Treatment of Light Atoms in *X*-Ray Structural Studies on Metal Carbonyl Clusters: a Critical View

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A significant 'sliding' of the C atoms towards the O atoms is observed on passing from isotropic to anisotropic refinement of the light atoms in conventional room temperature *X*-ray investigations on metal carbonyl clusters; differences in bond lengths are discussed with respect to results of neutron diffraction studies.

Carbon monoxide interacts with transition metal clusters, adopting a wide range of geometries. The capacity of the CO ligand to bond to metal atoms in terminal, double bridging, triple bridging, and in various asymmetric fashions, renders CO the most versatile ligand in cluster chemistry and certainly the most commonly encountered in all metal cluster structures.[1] Some well established relationships exist between structural parameters of the CO molecule and the way in which it is bonded to one or more metal atoms.[2] For instance, different degrees of π-back donation from metal atom d-orbitals into π^*-orbitals of the CO system are reflected by variations in the M–C and C–O bond lengths. Also, more efficient π-accepting capacity is attributed to bridging CO than to terminal CO groups; the latter usually show shorter M–C and C–O distances. In many cases subtle electronic effects (such as partial charge localization on metal atoms or change in the anionic charge on a metal polyhedron) within the same system or among entire classes of related compounds have been recognized by inspection and correlation of CO-ligand parameters. In the majority of these cases data from solid state structural investigations have been employed.

We now report that the use of different strategies for the treatment of conventional room temperature *X*-ray data sets may introduce a significant bias to such an extent that some speculations, based on comparison of M–C and C–O parameters, may become highly unreliable.

In the course of the investigation of the structure of $[NEt_4]_2[Co_6C(CO)_{13}]$[3] we first noted a systematic difference between Co–C and C–O bond lengths when the light atoms were assigned isotropic *vs.* anisotropic displacement ('thermal') parameters. Differences between the two kinds of models are not a novelty; however, the fact that a general lengthening of the Co–C distances was accompanied by an equivalent shortening of the C–O ones simply on passing from isotropic to anisotropic refinement of the C and O atoms was unexpected (Table 1). In other words the C-atoms were found to 'slide' along the M–O vectors, whose lengths remained almost unaltered (Figure 1). The bond length differences are

Table 1. Comparison of M–C and C–O bond lengths determined using isotropic and anisotropic models.

$[NEt_4]_2[Co_6C(CO)_{13}]$[a]				
$(\sin\theta/\lambda)_{max.}/Å^{-1}$	0.48		0.66	
$N_{obs.}$ $[F_0 > 5\sigma(F_0)]$	3261		5994	
	Iso.	Aniso.	Iso.	Aniso.
$N_{var.}$	251	471	251	471
R	0.044	0.028	0.047	0.030
R_w	0.052	0.030	0.054	0.032
Co–C_t/Å[d]	1.704(10)	1.762(7)	1.737(8)	1.760(4)
C–O_t/Å	1.180(13)	1.136(8)	1.156(10)	1.134(6)
Co–C_{br}/Å[d]	1.902(10)	1.930(6)	1.922(7)	1.928(4)
C–O_{br}/Å	1.195(13)	1.166(8)	1.174(10)	1.166(6)
$H_4Ru_4(CO)_{10}Ph_2P[CH_2]_3PPh_2$[b]				
$(\sin\theta/\lambda)_{max.}/Å^{-1}$	0.48		0.59	
$N_{obs.}$ $[F_0 > 5\sigma(F_0)]$	2059		3177	
	Iso.	Aniso.	Iso.	Aniso.
$N_{var.}$	200	300	200	300
R	0.043	0.033	0.048	0.039
R_w	0.045	0.034	0.049	0.038
Ru–C_t/Å	1.85(2)	1.89(2)	1.86(2)	1.90(1)
C–O_t/Å	1.16(2)	1.14(2)	1.16(2)	1.13(1)
Ru–C–O/°	176(2)	176(2)	176(2)	176(2)
$[(CH_2Ph)_2Me_2N][Ir_4(CO)_{11}SCN]$[c]				
$(\sin\theta/\lambda)_{max.}/Å^{-1}$	0.48		0.62	
$N_{obs.}$ $[F_0 > 6\sigma(F_0)]$	2132		3204	
	Iso.	Aniso.	Iso.	Aniso.
$N_{var.}$	220	330	220	330
R	0.028	0.025	0.035	0.032
R_w	0.035	0.031	0.041	0.036
Ir–C_t/Å	1.870(20)	1.908(20)	1.878(20)	1.911(20)
C–O_t/Å	1.170(20)	1.123(20)	1.151(20)	1.125(20)

[a] Ref. 3. [b] Ref. 4. [c] Ref. 5. [d] t = terminal, br = bridge.

Table 2. Comparison of M–C and C–O bond lengths obtained from *X*-ray and neutron diffraction data.

