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Vibrational Analysis and Mean Bond Displacements in $M(XY)_6$ Complexes

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Abstract: An empirical quadratic GVFF potential for $M(XY)_6$ molecules, coupled with explicit anharmonicities in the form of a Morse potential and a Urey–Bradley interaction between each nearest-neighbor nonbonded pair of X atoms, is used to model the stretching anharmonicities of the MX and XY bonds. Mean V–C, C–O, Co–C, and C–N bond displacements and mean square amplitudes are calculated for $V(CO)_6^-$ and $Co(CN)_6^{3-}$.

NMR chemical shifts of transition metal nuclei are very sensitive to the metal–ligand distance. Measures of the sensitivity of transition metal shielding to the metal–ligand distance are the observed large chemical shifts with temperature and upon isotopic substitution. For example, ^{59}Co shifts of 1.4 to 3 ppm/deg and ^{51}V shifts of 0.3 to 1.5 ppm/deg have been reported.[1] Isotope shifts are also large: −4.7, −6, and −10 ppm on D substitution in $\{CpM(CO)_3H\}$ for M = ^{51}V, ^{93}Nb, and ^{183}W, respectively.[2] Furthermore, the temperature coefficients of the shifts of ^{51}V in various vanadium carbonyl complexes show an interesting correlation with the chemical shifts at 300 K. A theory to interpret these very large shifts requires the knowledge of the mean bond length changes in these molecules in the form of various rovibrational averages, $\langle \Delta r \rangle$ and $\langle (\Delta r)^2 \rangle$. $V(CO)_6^-$ is a reasonable prototype of these octahedral complexes. In this paper we use the vibrational frequencies of $V(CO)_6^-$ to determine an empirical quadratic force field which is consistent with the ones which have been established for the analogous $M(CO)_6$ neutral molecules (M = Cr, Mo, W). We augment this with cubic force constants calculated using an anharmonic model for stretching and nonbonded interactions, a model which has been successful in reproducing the 10 stretching-mode anharmonicities that are presently known for SF_6. We calculate the thermal averages $\langle \Delta r \rangle$ and $\langle (\Delta r)^2 \rangle$ for V–C and C–O bonds in $V(CO)_6^-$ ($^{13/12}C$, $^{18/16}O$) and also for Co–C and C–N bonds in $Co(CN)_6^{3-}$ ($^{13/12}C$, $^{15/14}N$) for comparison.

The complete quadratic force field for the metal carbonyls $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ has been established by a comprehensive study of the vibrational spectra of the molecules $M(^{12}C^{16}O)_6$, $M(^{13}C^{16}O)_6$, and $M(^{12}C^{18}O)_6$ (M = Cr, Mo, W).[3] These studies lead to the important result that the interaction force constants are reasonably transferable from one $M(CO)_6$ molecule to another. The force field for $V(CO)_6^-$ has not been reported. Only the frequencies for the $^{12}C^{16}O$ species are known from the work of Abel et al.[4] However, it has been shown that in the $M(CO)_6$ series (M = Cr, Mo, W) most of the interaction force constants have equal or nearly equal magnitudes irrespective of M.[3] Therefore, we will determine the force field for $V(CO)_6^-$ with the assumption that these interaction force constants which are invariant in the Cr, Mo, and W hexacarbonyls can be used for $V(CO)_6^-$ to establish the off-diagonal symmetry force constants. That is, we will use the same values for $f_{MC,CO}$, $f^{cis}_{MC,CO'}$, $f_{MC,CO'}$, $f_{CO,\beta'}$, $f_{CO,\alpha'}$, $f_{CO,\alpha''}$, $f_{MC,\beta'}$, $f_{MC,\alpha'}$, $f_{MC,\alpha''}$, $f_{\alpha\beta'}$, $f_{\alpha\beta''}$, and $f_{\alpha\beta'''}$, as were reported for $Cr(CO)_6$. The displacement coordinates are designated in the same way as in ref 3. The CMC angles are labeled α and the MCO angle is labeled β. The quadratic force constants (shown in Table I) are the second derivatives of the potential energy with respect to Δr_{MC}, ΔR_{CO}, $\Delta\alpha_{CMC}$, and $\Delta\beta_{MCO}$.

