Gas-phase electronic absorption spectroscopy of substituted bis(η^6-benzene)chromium derivatives: Rydberg transitions in bis(η^6-anisole)chromium and bis(η^6-2,6-dimethylpyridine)chromium

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Gas-phase electronic absorption spectra of chromium bisarene complexes with oxygen- and nitrogen-containing ligands, (η^6-PhOMe)$_2$Cr (**1**) and (η^6-2,6-Me$_2$C$_5$H$_3$N)$_2$Cr (**2**), were first measured. Rydberg bands disappearing on going to the condensed-phase spectra were revealed. The first ionization potentials of complexes **1** and **2** (5.30 and 5.40 eV, respectively) were determined from the Rydberg frequencies. The Rydberg transitions were assigned and the corresponding Rydberg term values and quantum defects were determined. The effect of heteroatoms on the Rydberg structure parameters was revealed by comparing the spectra of complexes **1** and **2** with those of unsubstituted analogs. The appearance, in the ligand side chain, of an oxygen atom capable of being involved in conjugation with the π-electron system of the aromatic ring results in substantial broadening of the observed Rydberg bands. This can be associated with an increased ligand contribution to the HOMO of the sandwich compound. The influence of the oxygen atom on the ionization energy of the molecule is insignificant. In contrast to this, introduction of a nitrogen atom into the carbocycle leads to a noticeable increase in the ionization potential of the molecule, while the ligand contribution to the HOMO of the complex remains practically unchanged.

Key words: chromium bisarene complexes, anisole, 2,6-dimethylpyridine, electronic absorption spectra, Rydberg transitions, ionization potential, substituent effect.

Like ferrocene derivatives, bisarene chromium complexes are convenient model compounds for theoretical and experimental investigations of the nature of metal—ligand bonding in transition metal π-complexes. This is advanced by the high symmetry (point group D_{6h})[1] and closed 18-electron shell of unsubstituted bis(η^6-benzene)chromium. The electron shell of this complex has the configuration $^1A_{1g}$ [2—4]: ...$[e_{2g}(\mathrm{Bz}, 3d_{xy,x^2-y^2})]^4[a_{1g}(3d_{z^2})]^2$..., where the contributions of the benzene orbitals and of the 3d-levels of the metal atom to the MO of the sandwich molecule are given in parentheses. Specific spectral properties of (η^6-arene)$_2$Cr are governed by the nonbonding character of the totally symmetric HOMO, which is nearly completely composed of the Cr 3d$_{z^2}$-orbital.[2,3] Electronic absorption spectra of these complexes dramatically change on going from the gas phase to the condensed phase.[5—14] This is due to the appearance, in the gas-phase spectra, of relatively narrow bands corresponding to transitions of the nonbonding 3d$_{z^2}$-electron to Rydberg levels of the sandwich molecule. A clearly seen Rydberg structure makes the gas-phase absorption spectra of bisarene chromium complexes much more interesting and informative than the spectra obtained in the condensed phase.

The spectra of bis(η^6-benzene)chromium and its alkyl-substituted and halogen-substituted derivatives ex-

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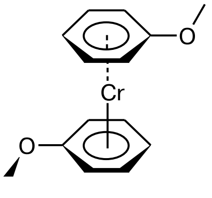
hibit series of bands that are described by the Rydberg formula

$$\nu_n = I - R/(n - \delta)^2 = I - R/(n^*)^2 = I - T, \quad (1)$$

where ν_n is the wavenumber of a series member, I is the ionization threshold equal to the energy of detachment of an electron 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).[15] Knowing the convergence limit of the Rydberg series, the first ionization potentials (IP) of $(\eta^6\text{-arene})_2Cr$ molecules can be determined with high accuracy.[7,11—13,16,17]

