

# Electron density distribution in the vanadocene crystal on the basis of X-ray diffraction data at 108 K

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## Abstract

Accurate molecular and crystal structure and experimental electron density distribution in the vanadocene single crystal were established on the basis of the precise X-ray diffraction data at 108 K. A characteristic asymmetry of the deformation electron density in the vicinity of the metal atom was found which is attributed to the different occupancies of the 3d-metal orbitals of the vanadium atom. A multipole analysis of the diffraction data was performed and the numerical values of the 3d-metal orbital occupancies in vanadocene were first calculated directly from these data. The results obtained are in agreement with the quantum-chemical calculations of vanadocene and other 3d-metallocenes.

**Keywords:** Vanadocene; X-ray structure; Charge density analysis

## 1. Introduction

3d-Metallocenes  $Cp_2M$ , where  $M = 3d$ -transition metal and  $Cp = C_5H_5$  ligand, represent a very important class of organometallic compounds and the interest in their atomic and electronic structure still remains very high despite an almost 40 years history of these studies [1–9]. As an important result of these studies, a close structural similarity in the 3d-metallocenes was elucidated. Thus, the crystals of monoclinic  $Cp_2Fe$ ,  $Cp_2Co$ ,  $Cp_2Ni$ , and  $Cp_2V$  were found to be isomorphous at room temperature and their crystal structures are very similar [10–13]. The electronic structure of the 3d-metallocene series may also be well explained in general features from the molecular-orbital (MO) diagram of ferrocene, the most important representative of these sandwich-like molecules, by subsequent removing of electrons from its occupied bonding and non-bonding  $a_{1g}$  and  $e_{2g}$  orbitals ( $Cp_2Mn$ ,  $Cp_2Cr$ ,  $Cp_2V$ ), or adding electrons to the antibonding  $e_{1g}$  orbital ( $Cp_2Co$ ,  $Cp_2Ni$ ) [14,15].

It is well established now, that direct information

about electron density distribution in crystals may be obtained from precise X-ray diffraction data [16–18]. Nevertheless, the charge density analysis in the metallocene series was absent until now mainly due to the complicated nature of their crystal disorder [3–6], Jahn–Teller distortions [19–21], and phase transitions on cooling the crystals [22,23]. We have found recently that the monoclinic structure of the vanadocene,  $Cp_2V$  (**1**) is ordered at 108 K [24], and the first accurate electron density distribution study of the  $Cp_2V$  crystal was undertaken at this temperature.

## 2. Results and discussion

The centrosymmetric  $Cp_2V$  molecules in crystal have an ideal staggered conformation of the Cp-rings (Fig. 1), as was found earlier in the two X-ray structural studies of **1** at room temperature [12,13]. However, in these two studies an essential rotational disorder of the Cp-rings was noted that would forbid observation of accurate data on the molecular geometry and electron density distribution. The ordered nature of the  $Cp_2V$  crystal structure at 108 K was proven in Ref. [24] by a careful analysis of the anisotropic displacement parameters. Thus, the largest eigenvalue  $L_1$  of the molecular

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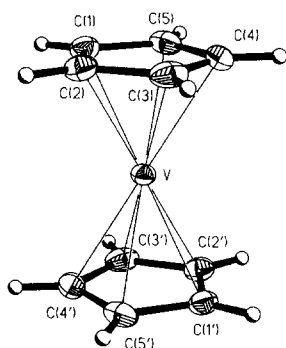


Fig. 1. General view of the vanadocene molecule in crystal with the representation of non-hydrogen atoms by the probability thermal ellipsoids ( $p = 50\%$ ), and atom numbering scheme.

libration tensor  $L$  in **1** was found to be  $31^{02}$ , that is the smallest value in the series of isomorphous  $Cp_2Co$ ,  $Cp_2Ni$ , and  $Cp_2V$  crystals at the same temperature.

