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Atomic Interactions in Ethylenebis(1-indenyl)zirconium Dichloride as Derived by Experimental Electron Density Analysis

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Synopsis

Topological analysis of the experimental electron density in the *racemic* ethylenebis(1-indenyl)zirconium dichloride, $C_{20}H_{16}Cl_2Zr$, has been performed. All the atomic interactions and a charge transfer from the Zr atom to the ligands were quantitatively characterized and the "ligand-opposed" charge concentrations around Zr were revealed using the Laplacian of the electron density and one-particle potential.

Abstract

Topological analysis of the experimental electron density in the *racemic* ethylenebis(1-indenyl)zirconium dichloride, $C_{20}H_{16}Cl_2Zr$, measured at 100(1) K, has been performed. The atomic charges calculated by the numerical integration of the electron density over the zero-flux atomic basins demonstrate the charge transfer of 2.25 e from the Zr atom to both indenyl ligands (0.39 e) and two *Cl* atoms (1.86 e). All the atomic interactions were quantitatively characterized in terms of the electron-density and the electronic energy-density features at the bond critical points. Only the Zr-C2 bond path significantly curved towards the C1-C2 bond was found; at the same time, the π-electrons of the C1-C2 bond are significantly involved in the metal-ligand interaction. The whole set of the electron density features allows the conclusion to be reached that the indenyl coordination can be approximately described as η^1 with slippage towards η^2. The "ligand-opposed" charge concentrations around the Zr atom were revealed using the Laplacian of the electron density and one-particle potential; they were linked to the orbital representations. Bonds in the indenyl ligand were characterize using the Cioslowski-Mixon bond order indices calculated directly from the experimental electron density.

Table 1d. Atomic positions (fractional coordinates) and equivalent atomic displacement parameters $U_{eq} = (U_{11} + U_{22} + U_{33})/3$ (Å^2)

Atom	X	Y	Z	U_{eq}
Zr	0.0	0.27096(1)	0.25	0.01050(3)
Cl	-0.13663(3)	0.42391(3)	0.18356(3)	0.01810(10)
C1	-0.00096(10)	0.07445(9)	0.13253(12)	0.01533(31)
C2	-0.09916(10)	0.13217(13)	0.05619(13)	0.01697(36)
C3	-0.09025(11)	0.24804(12)	0.00161(12)	0.01663(35)
C31	0.01387(10)	0.26197(11)	0.04039(11)	0.01540(30)
C4	0.06548(15)	0.35226(12)	0.00659(16)	0.02284(46)
C5	0.16771(16)	0.33559(14)	0.05595(19)	0.02611(54)
C6	0.22310(13)	0.23102(17)	0.14003(18)	0.02431(56)
C7	0.17602(11)	0.14139(12)	0.17343(14)	0.01834(36)
C71	0.06912(9)	0.15484(9)	0.12276(11)	0.01403(29)
C8	0.02364(15)	-0.04895(10)	0.20717(17)	0.02307(46)
H2	-0.17180	0.10198	0.04282	0.026(4)
H3	-0.15320	0.31013	-0.06578	0.021(4)
H4	0.02356	0.43001	-0.06134	0.022(4)
H5	0.21141	0.39981	0.03229	0.051(6)
H6	0.30431	0.21939	0.17729	0.034(5)
H7	0.21923	0.05591	0.22377	0.026(4)
H81	0.10523	-0.06382	0.26857	0.026(3)
H82	-0.00516	-0.12790	0.13891	0.035(4)

Table 2d. Atomic charges and kappa parameters from the multipole refinement

Atom	Atomic charge, e	κ
Zr	+1.33(7)	1.27(5)
Cl	- 0.77(4)	1.02(1)
C1	-0.15(3)	1.02(1)
C2, C3	-0.17(2)	1.02(1)
C4, C5, C6, C7	-0.16(2)	1.02(1)
C31, C71	-0.11(2)	1.02(1)
C8	+0.01(3)	1.01(1)
H2, H3	+0.28(2)	1.2*
H4, H5, H6, H7	+0.21(1)	1.2*
H81, H82	+0.03(2)	1.2*

* Kappa values for H atoms did not refine

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Fig.1d. Fragment of the electron density distribution in *rac*-EBIZD: density bridges of 0.31 e·Å^{-3} corresponding to the Zr-C2 contact are shown by arrows.

