*Inorg. Chem.* **2003**, *42*, 8128–8130

# Energy Density Distribution in Bridged Cobalt Complexes

**Markus Finger and Joachim Reinhold***

*Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, D-04103 Leipzig, Germany*

Received August 28, 2003

In the theory of atoms in molecules (AIM), the charge density is usually a suitable tool for bonding analyses. However, problems arise in some cases. So, no direct Co–Co bond is found in $Co_2(CO)_8$. It is shown that the energy density gives deeper insight into the bonding properties. This is demonstrated for $Co_2(CO)_8$, $Co_4(CO)_{12}$, and $Co_2(CO)_6(InMe)_2$. The strategy is not restricted to transition metal compounds; it should be useful to identify any weak bonding or antibonding interactions.

Bader's theory of atoms in molecules (AIM)[1] is nowadays widely accepted in population and bonding analyses. In this theory, a bond is generally indicated by the existence of a bond critical point (*bcp*) characterized by the minimum of the charge density $\rho$ along the path of maximum charge density between two atoms. More specific information concerning the nature of the molecular interactions is provided by the Laplacian $\nabla^2\rho$ of the charge density, distinguishing between regions of charge accumulation and charge depletion. It has been shown by Cremer and Kraka that the *energy* density *H*, resulting as the sum of the kinetic energy density *G* and the potential energy density *V*, is even more sensitive for analyzing bonding effects.[2,3] *Bcp*'s of negative energy density are assigned to be bonding.

Despite the capacity of the method, only a few AIM analyses for complexes featuring bonds between transition metal centers have been published. Among the considered systems, $Co_2(CO)_8$ received special attention. For this compound, the 18-electron rule predicts a direct Co−Co bond. However, this so-called bent bond is still a matter of controversy. Neither the molecular orbitals picture gives a clear answer, nor deformation density maps.[4,5] An AIM analysis could open a new view. But, as already pointed out by Low *et al.*[5] and Macchi *et al.*,[6] no Co−Co *bcp* exists (see Figure 1). Correspondingly, for the related $Co_4(CO)_{12}$ system (see Figure 2), Macchi *et al*. obtained Co−Co *bcp*'s only between the unbridged, but not between the bridged Co centers.[7]

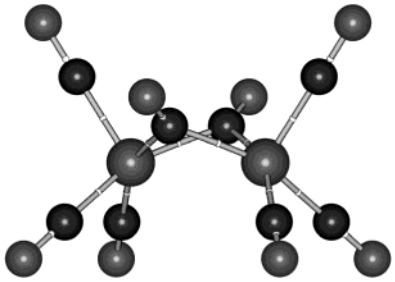

**Figure 1.** Structure of $Co_2(CO)_8$ (*bcp*'s are indicated by white dots).

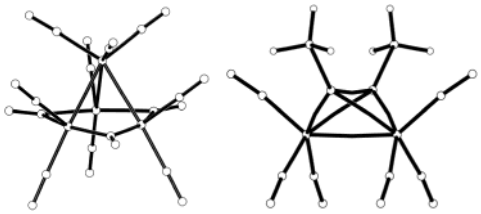

**Figure 2.** Structures of $Co_4(CO)_{12}$ and $Co_2(CO)_6(InMe)_2$.

Otherwise, *bcp*'s between bridged metal centers were found in the case of various bridging ligands except CO.[8] As expected, metal−metal bonds appear to be rather weak in comparison to metal−ligand bonds (see Table 1). The question arises, whether the charge density characteristics related to Co−Co bent bonds in $Co_2(CO)_8$ and $Co_4(CO)_{12}$ might be overwhelmed by the charge density related to the much stronger Co−CO bonds. Macchi *et al*. denied this conclusion for $Co_4(CO)_{12}$.[7]

To investigate the bent-bond problem in further detail, we have examined various charge and energy densities along lines crossing the respective bonding regions, i.e., the charge

* Author to whom correspondence should be addressed. E-mail: reinhold@quant1.chemie.uni-leipzig.de.