Parameters of Rydberg transitions contain information on the geometry of free sandwich molecules, delocalization degree of the d_{z^2}-orbital, configuration interactions, and other features of the electronic structure of metal complexes.[11—14,18—22] Therefore, analysis of the gas-phase electronic absorption spectra of bisarene chromium compounds provides a unique possibility of studying the influence of the nature and structure of the organic ligand on the electronic structure of sandwich compounds. Earlier,[23,24] we have shown that replacement of hydrogen atoms by fluorine or chlorine atoms in the benzene rings of $(\eta^6\text{-PhH})_2Cr$ causes a large shift and substantial broadening of the Rydberg bands. Broadening of a Rydberg transition can be due to an increase in the ligand contribution to the HOMO of the complex or to configuration interactions.[18—24] To analyze these effects in more detail, in this work we first studied the spectra of chromium complexes with two oxygen- and nitrogen-containing ligands, $(\eta^6\text{-PhOMe})_2Cr$ (**1**) and $(\eta^6\text{-2,6-Me}_2C_5H_3N)_2Cr$ (**2**).



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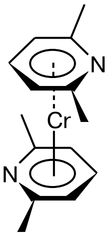

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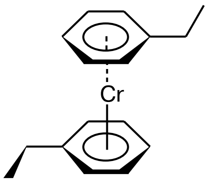
Anisole was used as the oxygen-containing ligand. In this compound the lone electron pair (LEP) of the oxygen atom is involved in conjugation with the aromatic π-system.[25] p—π-Conjugation can result in a change in the character of the interaction between the Cr $3d_{z^2}$-orbital and the anisole MO. In contrast to this, the unpaired electron of the nitrogen atom in the 2,6-dimethylpyridine molecule is involved in the ring π-system. It was of particular interest to analyze the changes in the gas-phase spectrum of the sandwich complex due to this type of substitution. For comparison we recorded the spectra of gaseous bis(η^6-ethylbenzene)chromium (**3**) and bis(η^6-*m*-xylene)chromium (**4**), which are unsubstituted analogs of the complexes **1** and **2**, respectively. Analysis of the Rydberg structures in the spectra of compounds **3** and **4** was reported earlier.[7,11,13]



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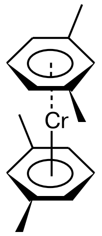

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Experimental

Metal complexes **1**—**4** were synthesized by low-temperature cocondensation of Cr atoms and an organic ligand, which allows individual bisarene compounds to be obtained.[26—29] The structures of the compounds under study were confirmed by elemental analysis and ^1H NMR spectroscopy data, which are consistent with the results obtained earlier for complexes **2** [26] and **1**, **3**, and **4**.[30] The complexes were purified by recrystallization followed by double vacuum sublimation.

Absorption spectra of gaseous compounds were recorded on a Specord UV—VIS spectrometer (Carl Zeiss, Germany) using an evacuated heated quartz cell at 80—140 °C. The best resolution of the spectrometer was 30 cm^{-1}. To reveal the Rydberg bands, the gas-phase spectra were compared with the absorption spectra of **1** and **2** in *n*-heptane, which were recorded on the same spectrometer in an evacuated quartz cell at room temperature. The gas-phase electronic spectra of complexes **1** and **2** were compared with the spectra of compounds **3** and **4**, which were also recorded on the same instrument. Analysis of the Rydberg series was performed by nonlinear regression methods.[31]

Results and Discussion

The gas-phase absorption spectrum of complex **1** exhibits five relatively broad bands, among which four disappear on going to the spectrum of a solution (Fig. 1). Disappearance of the absorption bands on going from the gas phase to the condensed phase is indicative of Rydberg nature of the corresponding transitions.[14,15] The wavenumbers of the Rydberg bands observed in the spectrum of complex **1** are listed in Table 1. Analysis of the Rydberg frequencies shows that three bands form a series that converges to an ionization threshold at 42770 cm^{-1} (5.30 eV). Information on the photoelectron spectrum of complex **1** is unavailable but the spectrum of complex $(\eta^6\text{-PhOMe})(\eta^6\text{-PhCN})Cr$ was reported.[32] The first IP of this compound is very similar to the IP of $(\eta^6\text{-PhMe})(\eta^6\text{-PhCN})Cr$ (5.75 and 5.73 eV, respectively), which allows one to expect similar values of the first IPs for complexes $(\eta^6\text{-PhOMe})_2Cr$ and $(\eta^6\text{-PhMe})_2Cr$. This assumption is

