$Cr(en)_3^{3+}$ impurity is *not* due to low-energy phonon modes.[7] Zeeman spectra[36] show that some of the fine structure is due to several inequivalent species whose $^2T_1$ energy levels are resolved but the $^2E(R_1,R_2)$ levels coalesce into *one* set of moderately broad R_1 and R_2 lines with bandwidths $\bar{\nu}_{1/2} \approx 3\ \mathrm{cm}^{-1}$.

The implication of section 4.2, that both the $^1T_1$ excited state and the higher lying charge-transfer state of $Co(en)_3^{3+}$ are expanded along the a_{1g} coordinate, is contrary to the conclusion of earlier workers.[18] Independently of our analysis of the RREP, we *would* expect the excited state associated with the higher energy transition to be expanded along a_{1g}. The intense absorption in $Co(en)_3^{3+}$ at 47 400 cm^{-1} must surely be a charge transfer from the nitrogen atoms to the metal e_g orbitals, e.g. $(e_g)^1(t_{2g})^6(t_{1u})^5 \leftarrow (t_{2g})^6(t_{1u})^6$. The charge separation will tend to shorten the Co–N bonds, but this effect is more than compensated by a large change in crystal field energy. For example, the change in the Co–N bond lengths is approximately

$$\delta R_0 \propto n(-18Dq(\mathrm{Co}^{2+}) + 24Dq(\mathrm{Co}^{3+})) - e^2/R_0 \qquad (9)$$

where we have assumed $Dq \propto 1/R^n$ and $n \approx 5$.[35] We therefore expect the charge-transfer state to be expanded along the a_{1g} coordinate.

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Registry No. $[Co(en)_3]^{3+}$, 14878-41-2; $[Rh(en)_3]^{3+}$, 16786-61-1; D_2, 7782-39-0; $[Co(en)_3]Cl_3$, 13408-73-6; $[Rh(en)_3]Cl_3$, 14023-02-0; $2[Co(en)_3]Cl_6{\cdot}6H_2O$, 15004-81-6; (+)-$Cr(en)_3^{3+}$, 41509-53-9; (±)-$Cr(en)_3^{3+}$, 15276-13-8.

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Effects of Rovibrational Averaging on the ^{93}Nb Chemical Shift in the $[Nb(CO)_6]^-$ Ion, Based on NMR and Vibrational Spectra

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We report the dependence of the ^{93}Nb NMR spectrum of $[Nb(CO)_6]^-$ in solution upon temperature (203–323 K) and upon isotopic replacement of $^{12}C^{16}O$ ligands by $^{13}C^{16}O$ and $^{12}C^{18}O$. The IR and Raman spectra of the hexacarbonyl anion are reported for the solid $[Et_4N]^+[Nb(CO)_6]^-$. In a comparative study of $[V(CO)_6]^-$, $[Nb(CO)_6]^-$, and $[Re(CO)_6]^+$ ions, force constants are calculated in a general quadratic valence force field constrained to be consistent with the interaction force constants in the corresponding neutral hexacarbonyl series $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$. The harmonic force field augmented with estimated anharmonic force constants is used to calculate mean NbC and CO bond displacements as a function of temperature and masses. The ^{93}Nb chemical shifts upon isotopic CO replacement are interpreted in terms of rovibrational averaging, and the empirical values of the electronic factors so obtained are found to be consistent with the observed temperature dependence of the shift.

Introduction

The temperature dependence[2-6] and isotope effects[5,7-12] of chemical shifts of transition-metal nuclei in diamagnetic complexes are very large compared to those for other nuclei (roughly in correlation to their ranges of chemical shifts).[13] We have shown that in the prototypical cases $[V(CO)_6]^-$ and $[Co(CN)_6]^{3-}$ the observed temperature coefficients of the ^{51}V and ^{59}Co chemical shifts in these complexes in solution can be attributed largely to the increase in the vibrationally averaged metal–ligand distance with increase in temperature rather than the decreased intermolecular effects on liquid expansion with temperature.[5] The chemical shifts due to isotopic replacement ($^{13/12}$C, $^{18/16}$O, and $^{15/14}$N) of neighboring atoms in these complexes have been interpreted consistently with the same rovibrational averaging model used for the temperature coefficients.

In this paper we report temperature dependence and isotope effects of ^{93}Nb chemical shifts in $[Nb(CO)_6]^-$, in a continuing study of trends in the low-spin d^6 metal hexacarbonyl ions. We measured the infrared and Raman spectra of $[Nb(CO)_6]^-$ and provide a harmonic force field analysis for this complex that is consistent within the series of neutral hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W)[14] and the hexacarbonyl ions $[M(CO)_6]^-$ (M = V, Nb) and $[Re(CO)_6]^+$. We used the quadratic force constants from this analysis with an anharmonic model used previously[15] to calculate mean bond displacements and mean square amplitudes in $[Nb(CO)_6]^-$ ion. These are used to interpret the NMR data. The results for ^{93}Nb are compared with those found previously for ^{51}V.

Experimental Section

Sample Preparation. $Na[Nb(CO)_6]$ was prepared by normal-pressure carbonylation of $NbCl_5$ with a Mg/Zn reductant[30] and converted to the more stable $[Et_4N][Nb(CO)_6]$ by treatment with $[Et_4N]Br$ in H_2O/CH_3OH (1/1), where $[Et_4N][Nb(CO)_6]$ is only sparingly soluble. For CO replacement, a 0.025 M solution, prepared under N_2 in highly purified THF, was cooled to 195 K (dry ice/ethanol) and irradiated for 20 min (high-pressure mercury lamp, 125 W) to yield red-violet $[Nb(CO)_5THF]^-$. After removal of the N_2/CO atmosphere via a vacuum line and injection of ^{13}CO or $C^{18}O$, respectively, the solution was warmed to 210 K and shaken, until the yellow color of the (hexacarbonyl)niobate was restored. Five more cycles of THF/CO replacement gave a sample that was 70% isotopically enriched. After filtration of small amounts of decomposition products, the solution was evaporated to dryness and the residue redissolved, for NMR measurements, in 3 mL of acetone-d_6.

