Photoelectron spectroscopy of mono and binuclear iron and chromium cyclooctatetraene complexes

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Abstract

The ultraviolet photoelectron spectra of mono and binuclear cyclooctatetraene (COT) complexes $(CO)_3FeCOT$ (**I**) $[(CO)_3Fe]_2COT$ (**II**), CpCrCOT (Cp: 1,3 cyclopentadienyl) (**III**) and $(CpCr)_2COT$ (**IV**) are reported. The interpretation of the low energy part of the spectra is followed by a discussion concerning the metal–ligand (COT) and metal–metal interactions. The calculated gas phase structure of CpCrCOT is presented and its main features are discussed. © 1998 Elsevier Science S.A. All rights reserved.

1. Introduction

Cyclooctatetraene (COT) as a ligand shows a great variety in complex chemistry as far as geometry and bonding are concerned. C_8H_8 can coordinate as a tub-shaped tetraolefine or as a planar aromatic anion $C_8H_8^{2-}$. Its haptocity may have the values 2, 4, 6 and 8, in binuclear complexes η^3 and η^5 coordination modes are also possible [1–3]. In addition, COT can function as a bridging ligand. The μ-cyclooctatetraene complexes may also serve as interesting prototypes of compounds containing a metal–metal multiple bond. However, in many molecules where metal–metal multiple bonds might exist, the presence of bridging groups renders the problem of bond order doubtful, because the bridging ligand may influence the metal–metal distance and may also provide an alternative possibility for electron pairing, apart from direct bonding. That is why methods other than diffraction techniques are needed to identify metal–metal multiple bonds. In principle, and under favorable conditions in practice, UV photoelectron spectroscopy (UPS) is one of the most

useful techniques, providing the most direct experimental information about the electronic structure of transition metal systems. For example, Geoffry and co-workers have made a combined X-ray and UPS investigation of titanium and zirconium sandwich complexes with substituted COT ligands and showed a novel coordination mode in one of the rings bonded to the zirconium [4].

Heck and co-workers reported detailed cyclic voltammetric, NMR, and ESR studies on μ-COT complexes of chromium and vanadium. They concluded that distinct metal–metal bonding, with the indication of a weak δ-interaction, is present in these kind of complexes [5].

Only a limited number of UPS investigations of this type of compound have been made so far [6,7]. Our intention was to draw some light on the geometry and electronic structure of mono and binuclear transition metal COT complexes by means of UPS and quantum chemical calculations.

Cyclooctatetraene complexes $(CO)_3FeCOT$ (**I**), $[(CO)_3Fe]_2COT$ (**II**), CpCrCOT (Cp: 1,3 cyclopentadienyl) (**III**) and $(CpCr)_2COT$ (**IV**) were examined by gas phase photoelectron spectroscopy. The structures of the -examined molecules are shown in Fig. 1. [8–11].
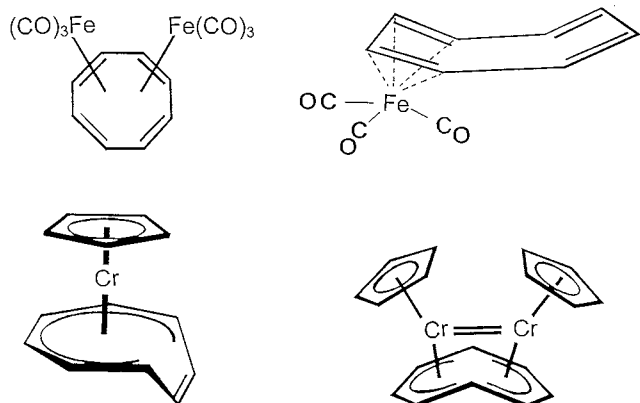
* Corresponding author.

Fig. 1. The structure of the examined molecules.

