Supramolecular, Bifurcated N-H···OC-M Bonding Explains Unusually Low ν_{CO} Frequencies in Metal Carbonyl Compounds: A Case Study[**]

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Dedicated to Professor M. Veith
on the occasion of his 60th birthday

Infrared spectroscopy has played a central part in the identification and elucidation of the structures of metal carbonyl compounds, with the ν_{CO} spectral region being the

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Supporting information for this article (including the crystallographic data for *cis*-[W(CO)$_4$(piperidine)$_2$], an ORTEP view, a powder X-ray diffraction pattern, and its IR spectrum (KBr pellet and pure solid)) is available on the WWW under http://www.angewandte.org or from the author.

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most diagnostic. In addition to the relationship derived from group theory between the stereochemistry of a metal carbonyl complex and the number and activity of its ν_{CO} modes, their frequency range correlates with the bonding mode of the CO ligands. In general, terminal CO groups absorb between 2100–1850 cm^{-1}, whereas doubly bridging CO ligands absorb between 1850–1750 cm^{-1} and triply bridging CO ligands absorb below 1730 cm^{-1}. This spectral shift arises as a consequence of the progressive decrease in C–O bond order.[1] Infrared spectroscopy is far more sensitive than X-ray diffraction to small changes in bond orders, despite the irreplaceable value of the latter for establishing the spatial arrangement of atoms and molecules in the solid state. We show below, in a case study, that an archetypal complex with terminal carbonyl ligands has unusual ν_{CO} frequencies below 1770 cm^{-1}, and that this observation can be rationalized by the presence of a remarkable and unexpected supramolecular, bifurcated N-H···OC-M network in the solid state.

Some metal complexes enjoy the privilege of being ubiquitous precursors to wide ranges of new molecules. This has been the case in metal–carbonyl chemistry with *cis*-[M(CO)$_4$(piperidine)$_2$] (M = Mo, W), which have been used for almost 30 years to prepare octahedral metal carbonyl complexes of the type *cis*-[M(CO)$_4$L$_2$]; the lability of the piperidine ligands allows the synthesis of the desired products under much milder conditions and in better yields than when starting from the parent hexacarbonyl compounds.[2,3] It is therefore not surprising that these complexes have been very highly cited and their synthesis has even been published several times—with only minor variations, since it simply results from the thermal or photochemical activation of [M(CO)$_6$] in the presence of excess piperidine [Eq. (1)].[4]

$$\mathrm{M(CO)_6} + \text{excess } \mathrm{NHC_5H_{10}} \xrightarrow[-2\,\mathrm{CO}]{\text{thermal or photochemical activation}} cis\text{-}[\mathrm{M(CO)_4(NHC_5H_{10})_2}] \qquad (1)$$

The most common characterization methods have been elemental analysis and IR spectroscopy in the ν_{CO} region, where four bands are expected for a C_{2v} local symmetry ($\Gamma_{vib} = 2\,A_1 + B_1 + B_2$). To the best of our knowledge, the only IR data available for *cis*-[W(CO)$_4$(piperidine)$_2$] are those published by Tripathi et al. who reported values of 2000, 1865, 1844, and 1814 cm^{-1} (in mulls, no intensities given),[4c] which are different from our own data (see below).

Recent studies on the reaction of *p*-benzoquinonediimine ligands with *cis*-[W(CO)$_4$(piperidine)$_2$] revealed an interesting metal-coordination-induced *para–ortho*-quinone isomerization and relocalization of the π system.[5] We were surprised to find a solid-state (KBr pellet) IR spectrum (see the Supporting Information) for *cis*-[W(CO)$_4$(piperidine)$_2$] with ν_{CO} bands down to 1768(vs) cm^{-1}, that is, at energies much lower than expected for terminal CO ligands in a neutral complex.[1,6] After performing purity controls and triggered by the lack of any previous report on this most unusual observation,[7] we grew single crystals of *cis*-[W(CO)$_4$(piperidine)$_2$] by slow diffusion of heptane into a THF solution and subjected them to an X-ray diffraction study. The ORTEP view of the crystal structure (see the Supporting Information) confirms that the piperidine ligands are in a *cis* arrangement and that all the carbonyl groups are of the linear type, with M–C–O angles of 174.1(4) and 179.1(3)°. Figure 1 also reveals the existence of a remarkable network of intermolecular bifurcated H-bonds. Figure 2 shows a projection of the structure in the *a*,*b* plane, with the channel-like 3D structure evident. Each octahedral complex molecule acts as a bridge between two other molecules: each N–H proton interacts with two carbonyl groups, each belonging to a different molecule. Conversely, each CO ligand *trans* to a piperidine