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Table I. Observed Frequencies (cm^{-1}) and Assignments for $[Nb(CO)_6]^-$ in $[Et_4N]^+[Nb(CO)_6]^-$ Microcrystalline Powder (Raman) and Nujol Mull (IR)

IR	Raman[a]	assgnt
384 s		ν_8 F_{1u}, ν(NbC)
420 m		$\nu_5 + \nu_{13}{}^{b,c}$?
494 m		ν_{12} ? F_{2u}, ν(NbCO)
568 vs		ν_7 F_{1u}, δ(NbCO)
936 m		$\nu_5 + \nu_7{}^b$
1860 vs[d]		ν_6 F_{1u}, ν(CO)
	94 vs	ν_{11} F_{2g}, δ[CNbC)
	384 vs	ν_2 A_{1g}, ν(NbC)
	411 m	ν_4 E_g, ν(NbC)
	446 m	
	1878, 1887 vs	ν_3 E_g, ν(CO)
	2019 m	ν_1 A_{1g}, ν(CO)

[a] In addition there are medium weak and weak peaks at 670, 851, 997, 1050, 1232, and 1453 cm^{-1}, which may be assigned to combinations and overtones with less certainty, e.g. 997 to $2\nu_{12}$. [b] This leads to $\nu_5 \sim 368$ cm^{-1} (F_{1g}, ν(NbCO)). The band at 936 cm^{-1} could have been assigned to $\nu_5 + \nu_{12}$; however, this would give $\nu_5 \sim 442$ cm^{-1}, which leads to a f_β value that is rather large and well outside of the other known values for hexacarbonyls. [c] This leads to $\nu_{13} \sim 52$ cm^{-1} (F_{2u}, ν(CNbC)). [d] Observed in THF solution (with shoulder at ca. 1870 cm^{-1}), this band is very broad in Nujol mull.

Table II. Summary of NMR Results

Temperature Dependence of (^{93}Nb) Chemical Shift

$\delta(300)^a$	compd	shift range, ppm	temp range, K	temp coeff ($d\sigma/dT$), ppm/deg
−2121	$[Et_4N][Nb(CO)_6]^\beta$	−2137/−2127	203/273	−0.15
		−2125/−2116	283/323	−0.22
−2017	η^5-$C_5H_5Nb(CO)_4{}^c$ (in THF)	−2056/−2030	203/273	−0.36
		−2025/−2006	283/323	−0.47
−2005	η^5-$C_5H_5Nb(CO)_4$ (in CH_2Cl_2)	−2028/−2005	240/300	−0.42

Isotope Shifts[d]

$^1\Delta[^{93}Nb(^{13/12}C)]$ in $[Nb(CO)_{6-n}(^{13}CO)_n]^-$	−0.173 (1) ppm/^{13}C
$^1\Delta[^{93}Nb(^{13/12}C)]$ in η^5-$C_5H_5Nb(CO)_{4-n}(^{13}CO)_n$	−0.373 ppm/^{13}C
$^2\Delta[^{93}Nb(^{18/16}O)]$ in $[Nb(CO)_{6-n}(C^{18}O)_n]^-$	−0.084 (2) ppm/^{18}O
$^1\Delta[^{93}Nb(^{2/1}H)]$ in η^5-$C_5H_5Nb(CO)_3H^-$	−6.0 ppm[e]

[a] ^{93}Nb chemical shift relative to a solution of $NbOCl_3$ in CH_3CN at 300 K. [b] Reference 27. [c] Reference 28, 29. [d] The isotope shifts, indicated for $\Delta n = 1$, are linear throughout within the limits of error (the estimated error is given in parentheses). All measurements have been carried out at 88.29 MHz. [e] Reference 9.

Spectra. IR spectra were obtained as Nujol mulls (CsI plates) on a Perkin-Elmer 325 spectrometer. Raman spectra of the microcrystalline, yellow powders were taken on a Jobin Yvon U 1000 spectrometer with the 647.1-nm beam of a Spectra Physics 2000 Kr laser. Laser power was 175 mW and (for the expanded sections) 65 mW. Points were spaced by 1 wavenumber, and the spectra were not smoothed. The 88.29-MHz ^{93}Nb NMR spectra of the ca. 0.17 M solutions in acetone-d_6, contained in spinning 10-mm-diameter tubes, were scanned on a Bruker AM 360 spectrometer. Typical measuring parameters were as follows: sweep width, 5 kHz (acquisition time = 3.2 s; resolution, 0.16 Hz/point), relaxation delay = 1 s, pulse width = 12.6 μs, scan number = 65. Chemical shifts δ (^{93}Nb) were referenced against $[Et_4N][NbCl_6]/CD_3CN$ (external standard) and are quoted with respect to $NbOCl_3/CH_3CN$ ($\delta = 0$); $\delta([NbCl_6]^-) = +460$ ppm.

Results and Discussion

The frequencies observed in the infrared and Raman spectra shown in Figure 1 are summarized in Table I. The temperature-dependent ^{93}Nb chemical shifts are summarized in Table II, and one example is shown in Figure 2, for a solution of $[Et_4N][Nb(CO)_6]$ in THF. The isotope shifts are found to be additive for successive replacement of $^{12}C^{16}O$ by either $^{13}C^{16}O$ or $^{12}C^{18}O$, giving rise to equally spaced peaks, one for each of the various isotopomers $[Nb(^{12}C^{16}O)_{6-n}(CO)_n{}^*]^-$, as seen in Figure 3a,b. The average isotope shifts are summarized in Table II.

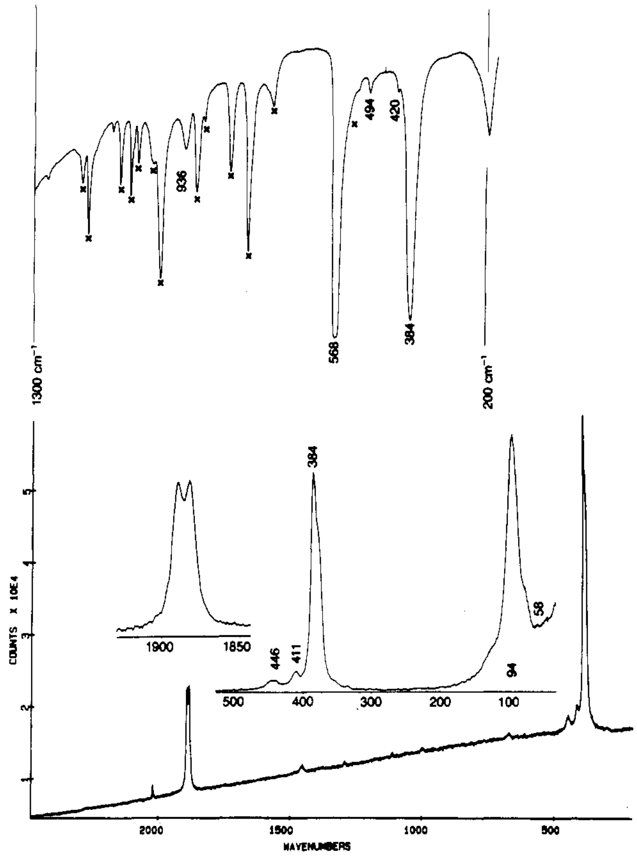

Figure 1. Infrared (top) and Raman (bottom) spectra of $[Et_4N]^+[Nb(CO)_6]^-$ solid (Nujol mull (IR) and microcrystalline powder (Raman)). $[Et_4N]^+$ peaks are marked ×.