Table 1
The elemental analysis data of the synthesized compounds

Compound	$C_{calc}\%$	$C_{found}\%$	$H_{calc}\%$	$H_{found}\%$
(CO)₃FeCOT (**I**)	54.14	54.20	3.31	3.28
[(CO)₃Fe]₂COT (**II**)	43.80	43.92	2.10	2.16
CpCrCOT (**III**)	70.57	70.64	5.93	5.85
(CpCr)₂COT (**IV**)	63.89	63.99	5.37	5.44

From the comparison of the two iron compounds (**I** and **II**), information concerning the connection between the two metal centers in the binuclear complex can be expected.
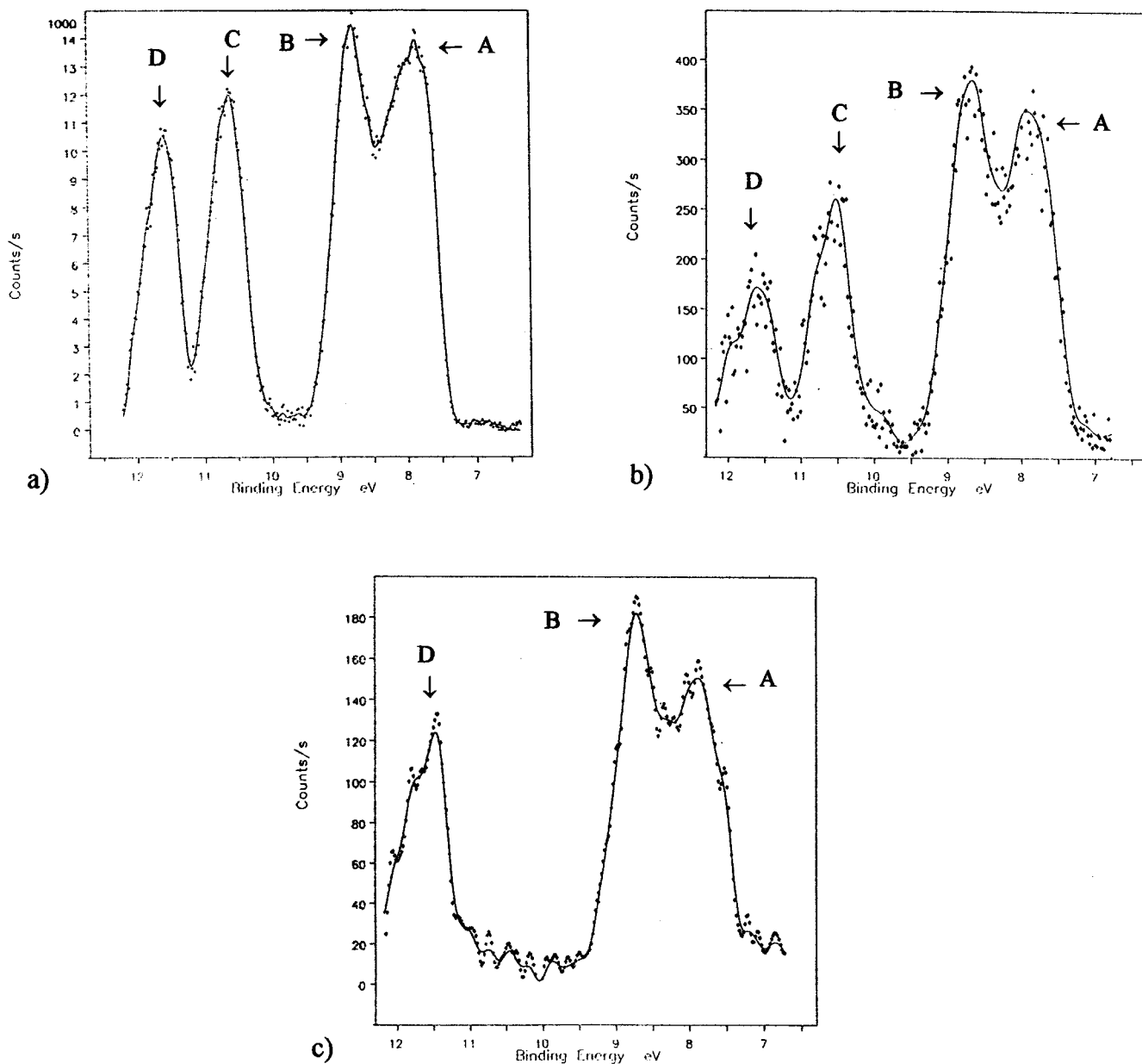