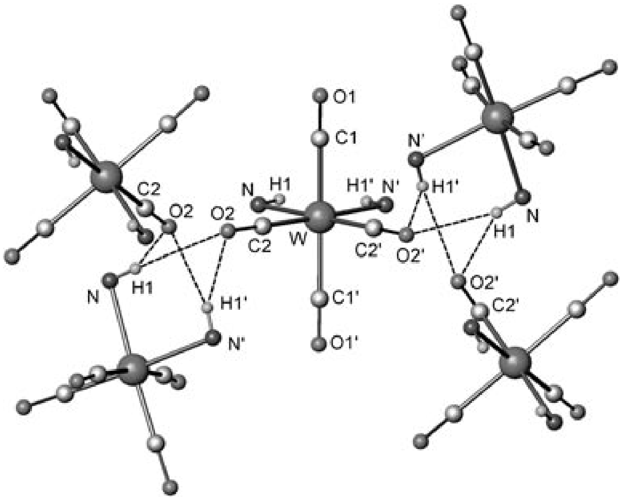

Figure 1. Partial view of the crystal structure of *cis*-[W(CO)$_4$(piperidine)$_2$] resulting from a bifurcated H-bonding network involving all the N–H protons and the CO ligands *trans* to the piperidine ligands. The carbon skeleton of the piperidine ligands has been omitted for clarity.

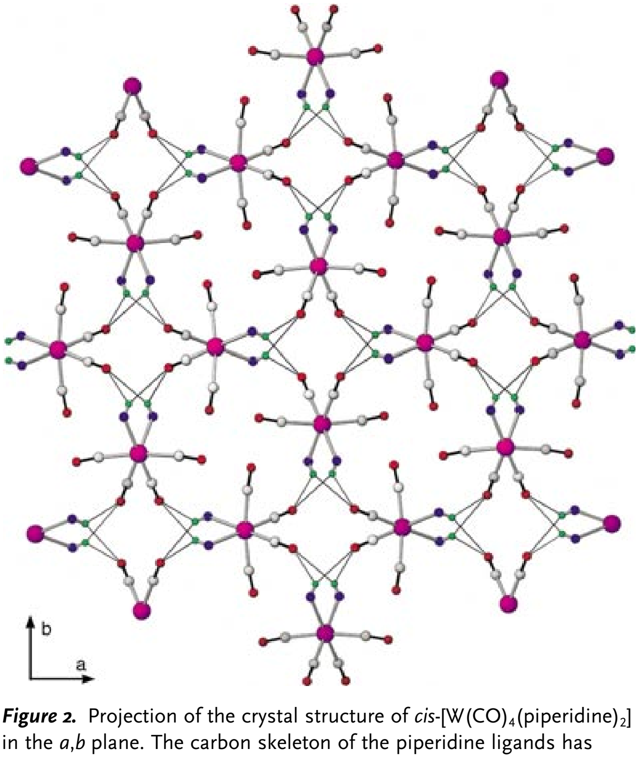

Figure 2. Projection of the crystal structure of *cis*-[W(CO)$_4$(piperidine)$_2$] in the *a*,*b* plane. The carbon skeleton of the piperidine ligands has been omitted for clarity. Color coding: W purple, O red, N blue, N–H green.