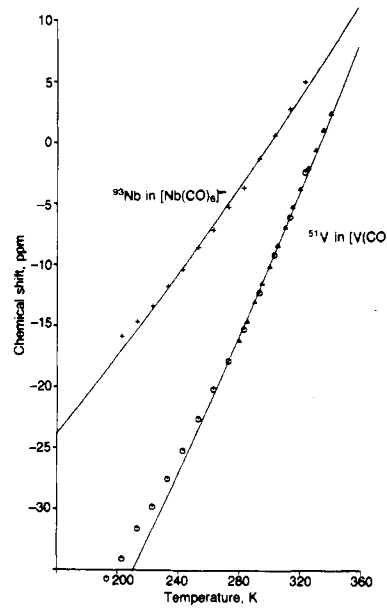

Figure 2. Observed temperature dependence of the ^{93}Nb chemical shift in $[Et_4N]^+[Nb(CO)_6]^-$ (ca. 0.05 M solution in THF) compared with calculated temperature dependence according to $\sigma_0(T) - \sigma_0(300\ K) = 6[-1.16 \times 10^3\{\langle\Delta r_{NbC}\rangle^T - \langle\Delta r_{NbC}\rangle^{300}\} - 8 \times 10^2\{\langle\Delta R_{CO}\rangle^T - \langle\Delta R_{CO}\rangle^{300}\}]$. The chemical shifts are in ppm relative to a solution at 300 K. The temperature dependence of ^{51}V chemical shift from ref 5 is also shown, for comparison.

In Figure 3a an alternate set of peaks (labeled *a* in the spectrum) are observed. This set of peaks, which is offset from the main set by 0.087 ppm, does not disappear with time and the alternate:main peak ratio seems to decrease monotonically with increasing number of ^{13}CO groups. Both the main set and the alternate set exhibit *the same* isotope shifts per ^{13}CO. Although

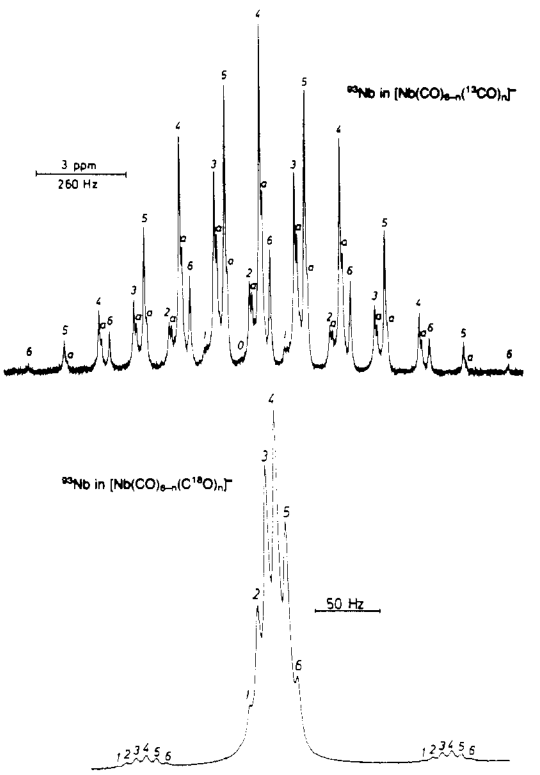

Figure 3. ^{93}Nb NMR spectra of $[Nb(CO)_6]^-$ ion (a) enriched in ^{13}CO and (b) enriched in C^{18}O taken at 88.29 MHz in acetone solution. Assignments refer to the isotopomers $[Nb(^{12}C^{16}O)_{6-n}(^{13}CO)_n]^-$ and $[Nb(^{12}C^{16}O)_{6-n}(C^{18}O)_n]^-$ respectively, for n = 0–6. The central group of signals in part b is flanked by the natural-abundance ^{13}C satellite doublets; $^1J(^{13}C-^{93}Nb)$ = 236 Hz. The peaks marked *a* in part a are discussed in the text.

the offset of 0.087 ppm is about the same magnitude as the ^{18}O-induced shift (−0.084 ppm/C^{18}O), mass spectra show that the ^{13}CO has not been contaminated by C^{18}O. In any case the constant offset would have been consistent only with a single ^{18}O substitution for each of the $(^{13}CO)_n$ (n = 0–5) isotopomers. This is not statistically possible. It is interesting to note that the ^{51}V spectrum of $[V(CO)_{6-n}(^{13}CO)_n]^-$ ion under higher resolution than the previously published spectrum also shows an alternate set of peaks offset by 0.106 ppm from the main set. Here too, both the main set and the alternate set exhibit the same isotope shifts per ^{13}CO, *and* there is no alternate peak for the n = 0 isotopomer. A possible explanation is that a fraction of the $[Nb(CO)_6]^-$ ions are involved in stable contact ion pairs with the cation $[Et_4N]^+$. If this is the case, and if the exchange between "free" ions and anions in ion pairs is sufficiently slow, then the alternate set of peaks in Figure 3a could be assigned to the ^{93}Nb in the ion pairs. The ^{13}C spectrum of $[Nb(CO)_{6-n}(^{13}CO)_n]^-[Et_4N]^+$ shows the typical decet pattern due to coupling with spin $^9/_2$ of ^{93}Nb, with *no* visible further splittings. Ion-pair formation would have a smaller effect (in ppm) on ^{13}C than on ^{93}Nb since the chemical shift range of ^{13}C is only 10% that of ^{93}Nb.

The low-spin d^6 metal hexacarbonyl ions $[V(CO)_6]^-$, $[Nb(CO)_6]^-$, and $[Re(CO)_6]^+$ may be expected to have electronic structures that are essentially the same as in the neutral isoelectronic analogues $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, respectively. The electronic spectra of these ions have been studied,[16,17] and infrared and Raman spectra for $[V(CO)_6]^-$ and $[Re(CO)_6]^+$ have been measured.[17] Since the vibrational spectra of the ^{13}C/^{12}C and ^{18}O/^{16}O isotopomers of $[Nb(CO)_6]^-$ have not been obtained, the present analysis makes the assumptions that the near-invariance of the interaction force constants and the consistencies observed in the neutrals can be carried over to the ions. Furthermore, when we use the same assumptions for the analysis of $[Re(CO)_6]^+$, we find that the series of hexacarbonyls $[V(CO)_6]^-$, $Cr(CO)_6$, $[Nb(CO)_6]^-$, $Mo(CO)_6$, $W(CO)_6$, and $[Re(CO)_6]^+$ have valence force constants that are consistent with one another.