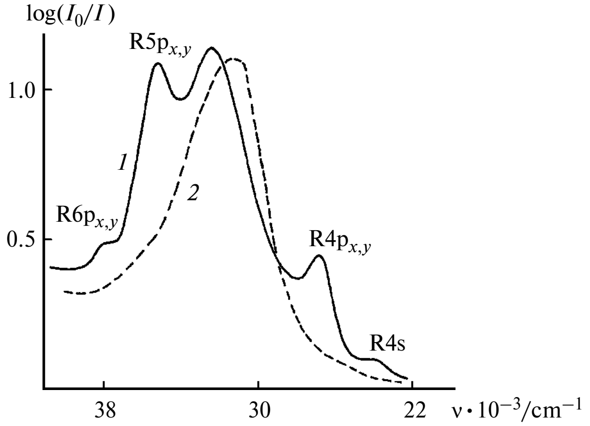


Fig. 1. Electronic absorption spectrum of bis(η^6-anisole)chromium in the gas phase (*1*) and in *n*-heptane (*2*).

in good agreement with the convergence limit value obtained for the series in the absorption spectrum of **1** (the first IP of (η^6-PhMe)$_2$Cr is 5.29 eV[13]). Noteworthy is that the ionization energy of the sandwich complex somewhat increases on going from system **3** to **1** (see Table 1). A reverse trend is observed for free ligands (the vertical IPs of ethylbenzene and anisole are 8.77[33] and 8.39[34] eV, respectively). This means that the difference in the energy shifts of the ground-state energy levels of the neutral molecule and the cation upon introduction of an O atom changes as a result of ligand coordination to the Cr atom.

The quantum defect δ 1.30 characterizing the series members with n = 5 and n = 6 is typical of transitions to the Rydberg p-levels,[5—14] being intermediate between the corresponding values for the Rnp$_{x,y}$- and Rnp$_z$-series in the spectra of alkyl-substituted bis(η^6-benzene)chromium derivatives.[7,10,11,13] This allows the bands at 34750 and 37800 cm^{-1} (see Table 1) to be assigned as transitions from the HOMO to the R5p and R6p levels, respectively. The first member of the p-series (ν = 26500 cm^{-1}) is characterized by a characteristic increase in the quantum defect (see Table 1) due to increased penetration of the lowest Rydberg orbital into the cation core.[9—12,35] Taking into account that the lowest p$_{x,y}$-bands in the spectra of all sandwich complexes with mono-substituted ligands studied earlier[7,11,13,14,20] are much more intense than the p$_z$-peaks, the Rydberg p-bands in the spectrum of complex **1** should be assigned to the $3d_{z^2} \rightarrow Rnp_{x,y}$ transitions. The long-wavelength shoulder (ν = 23300 cm^{-1}) corresponds to transition to the lowest Rydberg s-orbital. The corresponding term value (19470 cm^{-1}) is very similar to the *T*(R4s) value for complex **3** (19390 cm^{-1}, see Table 1).

Comparison of the spectra of complexes **1** and **3** (Figs 1 and 2) shows that introduction of an oxygen atom to the side chain of the aromatic ligand causes a substantial broadening of all Rydberg bands. A similar effect was observed for halogen-substituted (η^6-PhH)$_2$Cr derivatives.[23] The lone electron pair of the heteroatom involved

Table 1. Wavenumbers ν (cm^{-1}), term values *T* (cm^{-1}), effective principal quantum numbers n^*, quantum defects δ, and assignment of the Rydberg bands in the spectra of molecules **1** (I = 42770 cm^{-1}), **2** (I = 43570 cm^{-1}), **3** (I = 42330 cm^{-1}), and **4** (I = 41490 cm^{-1})

