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Mendeleev Commun., 2019, **29**, 346–348

Mendeleev Communications

Experimental study of X-ray charge density and the selection of reference points for a source function in η^6-(2-methyl-1,4-dihydro-2*H*-3,1-benzoxazine)tricarbonylchromium(0)

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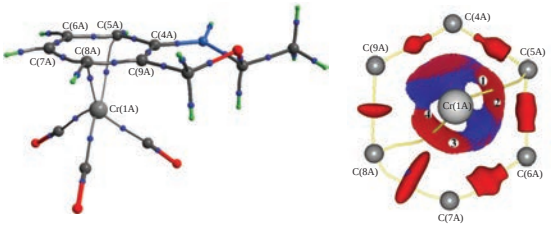
DOI: 10.1016/j.mencom.2019.05.036

An approach based on the simultaneous use of a source function and a noncovalent interaction index for studying interatomic interactions in the absence of bond critical points is offered. This approach comprises the selection of reference points for the source function on the noncovalent interaction index isosurface.



The Atoms In Molecules (AIM) theory[1] not always reproduces the expected interatomic bond paths and bond critical points [CP(3,–1)]. Obviously, it is observed in the complexes containing π-carbocyclic ligands.[2–8] A conclusion was made that the indicators of interatomic interactions different from bond paths and CP(3,–1) are required. A source function (SF)[9–11] and a noncovalent interaction (NCI)[12–14] index based on the reduced electron density gradient (RDG) are used as such indicators. The SF provides a measure of the relative importance of each atomic basin contribution to the density at a reference point (rp). Usually, the rps are selected in CP(3,–1), and in case of their absence on the middle of the corresponding interatomic distances. In turn, the NCI index reliably localizes the positions of observed critical points. We consider the isosurface of the NCI index, which can be used for searching space regions where CP(3,–1) could be located, but it was not found due to a small curvature of electron density. Here, we test the offered approach based on an example of the η^6-(2-methyl-1,4-dihydro-2*H*-3,1-benzoxazine)tricarbonylchromium(0) complex **1**.

According to the X-ray diffraction data† [Figure 1(*a*)], an asymmetric unit of complex **1** contains two independent molecules in common position, which have close geometric parameters (Table S1, see Online Supplementary Materials). The carbonyl groups in both independent molecules of complex **1** are disposed in an orientation close to eclipsed relative to the arene rings. The same orientation is observed in η^6-[(5-methyl-1,3-oxazolidin-3-yl)benzene]tricarbonylchromium(0)[22] complex. This orientation does not lead to a significant alternation of the C–C bonds in the arene ring, as distinct from staggered one.[2,23–25] The Cr–C_{arene} and Cr–C(CO) distances are 2.2019(5)–2.3383(5) and 1.8371(7)–1.8435(5) Å, respectively. Note that the hydrogen atoms in **1** are slightly shifted from the arene ring plane toward the metal atom

† *X-ray analysis*. The data were collected on an Agilent Xcalibur E diffractometer (graphite-monochromated MoKα radiation) at 100 K. The structure was solved by dual methods and was refined on F^2 using the SHELXTL[15] package. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and were refined in the riding model. SCALE3 ABSPACK[16] was used to perform area-detector scaling and absorption corrections.

Crystal data for **1**. M = 285.22, triclinic, space group $P\bar{1}$, a = 7.8714(1), b = 11.0927(1) and c = 13.8006(1) Å, α = 99.586(1)°, β = 93.650(1)°, γ = 91.223(1)°, V = 1185.14(2) Å^3, Z = 4, d_{calc} = 1.599 g cm^{-3}, μ = = 0.970 mm^{-1}, F(000) = 584. Intensities of 283260 reflections were measured (θ < 53.866°) and 29110 independent reflections (R_{int} = 0.0264) were used in further refinement, which converged to wR_2 = 0.1043 and GOF = 1.071 for all observed reflections [R_1 = 0.0388 was calculated against F for 22924 observed reflections with $I > 2\sigma(I)$]. The residual electron densities (max/min) and completeness data were 1.146/–1.111 e Å^{-3} and 1.0.