The fundamental frequencies for $V(CO)_6^-$ are then used to determine the following force constants: f_{CO}, $f^{c}_{CO,CO'}$, and $f_{CO,CO'}$,

Table I. Valence Force Constants for $V(CO)_6^-$

valence stretching force constants, mdyn Å^{-1}		valence angle bending force constants, mdyn Å rad^{-2}
f_{CO}	15.030	f_β = 0.4595
f_{MC}	2.160	$f_{\beta\beta'}$ = 0.1005
$f^{cis}_{CO,CO'}$	0.285	$f_{\beta\beta''}$ = 0.0005
$f^{t}_{CO,CO'}$	0.180	$f_{\beta\beta'''}$ = −0.005
$f^{c}_{MC,MC'}$	−0.025	$(f_\alpha - f_{\alpha\alpha''})$ = 0.50
$f^{t}_{MC,MC'}$	0.360	$(f_{\alpha\alpha'} - f_{\alpha\alpha'''})$ = 0.075
$f_{MC,CO}$	0.683	$(f_{\alpha\alpha''} - f^{iv}_{\alpha\alpha})$ = 0.01
$f^{c}_{MC,CO'}$	−0.052	
$f^{t}_{MC,CO'}$	−0.097	

Table II. Symmetry Force Constants and Frequencies for $V(CO)_6^-$

	symmetry force constants[a]			$V(^{12}C^{16}O)_6^-$ obsd[b]	$V(^{12}C^{16}O)_6^-$ calcd	$V(^{13}C^{16}O)_6^-$ calcd	$V(^{12}C^{18}O)_6^-$ calcd
A_{1g}	$\mathcal{F}_{11}$	16.35	ω_1	2036	2034.5	1987.0	1989.1
	$\mathcal{F}_{22}$	2.42		374	378.1	371.9	364.6
	$\mathcal{F}_{12}$	0.38					
E_g	$\mathcal{F}_{33}$	14.64	ω_3	1908	1907.7	1863.3	1864.8
	$\mathcal{F}_{44}$	2.57		393	391.4	385.0	377.5
	$\mathcal{F}_{34}$	0.69					
F_{1g}	$\mathcal{F}_{55}$	0.358		356	356.1	345.4	351.6
F_{1u}	$\mathcal{F}_{66}$	14.85	ω_6	1895	1897.9	1855.1	1853.2
	$\mathcal{F}_{77}$	1.80		650	655.1	643.1	651.9
	$\mathcal{F}_{88}$	0.55		460	454.4	445.5	445.9
	$\mathcal{F}_{99}$	0.65		92	91.8	91.3	87.9
	$\mathcal{F}_{67}$	0.78					
	$\mathcal{F}_{68}$	0					
	$\mathcal{F}_{69}$	0					
	$\mathcal{F}_{78}$	−0.18					
	$\mathcal{F}_{79}$	−0.3					
	$\mathcal{F}_{89}$	−0.21					
F_{2g}	$\mathcal{F}_{10,10}$	0.36		517	518.2	499.6	515.7
	$\mathcal{F}_{11,11}$	0.52		84	85.0	84.7	80.5
	$\mathcal{F}_{10,11}$	−0.52					
F_{2u}	$\mathcal{F}_{12,12}$	0.57		506	505.7	489.2	501.0
	$\mathcal{F}_{13,13}$	0.35			67.0	66.6	63.8
	$\mathcal{F}_{12,13}$	−0.11					

[a] Units are mydn Å^{-1} except mdyn rad^{-1} for $\mathcal{F}_{68}$, $\mathcal{F}_{69}$, $\mathcal{F}_{78}$, and $\mathcal{F}_{79}$, and mdyn Å rad^{-2} for $\mathcal{F}_{55}$, $\mathcal{F}_{88}$, $\mathcal{F}_{99}$, $\mathcal{F}_{89}$, $\mathcal{F}_{10,10}$, $\mathcal{F}_{10,11}$, $\mathcal{F}_{11,11}$, $\mathcal{F}_{12,12}$, $\mathcal{F}_{12,13}$, and $\mathcal{F}_{13,13}$. The definitions of the symmetry coordinates are the same as in ref 3. [b] From ref 4. Only the frequencies for vibrations 1, 3, and 6 have been corrected for anharmonicity; that is, harmonic frequencies rather than observed frequencies are given for these vibrations only.