moiety on each complex interacts with the two N–H protons from another molecule (Table 1). The observation that these H-bonding interactions selectively involve the two carbonyl ligands which are *trans* to the strong σ-donating/weak π-accepting piperidine ligands is perfectly consistent with their more electron-rich nature. This results in a) a considerable reduction in the electron density at these oxygen atoms, which leads therefore to ν_{CO} absorptions much more typical of bridging carbonyl groups or isocarbonyl linkages than of terminal CO ligands,[1] and b) an IR ν_{NH} vibration as low as 3254 cm^{-1} in KBr. The X-ray diffraction pattern of a microcrystalline powder of *cis*-[$W(CO)_4$(piperidine)$_2$] was recorded at 300 K and could be completely indexed on the basis of the extinction conditions of the tetragonal system in the space group $P4_32_12$ with $a = 11.864(1)$ and $c = 11.058(1)$ Å. This observation is in complete agreement with the data obtained from the single crystal study (see the Supporting Information). To ensure that no special matrix effect was caused by the KBr pellets, drops of a solution of the complex in THF were evaporated on a single crystal of KBr and the IR spectrum recorded. The ν_{CO} values found were almost identical (see the Supporting Information). These H-bonding interactions also remain in a Nujol mull (ν_{CO}: $\tilde{\nu} = 2005$(m), 1900(sh), 1874(vs), 1829(s), 1787(sh), 1769(vs) cm^{-1}, and these values are at variance with those reported in the literature,[4c]) but as expected, they disappear in solution, as shown by the IR spectrum showing four ν_{CO} absorptions in the usual range ($\tilde{\nu} = 1998$(w), 1920(w), 1860(vs), 1823(s) cm^{-1} in THF). The hydrogen-bonding capability of carbonyl ligands versus C–H bond donors is well-documented[8a,b] and increases with increasing basicity: terminal M-CO < μ_2-CO < μ_3-CO.[8c,d] A search of the Crystallographic Cambridge Data Base for analogous N–H···OC–M (M = Group 6 metal) interactions involving terminal carbonyl groups identified 225 hits with a median value of 2.582 Å (a value which is consistent with our data), but none for *cis*-[$M(CO)_4$(piperidine)$_2$] complexes. Interestingly, Kraihanzel and Cotton noted that the "solid-state spectrum of [$Mo(CO)_4$(ethylenediamine)$_2$] is strikingly different from the solution spectrum" and suggested that the extreme insolubility of this compound might be a result of NH···OC hydrogen bonding, but this was not (and has never been since) substantiated by X-ray diffraction data.[9] It was stated on the basis of the X-ray structure of *cis*-(diethylenetriamine)tricarbonylmolybdenum that "clearly, there are no strong intermolecular NH···O bonds".[10] Although Shiu et al. noted a low frequency ν_{CO} absorption at 1790 cm^{-1} in the solid-state spectrum of the complex [$Mo(CO)_4$(N-N)] (N-N = $PhCH_2NHCH_2CH_2NMe_2$), they concluded from the X-ray data that "an intermolecular H-bond between the N–H atom of one molecule and a carbonyl oxygen atom of another molecule is negligible in this compound".[11] However, such an intermolecular bonding interaction was cautiously discussed in [Mo(di-2-pyridylamine)$(CO)_4$] although it involved only one CO ligand,[12] whereas no H-bonding was observed in [Mo(bipy)(di-2-pyridylamine)$(CO)_3$].[13] An intermolecular N-H···O distance of 2.15 Å has been reported for the pyridine-4(1*H*)-thione complex [$W(C_5H_5NS)(CO)_5$] but no IR data are available, which precludes any correlation between H-bonding and ν_{CO} shifts.[14] The IR spectra of *cis*-[$W(CO)_4$(piperidine)$_2$] were compared to those of *cis*-[Mo(or W)$(CO)_4$(pyridine)$_2$] (in THF solution, KBr pellets, or Nujol mulls).[15a,b] As expected, the latter display no unusual features, which is consistent with the X-ray structure of the tungsten complex which shows "no particularly short intermolecular contacts".[15c] Although ion-pair interactions between an oxygen atom of a carbonylmetalate anion and its associated cation are known to produce significant ν_{CO} shifts to lower energies, this represents a very different situation to that involving a neutral molecule.[16]

Table 1: Selected bond lengths [Å] and angles [°] for *cis*-[$W(CO)_4$(piperidine)$_2$].

intramolecular data			
W-C1	2.038(4)	W-C2	1.951(4)
W-N	2.323(3)	C1-O1	1.140(5)
C2-O2	1.168(4)	N-H1	0.77(4)
C1-W-C1′	172.1(2)	C1-W-N′	92.6(1)
C1′-W-N′	93.2(1)	C2′-W-C2	90.7(2)
C2′-W-C1	87.65(15)	C2-W-C1	86.83(15)
C2′-W-N′	91.7(1)	C2-W-N′	177.5(1)
C2′-W-N	177.5(1)	C2-W-N	91.7(1)
N′-W-N	85.90(15)	W-N-H1	97(3)
O1-C1-W	174.1(4)	O2-C2-W	179.1(3)
hydrogen bonds			
O2-N	3.22(1), 3.14(1)	O2-N′	3.14(1), 3.22(1)
O2-H1	2.61(1), 2.50(1)	O2-H1′	2.50(1), 2.61(1)
O2-H1′-N′	141.5(2), 138.7(2)	O2-H1-N	137.7(2), 141.5(2)

Since the space group in which this molecule crystallizes is chiral, we investigated its nonlinear optical (NLO) properties, but no second order effect was observed.