The molecular geometry of **1** at 108 K is presented in Table 1. The V–C bond lengths are 2.260(1)–2.278(1) Å (mean value 2.269(6) Å) and C–C bond lengths 1.413(1)–1.423(1) Å (mean value 1.417(3) Å). The Cp-ring is planar within 0.001 Å and the distance from the metal atom to the ring center is 1.923 Å. These values, especially after correction for libration motion, are close to those found for vanadocene in the gas phase using the electron diffraction method: V–C 2.280(5) Å, C–C 1.434(3) Å, V-center of the ring 1.928(6) Å [25]. The C–H bond lengths are in the interval 0.94(2)–0.96(2) Å and displacements of these atoms from the carbon ring plane to the metal are small and hardly significant.

The deformation electron density (DED) map through the Cp-ring plane, obtained by a conventional 'X–X' method, is shown in Fig. 2. Distinct positive DED peaks at the C–C bond centers and at the C–H bonds were found with the heights of 0.40–0.50 and 0.20–0.30  $e \text{ \AA}^{-3}$  respectively, indicating a rather good quality of the experimental data.

The typical DED section through the molecular symmetry plane, containing V, C(5), and C(5') atoms, and the midpoints of the opposite C(2)–C(3) and C(2')–C(3') bonds of the ring is presented in Fig. 3. A

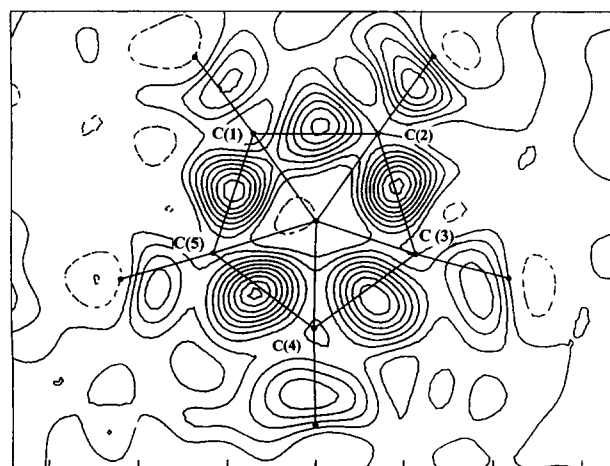


Fig. 2. Deformation electron density through Cp-ring plane. Contour intervals  $0.05 e \text{ \AA}^{-3}$ , negative contours dashed.

characteristic asymmetry of the electron density distribution near the vanadium atom was observed, that is quite usual for transition metal complexes. In this section, two positive DED maxima with the heights of about  $0.20 e \text{ \AA}^{-3}$  are directed to the rings' centers, two other maxima being located in the V-containing plane almost parallel to the Cp-rings. The negative DED peaks (about  $-0.40 e \text{ \AA}^{-3}$ ) were found along V–C and V-center C–C bond vectors. The general features of the DED maps through the other comparable sections were found to be almost the same. It is interesting to note some ellipticity of the DED sections through the middles of C–C bonds in the Fig. 3. This may reflect the contribution of the  $\pi$ -component in the corresponding bonds.

The section through the V-atom and parallel to Cp-ring planes is presented in Fig. 4. Four DED minima in the vicinity of the metal atom were located in this section together with the almost continuous 'ring-like' (centered at the V atom) distribution of the positive DED. The largest value of the DED maxima in this ring is equal to  $0.35 e \text{ \AA}^{-3}$ . It should be noted that the DED picture near the metal atom in **1** is similar to that for centrosymmetrical triple-decker complex Cp–V–Bz–V–Cp (where Bz =  $C_6H_6$ ) [16].

Table 1  
Molecular geometry of vanadocene at 108 K (libration corrected bond lengths are also given)

Bond	Bond length $d$ (Å)	Libration correction	Bond	Bond length $d$ (Å)	Libration correction	Bond	Angle (deg)
V–C(1)	2.273(1)	2.279	C(1)–C(2)	1.413(1)	1.422	C(2)–C(1)–C(5)	108.5(1)
V–C(2)	2.268(1)	2.270	C(2)–C(3)	1.417(1)	1.427	C(1)–C(2)–C(3)	107.7(1)
V–C(3)	2.260(1)	2.268	C(3)–C(4)	1.423(1)	1.432	C(2)–C(3)–C(4)	108.1(1)
V–C(4)	2.267(1)	2.275	C(4)–C(5)	1.418(1)	1.427	C(3)–C(4)–C(5)	107.7(1)
V–C(5)	2.278(1)	2.284	C(1)–C(5)	1.414(1)	1.424	C(1)–C(5)–C(4)	108.0(1)
Mean	2.269(6)	2.275		1.417(3)	1.426	Mean C–C–C	108.0(3)