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Table III. Evaluation of Approximate Cubic Force Constants for $M(CO)_6$-Type Molecules[a]

F_{ijk}	term		$V(CO)_6^-$	$Co(CN)_6^{3-}$
f_{rrr}	Δr_1^3	$(1/r_{MC})(F_3 + 3F - 3F') - 3a_{MC}K_{MC}$	−11.313	−11.343
$f_{rrr'}^{cis}$	$\Delta r_1^2 \Delta r_2$	$(1/4r_{MC})(F_3 - F + F')^b$	−0.093	−0.203
$f_{\alpha\alpha\alpha}$	$(r\Delta\alpha)^3$	$(1/4r_{MC})(F_3 - 3F - F')$	−0.109	−0.236
$f_{rr\alpha}$	$\Delta r_1^2(r_1\Delta\alpha_{1j})$	$(1/4r_{MC})(F_3 + 3F - 3F')$	−0.056	−0.122
$f_{rr'\alpha}$	$\Delta r_1 \Delta r_2(r\Delta\alpha_{12})$	$(1/4r_{MC})(F_3 + F + 3F')$	−0.078	−0.170
$f_{r\alpha\alpha}$	$\Delta r_1(r_1\Delta\alpha_{1j})^2$	$(1/4r_{MC})(F_3 + F - F')$	−0.075	−0.162
f_{RRR}	ΔR_1^3	$-3a_{CO}K_{CO}$ or $-3a_{CN}K_{CN}$	−108.9	−125.8

[a] $F_{ijk} \equiv (\partial^3 V/\partial\mathcal{R}_i\partial\mathcal{R}_j\partial\mathcal{R}_k)_e$ all in mdyn Å^{-2}, $F' \equiv (\partial V/\partial q)_0/q_0$, $F \equiv (\partial^2 V/\partial q^2)_0$, $F_3 \equiv q_0(\partial^3 V/\partial q^3)_0$. [b] Note the typographical error in this term in eq 1 of ref 7.

from ω_1, ω_3, and ω_6; f_{MC}, $f_{MC,MC'}$, and $f_{MC,MC}$ from ω_2, ω_4, and ω_7; f_β, $f_{\beta\beta'}$, $f_{\beta\beta''}$, and $f_{\beta\beta'''}$ from ω_5, ω_8, ω_{10}, and ω_{12}; and finally the linear combinations $(f_\alpha - f_{\alpha\alpha''})$, $(f_{\alpha\alpha'} - f_{\alpha\alpha'''})$, and $(f_{\alpha\alpha''} - f_{\alpha\alpha}^{iv})$ from ω_9, ω_{11}, and ω_{13}. Since ω_{13} was not observed, we used the same symmetry force constant $\mathcal{F}_{13,13}$ as in $Cr(CO)_6$. This fixes the sum $(f_\alpha - f_{\alpha\alpha''}) - 2(f_{\alpha\alpha'} - f_{\alpha\alpha'''})$. The complete set of force constants is given in Tables I and II. These are consistent with the set for Cr-, Mo-, and $W(CO)_6$ in that the values for $V(CO)_6^-$ are not drastically different and the relative magnitudes of cis vs. trans force constants and other such trends are preserved. The elements of the $\mathbf{G}_S$ matrix have been given by Jones et al.[5] Solution of the **GF** matrix problem reproduces the fundamental frequencies of $V(CO)_6^-$ to within ±2 cm^{-1}. Frequencies for the ^{13}C and ^{18}O isotopomers calculated with this set of force constants are also given in Table II.