Fig. 2. (a) The He(I) PE spectrum of **I** (below 12 eV); (b) the He(II) PE spectrum of **I** (below 12 eV); (c) the He(I) PE spectrum of **II** (below 12 eV).
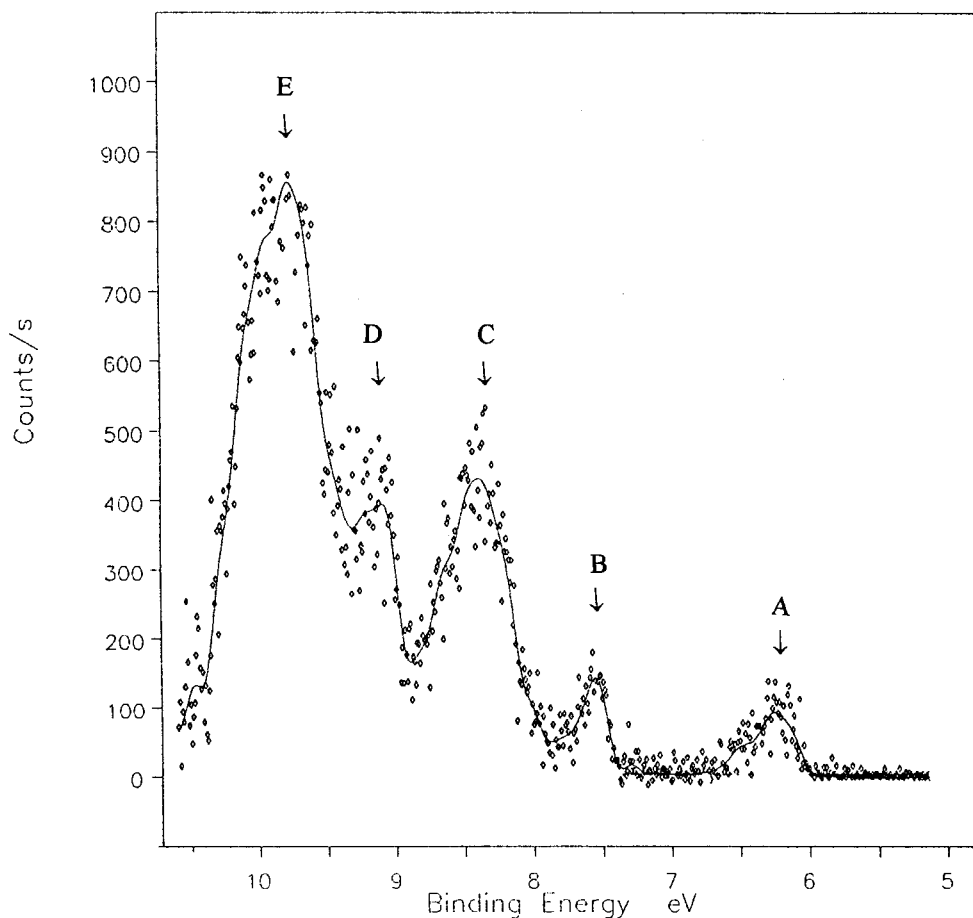
Fig. 3. The He(I) PE spectrum of **III** (below 10 eV).

The spectrum of the mononuclear η^6-chromium compound (**III**) related to that of CpCrBz (Bz: benzene) may reveal similarities between the electronic structure of these molecules. This complex was also investigated by ab initio quantum chemical calculations. It was hoped that the investigation of binuclear chromium complex (**IV**) gives further insight into the nature of the chromium–chromium bond.
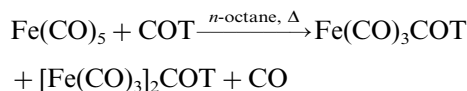
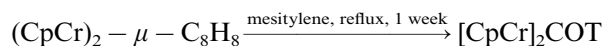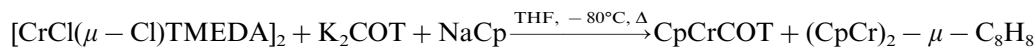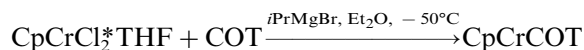## 2. Experimental

2.1. Preparation

All manipulations were carried out by using standard Schlenck technique under pure nitrogen atmosphere and in N_2-saturated solvents. Tetrahydrofuran (THF),

petroleum ether and diethylether (Et_2O) were freshly distilled from Na/benzophenone; n-octane and mesitylene were purified by refluxing on sodium metal. The purity of the synthesized compounds were checked by elemental analysis. The analysis data are given in Table 1.