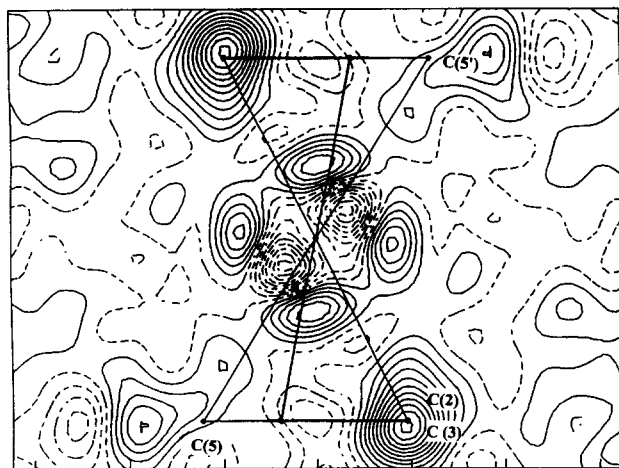


Fig. 3. DED section through the molecular symmetry plane, containing atoms V, C(5), C(5'), and midpoints of the opposite C(2)–C(3), and C(2')–C(3') bonds of the ring. Contours as in the Fig. 2.

The observed asphericity of the experimental DED distribution near the V-atom is caused by the preferential occupancy of the 3d-orbitals due to a relatively small overlap between the atomic 3d-metal and ligand orbitals, and agrees well with the MO treatment of the bonding in metallocenes. According to the numerous quantum-chemical calculations of these compounds (see for review in Ref. [15]), starting from the first MO calculation of the ferrocene by Shustorovitch and Dyatkina as early as 1961 [26], the metal 3d-orbitals, transforming as  $e_{1g}$ ,  $e_{2g}$ , and  $a_{1g}$  under axial molecular symmetry, will be split through the interaction with the corresponding ligand orbital combinations, and mainly metal 3d-molecular orbitals follow the sequence:

$$e_{2g}(d_{xy}, d_{x^2-y^2}) < a_{1g}(d_{z^2}) < e_{1g}(d_{xz}, d_{yz})$$

As a result, the  $e_{1g}$  pair becomes antibonding,  $e_{2g}$  bonding, and  $a_{1g}$  nonbonding orbitals in 3d-metallo-

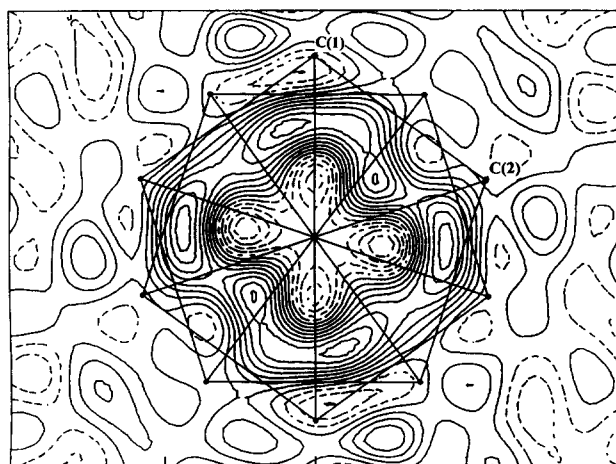


Fig. 4. DED section through V atom and parallel to Cp-ring plane. Contours as in the Fig. 2. The projection of the rings on this plane is shown for clarity with the C(1) and C(2) atoms numbering.

Table 2

3d-Occupancies in the vanadocene calculated from X-ray data in the multipole approximation

d orbital	Population (e)	Population (%)
$d_{x^2-y^2}$	0.64(8)	34
$d_{xz} + d_{yz}$	0.00(3)	0
$d_{xy}$	0.60(5)	32
$d_{z^2}$	0.64(7)	34

enes. It is essential that the  $a_{1g}$  molecular orbital is localized at the metal atom with the pure  $3d_{z^2}$  orbital contribution about 95%, but the metal contribution to the other  $e_{2g}$  and  $e_{1g}$  orbitals is smaller [15]. In accordance with this orbital sequence, the positive DED peaks directed to the ring centers (Fig. 3) should correspond to the occupied  $3d_{z^2}$  orbital, and the 'ring-like' positive DED to the occupied  $3d_{xy}$ , and  $3d_{x^2-y^2}$  orbitals, having essential atomic character.