The multipole refinement was carried out within the Hansen–Coppens formalism[17] using the MoPro program package.[18] Before the refinement, C–H bond distances were normalized to the values obtained in neutron diffraction analyses.[19] The level of the multipole expansion was hexadecapole for chromium atoms, octupole for all other non-hydrogen atoms, and one dipole for hydrogen atoms.

The refinement of compound **1** (θ < 51.42°) was carried out against F and converged to R = 0.0284, wR = 0.0206, GOF = 0.998 for 20457 merged reflections with $I > 2\sigma(I)$. The ratio of the number of reflections to the number of refined parameters was > 10. All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria.[20] Analysis of topology of experimental $\rho(r)$ function was carried out using the WinXPRO program package.[21] The residual electron densities around chromium atoms were no greater than ~0.789 e Å^{-3}.

CCDC 1881904 (for IAM refinement) and 1881905 (for multipole refinement) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

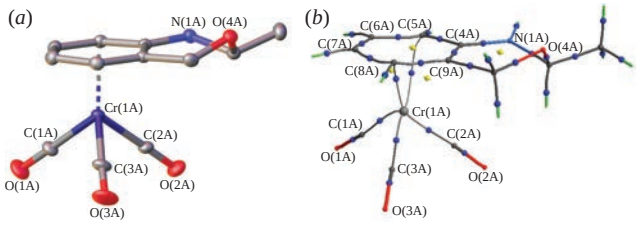


Figure 1 (*a*) Molecular structure and (*b*) experimental molecular graph of an independent molecule of complex **1**. The critical points [blue CP(3,–1) and yellow CP(3,+1)] are presented by points.

(0.1076–0.2267 Å). Such geometrical parameters are typical of tricarbonyl(η^6-arene)chromium complexes.

According to the AIM theory[1] (Table S2), all Cr–C bonds in the coordination sphere of **1** are intermediate interactions [$\nabla^2\rho(r) > 0$, $h_e(r) < 0$], whereas the O–C ones are shared interactions [$\nabla^2\rho(r) < 0$, $h_e(r) < 0$]. The topological parameters of electron density (ED) in **1** are in good agreement with analogous ones for tricarbonyl(η^6-arene)chromium complexes.[2,23]

An analysis of the experimental molecular graph of an independent molecule of complex **1** has shown that there are only two bond paths and CP(3,–1) between the chromium atom and the arene fragment of the molecule [Figure 1(*b*)]. Note that three bond paths and CP(3,–1) are found in another independent molecule of complex **1** between analogous fragments. Thus, the quantity of observed bond paths and bond critical points is much less than expected. As pointed out previously, the AIM bond–path analysis is an insensitive indicator for systems containing a very flat change of ED. Really high values of ellipticity (ε)[26] in CP(3,–1) between the chromium atom and the arene fragment indicate a small curvature of ED [ε = 1.06 and 2.92 for Cr(1A)–C(5A) and Cr(1A)–C(8A) interactions, respectively], which essentially complicates a search for all expected critical points and bond paths. For the characterization of Cr–η^6-arene interactions, we used the SF both in CP(3,–1) and on the middle of the corresponding distances and also on the NCI index isosurface. In this work, we first used the selection of the rps for the SF on the NCI index isosurface. The source function percentage contributions in CP(3,–1) of the Cr–C_{arene} fragment are presented in Table S3 (see Online Supplementary Materials). All contributions in the CP(3,–1) of chromium and carbon atoms of the arene fragment have positive values. Consequently, the Cr–η^6-arene interaction occurs in these rps. However, the absence of four expected CP(3,–1) between the chromium atom and the arene fragment does not allow us to carry out such investigation completely. Therefore, we have selected the rps for the SF on the middle of the Cr(1)–C(4A–9A) distances. Unexpectedly, we have found that the carbon atom contributions in the SF at selected rps have negative values for Cr(1A)–C(4A,C6A,C8A,C9A) bonds (Table S4). In other words, a depletion of charge density is observed for these carbon atoms from corresponding rps. Such data lead to complications in their interpretation.