Fig. 2d. Electron density in the planes, perpendicular to the C-C bonds of indenyl at the bond critical points. Vertical direction is perpendicular to the ring plane. Line interval is 0.1 eÅ^{-3}.

Fig. 3d. Residual maps around the Zr atom (a) and in the mean-square plane going through the indenyl ligand (b). Line interval is 0.1 e·Å^{-3}, excessive density values are solid.

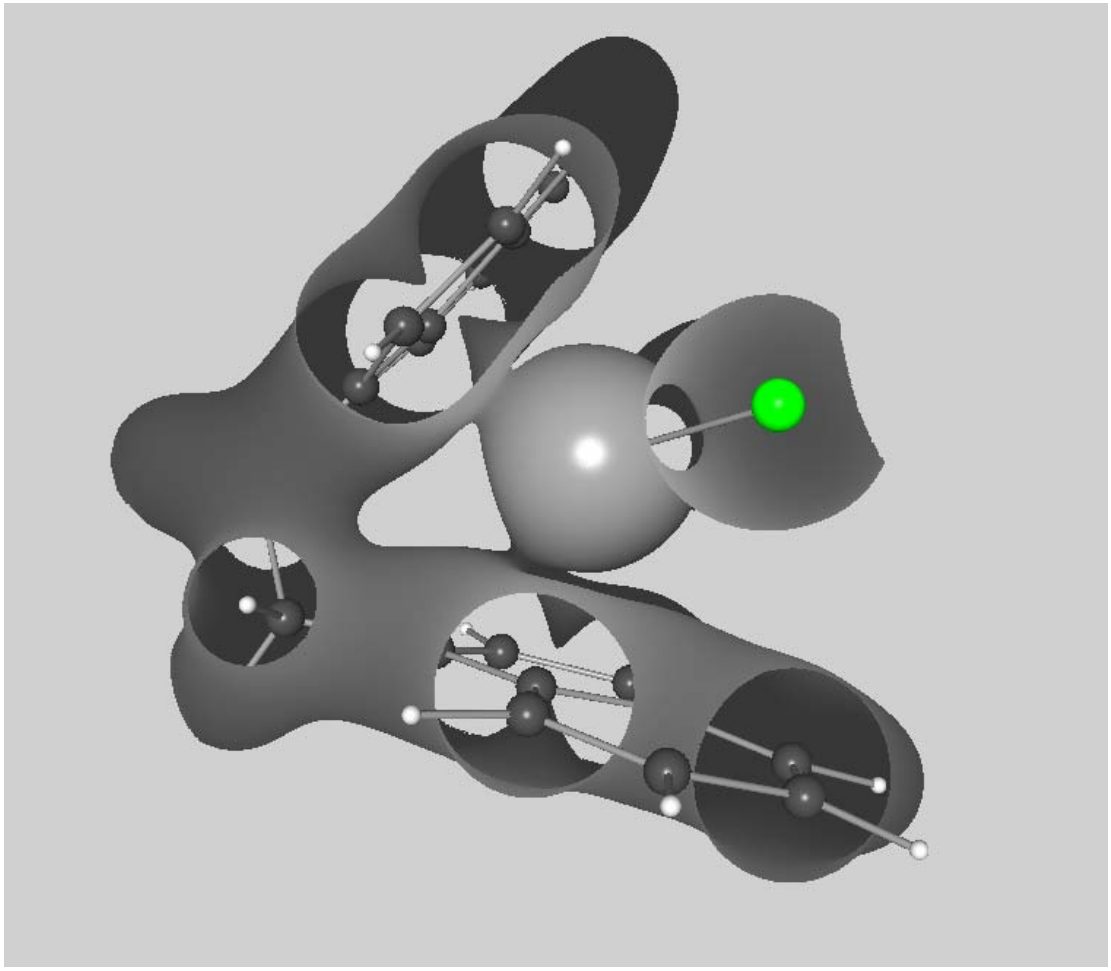

Fig. 1d

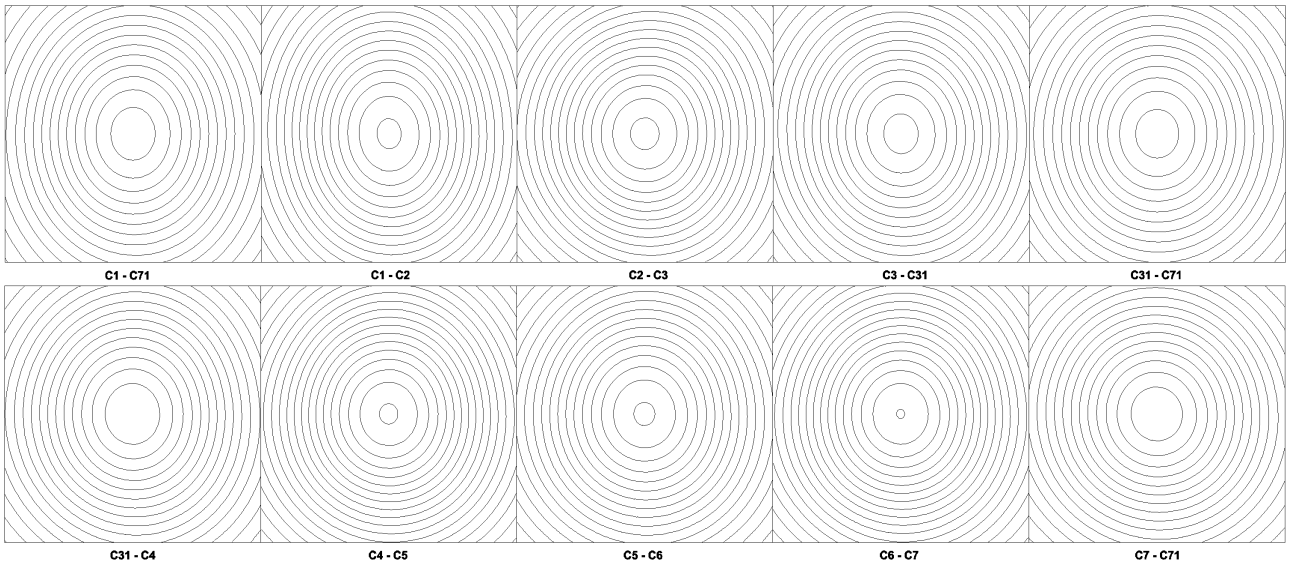

Fig. 2d

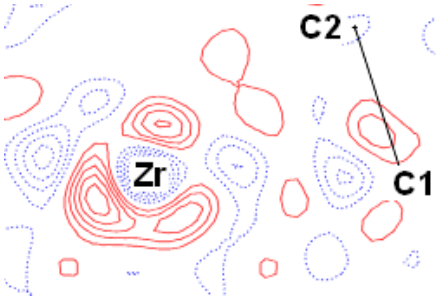

Fig. 3d_a

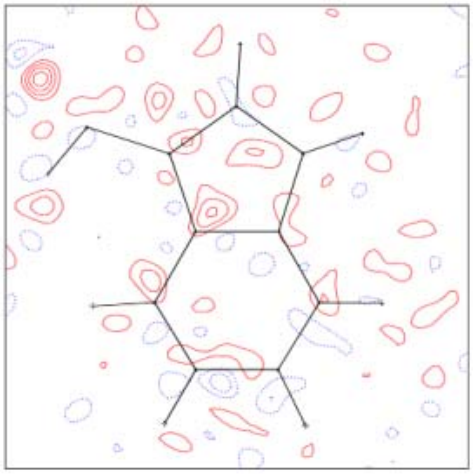

Fig. 3d_b