It is known, that numerical characteristics of the 3d-orbital occupancies of the central atom in the transition metal complexes may be evaluated from the analysis of X-ray diffraction data via refinement of these data in the multipole approximation [27,28]. This approach was used in the present paper for **1**, and results of the analysis are given in Table 2.

The results obtained agree well with the general features of the DED maps (see Figs. 3 and 4), and with other experimental and quantum-chemical data for vanadocene [29,30]. According to the electron density maps and multipole analysis, the ground state of the metal atom in **1** is the high-spin  $^4A_{2g}$  one; that is in agreement with the spectral data (see Refs. [14,15]). The depopulation of the 3d-electron density in complex **1** should be noted. The total number of 3d-electrons is 1.88(7) instead of 3.0 for the spherical atom, and the most depopulated ones in comparison with the spherical atom are the  $e_{1g}$  orbitals. This result was also mentioned for other 3d-metal complexes [28], and it may reflect some contribution of the covalent metal–ligand interaction. Thus, very recent valence level photoelectron cross-sections data for 3d-metallocenes, including vanadocene, give evidence for 3d-orbital covalency in the  $e_{1g}$  orbitals [31]. For molecule **1**, the so-called back  $\pi$ -donation from the metal to the ligand may also be important.

### 3. Experimental and calculation details

Experimental diffraction data were obtained at 108 K for a single crystal of **1** with the linear dimensions about  $0.3 \times 0.3 \times 0.3 \text{ mm}^3$  using a four-circle Nicolet R3m/V diffractometer (monochromatized Mo  $K\alpha$  radiation).

Crystals of **1** are monoclinic at 108 K:  $a = 5.7208(6)$ ,  $b = 8.211(1)$ ,  $c = 8.831(1)$  Å  $\beta = 90.94(1)^\circ$ ,  $V = 414.77(9)$  Å<sup>3</sup>,  $Z = 4$ , space group  $P2_1/n$ .

The total number of 7105 reflections were measured using Wyckoff-type scan in the full sphere of the reciprocal space with  $2\theta < 90^\circ$ . After averaging the data ( $R_{\text{int}} = 0.025$ ) and empirical absorption correction (the min/max transmission coefficients were found to be 0.82/0.95), 2783 independent observed reflections with  $|F| > 4.0 \sigma(F)$  were used in the structure refinement by a full-matrix least squares to the final values of  $R = 0.032$ ,  $R_w = 0.038$ , and GOF = 1.15 in the anisotropic–isotropic (H atoms) approximation. The quasi-high-order refinement using the weighting scheme of Dunitz and Seiler [32] with the  $B = 5.0$  converged at  $R = 0.031$ ,  $R_w = 0.036$ , and GOF = 1.18; H-atom parameters during this procedure were fixed. The high-order refinement of the structure using diffraction data with  $\sin \theta/\lambda > 0.65$  Å<sup>-1</sup> was also carried out, and resulted in nearly the same atomic parameters as previous ones. DED maps were obtained with a conventional ‘X–X’ method using high-order refined atomic model and low-angle diffraction data ( $\sin \theta/\lambda < 0.70$  Å<sup>-1</sup>). All calculations were made with Micro-VAX-II computer using SHELXTL PLUS programs.

The multipole calculations were performed using the MOLLY program, adapted for a personal computer. The multipole population parameters were refined up to hexadecapole level ( $l = 4$ ) for V and C atoms, and dipole level ( $l = 2$ ) for H atoms with the inclusion the metal 4s-orbital contribution to the X-ray scattering; that resulted in the lowest  $R$ -values and goodness of fit ( $R = 0.017$ ,  $R_w = 0.027$ , GOF = 0.98). The obtained multipole population coefficients were recalculated to the d-electron orbital occupancies using the procedure described in Ref. [28].

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