(1) Bader, R. F. W. *Atoms in Molecules*; Clarendon Press: Oxford, 1990.
(2) (a) Cremer, D.; Kraka, E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 627. (b) Cremer, D.; Kraka, E. *Croat. Chem. Acta* **1984**, *57*, 1259.
(3) In detail, the energy densities are as follows: kinetic energy density $G(\mathbf{r}) = {}^1/_2 N \int \nabla\Psi^* \nabla\Psi \, d\mathbf{r}'$, potential energy density $V(\mathbf{r}) = N \int \Psi^* (-\mathbf{r}\nabla V_o)\Psi \, d\mathbf{r}'$, (total) energy density $H(\mathbf{r}) = G(\mathbf{r}) + V(\mathbf{r})$, where $\mathbf{r}'$ indicates integration over the coordinates of all electrons but one. $V_o$ is the potential operator.[1,2] The energy densities are connected with the Laplacian of the charge density by Bader's formula $2G(\mathbf{r}) + V(\mathbf{r}) = {}^1/_4 \nabla^2\rho(\mathbf{r}) = -L(\mathbf{r})$.[1]
(4) Leung, P. C.; Coppens, P. *Acta Crystallogr.* **1983**, *B 39*, 535.
(5) Low, A. A.; Kunze, K. L.; MacDougall, P. J.; Hall, M. B. *Inorg. Chem.* **1991**, *30*, 1079.
(6) Macchi, P.; Sironi, A. *Coord. Chem. Rev.* **2003**, *238/239*, 363.
(7) Macchi, P.; Garlaschelli, L.; Martinengo, S.; Sironi, A. *J. Am. Chem. Soc.* **1999**, *121*, 10428.
(8) (a) Bianchi, R.; Gervasio, G.; Marabello, D. *Helv. Chim. Acta* **2001**, *84*, 722. (b) Bianchi, R.; Gervasio, G.; Marabello, D. *Acta Crystallogr.* **2001**, *B57*, 638. (c) Uhl, W.; Melle, S.; Frenking, G.; Hartmann, M. *Inorg. Chem.* **2001**, *40*, 750.



10.1021/ic035011i CCC: $25.00 
Published on Web 11/13/2003

**Table 1.** Examples of *bcp* Characteristics of Metal−Metal Bonds in Binuclear Complexes ($\rho$ and $H$ in au/Å$^{-3}$, $\nabla^2\rho$ in au/Å$^{-5}$)[a]

| | | $d$[b] | $\rho_c$ | $\nabla^2\rho_c$ | $H_c$ |
|---|---|---|---|---|---|
| Unbridged Metal−Metal Bonds | | | | | |
| $Mn_2(CO)_{10}$ | exptl[c] | 290.4 | 0.190 | 0.815 | −0.031 |
| $Co_2(CO)_6(AsPh_3)_2$ | exptl[d] | 264.3 | 0.204 | 1.344 | −0.025 |
| | calcd[d] | 264.0 | 0.271 | 0.043 | −0.090 |
| $Co_4(CO)_{11}(PPh_3)$ | exptl[7] | 252.8 | 0.252 | 1.81 | −0.039 |
| $Co_4(CO)_{12}$ | calcd[7] | 252.0 | 0.355 | −0.11 | −0.152 |
| $Co_2(CO)_8$ ($D_{3d}$) | calcd[6] | 274.6 | 0.227 | 0.06 | −0.063 |
| Bridged Metal−Metal Bonds | | | | | |
| $Co_2(CO)_7(C_2O_4H_2)$ | exptl[8a] | 242.2 | 0.76 | 2.0 | −0.46 |
| $Co_2(CO)_7(C_2O_4H_2)$ | exptl[8b] | 244.0 | 0.46 | 3.4 | |
| $Ni_2Cp_2(InCH_3)_2$ | calcd[8c] | 249.1 | 0.282 | 0.809 | −0.074 |
| $Ni_2Cp_2(GaCH_3)_2$ | calcd[8c] | 244.9 | 0.300 | 1.118 | −0.075 |
| Co−CO (terminal) | calcd[e] | | 0.927 | 12.76 | −0.34 |

[a] For comparison, a metal−ligand bond in $Co_2(CO)_8$ is included. [b] M−M bond length in pm. [c] Bianchi, R.; Gervasio, G.; Marabello, D. *Inorg. Chem.* **2000**, *39*, 2360. [d] Macchi, P.; Proserpio, M.; Sironi, A. *J. Am. Chem. Soc.* **1998,** *120*, 13429. [e] This work.

density $\rho$, the energy density[9] $L$ related to the Laplacian $\nabla^2\rho$ of the charge density, the kinetic energy density $G$, the potential energy density $V$, and the (total) energy density $H$.