In the case of the metal hexacarbonyls the anharmonic corrections X_{ij} for all but ν_1, ν_3, and ν_6 are negligible.[14] To calculate anharmonic corrections for these C–O stretching fundamentals, it is necessary to use ternary combination bands (which were not observed here), but we can estimate these X_{ij} values by taking the anharmonic defects to be three-fourths that in the corresponding neutral hexacarbonyls, a factor consistent with values for $[V(CO)_6]^-$ and $[Re(CO)_6]^+$ based on $Cr(CO)_6$ and $W(CO)_6$, respectively;[17] that is, $(\omega_i - \nu_i)$ are 15, 14, and 32 cm^{-1} for i = 1, 3, and 6, respectivley, for $[Nb(CO)_6]^-$ based on 20.5, 18.5, and 42.8 cm^{-1} for $Mo(CO)_6$ in solution.[14]

Off-diagonal matrix elements of the symmetry force constant matrix $\mathcal{F}$ were taken to be the same as for the corresponding neutral hexacarbonyl, $Mo(CO)_6$, except that $\mathcal{F}_{78}$, $\mathcal{F}_{79}$, and $\mathcal{F}_{89}$ were assigned the same values as for $[V(CO)_6]^-$, i.e., taken from $Cr(CO)_6$. These off-diagonal elements correspond to linear combinations of interaction force constants of different internal coordinates, such as $f_{MC,CO}$ or $f_{\alpha\beta'}$. Jones et al. have shown that these quantities are essentially the same for all three neutral hexacarbonyls within their standard deviations.[14] Initial values for all symmetry force constants were taken directly from $Mo(CO)_6$, except for three involving f_{CO} ($\mathcal{F}_{11}$, $\mathcal{F}_{33}$, and $\mathcal{F}_{66}$), which were taken initially from $[V(CO)_6]^-$ since they are known to be substantially different for the anion. With these, the assignments shown in Table I become obvious for all strong peaks and for ν_1, which is substantially less intense than ν_3 as it is in all other hexacarbonyls. The IR-forbidden ν_{12} band has been observed in other hexacarbonyls in the solid and is tentatively assigned to 494 cm^{-1}. As in other hexacarbonyls, the combination $\nu_5 + \nu_7$ provides the estimate for ν_5. The peak at 446 cm^{-1} in the Raman spectrum is unassigned. On one hand, the set of $[Nb(CO)_6]^-$ frequencies by itself is not overcomplete as would be necessary for assignment of all bands with confidence. On the other hand, these frequencies are almost redundant information when $Nb(CO)_6^-$ is considered as part of the series of hexacarbonyls. The completely predictable change of f_{CO} in going from $Mo(CO)_6$ to $[Nb(CO)_6]^-$ is found also in going from $Cr(CO)_6$ to $[V(CO)_6]^-$.

The results of the force field analyses are shown in Table III.[18] The valence force constants are compared for the series of hexacarbonyls in Table IV. For those in a given transition series there is a sizable decrease in f_{CO} with net negative charge on the complex (and a sizable increase of f_{CO} with net positive charge, as in $[Re(CO)_6]^+$ compared to $W(CO)_6$. This indicates significantly stronger metal–ligand π bonding for $[Nb(CO)_6]^-$ and $[V(CO)_6]^-$ than for the corresponding neutrals, and significantly weaker metal–ligand π bonding in $[Re(CO)_6]^+$, where the f_{CO} value is nearly as large as in free CO. Since the ionic species are observed in condensed phase, there may be systematic errors in these force constants. There is a slight increase in f_{MC} with net negative charge. All other changes are small.

The anharmonic force constants were determined by a method described elsewhere,[15,19] using the following parameters: r_{NbC} = 2.02 Å,[20] r_{CO} = 1.145 Å, a_{NbC} = 1.725 Å^{-1}, a_{CO} = 2.416 Å^{-1}, K_{NbC} = 2.09 mdyn Å^{-1}, K_{CO} = 15.03 mdyn Å^{-1}, and F = 0.065 mdyn

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[18] For $[Re(CO)_6]^+$ the following symmetry force constants reproduce the frequencies observed by ref 17 to within 1 cm^{-1}, listed in the same order and in the same units as for $[Nb(CO)_6]^-$ in Table III. A_{1g} (19.30, 3.33, 0.36), E_g (18.45, 3.04, 0.82), F_{1g} (0.355), F_{1u} (18.85, 1.63, 0.41, 0.99 and 0.91, 0, 0, −0.04, −0.3, −0.34), F_{2g} (0.39, 0.39, −0.13), F_{2u} (0.61, 0.33, −0.14). All off-diagonal elements were assumed to be the same as for $W(CO)_6$ values in the gas phase. The ReC and CO bond lengths used were those found by X-ray diffraction in $[Re(CO)_6]^+[Re_2F_{11}]^-$, respectively 2.01 (4) and 1.13(3) Å (Bruce, D. M.; Holloway, J. H.; Russell, D. R. *J. Chem. Soc. Chem. Commun.* **1973**, 321–322.)

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Table III. Symmetry Force Constants and Frequencies for $[Nb(CO)_6]^-$

symmetry force const[d]				$[Nb(^{12}C^{16}O)_6]^-$		$[Nb(^{13}C^{16}O)_6]^-$	$[Nb(^{12}C^{18}O)_6]^-$
				obsd	calcd	calcd	calcd
A_{1g}	$\mathcal{F}_{11}$	16.30	ω_1[a]	2034	2034.6	1986.9	1989.4
	$\mathcal{F}_{22}$	2.50		384	383.8	377.6	370.0
	$\mathcal{F}_{12}$	0.36[c]					
E_g	$\mathcal{F}_{33}$	14.43	ω_3	1901	1901.1	1856.4	1859.0
	$\mathcal{F}_{44}$	2.85		411	410.9	404.3	396.2
	$\mathcal{F}_{34}$	0.68[c]					
F_{1g}	$\mathcal{F}_{55}$	0.392		~368	367.9	356.9	363.1
F_{1u}	$\mathcal{F}_{66}$	15.0	ω_6	1892	1892.3	1850.4	1846.6
	$\mathcal{F}_{77}$	1.44		568	567.2	551.8	564.5
	$\mathcal{F}_{88}$	0.47		384	384.9	379.5	376.6
	$\mathcal{F}_{99}$	0.83		*b*	89.8	89.4	85.9
	$\mathcal{F}_{67}$	0.88					
	$\mathcal{F}_{68}$	0[c]					
	$\mathcal{F}_{69}$	0					
	$\mathcal{F}_{78}$	−0.18					
	$\mathcal{F}_{79}$	−0.3					
	$\mathcal{F}_{89}$	−0.21					
F_{2g}	$\mathcal{F}_{10,10}$	0.44			501.8	484.3	498.7
	$\mathcal{F}_{11,11}$	0.48		94	94.1	93.7	89.3
	$\mathcal{F}_{10,11}$	−0.11[c]					
F_{2u}	$\mathcal{F}_{12,12}$	0.49		494	494.1	477.6	490.0
	$\mathcal{F}_{13,13}$	0.40			60.4	60.1	57.4
	$\mathcal{F}_{12,13}$	−0.19[c]					