ν		*T*		n^*		δ		Assignment
1	**3**	**1**	**3**	**1**	**3**	**1**	**3**	
23300 sh	22940	19470	19390	2.37	2.38	1.63	1.62	R4s
26500	25250	16270	17080	2.60	2.53	1.40	1.47	R4$p_{x,y}$
34750	33900	8020	8430	3.70	3.61	1.30	1.39	R5$p_{x,y}$
37800 sh	37160	4970	5170	4.70	4.61	1.30	1.39	R6$p_{x,y}$
2	**4**	**2**	**4**	**2**	**4**	**2**	**4**	
23200	22500	20370	18990	2.32	2.40	1.68	1.60	R4s
—	24600	—	16890	—	2.57	—	1.43	R4$p_{x,y}$
—	24870	—	16620	—	2.71	—	1.29	R4$p_{x,y}$
32230 sh	29100	11340	12390	3.11	2.98	0.89	1.02	R4d
34870	32580 sh	8700	8910	3.55	3.51	1.45	1.49	R5$p_{x,y}$
35300 sh	32980	8270	8510	3.64	3.59	1.36	1.41	R5$p_{x,y}$
35900 sh	33870	7670	7620	3.78	3.79	1.22	1.21	R5p_z
37180 sh	34750 sh	6390	6740	4.14	4.04	0.86	0.96	R5d
38300	36280	5270	5210	4.56	4.59	1.44	1.41	R6$p_{x,y}$
38830	36730	4740	4760	4.81	4.80	1.19	1.20	R6p_z
39970	37930	3600	3560	5.52	5.55	1.48	1.45	R7$p_{x,y}$
40300	38200 sh	3270	3290	5.79	5.78	1.21	1.22	R7p_z
41000	38940	2570	2550	6.53	6.56	1.47	1.44	R8$p_{x,y}$
41200	39110 sh	2370	2380	6.80	6.79	1.20	1.21	R8p_z
41680	39600	1890	1890	7.62	7.62	1.38	1.38	R9$p_{x,y}$
42070 sh	40000	1500	1490	8.55	8.58	1.45	1.42	R10$p_{x,y}$

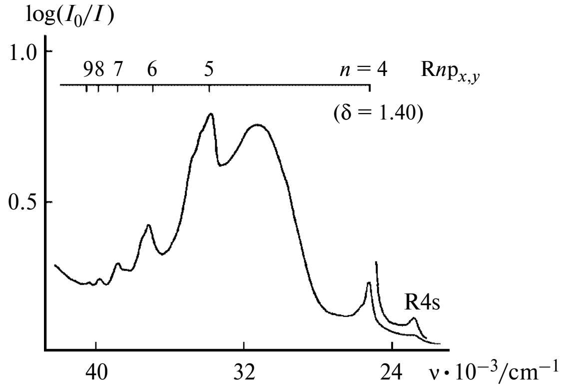
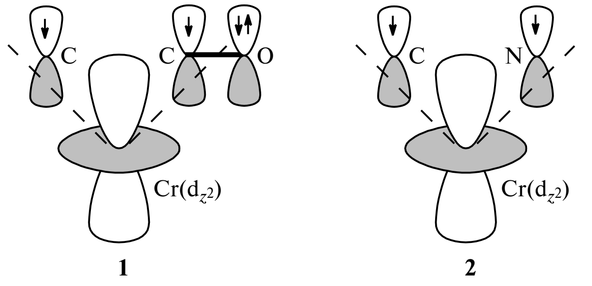


Fig. 2. Gas-phase electronic absorption spectrum of bis(η^6-ethylbenzene)chromium.

in conjugation with the π-system of the aromatic ring changes the pattern of the interaction between the Cr $3d_{z^2}$-orbital and the ligand MO. In the unsubstituted complex the nodal $3d_{z^2}$ surface intersects the totally symmetric benzene π-MO in the region of maximum electron density.[36] This is, in particular, the reason for the nonbonding character of the HOMO of (η^6-PhH)$_2$Cr. Violation of symmetry of the π-electron system of the ligand as a result of conjugation with the electron pair of the heteroatom (Fig. 3) causes strengthening of the interaction between the $3d_{z^2}$-orbital and the MO of the organic fragment, which affects the Rydberg structure. Even greater broadening of the Rydberg bands in the spectra of sandwich complexes was observed on the opening of the carbocycle;[21] this was associated with delocalization of the $3d_{z^2}$-electrons.