Compounds **I** and **II** were prepared by standard literature methods based on the direct reaction of cyclooctatetraene and $Fe(CO)_5$ [12]. The products were separated on an alumina column with petroleum ether eluent.

$$Fe(CO)_5 + COT \xrightarrow{n\text{-octane, }\Delta} Fe(CO)_3COT$$

$$+ [Fe(CO)_3]_2COT + CO$$

The cyclooctatetraene chromium compounds (**III** and **IV**) were prepared by using Heck's method reported in the literature [13,14].

$$CpCrCl_2 \cdot THF + COT \xrightarrow{\textit{iPrMgBr, Et}_2O, \, -50°C} CpCrCOT$$

$$[CrCl(\mu - Cl)TMEDA]_2 + K_2COT + NaCp \xrightarrow{THF, \, -80°C, \, \Delta} CpCrCOT + (CpCr)_2 - \mu - C_8H_8$$

$$(CpCr)_2 - \mu - C_8H_8 \xrightarrow{\text{mesitylene, reflux, 1 week}} [CpCr]_2COT$$

All photoelectron (PE) experiments were carried out on an ATOMKI ESA-32 photoelectron spectrometer [15] by using a heated direct inlet probe. The spectra were recorded digitally and were smoothed with the help of Fourier transformation method [16]. The low energy region of the spectra of **II** and **IV** were accumulated from 40 scans. All spectra were calibrated by using argon as internal standard. Maximum errors in ionization energies are estimated less than 0.1 eV.

2.2. Computational details

Ab initio calculations were carried out on CpCrCOT, using double zeta basis set of Wachters [17]. The calculations have been performed at the restricted open-shell Hartree–Fock level. Because of convergence problems, Pulay's DIIS converger was not applied in the SCF iterations. Full geometry optimizations were done using Biosym's Turbomole v235 program system of Ahlrichs et al. on an IBM RS/6000 model 580 computer. For the geometry optimizations, natural coordinates were used. The internal coordinates describing the ring systems were defined the usual way using Fogarasi's intc program [18,19]. The relative position of the Cp, COT rings and the chromium atom were defined by using dummy atoms in the center of the rings. Four rocking and a torsion coordinate were used to describe the relative position of the rings. The place of the central atom was defined by two stretching and two linear bending internal coordinates. All calculations were performed utilizing the symmetry of the molecule (C_s). This premise was sufficiently backed up by the experimental studies and proved by the absence of imaginary frequencies. The use of symmetry resulted in a serious reduction of the computational cost.

3. Results and discussion

3.1. Photoelectron spectra

The He(I) and He(II) photoelectron spectra of **I** and the He(I) photoelectron spectra of **II**, **III** and **IV** (below 12 eV) are shown in Figs. 2 and 3. The points represent the experimental data and the continuous line is a fit to these points. Ionization energies (IE) together with those of related compounds are given in Table 2.

3.1.1. PE spectra of $(CO)_3FeCOT$ and $[(CO)_3Fe]_2COT$

The He(I) photoelectron spectrum of **I** has been published by Green et al. [20]. Their interpretation is based on a model that is composed of a Fe(diene)(CO)$_3$ unit plus a free diene system. The first band composed by two overlapping peaks is related to ionizations from orbitals mainly localized on the metal atom, and from the $1a_2$ orbitals of the complexed and free ligands. The next band is assigned to the higher π-ionization of the diene, while the third band arises from the ionization of the $1b_1$ level of the free ligand. We used this derivative as a reference compound and recorded its PE spectrum for the sake of the uniformity. In addition, He(II) spectrum was also registered in order to confirm the d-orbital involvement in the corresponding molecular orbitals (MO). Our results agree well with the above literature data (see Table 3), the relative band intensity changes related to d-orbital ionizations (7.8 and 8.7 eV) are in accord with the assignment. The ratio of the intensity of the first band relative to the peak at 11.6 eV (A + B/D in Table 3) in the He(I) and He(II) spectra is