[a] See text for anharmonic corrections to ν_1, ν_3, and ν_6. [b] ν_9 is frequently observed in the Raman spectrum in the solid.[14] In this case there is a shoulder at ~80 cm^{-1} that could be consistent with this. [c] These off-diagonal matrix elements were taken to be the same as for $Mo(CO)_6$ except $\mathcal{F}_{78}$, $\mathcal{F}_{79}$, and $\mathcal{F}_{89}$ are the same as used for $[V(CO)_6]^-$, i.e., taken from $Cr(CO)_6$. [d] Units are mdyn $Å^{-1}$ 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 14.

Table IV. Valence Force Constants of Hexacarbonyls[a]

	V	Cr[b]	Nb	Mo[b]	W[b]	Re
f_{CO}	15.03	17.24	15.03	17.33	17.22	18.79
$f^{c}_{COCO'}$	0.285	0.21	0.31	0.22	0.22	0.14
$f^{t}_{COCO'}$	0.18[c]	0.02	0.03	−0.06	0	−0.06
f_{MC}	2.16	2.08	2.09	1.96	2.36	2.38
$f^{c}_{MCMC'}$	−0.025	−0.018	−0.058	0.031	0.049	0.048
$f^{t}_{MCMC'}$	0.36	0.44	0.65[c]	0.53	0.56	0.76
f_{β}	0.460	0.476	0.447	0.454	0.476	0.44
$f_{\beta\beta'}$	0.100	0.094	0.031	0.061	0.079	0.068
$f_{\beta\beta''}$	0.0005	0.004	0.012	0.023	0.006	0.009
$f_{\beta\beta'''}$	−0.005	−0.01	−0.005	−0.017	−0.04	−0.05
$(f_{\alpha} - f_{\alpha\alpha''})$	0.50	0.57	0.61	0.61	0.63	0.66
$(f_{\alpha\alpha'} - f_{\alpha\alpha'''})$	0.08	0.11	0.11	0.11	0.15	0.16
$(f_{\alpha} - f^{tv}_{\alpha\alpha})$	0.51	0.56	0.55	0.48	0.51	0.52

[a] All other interaction force constants (between different types of internal coordinates, e.g. $f_{\alpha\beta}$, $f_{MC,CO}$) for the ions are taken to be identical with the values for the neutrals.[14] [b] Reference 14. [c] Seems large compared to rest of series but is not inconsistent.

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

	T, K	$\langle \Delta r \rangle_{vib}$	$\langle \Delta r \rangle_{rot}$	$\langle \Delta r \rangle$	$\langle (\Delta r)^2 \rangle$
$Nb(^{12}C^{16}O)_6^-$	300	11.5145	0.4101	11.9246	3.5187
$Nb(^{13}C^{16}O)_6^-$	300	−0.12	+0.0	−0.12	−0.044
$Nb(^{12}C^{18}O)_6^-$	300	−0.007	+0.0	−0.007	−0.007
$Nb(^{12}C^{16}O)_6^-$	200	−2.33	−0.14	−2.47	−0.61
	240	−1.45	−0.08	−1.53	−0.38
	280	−0.50	−0.03	−0.53	−0.13
	320	+0.51	+0.03	+0.54	+0.14
	360	+1.56	+0.08	+1.64	+0.42
	400	+2.65	+0.14	+2.79	+0.71
	T, K	$\langle \Delta R \rangle_{vib}$	$\langle \Delta R \rangle_{rot}$	$\langle \Delta R \rangle$	$\langle (\Delta R)^2 \rangle$
$Nb(^{12}C^{16}O)_6^-$	300	4.3355	0.1109	4.4464	1.2872
$Nb(^{13}C^{16}O)_6^-$	300	−0.09	+0.0	−0.09	−0.028
$Nb(^{12}C^{18}O)_6^-$	300	−0.11	+0.0	−0.11	−0.032
$Nb(^{12}C^{16}O)_6^-$	200	−0.001	−0.04	−0.04	−0.001
	400	+0.01	+0.04	+0.05	+0.004

[a] Δr refers to the Nb–C bond and ΔR to the CO bond; all are in 10^{-3} Å. The absolute magnitudes for the $[Nb(^{12}C^{16}O)_6]^-$ are given at the top of each column. All other entries are changes relative to that value.

$Å^{-1}$.[21] As in previous work,[15] the vibrational contributions to the mean bond displacement are calculated by using the method of Bartell,[22] with the equations derived specifically for $M(CO)_6$ molecular types. Details are shown in a previous reference.[15] With the equations shown there, the temperature dependence of $\langle \Delta r_{NbC} \rangle$ and $\langle \Delta R_{CO} \rangle$ can be calculated for the isotopomers. The results are shown in Table V. The *changes* with mass and with temperature of the mean bond displacements and the mean square amplitudes are directly expressible in terms of the anharmonic force field parameters. These changes are calculated and shown in Table V. Also shown are the absolute magnitudes of the rotational and vibrational contributions for the $[Nb(^{12}C^{16}O)_6]^-$ ion at 300 K.

