Experimental charge density study of the Mn–Mn bond in $Mn_2(CO)_{10}$ at 120 K

R. Bianchi,[a] G. Gervasio[b]† and D. Marabello[b]

[a] *Centro CNR per lo Studio delle Relazioni tra Struttura e Reattività Chimica, Milano, Italy*
[b] *Dipartimento di Chimica I.F.M. dell'Università, Torino, Italy*

This paper presents an analysis of the charge density, $\rho(r)$, for the Mn–Mn bond in $Mn_2(CO)_{10}$, determined by a multipole model from accurate X-ray data measured at 120 K.

The experimental deformation charge densities of some binuclear metal carbonyls, $[CpFe(CO)_2]_2$, $(\mu\text{-}CH_2)[CpMn(CO)_2]_2$ and $Mn_2(CO)_{10}$, were determined by X-ray diffraction some years ago.[1–3] The theoretical deformation densities for other similar complexes, $Fe_2(CO)_9$ and $Co_2(CO)_8$, and for $Mn_2(CO)_{10}$ were also reported in refs. 4 and 5.

In all the three complexes examined by X-ray diffraction, the deformation maps showed no evidence of significant density accumulation in the metal–metal bonding region. This result was justified by the presence of bridging groups (CH_2 or CO), which join the two metallic fragments to form the entire molecule. This explanation was also supported by the theoretical calculations made for $Fe_2(CO)_9$ and $Co_2(CO)_8$. However, in the case of $Mn_2(CO)_{10}$, which has only terminal carbonyl groups, two Mn–Mn bonding hypotheses were considered: the first is a direct metal–metal bond and the second is an interaction between the d_{xz} or d_{yz} orbitals of one manganese and the π^* orbital of the equatorial carbonyls of the other manganese.[3,6,7] The last hypothesis could be also supported by the bending of equatorial carbonyls towards the opposite Mn atom. Note that the above two hypotheses are not supported by experimental evidence, but a theoretical study, based on Bader's quantum theory of atoms in molecules (QTAM),[8] proved the existence of the Mn–Mn bond in $Mn_2(CO)_{10}$.[9]

Here we report the experimental charge density of the title compound, determined by accurate X-ray data, measured at 120 K and interpreted by the aspherical-atom formalism developed by Stewart.[10] Further, the results of the Bader analysis on the experimental charge density are reported, in order to confirm the existence of the Mn–Mn bond. This is the first topological analysis of the experimental charge density in binuclear metal complexes.

A crystal of $Mn_2(CO)_{10}$ recrystallized from a light petroleum solution was made spherical to a diameter of 0.51 mm and put in a Lindemann glass capillary. The intensity data were collected on a Siemens P4 diffractometer equipped with a low temperature device using liquid nitrogen. 20507 reflections were collected at 120 K, up to $2\theta = 110°$, with Mo-Kα radiation ($\lambda = 0.71073$ Å) and with the θ–2θ scan method. Other experimental data are summarized in Table 1. Further information on data collection will be given in the full paper. However, our data collection is not better than that of ref. 3, because they measured the low-order reflections ($\sin\theta/\lambda < 0.76$ Å^{-1}) with the same crystal but two different X-ray wavelengths, Ag-Kα and Mo-Kα.

The quantity minimized in the multipole refinement was $\Sigma w(|F_o|^2 - k^2|F_c|^2)^2$ based on 6217 independent reflections with $I > 2\sigma(I)$ and weights $w = 1/\sigma^2(|F_o|^2)$. The data were corrected for absorption effects, extinction corrections were not introduced and the anomalous dispersion was considered only for the Mn atom. The final aspherical fit to X-ray data was obtained with the following multipole model (POP). Each pseudoatom is assigned a small finite multipole expansion of the atomic form factor. The multipole expansion included two monopoles for C and O atoms and three monopoles for Mn atom and the higher terms were up to the octupole level, except for Mn (up to hexadecapole level). The monopoles consist of shells constructed from the canonical SCF s-, p- and d-orbitals.[11] For the higher multipoles, Slater-type radial functions with fixed standard molecular exponents were used for all carbons and oxygens[12] and the radial exponents of Mn atom were determined in the refinement procedure. All calculations were performed using a modified version of the VALRAY program.[13] The final agreement factors and some other refinement information are listed in Table 1.
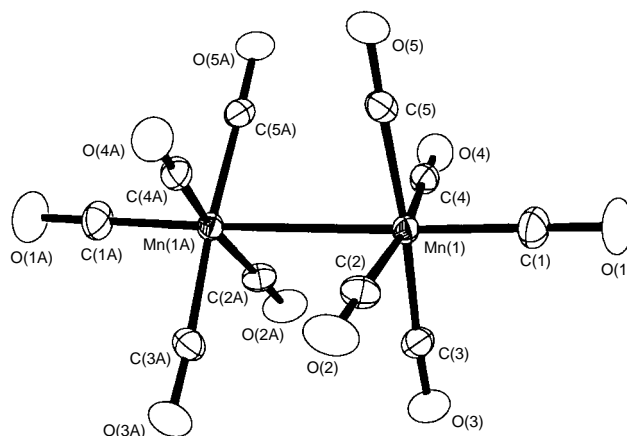
Table 1 Crystal data and multipole POP refinement information