In order to calculate mean V–C and C–O bond displacements, we need some reasonable estimate of the anharmonicity of the bonds. Here we extend the method of Krohn and Overend for SF_6,[6] which we have successfully applied to other molecules of this type (SeF_6, TeF_6, $PtCl_6^{2-}$, and $PtBr_6^{2-}$).[7] We assume, as they did, that the anharmonicity can be described by a stretching Morse anharmonicity combined with nonbonded interactions. In this way we can derive the expressions for the cubic force constants as shown in Table III. The Morse parameters $a_{VC} = 1.711$ Å^{-1} and $a_{CO} = 2.416$ Å^{-1} are calculated by the method of Herschbach and Laurie[8] using the bond lengths $r_e(CO) = 1.146$ Å and $r_e(VC) = 1.931$ Å in $V(CO)_6^-$ from the X-ray crystal structure.[9] $K_{VC} = 2.16$ mdyn/Å and $K_{CO} = 15.03$ mdyn/Å were estimated from the f_{MC} and f_{CO} values found in this vibrational analysis (see Table I). We neglect all contributions of nonbonded interactions to the cubic force constants involving the C–O stretch, so the entire anharmonicity of the CO bond is due to Morse anharmonicity. Terms other than those types shown in Table III are neglected. The nonbonded interaction constant $F(C\cdots C)$ in Table III is obtained from the symmetry force constant $\mathcal{F}_{22} = K_{MC} + 4F$. For $V(CO)_6^-$ $F = 0.065$ mdyn/Å and F' and F_3 are taken to be −0.0065 and −0.65 mdyn/Å according to the usual recipe in which $F' \approx -0.1F$, $F_3 \approx -10F$.

The vibrational contributions to the mean bond displacements are calculated using the method of Bartell[10] as implemented in our previous work,[11] from which the following is easily derived:

$$\langle \partial V/\partial z_k \rangle = \sum_{j=1}^{12} F_{kj}\langle \mathcal{R}_j \rangle + \sum_{i=1}^{12}\sum_{j=13}^{36} -\frac{F_{ij}}{2r}\langle \mathcal{R}_i\mathcal{R}_j\rangle \epsilon_{kj} + \sum_{i=13}^{36}\sum_{j=13}^{36} -\frac{F_{ij}}{4r}\langle \mathcal{R}_i\mathcal{R}_j\rangle(\epsilon_{ki} + \epsilon_{kj}) + \sum_{i=1}^{36}\sum_{j=1}^{36} \frac{F_{kij}}{2}\langle \mathcal{R}_i\mathcal{R}_j\rangle \quad k = 1 \text{ to } 12 \quad (1)$$

Here $\mathcal{R}_i$ stands for the curvilinear internal coordinates ΔR_{CO} or Δr_{MC} for $i = 1$ to 6 and $i = 7$ to 12, respectively, $\Delta\alpha$ for $i = 13$ to 24, and $\Delta\beta$ for $i = 25$ to 36. $r = r_e(CO)$ for $k = 1$ to 6 and $r = r_e(MC)$ for $k = 7$ to 12. $\epsilon_{kj} = 1$ if the bond to atom k is in the jth bond angle deformation; otherwise $\epsilon_{kj} = 0$. F_{ij} stands for $(\partial^2 V/\partial\mathcal{R}_i\partial\mathcal{R}_j)$ and F_{kij} for $(\partial^3 V/\partial\mathcal{R}_k\partial\mathcal{R}_i\partial\mathcal{R}_j)$, given in Tables I and III, respectively. As in previous work, in eq 7 we have neglected the averages $\langle \mathcal{R}_k\mathcal{R}_i\mathcal{R}_j\rangle$ and also set the sums over $\langle\Delta\alpha\rangle$ and $\langle\Delta\beta\rangle$ to zero. Upon setting $\langle \partial V/\partial z_k\rangle = 0$, i.e., applying Ehrenfest's theorem, we obtain the set of coupled equations:

$$\sum_{i=1}^{12} F_{ki}\langle \mathcal{R}_i \rangle = \Sigma_k \qquad k = 1 \text{ to } 12 \quad (2)$$

Thus,

$$\langle \boldsymbol{R} \rangle = \mathbf{F}^{-1}\boldsymbol{\Sigma} \quad (3)$$

The column vector $\langle \boldsymbol{R}\rangle$ contains the 12 desired mean displacements $\langle \mathcal{R}_i\rangle$ of the CO and the MC bonds. The vector $\boldsymbol{\Sigma}$ contains the elements

$$\Sigma_k = \sum_{i=1}^{12}\sum_{j=13}^{36} \frac{F_{ij}}{2r}\langle \mathcal{R}_i\mathcal{R}_j\rangle\epsilon_{kj} + \sum_{i=13}^{36}\sum_{j=13}^{36}\frac{F_{ij}}{4r}\langle \mathcal{R}_i\mathcal{R}_j\rangle(\epsilon_{kj} + \epsilon_{ki}) + \sum_{i=1}^{36}\sum_{j=1}^{36}\frac{-F_{kij}}{2}\langle \mathcal{R}_i\mathcal{R}_j\rangle \qquad k = 1 \text{ to } 12 \quad (4)$$