DFT calculations in the idealized experimental structures[4,7,10] applying the B3LYP[11] functionals were performed using the Gaussian98 program package.[12] For cobalt and indium a (14s,11p,6d,3f)/[8s,6p,4d,1f] and a (19s,15p,9d)/[8s,7p,5d], respectively, all-electron basis[13] was used, whereas for the other atoms the standard 6-31G* basis sets[14] were used throughout. The bonding analyses were undertaken with EXTREME contained in the AIMPAC package[15] of Bader.

In Figure 3, the results for $Co_2(CO)_8$ are presented. The densities along the 2-fold symmetry axis are displayed in dependence on the distance from the Co−Co vector. The maximum of the charge density $\rho$, which is a minimum in the perpendicular plane, represents a ring critical point. The minimum of $L$ indicates repulsive interactions between the cobalt−ligand bonds. The energy densities $G$ and $V$ also show extrema in this area. The energy density $H$, however,

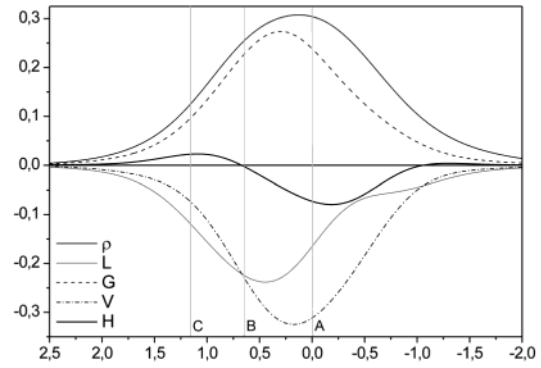


**Figure 3.** Charge density $\rho$ and energy densities (in au/Å$^{-3}$) along the 2-fold axis in $Co_2(CO)_8$. $L$ is equivalent to the negative of the Laplacian, and $G$ and $V$ are the kinetic and potential energy densities, respectively, whereas $H$ sums up both contributions. Lines A, B, and C indicate the positions of the Co−Co, C−C, and O−O connecting vectors, respectively.

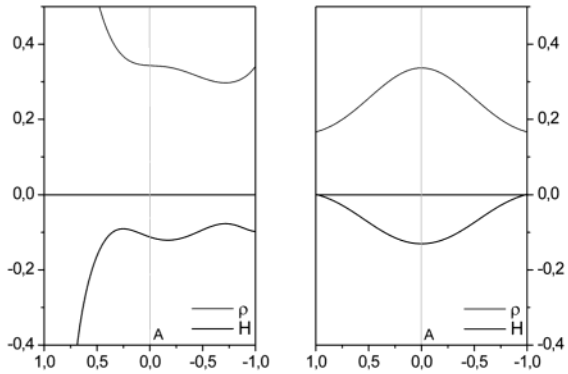


**Figure 4.** Charge density $\rho$ and energy density $H$ (in au/Å$^{-3}$) in $Co_4(CO)_{12}$ along a line perpendicular to the Co−Co bonds. For the bridged bond (left), this line points from the bridging CO "inside"; for the unbridged bond (right), it is normal to the symmetry plane. Line A indicates the position of the Co−Co vector.

turns out to be more sensitive than its individual contributions. It shows a distinct minimum in the bent-bond region and a maximum between the bridging CO's.

The formation of a chemical bond is connected with a decrease of the total energy of the system. The larger this energy decrease, the more stable is the resulting bond. By examining the energy density $H$, the local contributions to the total molecular electronic energy can be discussed. Attractive interactions are represented by negative values of $H$, contributing to the decrease of the total molecular energy. Accordingly, we interpret the obtained minimum of $H$, which is also a minimum in the perpendicular plane, as a direct Co−Co bonding interaction, not only supporting the prediction of the 18-electron rule but also showing a slight but distinct bending. Contrary, repulsive interactions are connected with positive values of $H$ having an increasing effect on the total molecular energy. Consequently, the maximum of $H$ clearly indicates repulsive interactions between the two bridging CO's. This agrees with results recently obtained in a different way for derivatives of $Fe_2(CO)_9$.[16]

The essential results for $Co_4(CO)_{12}$ are presented in Figure 4. Again, a slightly bent direct bonding interaction between

(9) $L = -^1/_4\nabla^2\rho$ is used instead of the Laplacian to allow the simultaneous presentation of all densities in one graph.