If ν_1, ν_3, and ν_6 are used directly without estimation of the anharmonic defect, a slightly different set of valence force constants f_{CO}, $f^{c}_{CO,CO}$, and $f^{t}_{CO,CO}$ are obtained. A smaller opposite bond interaction is obtained by using corrected frequencies. For the purposes of this application, either set can be used in the interpretation of the NMR data; these parameters affect primarily the vibrational contribution to the CO bond displacement, $\langle \Delta R_{CO} \rangle_{vib}$. The ^{93}Nb chemical shift with temperature largely depends on the change in $\langle \Delta r_{NbC} \rangle$ with temperature and only slightly on the temperature shift of $\langle \Delta R_{CO} \rangle$. In any case, the change of $\langle \Delta R_{CO} \rangle$ with temperature is primarily due to the rotational contribution, which is 84% of the change in the range 200–400 K. For this reason, that one of the frequencies ν_6 is taken from solution or that the ν_3 peaks are split in the solid (1878 and

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(21) The Morse parameters $a_{NbC} = 1.725$ and $a_{CO} = 2.416$ $Å^{-1}$ were estimated by using the parameters of Herschbach and Laurie for the representative elements (Herschbach, D. R.; Laurie, V. W. *J. Chem. Phys.* **1961**, *35*, 458–463) with bond lengths $r(CO) = 1.145$ and $r(NbC) = 2.02$ Å.[20] The Urey–Bradley K constants, $K_{NbC} = 2.09$ and $K_{CO} = 15.03$ mdyn $Å^{-1}$ were estimated from the f_{MC} and f_{CO} values found in the vibrational analysis. The latter is the same as was used for $[V(CO)_6]^-$. We assume the anharmonicity of the CO bond to be entirely due to Morse anharmonicity, neglecting nonbonded C–O or O–O interactions. The nonbonded quadratic force constant F is taken to be the same as in the $[V(CO)_6]^-$ ion.[15] The linear and cubic nonbonded force constants F' and F_3 are then taken to be $-0.1F$ and $-10F$ according to the usual receipe.

(22) Bartell, L. S. *J. Chem. Phys.* **1963**, *38*, 1827–1833; **1979**, *70*, 4581–4584.

1887 $\mathrm{cm^{-1}}$, likely due to site effects) is not of significance to this application, a small site shift or solvent shift of the frequencies will affect the interpretation of the ^{93}Nb chemical shifts in an insignificant way.

It is interesting to compare these results with those for $[\mathrm{V(CO)_6}]^-$.[15] As in the study of $\mathrm{SeF_6}$ and $\mathrm{TeF_6}$,[19] the MC mean bond displacements in the transition-metal complex ions $[\mathrm{V(CO)_6}]^-$ and $[\mathrm{Nb(CO)_6}]^-$ and their temperature dependence increase with increasing size of the central atom. The Nb–C equilibrium bond length is somewhat longer, f_{NbC} is somewhat smaller, and the Morse parameter is slightly larger for the NbC bond, leading to a somewhat larger $\mathrm{d}\langle\Delta r\rangle/\mathrm{d}T$ in going from VC to NbC. The isotopic replacement of ^{12}C by ^{13}C leads to a change in $\langle\Delta r_{\mathrm{NbC}}\rangle$ of 1.2×10^{-4} Å, which is essentially the same as in $[\mathrm{V(CO)_6}]^-$.

The ^{93}Nb shielding in the isolated $[\mathrm{Nb(CO)_6}]^-$ complex ion can be expanded in terms of the internal coordinates of the molecule

$$\sigma(T) = \sigma_{\mathrm{e}} + (\partial\sigma/\partial(\Delta r))_{\mathrm{e}}\langle\Delta r_{\mathrm{NbC}}\rangle^T + \tfrac{1}{2}(\partial^2\sigma/\partial(\Delta r)^2)_{\mathrm{e}}\langle(\Delta r_{\mathrm{NbC}})^2\rangle^T + \ldots \quad (1)$$

The intermolecular effects on the complex ion in solution also give rise to a temperature dependence of the shielding. Although this contribution is not negligible in absolute magnitude, it is negligible relative to the effects of rovibrational averaging.[15] The temperature and mass dependence of the ^{93}Nb chemical shift in $[\mathrm{Nb(CO)_6}]^-$ can thus be interpreted by fitting the temperature and mass dependence of $\langle\Delta r\rangle$ and $\langle(\Delta r)^2\rangle$ to the experimental NMR data by means of the above equation. A two-parameter fit to the ^{13}C-induced isotope shift and to the temperature-dependent chemical shift leads to $(\partial\sigma^{\mathrm{Nb}}/\partial(\Delta r_{\mathrm{NbC}}))_{\mathrm{e}} \approx -0.625 \times 10^3$ ppm $\mathrm{Å^{-1}}$ and $^1/_2(\partial\sigma^{\mathrm{Nb}}/\partial(\Delta \mathrm{r}_{\mathrm{NbC}}{}^2)) \approx -2.18 \times 10^3$ ppm $\mathrm{Å^{-2}}$. Although these parameters can lead to complete agreement with experiment, the approximations involved in the modeling of the cubic force constants preclude attaching significance to these values, which may merely be compensating for inadequacies in the anharmonic force field. A practical approach is to obtain an *effective* $(\partial\sigma^{\mathrm{Nb}}/\partial(\Delta r_{\mathrm{NbC}}))_{\mathrm{e}}$ from the isotope shift and the temperature dependence by using only one term. Thus

$$^1\Delta[^{93}\mathrm{Nb}(^{13/12}\mathrm{C})] \simeq (\partial\sigma^{\mathrm{Nb}}/\partial(\Delta r_{\mathrm{NbC}}))_{\mathrm{e}}[\langle\Delta r_{\mathrm{Nb^{12}C}}\rangle - \langle\Delta r_{\mathrm{Nb^{13}C}}\rangle]$$

and

$$\sigma^{\mathrm{Nb}}(320\ \mathrm{K}) - \sigma^{\mathrm{Nb}}(200\ \mathrm{K}) \approx 6(\partial\sigma^{\mathrm{Nb}}/\partial(\Delta r_{\mathrm{NbC}}))_{\mathrm{e}}[\langle\Delta r\rangle^{320} - \langle\Delta r\rangle^{200}]$$

The isotope shift gives $(\partial\sigma^{\mathrm{Nb}}/\partial(\Delta r_{\mathrm{NbC}}))_{\mathrm{e}} \approx -1.42 \times 10^3$ ppm/Å, and the temperature shift gives $(\partial\sigma^{\mathrm{Nb}}/\partial(\Delta r_{\mathrm{NbC}}))_{\mathrm{e}} \approx -1.16 \times 10^3$ ppm/Å. The latter gives the curve in Figure 2, indistinguishable from the curve using -0.625×10^3 ppm $\mathrm{Å^{-1}}$ and -2.18×10^3 ppm $\mathrm{Å^{-2}}$ as first and second derivatives. The inadequacies in the anharmonic force field could easily account for the 20% difference between these two values, so we report an average effective parameter, $(\partial\sigma^{\mathrm{Nb}}/\partial(\Delta r_{\mathrm{NbC}}))_{\mathrm{e}} \approx -1.3 \times 10^3$ ppm/Å. A discussion of the relationship between this effective parameter and the true derivatives is given in ref 19. From

$$^2\Delta[^{93}\mathrm{Nb}(^{18/16}\mathrm{O})] \simeq (\partial\sigma^{\mathrm{Nb}}/\partial(\Delta R_{\mathrm{CO}}))_{\mathrm{e}}[\langle\Delta R_{\mathrm{C^{16}O}}\rangle - \langle\Delta R_{\mathrm{C^{18}O}}\rangle]$$

we also estimate $(\partial\sigma^{\mathrm{Nb}}/\partial(\Delta R_{\mathrm{CO}}))_{\mathrm{e}} \approx -8 \times 10^2$ ppm/Å.