1 **2**

Fig. 3. Mutual arrangement of the Cr $3d_{z^2}$-orbital and the p_z-orbitals of carbon atom and heteroatom for complexes **1** and **2** (shown is the section by the plane passing through the nuclei of the ring atoms in positions 1 and 4 and the nucleus of the Cr atom; dashed lines denote the $3d_{z^2}$ nodal surface).

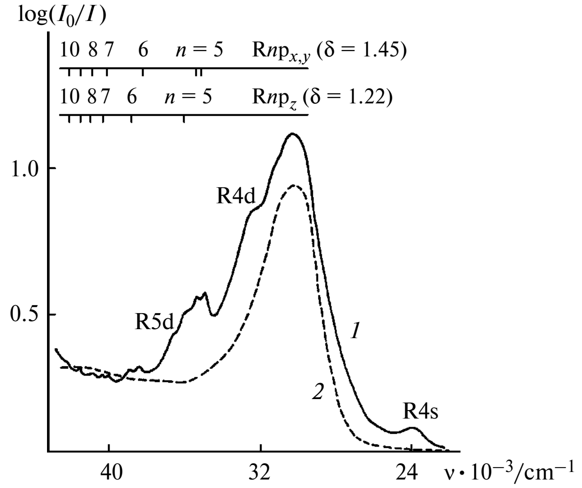


Fig. 4. Electronic absorption spectrum of bis(η^6-2,6-dimethylpyridine)chromium in the gas phase (*1*) and in *n*-heptane (*2*).

In contrast to compound **1**, almost no symmetry violation of the ligand π-system occurs in molecule **2** (see Fig. 3). Therefore, one can expect that the gas-phase absorption spectrum of **2** will exhibit narrow Rydberg bands. Indeed, a resolved Rydberg structure is observed in the short-wavelength region of the spectrum (Fig. 4). This feature disappears on going to the spectrum of a solution. Using regression analysis methods, the following two series were revealed:

$$\nu_n(\text{см}^{-1}) = 43570 - 109737/(n - 1.45)^2; \quad n = 5 - 10,\ r = 0.99995,\ s = 30\ \text{см}^{-1}, \qquad (2)$$

$$\nu_n(\text{см}^{-1}) = 43600 - 109737/(n - 1.22)^2; \quad n = 5 - 8,\ r = 0.99990,\ s = 30\ \text{см}^{-1}, \qquad (3)$$

where r is the correlation coefficient and s is the standard deviation. Both series converge to the same ionization threshold corresponding to the first IP of the sandwich molecule. The ionization energy calculated from the Rydberg frequencies (5.40 eV) is in good agreement with the photoelectron spectroscopy data[37] (5.43 eV).

The quantum defects of the series in the spectrum of complex **2** (see Eqns (2) and (3)) are nearly equal to the δ value for the unsubstituted analog, **4** (Fig. 5). The series in the spectrum of **2** should therefore be assigned unambiguously to transitions to the Rnp$_{x,y}$ and Rnp$_z$ levels, respectively. Indeed, in the spectra of molecules **2** and **4** the peaks corresponding to the R5p$_{x,y}$ transition are split into p$_x$- and p$_y$-components (see Figs 4 and 5, respectively). In addition to the Rnp bands two clearly defined shoulders at 32230 and 37180 cm^{-1} are observed in the short-wavelength region of the spectrum of **2**. Comparison of the corresponding term values with the data obtained for complex **4** (see Table 1) shows that the shoulders correspond to transitions to the R4d- and R5d-orbitals, respectively.