All the mean square amplitudes $\langle \mathcal{R}_i\mathcal{R}_j\rangle$ such as $\langle \Delta r_1^2\rangle$ or $\langle \Delta r_1 \Delta\alpha_{12}\rangle$, etc., including all cross-terms are evaluated as

$$\langle \mathcal{R}_i\mathcal{R}_j\rangle = \sum_s L_{is}\langle Q_s^2\rangle L_{sj} \quad (5)$$

where

$$\langle Q_s^2\rangle = (h/8\pi^2 c\omega_s)\coth(hc\omega_s/2kT) \quad (6)$$

The above equations therefore allow us to calculate $\langle \Delta r_{MC}\rangle$ and $\langle \Delta R_{CO}\rangle$ as a function of temperature and masses. We need the inverse $\mathbf{F}^{-1}$ of the force constant matrix for *stretches only*, for

Table IV. Mean Bond Displacements and Mean Square Amplitudes for the V–C Bond and the C–O Bond in $V(CO)_6^-$ [a]

	T	$\langle\Delta r\rangle_{vib}$	$\langle\Delta r\rangle_{rot}$	$\langle\Delta r\rangle$	$\langle(\Delta r)^2\rangle$
$V(^{12}C^{16}O)_6^-$	300	11.6443	0.4432	12.0875	3.2451
$V(^{13}C^{16}O)_6^-$	300	11.5170	0.4432	11.9602	3.2016
$V(^{12}C^{18}O)_6^-$	300	11.6379	0.4432	12.0810	3.2380
$V(^{12}C^{16}O)_6^-$	200	9.5167	0.2954	9.8122	2.7734
	240	10.3115	0.3545	10.6661	2.9453
	280	11.1844	0.4136	11.5980	3.1406
	320	12.1172	0.4727	12.5900	3.3535
	360	13.0960	0.5318	13.6278	3.5798
	400	14.1104	0.5909	14.7013	3.8167
		$\langle\Delta R\rangle_{vib}$	$\langle\Delta R\rangle_{rot}$	$\langle\Delta R\rangle$	$\langle(\Delta R)^2\rangle$
$V(^{12}C^{16}O)_6^-$	300	4.2967	0.1105	4.4073	1.2828
$V(^{13}C^{16}O)_6^-$	300	4.2026	0.1105	4.3131	1.2549
$V(^{12}C^{18}O)_6^-$	300	4.1904	0.1105	4.3009	1.2513
$V(^{12}C^{16}O)_6^-$	200	4.2958	0.0737	4.3694	1.2817
	400	4.3077	0.1474	4.4551	1.2862

[a] Δr refers to the V–C bond and ΔR to the CO bond; all are in 10^{-3} Å.

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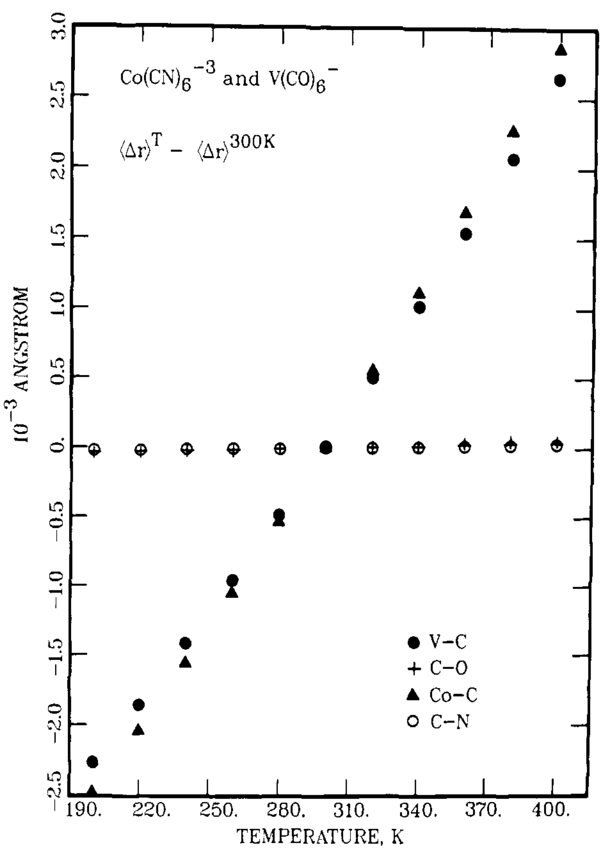