The vibrational analysis of $[\mathrm{Re(CO)_6}]^+$, which we have done also, would be useful for interpretation of the ^{185}Re or ^{187}Re NMR shifts. The ^{185}Re and ^{187}Re NMR spectra for the $[\mathrm{Re(CO)_6}]^+$ ion in solution have been previously reported by us.[23] Unfortunately, the very high electric quadrupole moment of these nuclei (2.8 and 2.6×10^{-28} $\mathrm{m^2}$ compared to -0.05×10^{-28} $\mathrm{m^2}$ for ^{51}V) leads to very efficient quadrupolar relaxation, giving rise to broad lines that make the determination of isotope shifts and temperature shifts unfeasible.

The contribution to the temperature dependence of the ^{93}Nb chemical shift from the extension of the CO bond is much smaller than that from the Nb–C extension. The rotational contribution to the latter is also small. Thus, in large part, both the isotope effect and the temperature coefficient of the ^{93}Nb chemical shift are determined by the common electronic factor, $(\partial\sigma^{\mathrm{Nb}}/\partial(\Delta r_{\mathrm{NbC}}))_{\mathrm{e}}$. Examination of the data in Table II reveals that the ratio of the ^{13}C-induced isotope shift to the temperature coefficient in $[\mathrm{Nb(CO)_6}]^-$ ion is roughly the same as the ratio for the $\mathrm{CpNb(CO)_4}$ molecule, implying that the ratio of the dynamic averages

$$\frac{\langle\Delta r_{\mathrm{Nb^{12}C}}\rangle^{300} - \langle\Delta r_{\mathrm{Nb^{13}C}}\rangle^{300}}{\langle\Delta r_{\mathrm{Nb^{12}C}}\rangle^{320} - \langle\Delta r_{\mathrm{Nb^{12}C}}\rangle^{200}}$$

is roughly the same for both complexes. The ^{13}C-induced ^{93}Nb isotope shifts in these two complexes are in the ratio $(-0.373/-0.173) \approx 2$, from which we estimate that the derivative $(\partial\sigma^{\mathrm{Nb}}/\partial(\Delta r_{\mathrm{NbC}}))_{\mathrm{e}}$ in the less shielded environment $\mathrm{CpNb(CO)_4}$ is 2 times as large as that in $[\mathrm{Nb(CO)_6}]^-$. This is similar to the trend found in the corresponding derivatives of ^{51}V shielding in the $\mathrm{CpV(CO)_4}$ and $[\mathrm{V(CO)_6}]^-$ complexes.[14] The less shielded nuclei have greater temperature coefficients. This is to be expected if the paramagnetic term in the shielding dominates $(\partial\sigma/\partial(\Delta r))_{\mathrm{e}}$ for transition metal nuclei. It is of interest also to note that the magnitude of $(\partial\sigma/\partial(\Delta r))_{\mathrm{e}}$ for ^{93}Nb is somewhat less than that of ^{51}V in the hexacarbonyl anion, -1.3×10^3 vs -2.1×10^3 ppm/Å. That this is consistent with the larger chemical shift range of ^{51}V (6000 ppm) compared to ^{93}Nb (5000 ppm) is by itself not significant in view of the greater number of ^{51}V NMR measurements compared to ^{93}Nb measurements.

The shifts induced by replacement of H by D in the hydrides $\mathrm{CpM(CO)_3H}$ are very large. For M = V, Nb, and W they are respectively -4.7,[12] -6.0,[9] and -10 ppm.[7] At this time we are unable to perform the rovibrational averaging for these $\mathrm{CpM(CO)_3H}$ molecules so as to estimate $(\partial\sigma^{\mathrm{M}}/\partial(\Delta r_{\mathrm{MH}}))_{\mathrm{e}}$ from the approximate relationship

$$^1\Delta[\mathrm{M}(^{2/1}\mathrm{H})] \simeq (\partial\sigma^{\mathrm{M}}/\partial(\Delta r_{\mathrm{MH}}))_{\mathrm{e}}[\langle\Delta r_{\mathrm{MH}}\rangle - \langle\Delta r_{\mathrm{MD}}\rangle]$$

However, it has been previously shown that a rough estimate of $[\langle\Delta r_{\mathrm{MH}}\rangle - \langle\Delta r_{\mathrm{MD}}\rangle]$ can be made from the isotopic masses and the M–H bond length.[24] Using $r_{\mathrm{NbH}} \approx 1.66$ Å and $r_{\mathrm{VH}} \approx 1.54$ Å,[25] we estimate $\langle\Delta r_{\mathrm{NbH}}\rangle \approx 2.38 \times 10^{-2}$ Å, $\langle\Delta r_{\mathrm{VH}}\rangle \approx 2.45 \times 10^{-2}$ Å, and

$$(\partial\sigma^{\mathrm{Nb}}/\partial(\Delta r_{\mathrm{NbH}}))_{\mathrm{e}} \approx -1.0 \times 10^3\ \mathrm{ppm/Å}$$

$$(\partial\sigma^{\mathrm{V}}/\partial(\Delta r_{\mathrm{VH}}))_{\mathrm{e}} \approx -8 \times 10^2\ \mathrm{ppm/Å}$$

These derivatives are smaller than those involving the stretches of Nb–C or V–C bonds, which we had estimated to be -1.3×10^3 and -2.1×10^3 ppm/Å, respectively. For ^{183}W in $\mathrm{CpW(CO)_3H}$ a bond length of 1.62 Å estimated from the sum of covalent radii is short compared to 1.68 Å, which is typical of known ReH bond lengths and those of other third transition series hydrides.[25] The latter results in an estimate for $(\partial\sigma^{\mathrm{W}}/\partial(\Delta r_{\mathrm{WH}}))_{\mathrm{e}}$ of $\approx -1.6 \times 10^3$ ppm/Å.