Table 2
Vertical IEs (eV) of the investigated cyclooctatetraene derivatives in the low-energy part of the PE spectrum

$(CO)_3FeCOT$	$[(CO)_3Fe]_2COT$	CpCrCOT	$(CpCr)_2COT$
7.8	7.7	6.2–6.4	5.8
8.7	8.6	7.5	6.0
10.6	11.5	8.5	6.2
11.6		9.1	8.0
		9.7	9.3
			9.8

Table 3
IEs (eV) of **I**, **II** and $Fe(CO)_3(C_4H_6)$ in the low-energy part of the PE spectrum

Bands	A	B	C	D
$(CO)_3FeCOT$ (**I**)[a]	7.84	8.74	10.61	11 63
$(CO)_3FeCOT$ (**I**)	7.8	8.7	10.6	11.6
$[(CO)_3Fe]_2COT$ (**II**)	7.7	8.6		11.5
$Fe(CO)_3(C_4H_6)$[a]	8.67	9.82	11.43	12.56

[a] [20]

Table 4
Ionisation energies (eV) of **III** and CpCrBz in the low energy part of the PE spectrum

Band	A	B	C	D	E
Ionizations	d^{-1}	d^{-1}	π^{-1}	π^{-1}	π^{-1}
CpCrCOT (**III**)	6.2–6.4	7.5	8.5	9.1	9.7
CpCrBz[a]	6.20[b]	7.15[c]	8.76[d]	9.17[d]	9.68[e]

[a] [23]; [b] $^1A_1 + {}^3E_2$; [c] $^1E_2$.
[d] e_{1g}-type orbital deriving from the highest 'π' orbital of the aromatic ligand.
[e] e_{1u}-type orbital deriving from the highest 'π' orbital of the aromatic ligand.

3.1:7.7, indicating a substantial d character of the corresponding orbitals.

The comparison of the PE spectra of the mono and binuclear iron complexes show that within the experimental error the first and second IEs are equal, indicating a similar electronic structure in the close proximity of the Fe atoms. However, the band at 10.6 eV (band C in Fig. 2) is shifted to higher values in the spectrum of **II** as a consequence of further interactions resulted by the ligation of the free diene by the other $Fe(CO)_3$ moiety in the binuclear complex.

On the basis of early ^{1}H-NMR studies [21] in the solution of compound **II** an equilibrium can be suggested between an iron–iron bonded species (**II**.a) and a complex with two independent $Fe(CO)_3$ groups (**II**.b). Our UPS results suggests that in the gaseous phase, at the temperature of the inlet probe (210°C), the preferred structure is that of **II**.b; consequently COT acts as a bis-η^4-ligand bridging the two iron atoms and no direct bonding exists between them.

3.1.2. PE spectra of CpCrCOT and (CpCr)₂COT

In the case of the mononuclear Cr complex (**III**), a coordination mode of η^6 for the cyclooctatetraene ligand is generally accepted [22]. This means that the central atom is bound to six quasi-planar carbon atoms. Accordingly, there is a benzene-like, six-membered delocalized electronic system around the Cr atom. Although this structure is widely used in the literature, no exact structural data are available according to our best knowledge. That is why we have performed quantum chemical calculations concerning its gas phase structure, which is in accord with the proposed geometry (see below).