In conclusion, we have shown that supramolecular H-bonding interactions can dramatically affect the ν_{CO} frequencies of metal–carbonyl compounds, and consequently can make structural assignments based on vibrational spectroscopy alone misleading or incorrect. In a case study, we have established that the long-known and archetypal carbonyl complex *cis*-[$W(CO)_4$(piperidine)$_2$] displays most unusual, low-frequency ν_{CO} absorptions in the solid state which are not the result of the strong σ-donor/weak π-acceptor properties of the amine ligands but of supramolecular interactions involving the piperidine N–H proton and the carbonyl oxygen atom of the two CO ligands *trans* to the piperidine ligands. Although the crystal structure of *cis*-[$Mo(CO)_4$(piperidine)$_2$] was reported very recently, no mention was made of either intermolecular H-bonding interactions or unusual IR data in the solid state.[17] We examined a freshly prepared sample of *cis*-[$Mo(CO)_4$(piperidine)$_2$] and found that the IR spectra recorded in KBr pellets or Nujol mull were very similar to those of the tungsten derivative (see Experimental section), but at variance with literature values.[4f] It is therefore most likely that similar intermolecular N-H···O interactions are also present in the Mo derivative. It would not be surprising that other metal–carbonyl complexes containing H-bond donors, even with the less-basic terminal CO ligands, reveal similar features to *cis*-[$W(CO)_4$(piperidine)$_2$]. In other cases where solid-state IR data have been reported for complexes of the type *cis*-[W(CO)$_4$(amine)$_2$] and low values found for their ν_{CO} frequencies, no comment was made or explanation offered.[18] Such questions are of clear relevance to crystal engineering. In a different context, it is interesting to note that the activation of organic carbonyl compounds by double H-bonding is increasingly used in asymmetric catalysis.[19]

Experimental Section

All reactions were carried out under purified N_2 in freshly distilled solvents by using Schlenk techniques. A solution of *cis*-[W(CO)$_4$(piperidine)$_2$], prepared by a slightly modified standard procedure[4d] (using xylene as a solvent), in THF was layered with heptane and unsolvated, pale yellow crystals were obtained by slow diffusion. $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN, 298 K): $\delta = 211.23$ (s), 210.93 ppm (s, CO). These values are consistent with those reported for similar complexes.[20]

Crystal data: $C_{14}H_{22}N_2O_4W$, $M_r = 466.19$, tetragonal, space group $P4_32_12$, $a = 11.936(1)$, $b = 11.936(1)$, $c = 11.210(1)$ Å, $U = 1597.1(2)$ Å^3, $Z = 4$, $\mu(\mathrm{Mo}_{K\alpha}$, $\lambda = 0.71073$ Å$) = 7.249$ mm^{-1}, $T = 173$ K, 2339 unique reflections collected, $R = 0.0224$ for 2173 reflections with $I > 2\sigma(I)$, wR2 = 0.0559. Data collection on a Nonius Kappa-CCD area detector diffractometer using Denzo software. The structure was solved by direct methods (SIR97) with full-matrix least-squares refinement on F^2 using SHELXL97 software. The absorption was corrected empirically.[21] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms, except H1, which was found by Fourier differences, were generated according to the stereochemistry and refined using a riding model in SHELXL97.[22] CCDC 234274 contains the supplementary crystallographic data (excluding structure factors). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

The IR spectrum of solid *cis*-[W(CO)$_4$(piperidine)$_2$], deposited by evaporation of a THF solution on a single crystal of KBr, contains the expected four ν_{CO} absorptions at $\tilde{\nu} = 2004$(m), 1875(vs), 1830(s), 1774(vs) cm^{-1}, similar to those found for this complex in a KBr pellet.[6]

The complex *cis*-[Mo(CO)$_4$(piperidine)$_2$] was prepared in a similar manner to the W complex (shorter reaction times) and its IR spectrum was recorded for comparison: ν_{CO} (KBr): $\tilde{\nu} = 2012$(mw), 1913(sh), 1887(vs), 1838(s), 1792(sh), 1774(vs) cm^{-1}. ν_{CO} (solid deposited by evaporation of a THF solution on a single crystal of KBr): $\tilde{\nu} = 2010$(mw), 1942(w), 1911(sh), 1882(vs), 1835(s), 1778(vs) cm^{-1}.

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