Lattice type; space group	monoclinic; $C2/c$
a/Å	17.314(4)
b/Å	6.898(1)
c/Å	14.110(3)
$\beta/°$	126.94(3)
Z	4
N_o (number of reflections)	6217
N_p (number of parameters)	290
$R(\text{int}) = \Sigma||F_o|^2 - |F_o|^2(\text{mean})|/\Sigma|F_o|^2$	0.033
$R(\text{sigma}) = \Sigma[\sigma(|F_o|^2)]/\Sigma|F_o|^2$	0.039
$R(F) = \Sigma||F_o| - k|F_c||/\Sigma|F_o|$	0.0326
$wR(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$	0.0216
$R(F^2) = \Sigma||F_o|^2 - k^2|F_c|^2|/\Sigma|F_o|^2$	0.0424
$wR(F^2) = [\Sigma w(|F_o|^2 - k^2|F_c|^2)^2/\Sigma w|F_o|^4]^{1/2}$	0.0403
$S = [\Sigma w(|F_o|^2 - k^2|F_c|^2)^2/(N_o - N_p)]^{1/2}$	1.209
k (scale factor)	0.2477(5)
$(\text{shift/e.s.d.})_{max}$	< 0.02

Fig. 1 An ORTEP plot (30% probability) of the entire molecule of $Mn_2(CO)_{10}$.[16] The molecule has crystallographic C_2 symmetry with the two-fold axis passing through the middle of the Mn–Mn bond. Each Mn atom links four equatorial and one axial CO groups in a pseudo-octahedral environment. The equatorial CO groups of the two Mn atoms are staggered [51° between the CO(1)–Mn(1)–CO(2) and CO(1A)–Mn(1A)–CO(2A) planes]. The Mn–Mn bond distance is 2.9042(8) Å; this value is in keeping with the observed dependence on the temperature [2.923(3) Å r.t., 2.9042(8) Å 120 K, 2.8950(6) Å 74 K].[3]
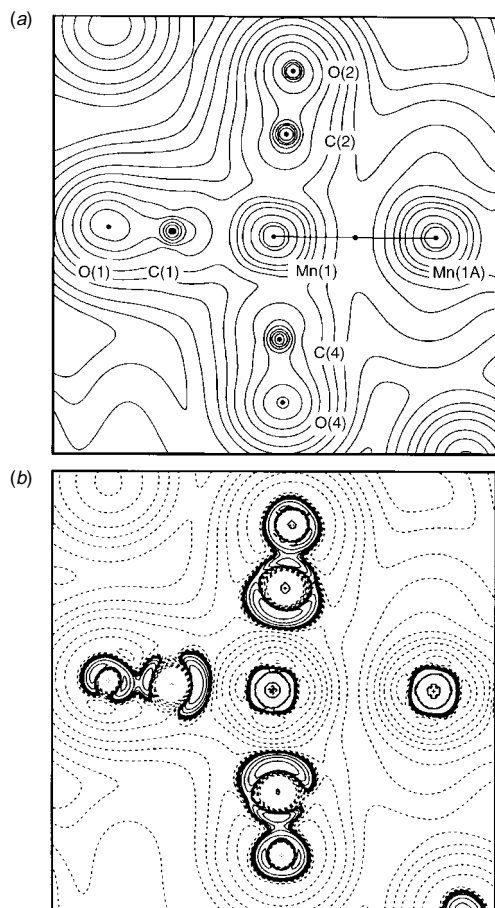
Fig. 2 Experimental charge density, $\nabla\rho(\mathbf{r})$ (*a*), and its Laplacian, $\nabla^2\rho(\mathbf{r})$ (*b*), on the plane defined by Mn(1), Mn(1A) and C(2). The absolute values of the contours (atomic units) increase from the outermost one inwards in steps of 2×10^n, 4×10^n and 8×10^n with n beginning at -3 and increasing in steps of 1. It has been shown that a necessary and sufficient condition for two atoms to be involved in a bonding interaction is the existence in $\nabla\rho(\mathbf{r})$ of a line linking the nuclei along which the charge density is at a maximum with respect to any lateral displacement. Such a line is called a bond path, and the interatomic critical point $\mathbf{r}_c$ [where $\nabla\rho(\mathbf{r}_c) = 0$] occurring on it is a bond critical point (bcp). At the bcp, there are two negative curvatures (λ_1 and λ_2) that determine the contraction of ρ towards $\mathbf{r}_c$ in the directions perpendicular to the bond path, and one positive curvature, λ_3, parallel to the interaction line. The values of $\rho(\mathbf{r}_c)$ and of $\nabla^2\rho(\mathbf{r}_c) = \lambda_1 + \lambda_2 + \lambda_3$ characterize the atomic interaction. In (*a*) the bond paths of $\nabla\rho(\mathbf{r})$ which originate at bcp are superimposed on the same map and the bcp position is denoted by a black dot. In (*b*) positive values are denoted by dashed contours, negative values are denoted by solid contours.