As far as ionization energies are concerned, with the exception of IE$_2$ (7.5 versus 7.15 eV) the PE spectra of **III** and CpCrBz [23] exhibit good agreement in the energy range below 10 eV. The corresponding pairs of IE values are: 6.2–6.4 eV versus 6.20 eV, 8.5 versus 8.76 eV, 9.1 versus 9.17 eV, and 9.7 versus 9.68 eV (see Table 4). The
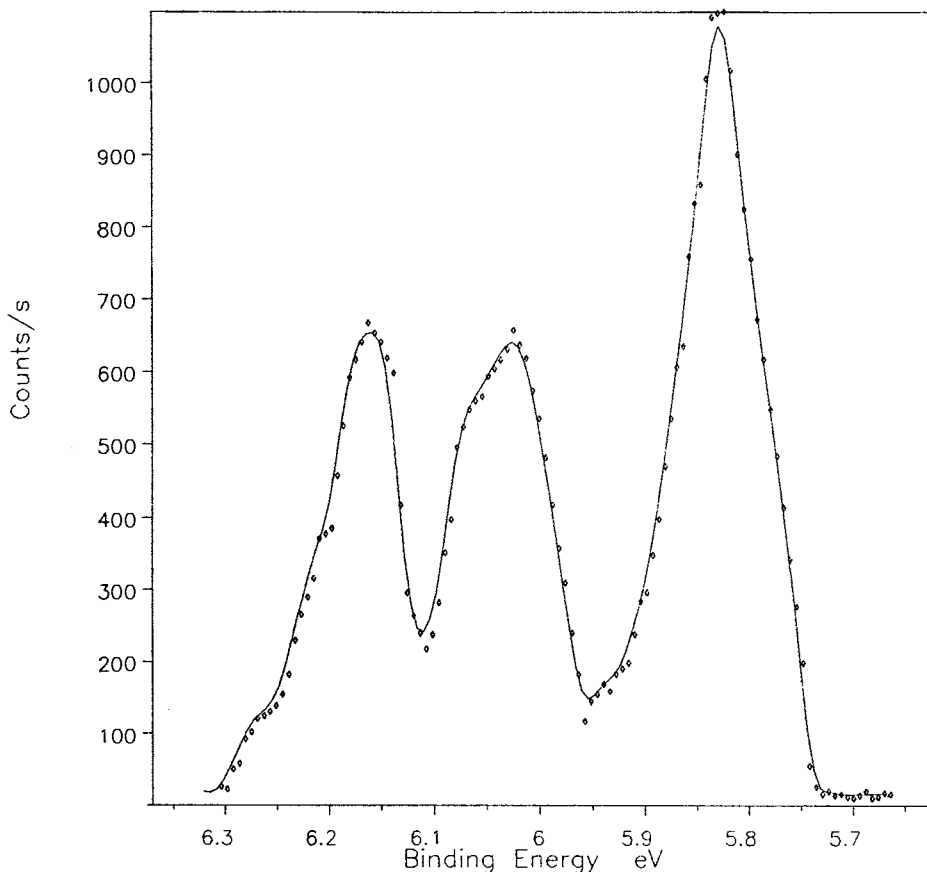

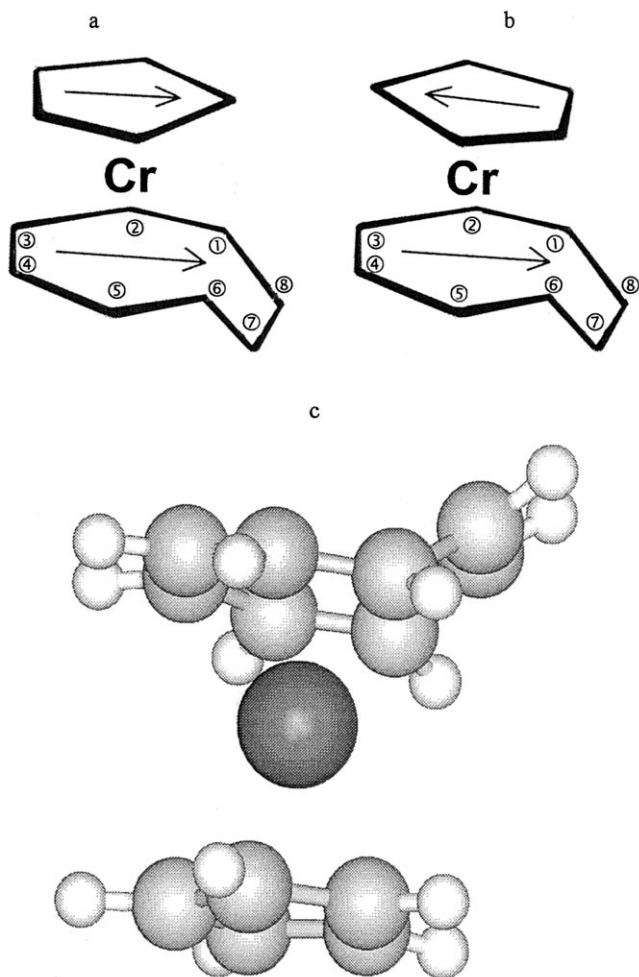Fig. 4. The low-energy part of the He(I) PE spectrum of **IV**.