Summary and Conclusions

In this work, we find that the ^{93}Nb NMR chemical shift changes dramatically with temperature and isotopic mass of the ligands, and these changes are completely consistent with the vibrational averaging that occurs within the NMR time scale. The effects observed here occur in all molecular systems. By a favorable combination of very large ^{93}Nb chemical shifts and high sensitivity of the electronic structure of transition-metal complexes to metal–ligand distance, these effects are very dramatic in $[\mathrm{Nb(CO)_6}]^-$, thereby allowing quantitative measurements and interpretation. The vibrational averages are carried out by using a method that has been developed and shown to be successful in interpreting the temperature and mass effects on bond lengths

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(25) Covalent radii of V, Nb, and H (1.22, 1.34, and 0.32 Å, respectively) were used. It is known that M–H bond lengths in transition-metal compounds are typical of a normal covalent bond: Frenz, B. A.; Ibers, J. A. In *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Dekker: New York, 1971; Vol. 1, p 33.

in other molecules, using a vibrational force field that is obtained from the IR and Raman spectra of the anion and is consistent with the hexacarbonyl anion, cation, and neutrals of adjacent transition metals. We find the magnitude of the one-bond isotope shift of ^{93}Nb is completely consistent with the temperature dependence of the ^{93}Nb chemical shift in $[Nb(CO)_6]^-$ ion. A single parameter, $(\partial\sigma^{Nb}/\partial(\Delta r_{NbC}))_e$, which describes the sensitivity of the ^{93}Nb chemical shift to Nb–C bond extension, reproduces both the magnitude of the ^{13}C-induced isotope effect and the shape of the temperature dependence of the ^{93}Nb shift. A small correction to the latter is provided by the much smaller sensitivity of the ^{93}Nb chemical shift to the C–O bond extension, which is obtained from the ^{18}O-induced shifts. On the other hand, the very large D-induced isotope shifts of the metal M in the hydrides $[CpM(CO)_3H]$, respectively −4.7, −6.0, and −10 ppm for M = ^{51}V, ^{93}Nb, and ^{183}W, can be interpreted with analogous parameters $(\partial\sigma^M/\partial(\Delta r_{MH}))_e$ describing the sensitivity of the M chemical shift to M–H bond extension, which are smaller than those for M–C bond extension in the same compounds and are consistent within the series of hydrides. With these results we believe that the signs and magnitudes of the temperature dependence of transition-metal shifts and their isotope effects are generally understood. What remains to be determined are the general magnitudes of the derivatives $(\partial\sigma^M/\partial(\Delta r))$, $(\partial^2\sigma^M/\partial(\Delta r)^2)$, etc., by ab initio calculations such as those used for ^{55}Mn shielding in $Mn(CO)_5L$ complexes.[26]

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Ruthenium(II) Cluster Complexes: A Series of Homooligonuclear Complexes Based on Bidentate Bridging Ligands

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The preparation and properties of trimetallic and tetrametallic cluster complexes containing ruthenium(II) metal centers bridged by 2,2′-bipyrimidine (bpm) and 2,3-bis(2-pyridyl)quinoxaline (bpq) are reported. The tetrametallic clusters are symmetrical complexes containing a central ruthenium(II) coordinated to three $(BL)Ru(bpy)_2^{2+}$ "ligands", where BL is bpm or bpq and bpy is 2,2′-bipyridine. The trimetallic clusters are asymmetric and are of the general formula $[(bpy)Ru(BLRu(bpy)_2)_2]^{6+}$. The complexes exhibit low-energy MLCT transitions assigned as $d\pi(Ru(outer)) \rightarrow \pi^*(BL)$. The MLCT maxima of the tetrametallic complexes were at slightly higher energies than those for their trimetallic analogues. For example, λ_{max} for $[Ru(bpqRu(bpy)_2)_3]^{8+}$ was located at 618 nm; that of $[(bpy)Ru(bpqRu(bpy)_2)_2]^{3+}$ was located at 621 nm. The $E_{1/2}$ values were determined by cyclic voltammetry. The first oxidation in the case of $[(bpy)Ru(bpqRu(bpy)_2)_2]^{6+}$ was located at $E_{1/2}(1) = 1.57$ V, and the second, at $E_{1/2}(2) = 1.83$ V vs. SSCE. The wave associated with $E_{1/2}(1)$ had about twice the peak current as the wave at $E_{1/2}(2)$ and, hence, was assigned to the Ru(III/II) redox couple of the outer ruthenium(II) components. The low-energy MLCT transitions for the mononuclear precursors $(Ru(bpy)_x(BL)_{3-x}$, $x = 1-3)$ and the multimetallic complexes were found to parallel $\Delta E_{1/2}$, the difference between $E_{1/2}$ values for the first oxidation and the first reduction. The excellent correlation (slope 1, correlation coefficient 0.99) indicates that either the energy of the lowest MLCT transition or $\Delta E_{1/2}$ can be used to measure the energy gap between the $d\pi$ and π^* energy levels.

Introduction

Several years ago we began a research program to develop multielectron-transfer catalysts that were photochemically and electrochemically active. We have successfully synthesized monometallic[1,2] precursor and multimetallic[3] metal complexes based on bidentate bridging ligands, which were chosen to add stability to the compounds. The bridging ligands used in our studies have been nitrogen-based heterocycles with both π-donor and π-acceptor properties, and the metal center has normally been ruthenium(II), although recently we have reported mixed-metal complexes containing both platinum(II) and ruthenium(II).[4–6]

A number of other workers have also contributed in this area. Dose and Wilson[7] reported the preparation and properties of $[Ru(bpy)_2(bpm)]^{2+}$ and $[(Ru(bpy)_2)_2bpm]^{4+}$, where bpm is 2,2′-bipyrimidine and bpy is 2,2′-bipyridine. Hunziker and Ludi reported the preparation of the tetranuclear complex $[Ru(bpmRu(bpy)_2)_3]^{8+}$, where bpm ligands served to bridge the central ruthenium(II) to the outer three ruthenium(II) centers.[8] Bimetallic and tetrametallic complexes were recently reported by Schmehl and co-workers.[9] The bridging ligand used by these investigators contained a p-$CH_2C_6H_4CH_2$ unit attached to two bipyridine molecules in the 4-position of the heterocyclic rings. Gafney and co-workers[10] have reported similar monometallic and bimetallic ruthenium(II) complexes based on the ligand 2,3-bis(2-pyridyl)pyrazine (bpp) and more recently Petersen and co-workers reported the preparation and properties of $Ru(bpp)_3^{2+}$.[11] Simlar complexes based on the ligand 2,2′-bibenzimidazole ($BiBzImH_2$) were reported by Haga.[12] The π-donor

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