	4s
23030	14560	2.75	23300	14340	2.77	$4p_{x,y}$
30400[a]	7190	3.91	29200	8440	3.61	$5p_{x,y}$
30640	6950	3.97	—	—	—	$5p_z$
33280	4310	5.05	32700	4940	4.71	6p
34600	2990	6.06	34300	3340	5.73	7p
35380	2210	7.05	35230	2410	6.75	8p
35890[a]	1700	8.03	35770[a]	1870	7.66	9p
36260[a]	1330	9.08	—	—	—	10p

[a] Shoulder.

of $(\eta^6\text{-}C_6H_6)_2Cr$.[9] At the same time, assuming the additive character of the influence of methyl substituents on the Rydberg parameters and based on the available data for compounds with one, two, and three Me groups in the ligands,[9] we can expect an increase in these characteristics on going to complex **1**. Therefore, in this case, the influence of methyl substituents is not additive and monotonic. A quite different picture is observed for the lower Rydberg transitions.

The long-wave region of the spectrum of molecule **1** contains one intense Rydberg band with a maximum at 23030 cm^{-1}. In the spectra of all previously studied chromium bisarene complexes[1—9] the strong *R*4p bands are due to the components polarized along axes *x* and *y* and the $R4p_z$ transitions are low-intensity or are not observed at all. Hence, the peak at 23030 cm^{-1} should be assigned to the excitation $3d_{z^2}\rightarrow R4p_{x,y}$. The corresponding term value (see Table 2) is much lower than the $T(R4p_{x,y})$ values in the series of the studied methyl-substituted complexes.[9] Unlike $T(R5p_{x,y})$, the $T(R4p_{x,y})$ values change monotonically with an increase in the number of methyl substituents.

Several shoulders (see Fig. 1) corresponding to the vibronic components of the Rydberg transition can be picked out at the short-wave wing of the $R4p_{x,y}$ band. By analogy to $(\eta^6\text{-}C_6H_6)_2Cr$ [8] and previously[9] studied methyl-substituted derivatives, the appearance of totally-symmetric stretching vibrations metal—ligand and totally-symmetric out-of-plane vibrations of the methyl groups should be expected in the structure of the Rydberg transitions of molecule **1**. Several weakly pronounced shoulders due to the vibronic components are also seen at the short-wave shoulder of the $R5p_z$ band.

The longest-wave Rydberg band in the spectra of the chromium bisarene complexes is resulted from the $3d_{z^2}\rightarrow R4s$ transition. This transition is forbidden by the selection rules for complex **1**, whose symmetry of the carbon core can correspond to point groups D_{6h}, D_{6d}, or D_6. The spectrum of molecule **1** (see Fig. 1) exhibits only a very weak shoulder at 21500 cm^{-1}, which corresponds to the *R*4s components resolved due to the vibronic interaction. A comparison of the $T(R4s)$ values characteristic of complex **1** (see Table 2) and other methyl-substituted derivatives of $(\eta^6\text{-}C_6H_6)_2Cr$ [9] shows that the term values decrease monotonically with the number of methyl groups in the cycle, as $T(R4p_{x,y})$.

A special character of changing the terms of the lowest Rydberg MO can be related to the fact that for $n = 4$ the sizes of clouds of the Rydberg electron and molecular core[23] are comparable. Therefore, the Rydberg orbitals for $n = 4$ behave during methylation like nonbonding valent MO for which the ionization energy decreases monotonically.[21,24] A stronger penetration of the lowest Rydberg orbitals into the molecular core results in the situation where the $R4p_{x,y}$ band for most $(\eta^6\text{-}C_6H_6)_2Cr$ derivatives is shifted to the long-wave spectral region relatively to the calculated value.[3—9] For complex **1**, the $\nu(R4p_{x,y})$ frequency calculated from the quantum defect of the $R5p_{x,y}$ transition is 24630 cm^{-1}, which exceeds the experimental value by 1600 cm^{-1} (see Table 2).

Since the first IPs of compounds **1** and **2** are almost equal, we can expect that the lowest Rydberg transitions in the spectra of **1** and **2** are characterized by close term values. Two Rydberg bands are observed in the long-wave region of the gas-phase spectrum of **2** (see Fig. 2). The peak at 23300 cm^{-1} has a higher intensity and, by analogy to other chromium bisarene complexes, should be assigned to the $3d_{z^2}\rightarrow R4p_{x,y}$ transition. In fact, the corresponding term value is very close to the $T(R4p_{x,y})$ value for compound **1** (see Table 2). The shoulder at 22000 cm^{-1} (see Fig. 2) can correspond to the *R*4s transition only. The $T(R4s)$ value somewhat decreases when Me is replaced by Et. This implies that the Rydberg 4s MO in molecules of the chromium bisarene complexes is more sensitive to the influence of the substituent than the valent occupied non-bonding $3d_{z^2}$ MO.

Note that the ratio of intensities of the bands corresponding to the $R4s/R4p_{x,y}$ transitions for complex **2** is much higher than that for **1** (see Figs. 1 and 2), which is related to the symmetry of molecule **2**. The terminal methyl groups of the ethyl substituents of the C_6Et_6 fragment can differently be oriented relatively to the plane of the aromatic cycle,[25] due to which a set of complexes **2** with different symmetries of the carbon core appears in the gas phase. Evidently, the contribution to the observed Rydberg structure can also be made by low-symmetry molecules for which the $3d_{z^2}\rightarrow R4s$ transition is allowed by the selection rules.

Unlike Me substitution, when H atoms are completely substituted by Et in $(\eta^6\text{-}C_6H_6)_2Cr$, the terms of the Rydberg transitions for $n > 4$ do not substantially change. A considerable increase in the $T(Rnp)$ parameters when Me are substituted by Et (see Table 2) indicates an enhancement of the bond of the Rydberg electron with the cation core. This is a result of an increase in the size of the electron shell and enhancement of the polarizability of the core of the sandwich molecule on going from complex **1** to compound **2**.

In fact, the nonmonotonic change in the term values for $n > 4$ with an increase in the number of methyl groups in ligands of the chromium bisarene complexes mentioned above indicates that the influence of alkyl substituents on the *T* value includes at least two opposite mechanisms. On the one hand, the inductive effect results in an enhancement of the interelectron repulsion[24] and, hence, in a decrease in IP and *T*. On the other hand, an increase in the size of the electron shell and polarizability value of the core when alkyl groups are introduced enhances the interaction of the Rydberg electron with the core shell[26] and, hence, increases the term values. The character of changing *T* indicates that the first mechanism is predominant for the lower Rydberg levels of the bisarene chromium complexes, and the

second mechanism is significant for higher principal quantum numbers n^*.

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