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Metal–Metal Frequencies and Force Constants for the Group Six Carbonyl Anions, $Cr_2(CO)_{10}^{2-}$, $Mo_2(CO)_{10}^{2-}$, and $W_2(CO)_{10}^{2-}$

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Transition metal M–M bond strengths are generally thought to increase going down a group of the periodic table. However, this impression is for the most part based on chemical properties and not on precise physical data. It is therefore interesting to inspect the trends in force constants going down a group. Homonuclear neutral compounds containing group seven metals $M_2(CO)_{10}$ (M = Mn, Tc, and Re), have been investigated previously [1] and heteronuclear dimetallic compounds between group six and seven metals have been investigated [2, 3]. In both cases an increase in force constant was noted on going to heavier members of the series. In the present paper we investigate the M–M stretching frequencies and force constants for the group six dianions $M_2(CO)_{10}^{2-}$.

Experimental

Compounds were made by published methods and their identity was checked by infrared spectroscopy. Solvents were dried over molecular sieves and were purged with dry nitrogen before use. Raman spectra were obtained using 514.5 nm incident laser radiation on fresh solutions or powdered samples contained in 12 mm rotating sample tubes. Details of the sample spinner and the backscattering Raman experimental arrangement are available in the literature [4]. The spectra were collected with a digital data acquisition system which allowed accurate determination of peak positions relative to the exciting line. For sharp features the estimated accuracy is 1.0 cm^{-1} and the precision is about 0.5 cm^{-1}.

Results and Discussion

Powdered samples of $[(C_2H_5)_4N]_2[Cr_2(CO)_{10}]$, $[(C_2H_5)_4N]_2[Mo_2(CO)_{10}]$, $[(C_2H_5)_4N]_2[W_2(CO)_{10}]$, and $Na_2[W_2(CO)_{10}]$ showed strong to medium intensity Raman bands at 160, 140, 115, and 110 cm^{-1} respectively. In addition, an acetone solution of $[Et_4N]_2[Cr_2(CO)_{10}]$ revealed a polarized band at 158 cm^{-1}, and an ethanol solution of $Na_2[W_2(CO)_{10}]$ displayed a polarized Raman band at 109 cm^{-1}. These results are consistent with the assignment of these observed bands to metal–metal stretching modes. Harris and Gray have previously observed a 109 cm^{-1} Raman feature for $W_2(CO)_{10}^{2-}$ which they attribute to a tungsten–tungsten stretch. It is possible that the modes lower than 120 cm^{-1} may be associated with C–M–C deformations, however the likelihood of confusion with the M–M stretch is minimized for data on the tungsten compounds because no intense C–M–C deformation features are evident in the Raman spectra of the chromium and molybdenum compounds in the vicinity of 100 cm^{-1}. Also, the systematic trend in the observed M–M frequencies for these three carbonyl anions lends weight to the assignment for the tungsten compound. Complete Raman frequency data are given in Table I for the anions in the various salts. There is some ambiguity in subtracting the cation modes for the tetraethylammonium salts, and some variation in the quality of the spectra which were obtainable, so great significance should not be attached to the apparent difference in complexity of the spectra.

TABLE I. Raman Data on $[R]_2[M_2(CO)_{10}]$.

R = Et_4N^+, M = Cr (cm^{-1})	R = Et_4N^+, M = Mo (cm^{-1})	R = Et_4N^+, M = W (cm^{-1})	R = Na^+, M = W (cm^{-1})
2010 (m)	2070 (w)	2022 (w)	2027 (s)
$\sim$1880 (s)	$\sim$2010 (vw)	1858 (s)	2000 (vw)
1856 (m)	1973 (m)	595 (m)	1961 (vw)
1825 (m)	1964 (m)	525 (m)	1925 (vw)
1805 (m)	$\sim$1880 (s)	452 (m)	1897 (s)
489 w	1870 (s)	428 (w)	1857 w
431 w	1858 (s)	406 (w)	1767 (w)
414 m	1849 (s)	111 (m)	1708 (w)
160 (s)	$\sim$500 (w)	60 (w)	595 (m)
$\sim$78 m	$\sim$425 (w)		550 (vw)
	138 (m)		485 (vw)
	60 ?		460 (s)
			432 (m)
			414 (m)
			411 (vs)
			110 (s)
			41 (w)