Fig. 5. (a) and (b) The two hypothetical structures of **III**. (c) The calculated structure of **III**.

higher value of IE$_2$ in compound **III** can be related to the different π-donor capabilities of η^6-COT and η^6-Bz ligands. This idea can be related to the fact that the chromium atom is immersed deeper in the COT ring system than in the benzene of CpCrBz, as discussed Section 3.2.

The low-energy part of the photoelectron spectrum of the binuclear chromium complex (**IV**) contains three well distinguishable bands with approximately 2:1:1 relative intensity ratios (Fig. 4). This spectral feature can be interpreted as follows: the peak of smallest IE can be attributed to ionization from the d-type lone pairs localized on the two chromium atoms, while the other two peaks belong to Cr–Cr bonding molecular orbitals. This indicates that there is a double bond between the two chromium atoms. The measured stabilization energy associated with the formation of the bonding orbitals is only 0.2–0.4 eV, as a consequence of the relatively small overlap between the d orbitals.

The electronic structure of this binuclear chromium complex was described in the excellent article of Heck and co-workers [5]. According to their interpretation, the overlap of the 2a$_1$ and the b$_2$ fragment orbitals [24] results in the formation of a σ and a π bond, respectively. The overlap of the 1a$_1$ orbitals leads to the δ and δ^* orbitals, which are both doubly occupied. Consequently, the total bond order is two. Our description, based on the PE experiment is just slightly different: the splitting of the $\delta-\delta^*$ is negligable since the overlap between the 1a$_1$ orbitals of the fragments is not substantial. This quasi-degeneracy results in the absence of splitted bands related to the HOMO of the molecule.

3.2. Quantum chemical calculations of CpCrCOT

Two initial geometries were studied:
1. one with the Cp-carbon atom in the mirror plane being in the same direction as the COT diene carbons (Fig. 5(a)),
2. the other geometry with these carbon atoms pointing the other way (Fig. 5(b)).

Full geometry optimizations were done starting from both possible conformations. Both calculations converged, but only the latter one led to appropriate results. This indicates that the correct position of the polyene rings is such that the carbon atoms described above point to the opposite direction (Fig. 5(b)). The optimized geometry is represented in Fig. 5(c). Some characteristic parameters of the calculated geometry of **III** are summarized in Table 5. The distance of the central chromium atom and the ligand rings differs significantly. Note, however, that the values of the Cr–C bond lengths are much closer. The COT ring is much more spacious than the Cp ring, so the central chromium atom is closer to the ring plane in this case. The calculated Cp C–C bond lengths are in accord with the aromatic nature of the ring.

The C(1)–C(6) distance is ca. 3 Å in the COT ring, so the six-membered pseudo-ring is much more open than the benzene ring, resulting in much closer contact between the central chromium and the ring system. The other C–C

Table 5
The calculated geometry of **III**

Metal-to-ring distances (Å)	C–C bonds (Å)				
	COT				Cp
$r_{(Cp,Cr)} = 2.02$					
$r_{(COT,Cr)} = 1.46$	$r_{(C-C)} = 1.33$	$r_{(C-C)} = 1.46$	$r_{(aromatic\ C-C)} = 1.41$		$r_{(C-C)} = 1.42$

distances in the planar part of the COT ring show a delocalized π-electronic system, while the C(7)–C(8) bond length corresponds to an olefinic double bond.

Acknowledgements

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