$[(Ph_3P)_2N][HCo_6(CO)_{15}]$[a]		
	X-Ray	Neutron
$(\sin\theta/\lambda)_{max.}/Å^{-1}$	0.54	0.52(0.58)[b]
$N_{obs.}$ $[F_0^2 > 3\sigma(F_0^2)]$	4966	3574
T/K	177	80
C and O refinement	Iso.	Aniso.
$N_{var.}$	244	463
Co–C_t/Å[g]	1.747(12)	1.768(13)
C–O_t/Å	1.160(16)	1.143(7)
Co–C_{br}/Å 'long'[c,g]	2.169(14)	2.186(13)
'short'	1.777(14)	1.830(14)
C–O_{br}	1.202(20)	1.157(8)
Co–C_{br}[d]	1.876(11)	1.922(13)
C–O_{br}[d]	1.195(13)	1.169(7)
$Co_3(CO)_9CH$[e]		
	X-Ray	Neutron
$(\sin\theta/\lambda)_{max.}$ $Å^{-1}$	0.59	0.61(0.79)[b]
$N_{obs.}$ [*X*-ray: $F_0^2 > 3\sigma(F_0^2)$; neutron: all data]	2159	3781
T/K	92	92
C and O refinement	Aniso.	Aniso.
Co–C_t[d]/Å	1.837(2)	1.837(1)
C–O_t/Å	1.134(2)	1.136(1)
Co–C_t/Å	1.796(2)	1.798(1)
C–O_t/Å	1.136(3)	1.137(1)

[a] Ref. 7. [b] Only strong reflections were measured between the lower and upper $(\sin\theta/\lambda)_{max.}$ values. [c] Distances averaged for 'asymmetric' CO bridges. [d] Symmetric CO bridge. [e] Ref. 8. [f] Two sets of non-equivalent terminal CO groups were present. [g] t = terminal, br = bridge.

of the order of 0.05 Å or less, which is close to the detectable limit, but since they do appear to be significant we have initiated a systematic investigation of other metal carbonyl clusters (test cases are reported in Table 1), which has led us to the conclusion that this effect is generally observed when data of sufficient quality are available. It must be noted that bridging CO ligands, when present, behave in much the same way as terminal CO ligands, although the 'sliding' effect of the C atoms towards the O atoms is less pronounced. This difference in behaviour may reflect the different electronic situations of the two types of bonding modes. No differences were detected for the heavy atoms. We have also demonstrated, by varying the $(\sin\theta/\lambda)$ cutoff, that the difference between the two kinds of refinements decreases, as expected, with increasing $(\sin\theta/\lambda)_{max.}$, although coincidence could not be achieved (Table 1).

The exclusion of high order data from least squares refinements is known to affect both displacement and positional parameters because of the inadequacy of the spherical atom scattering factor for low order reflections.[6] However, this fact does not seem to account for significant changes in the bond length distribution of the kind described here. [As a first consequence, the usual practice of adopting a limit of 2θ = 40° for accepting *X*-ray data on poorly diffracting or decaying carbonyl cluster crystals (which gives a barely adequate resolution of *ca.* 1 Å with Mo-K_α radiation) must be regarded with great suspicion when details beyond the pure metal framework and ligand distribution are sought.]

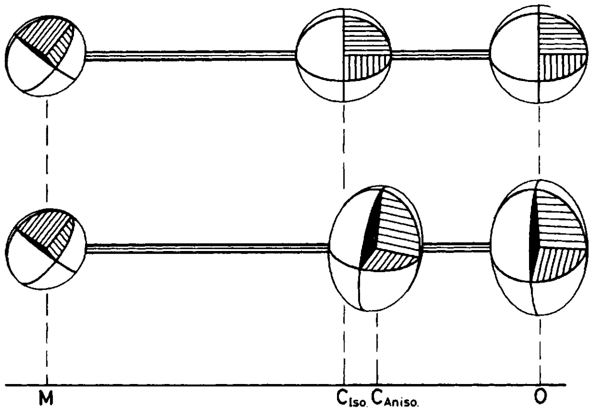

Figure 1. Schematic representation of the 'sliding' effect on a terminally bound CO group.

An examination of the results of neutron diffraction structure determinations in the very few cases for which comparison with good quality *X*-ray data are also available seems to indicate that positions of the C atoms as obtained from anisotropic refinement (even of fairly limited data sets) are closer to the nuclear positions derived from neutron data. A striking case[7] is that of $[(Ph_3P)_2N][HCo_6(CO)_{15}]$ where the same kinds of systematic differences are observed between M–C and C–O distances determined from isotropic refinement of *X*-ray data (at 177 K) and anisotropic refinement of neutron data (at 80 K), respectively. Conversely, a very good match of *X*-ray and neutron data is observed in the case of $Co_3(CO)_9CH$[8] where both structure models were treated with full anisotropy (Table 2) and the data were obtained at an identical temperature (92 K).

Differences between *X*-ray and neutron derived atomic positions are well established as being due to the fact that the *X*-ray positions lie at electron density 'centroids' which are influenced by valence electrons. This 'asphericity shift,' first noticed for H-atoms in organic structures, has been observed also for first row atoms in pronounced asymmetric bonding environments or when heavy atoms dominate the *X*-ray scattering.[9] Differences can be reduced by refining the nuclear positions on high-angle *X*-ray data alone assuming that these are dominated by the inner-core electrons.[9] Unfortunately this procedure is very often not feasible for conventional room temperature *X*-ray data collected on metal clusters because of both the paucity of measurable high-order data and the large number of atoms involved.

Our preliminary survey seems to indicate that this 'sliding' effect, though caused by the refinement procedure chosen, reflects a peculiar geometric and/or electronic situation present in metal-bound CO groups (and, presumably, in other metal-co-ordinated light molecules). Clearly, when accuracy in conventional *X*-ray work on metal clusters is desired, great care must be taken in the choice of the refinement strategies: whenever possible the largest $\sin\theta/\lambda$ range should be covered and light atoms refined anisotropically.

We thank Prof. V. G. Albano, Prof. K. N. Trueblood, and Dr. R. K. McMullan for helpful discussions, and M.P.I. (Italy) and the U.S. Department of Energy for support.

Received, 22nd September 1986; Com. 1355

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