The total electron density, $\rho(\mathbf{r})$, based on the multipole model, the gradient and Hessian of $\rho(\mathbf{r})$ were calculated with a direct space lattice sum. The topological analysis of $\rho(\mathbf{r})$ (search of critical points and bond paths[14]) was carried out using the TOPOND program,[15] interfaced to VALRAY. The topology of $\rho(\mathbf{r})$ has been fully described by Bader in the QTAM.

The molecular structure, with the atomic labeling, is shown in Fig. 1. The largest peak in the residual density (based on $F_{\text{obs}} - F_{\text{multipole}}$) is 0.33 e Å^{-3} and it is close to the Mn position. We observe a slightly positive and not significant deformation density of 0.1(1) e Å^{-3} (total density minus free spherical atoms) at the midpoint of the Mn–Mn bond. On the other hand

a very small deformation density has also been observed between the two metal atoms in previous works.[1,3]

Fig. 2 shows the total electron density map and its Laplacian, derived from the multipole POP model, in the plane containing the axial [C(1)–O(1)], the two equatorial carbonyl groups [C(2)–O(2) and C(4)–O(4)] and the two Mn atoms. The number of bcps we found in the experimental electron density corresponds to the expected number of bonds for $Mn_2(CO)_{10}$, including the interaction between the two Mn atoms as illustrated in Fig. 2(*a*). The density at the bcp between the two heavy atoms is 0.190(4) e Å^{-3}. No bcps were found for any cross interaction between one metal and the equatorial COs linked to the other metal atom. The positive value of $\nabla^2\rho(\mathbf{r})$ at the Mn—Mn bcp [0.815(8) e Å^{-5}; Fig. 2(*b*)] indicates an unshared interaction[14] between the two Mn atoms: the density is contracted towards each Mn nucleus. Indeed, one finds that $\lambda_3 = 1.209(3)$ e Å^{-5} is here dominant with respect to $\lambda_1 = \lambda_2 = -0.199(3)$ e Å^{-5}. This behaviour is similar to that found in the ionic and van der Waals interactions and clearly indicates a totally different nature with respect to a typical covalent interaction.

In conclusion, an accurate description of the total electron density has been obtained from a multipole analysis of the X-ray data. The low temperature (120 K) at which the diffraction experiment was performed allowed us to obtain a significant total electron density in the metal–metal region and the Bader analysis of this density was a useful tool to characterize the nature of their interaction.

Notes and References

1 A. Mitschler, B. Rees and M. S. Lehmann, *J. Am. Chem. Soc.*, 1978, **100**, 3390.
2 D. A. Clemente, M. Cingi Biagini, B. Rees and W. A. Hermann, *Inorg. Chem.*, 1982, **21**, 3741.
3 M. Martin, B. Rees and A. Mitschler, *Acta Crystallogr.*, *Sect. B*, 1982, **38**, 6.
4 W. Heiser, E. J. Baerends and P. Ros, *Discuss. Faraday Soc.,* 1980, **14**, 211.
5 A. Veillard and M.-M. Rhomer, *Int. J. Quantum Chem.,* 1992, **42**, 965.
6 R. Bau, S. W. Kirtley, T. N. Sorrel and S. Winark, *J. Am. Chem. Soc.*, 1974, **96**, 988.
7 D. A. Brown, W. J. Chambers, N. J. Fitzpatrick and R. M. Rawlinson, *J. Chem. Soc. A*, 1971, 720.
8 R. F. W. Bader, *Atoms in molecules—a Quantum Theory,* Oxford University Press, Oxford, 1990.
9 P. J. McDougall, Ph.D. Thesis, McMaster University, 1989; P. J. McDougall and M. B. Hall, *Trans. Am. Crystallogr. Assoc.*, 1990, **26**, 101.
10 R. F. Stewart, *Acta Crystallogr.*, *Sect. A,* 1976, **32**, 565.
11 E. Clementi and C. Roetti, *At. Data Nucl. Data Tables,* 1974, **14**, 177.
12 W. J. Hehre, R. Ditchfield, R. F. Stewart and J. A. Pople, *J. Chem. Phys.*, 1970, **51**, 2769.
13 R. F. Stewart and M. A. Spackman, VALRAY User's Manual, Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA, 1983.
14 R. F. W. Bader and H. Essen, *J. Chem. Phys.*, 1984, **80**, 1943.
15 C. Gatti, V. R. Saunders and C. Roetti, *J. Chem. Phys.*, 1993, **101**, 10686.
16 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.