(10) Uhl, W.; Keimling, S. U.; Hiller, W.; Neumayer, M. *Chem. Ber.* **1996**, *129*, 397.

(11) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B 37*, 785.

(12) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11.3; Gaussian Inc.: Pittsburgh, PA, 1998.

(13) (a) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033. (b) Bauschlicher, C. W., Jr.; Langhoff, S. R.; Barnes, L. A. *J. Chem. Phys.* **1989**, *91*, 2399. (c) Ahlrichs, R.; May, K. *Phys. Chem. Chem. Phys.* **2000**, *2*, 943.

(14) Hehre, W. J.; Radom, L.; Schleyer, P.v. R.; Pople, J. *Ab-initio Molecular Orbital Theory*; Wiley: New York, 1986.

(15) Biegler-König, F. W.; Bader, R. F. W.; Tang, T.-H. *J. Comput. Chem.* **1982**, *3*, 317.

(16) (a) Barthel, A.; Mealli, C.; Uhl, W.; Reinhold, J. *Organometallics* **2001**, *20*, 786. (b) Reinhold, J.; Barthel, A.; Mealli, C. *Coord. Chem. Rev.* **2003**, *238/239*, 333.

the bridged Co centers is indicated by the minimum of *H*. For the unbridged bonds, the minimum of *H* corresponds to the *bcp* position situated between the two Co centers (line A). Remarkably, for both cases, comparable charge and energy characteristics result.[17]

We extended the investigations to $Co_2(CO)_6(\mu\text{-InMe})_2$, a derivative of $Co_2(CO)_8$, in which the bridging CO's are substituted by indyl ligands. Now, a *bcp* between the two Co centers results. This is somewhat surprising, because the Co−Co distance is around 30 pm longer than in the parent compound, for which no *bcp* exists. The energy density *H*, however, shows a similar minimum for both systems (compare Figure 5 with Figure 3). The only difference is that the direct Co−Co bond is not bent. By using a sufficiently extended (*triple-ζ*) basis set for In, an additional weak bonding interaction between the two In centers is found, indicated by a *bcp* and a flat minimum of *H*. Thus, the bridging moiety in $Co_2(CO)_6(\mu\text{-InR})_2$ can be considered as a $Co_2In_2$ cluster unit, which has been assumed by Uhl *et al.*[10] for $R = C(SiMe_3)_3$.

It has turned out that, in many cases, the investigation of the topology of the *charge* density is an appropriate way for bonding analyses. However, weak bonding interactions as metal−metal bonds might be overwhelmed. In such cases, the *energy* density can be a valuable tool for a careful and sensitive bonding analysis. The strategy is not restricted to transition metal compounds; it should be useful to identify any weak bonding or antibonding interactions.

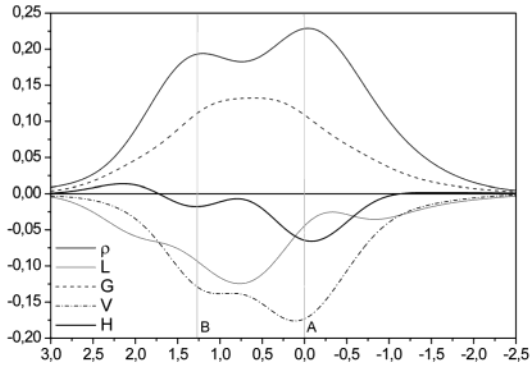


**Figure 5.** Charge and energy densities (in au/Å$^{-3}$) along the 2-fold axis in $Co_2(CO)_6(\mu\text{-InMe})_2$. Lines A and B indicate the positions of the Co−Co and In−In connecting vectors, respectively.

**Acknowledgment.** We thank the Fonds der Chemischen Industrie for financial support.

IC035011I

(17) The differences in the charge densities obtained by Macchi *et al.*[7] seem to be caused by using Hartree−Fock densities.