The M–M stretch has a totally symmetric representation and can only mix with other totally symmetric vibrations; thus, the normal coordinate analysis was performed only on the A_1 vibrations. The calculation was initially simplified by adopting a simple valence force field, in which no off-diagonal elements are evaluated. A series of calculations was performed in which different frequencies were assigned to the A_1 modes in the 345–673 cm^{-1} and the 40–100 cm^{-1} ranges. These calculations were designed to determine the extent to which the M–M force constants might be influenced by incorrect assignments. The results agree with previous work on similar molecules [1–3] which shows that the M–M force constant is insensitive to variations in the frequencies of the mid-frequency A_1 modes. However, k(MM) is sensitive to the value picked for the symmetric CMC deformation frequency which occurs below 100 cm^{-1}. Within the constraints of the simple valence force field approximation it is not possible to refine the force constants when the totally symmetric C–M–C deformation is assigned to a frequency higher than 80 cm^{-1}. Also, when this mode is assigned between 60 and 75 cm^{-1} the M–M stretching frequency cannot be fit exactly. Based on the reasonable assumption [2, 3] that the symmetric C–M–C deformation occurs at 50 cm^{-1} for the chromium and molybdenum compounds and 40 cm^{-1} for the tungsten compound simple valence force constants were calculated. The resulting values of k(MM) are given in Table II.

TABLE II. Metal–Metal Frequencies and Force Constants, for Single-Bonded Dimetal Carbonyls

	ν_{MM} (cm^{-1})	k_{MM} (mdyn/Å)	Ref.
$Mn_2(CO)_{10}$	160	0.59	1
$Tc_2(CO)_{10}$	148	0.72	1
$Re_2(CO)_{10}$	122	0.82	1
$Cr_2(CO)_{10}^{2-}$	160	0.60	a
$Mo_2(CO)_{10}^{2-}$	138	0.68	a
$W_2(CO)_{10}^{2-}$	111	0.73	a
$(OC)_5Cr\text{-}Re(CO)_5^-$	146	0.67	3
$(OC)_5Mo\text{-}Re(CO)_5^-$	130	0.72	3
$(OC)_5W\text{-}Re(CO)_5^-$	109	0.74	3
$(OC)_5CrMn(CO)_5^-$	153	0.50	2
$(OC)_5MoMn(CO)_5^-$	150	0.60	2
$(OC)_5WMn(CO)_5^-$	149	0.71	2
$(OC)_5ReMn(CO)_5$	157	0.81	1

[a] This work.

In a second set of calculations an off-diagonal element was introduced for the interaction of the M–M stretch with the M–M–$C_{equatorial}$ deformation. Judging from the Jacobian matrix elements ($\partial\nu_{MM}/\partial k$), this interaction constant and the C_{axial}-$MC_{equatorial}$ primary deformation constant strongly influence the calculated value of ν_{MM}. As with the simple valence force field calculation, there is relatively little influence on k(MM) if the symmetric CMC deformation frequency is held below 70 cm^{-1}. A third set of calculations was performed with a Urrey–Bradley force field. As expected, the values of k(MM) are lower, but the previously found trends in k(MM) are the same. Finally we note that a simple M–M diatomic model yields k(MM) values of 0.39, 0.54 and 0.67 mdyn/Å for the Cr_2, Mo_2, and W_2 compounds, respectively. This exaggerated trend in force constants when attached CO ligands are ignored, has been observed and commented upon previously [1].

The present results demonstrate an increase in bond strength as judged by M–M force constants from $Cr_2(CO)_{10}^{2-}$ to $Mo_2(CO)_{10}^{2-}$ to $W_2(CO)_{10}^{2-}$. It will be noted in Table II that the range in force constants (and frequencies) is greater than $Mn_2(CO)_{10}$ to $Re_2(CO)_{10}$ than in the series from $Cr_2(CO)_{10}^{2-}$ to $W_2(CO)_{10}^{2-}$. The large difference in the two ranges appears to be outside uncertainties in the force constants. Therefore it is concluded that there is a greater increase in the metal–metal bond strength going down the series of neutral Group VII carbonyls than going from the lightest to the heaviest dianonic Group VI carbonyl.

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