Figure 1. *Mean bond displacements in* $V(CO)_6^-$ *and* $Co(CN)_6^{3-}$.

which the redundancy condition is not a problem. For $k = 1$ to 6 we obtain the same value of $\langle \Delta R_{CO} \rangle$, and for $k = 7$ to 12 we obtain the same value of $\langle \Delta r_{MC} \rangle$, as dictated by symmetry. The results of these calculations are given in Table IV. The rotational contributions to the mean bond displacements are calculated by the usual method.[11]

We find the temperature dependence of $\langle \Delta R_{CO} \rangle$ and $\langle \Delta r_{VC} \rangle$ to be:

$$\langle \Delta R_{CO} \rangle^{400K} - \langle \Delta R_{CO} \rangle^{200K} = 1.20 \times 10^{-5}\ \text{Å due to vibration plus } 7.36 \times 10^{-5}\ \text{Å due to rotation (86\% rotation)}$$

$$\langle \Delta r_{VC} \rangle^{400} - \langle \Delta r_{VC} \rangle^{200} = 4.59 \times 10^{-3}\ \text{Å due to vibration plus } 2.95 \times 10^{-4}\ \text{Å due torotation (only 6 \% rotation)}$$

We have shown in Figure 1 the temperature dependence of the VC and CO bond displacements. The mass dependence of the V–C and C–O bond displacements at 300 K are given by:

$$\langle \Delta r \rangle_{^{51}V-^{12}C} - \langle \Delta r \rangle_{^{51}V-^{13}C} = 1.27 \times 10^{-4}\ \text{Å for } ^{16}\text{O isotopomers}$$

$$\langle \Delta r \rangle_{^{51}V-^{12}C(^{16}O)} - \langle \Delta r \rangle_{^{51}V-^{12}C(^{18}O)} = 6 \times 10^{-6}\ \text{Å}$$

$$\langle \Delta R \rangle_{^{12}C-^{16}O} - \langle \Delta R \rangle_{^{13}C-^{16}O} = 9.4 \times 10^{-5}\ \text{Å}$$

$$\langle \Delta R \rangle_{^{12}C-^{16}O} - \langle \Delta R \rangle_{^{12}C-^{18}O} = 1.06 \times 10^{-4}\ \text{Å}$$

We have applied the same theoretical calculation to the $Co(CN)_6^{3-}$ ion using the quadratic force field of Jones et al.[12] and using the molecular geometry from X-ray data: $r(\text{Co–C}) = 1.89$ Å and $r(\text{C–N}) = 1.5$ Å.[13] Morse parameters used are $a_{CoC} =$ 1.736 and $a_{CN} = 2.406$ Å^{-1}, respectively. K_{CoC} and K_{CN} are assigned the values 2.084 and 17.425 mdyn Å^{-1}, estimated from f_{CoC} and f_{CN} given by Jones.[12] The nonbonded interaction constant $F(\text{C}\cdots\text{C}) = 0.138$ mdyn/Å is obtained from $\mathcal{F}_{22} = K_{MC} + 4F$ using the experimental value of the symmetry force constant $\mathcal{F}_{22}$. The results are presented in Table V. We find the temperature dependence of $\langle \Delta R_{CN} \rangle$ to be very similar to that of $\langle \Delta R_{CO} \rangle$:

Table V. Mean Bond Displacements and Mean Square Amplitudes for the Co–C Bond and the C–N Bond in $Co(CN)_6^{3-}$ [a]