At $n \geq 5$, the term values for the Rydberg p-bands in the spectra of complexes **2** and **4** are very similar (see Table 1). Therefore, introduction of a nitrogen atom into the ring has a little effect on the character of interaction between the Rydberg electron and the cation core. However, replacement of *m*-xylene by 2,6-dimethylpyridine

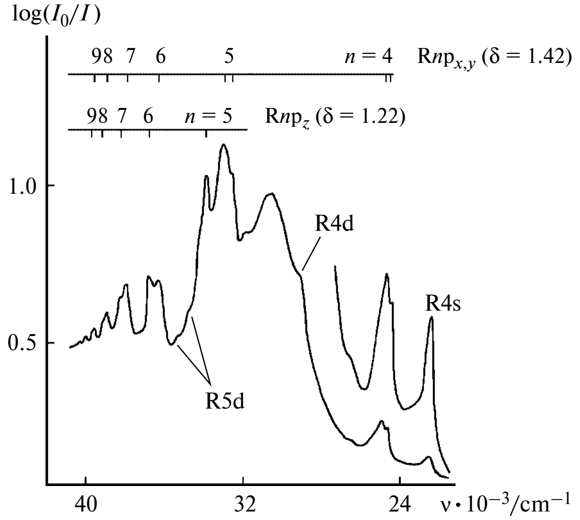


Fig. 5. Gas-phase electronic absorption spectrum of bis(η^6-*m*-xylene)chromium.

in the sandwich compound causes an appreciable increase (by more than 2000 cm^{-1}) in the IP due to the high electronegativity of nitrogen. A similar effect was also observed upon introduction of a nitrogen atom in the free ligand (IPs of *m*-xylene and 2,6-dimethylpyridine are 8.56[34] and 8.87[38] eV, respectively). As a result, all Rydberg bands are shifted toward the short-wavelength region on going from complex **4** to **2**. This changes the character of exhibition of the lowest Rydberg excitations in the spectrum of **2**. The shift of the R4p and R4s transitions leads to strengthening of the interaction between these excitations and higher valence excitations that contribute to the broad intense band with a maximum near 30000 cm^{-1} observed both in the gas phase and the condensed phase (see Fig. 4). The R4s band in the spectrum of complex **2** is much broader than in the spectrum of complex **4** (see Figs 4 and 5). The *T*(R4s) values increases by ~1400 cm^{-1} on going from complex **4** to **2** (see Table 1) due to the mutual repulsion between the R4s state and an upper valence excited level in molecule **2**. As to the R4p states, configuration interactions cause so large broadening that the corresponding Rydberg bands are not observed in the gas-phase absorption spectrum (see Fig. 4).

Thus, different reasons are responsible for broadening of the Rydberg bands in the spectra of complexes **1** and **2** compared to the corresponding bands in the spectra of unsubstituted analogs **3** and **4**. Namely, this is delocalization of the 3d$_{z^2}$-electron due to symmetry violation of the π-electron system for complex **1** and mixing of the Rydberg and valence electronic-excited states for complex **2**. The resolved short-wavelength Rydberg structure in the spectrum of complex **2** (see Fig. 4) indicates minor changes in the character of interaction between the Cr 3d$_{z^2}$-orbital and the ligand MO upon introduction of a nitrogen atom into the aromatic ring.

The results obtained demonstrate high sensitivity of the Rydberg transitions in the gas-phase absorption spectra of sandwich compounds to electronic structure disturbances induced by heteroatoms in the organic fragment of metal complexes. The Rydberg series permits determination of the first IPs of (η^6-arene)$_2$Cr using conventional UV spectrometers. Analysis of changes in the Rydberg parameters upon replacement of one ligand by another allows one to reveal the influence of the structure of the organic fragment on the extent of involvement of the Cr 3d$_{z^2}$-orbital in chemical bonding, on the energy characteristics of the Rydberg states of the sandwich molecule, and on the configuration interactions. This information is necessary to gain a better insight into the electronic structure of sandwich complexes and the mechanisms of photophysical and photochemical processes involving sandwich molecules.

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