Therefore, we have decided to compare the locus of the rps relatively the NCI index isosurface [Figure 2(*a*),(*b*)]. The reference points lie near the NCI index isosurface. However, the analysis of the coordinates of the rps and the NCI index isosurface has shown that the rps do not lie exactly on this isosurface. Thus, we do not reliably know in what space region (ED concentration or depletion) the selected rps are disposed. To avoid such an uncertainty, we used the NCI index isosurface for the selection of rps. Note that the NCI index isosurface denotes regions of ED concentrations ($\lambda_2 < 0$, attraction) and depletions ($\lambda_2 > 0$, repulsion). In addition, we can select much more rps on the isosurface and analyze more carefully the SF values. The disposition of the rps on the NCI index isosurface and the SF values for the Cr–C_{arene} fragment are presented in Figure 2(*c*),(*d*) and Table S5. As we can see, all values are positive as distinct from analogous ones in Table S4. Additional nine randomly selected rps in the regions of ED concentrations ($\lambda_2 < 0$) for the SF showed a similar result (Table S6). Thus, the rps selected both on the NCI index isosurface and in CP(3,–1) unambiguously denote η^6-interaction between chromium and arene ligand in **1**, as distinct from data obtained for the SF on the middle of the Cr–C_{arene} distances. Obviously, in the general case, the ED concentration regions are not disposed on the middle of the Cr–C_{arene} distances. Therefore, the easiest way of the rp selection [at absence CP(3,–1)] not always is reliable and rational.

In conclusion, based on an example of the η^6-(2-methyl-1,4-dihydro-2*H*-3,1-benzoxazine)tricarbonylchromium(0) complex, we have shown that the rps selected on the NCI index isosurface for the SF are the best alternative, as compared to analogous points selected on the middle of the Cr–C_{arene} distances. This selection of the rps for the SF on the NCI index isosurface makes it possible to more reliably and reasonably interpret the Cr–η^6-arene interactions in the absence of bond critical points.

This work was supported by the Russian Science Foundation (project no. 18-13-00356). The X-ray study was carried out using the equipment of the Analytical Center of the G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences.

Online Supplementary Materials

Supplementary data associated with this article [geometrical and topological parameters, the SF values selected in CP(3,–1), on the middle of the Cr–C_{arene} distances and on the NCI index isosurface and also description of synthesis of **1**] can be found in the online version at doi: 10.1016/j.mencom.2019.05.036.

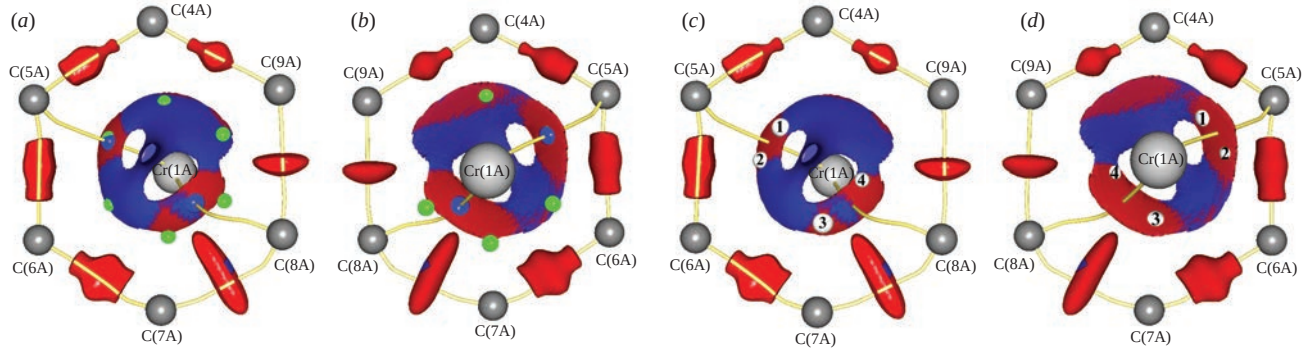


Figure 2 Experimental NCI isosurfaces (0.15 a.u.) for the Cr–C_{arene} fragment in **1** [(*a*),(*c*) Cr behind arene and (*b*),(*d*) Cr before arene]. The surface between Cr and arene is colored on a red–blue scale according to the values of sign(λ_2)ρ ranging from –2.67 to 1.94 a.u. Blue points are CP(3,–1), green points are middle of the Cr–C_{arene} distances and grey points (1–4) are rps on the NCI index isosurface.

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Received: 29th November 2018; Com. 18/5751