	T	$\langle \Delta r \rangle_{vib}$	$\langle \Delta r \rangle_{rot}$	$\langle \Delta r \rangle$	$\langle (\Delta r)^2 \rangle$
$Co(^{12}C^{14}N)_6^{3-}$	300	12.2011	0.4158	12.6169	3.1316
$Co(^{13}C^{14}N)_6^{3-}$	300	12.0791	0.4158	12.4949	3.0896
$Co(^{12}C^{15}N)_6^{3-}$	300	12.1968	0.4158	12.6127	3.1264
$CO(^{12}C^{14}N)_6^{3-}$	200	9.8399	0.2772	10.1171	2.6831
	240	10.7228	0.3327	11.0554	2.8447
	280	11.6915	0.3881	12.0796	3.0311
	320	12.7246	0.4436	13.1681	3.2361
	360	13.8061	0.4990	14.3051	3.4551
	400	14.9247	0.5545	15.4791	3.6849
		$\langle \Delta R \rangle_{vib}$	$\langle \Delta R \rangle_{rot}$	$\langle \Delta R \rangle$	$\langle (\Delta R)^2 \rangle$
$Co(^{12}C^{14}N)_6^{3-}$	300	4.2865	0.1021	4.3886	1.2129
$Co(^{13}C^{14}N)_6^{3-}$	300	4.1986	0.1021	4.3006	1.1882
$Co(^{12}C^{15}N)_6^{3-}$	300	4.2168	0.1021	4.3189	1.1936
$Co(^{12}C^{14}N)_6^{3-}$	200	4.2949	0.0681	4.3630	1.2117
	400	4.2827	0.1361	4.4419	1.2152

[a] Δr refers to the Co–C bond and ΔR to the C–N bond; all are in 10^{-3} Å.

$$\langle \Delta R_{CN} \rangle^{400K} - \langle \Delta R_{CN} \rangle^{200K} = -1.2 \times 10^{-5}\ \text{Å due to vibration plus } 6.8 \times 10^{-5}\ \text{Å due to rotation (120\% rotation)}$$

$$\langle \Delta r_{CoC} \rangle^{400} - \langle \Delta r_{CoC} \rangle^{200} = 5.08 \times 10^{-3}\ \text{Å due to vibration plus } 2.77 \times 10^{-4}\ \text{Å due to rotation (5\% rotation)}$$

The mass dependence of the Co–C and C–N bonds at 300 K are given by:

$$\langle \Delta r \rangle_{^{59}Co-^{12}C} - \langle \Delta r \rangle_{^{59}Co-^{13}C} = 1.22 \times 10^{-4}\ \text{Å for } ^{14}\text{N isotopomers}$$

$$\langle \Delta r \rangle_{^{59}Co-^{12}C(^{14}N)} - \langle \Delta r \rangle_{^{59}Co^{12}C(^{15}N)} = 4.2 \times 10^{-6}\ \text{Å}$$

$$\langle \Delta R \rangle_{^{12}C-^{14}N} - \langle \Delta R \rangle_{^{13}C-^{14}N} = 8.8 \times 10^{-5}\ \text{Å}$$

$$\langle \Delta R \rangle_{^{12}C-^{14}N} - \langle \Delta R \rangle_{^{12}C-^{15}N} = 6.9 \times 10^{-5}\ \text{Å}$$

It is worthwhile noting in Figure 1 that the temperature dependence of the M–C bond displacements is nearly two orders of magnitude larger than that of the CO or CN bond displacements, although the ^{13}C-induced changes are only 1.4 times as large for the M–C bonds as for the CO or CN bonds. Since the electron distribution in transition metal complexes is known to be sensitive to the metal–ligand distance, these results indicate that the optical absorption bands of these complexes should exhibit a measurable temperature dependence. The change in the position of the $^1A_{1g} \rightarrow {}^1T_{1g}$ absorption maximum in the $Co(CN)_6^{3-}$ complex has been noted in aqueous solution, a change of about 4 nm in the range 0–90 °C.[14]

The observed temperature and mass dependence of ^{51}V and ^{59}Co NMR chemical shifts in $V(CO)_6^-$ and $Co(CN)_6^{3-}$ are interpreted in the following paper in terms of the calculated temperature and mass dependence of $\langle \Delta r_{VC} \rangle$, $\langle \Delta R_{CO} \rangle$, $\langle \Delta r_{CoC} \rangle$, and $\langle \Delta R_{CN} \rangle$.

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