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The Vibrational Spectra of the Cyanide Ligand Revisited: Terminal Cyanides

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A comparison is made between the vibrational characteristics of the carbonyl and cyanide ligands. There are significant differences; the latter has a smaller dipole moment and a larger quadrupole moment associated with the bond stretch. This quadrupole moment may be linked to the observation that the totally symmetric ν(CN) mode does not lie at the highest frequency for some cyanide complexes. There are problems with the π-bonding model commonly used to interpret the ν(CN) data. For instance, for the first transition row hexacyanoanions, the spectra are almost independent of t_{2g} occupancy but are very sensitive to the formal charge. It is suggested that the observed ν(CN) frequency shifts on complex formation are in large measure determined by the effective charge on the cation to which the cyanide group is attached, and a new model, the Internal Vibrational Stark Effect, is suggested to account for this. The model is supported by DFT calculations. Raman spectra of some cubic cyano species are reported, along with polarization and intensity data.

Introduction

This paper is devoted to a study of the vibrational properties of metal complexes containing terminal CN$^-$ ligands. Cyanide complexes are of great current interest, but the details are well-known and will not be rehearsed here. Despite this interest, it cannot be said that the ν(CN) spectra of complex cyanides are well-understood, although such an understanding would clearly be of widespread value. For many species, only solid complexes can be studied; seldom are reliable Raman data available.[1,2] Because anionic species are often highly charged, seldom are the associated cations totally innocent.[3] So, where mixed-solvent studies have been made, frequencies show a dielectric constant dependence.[4] In the solid, a CN bond length in an anion may vary with the associated cation. Bridge species are common—and of current interest—and usually, but not always, show frequencies above those of the corresponding unbridged compound.[2] The bridged species present particular problems, and so, the present work is limited to complexes with terminal CN groups; the case of bridging cyanides will be discussed elsewhere. Formally, of course, there is a relationship between transition metal cyanides and the much better understood transition metal carbonyls. The CN$^-$ and CO ligands are isoelectronic, strong field, ligands; cyanide and carbonyl complexes can often be found with the same symmetries.[5] Similar vibrational analyses have been adopted for each (in particular, exploiting the fact that the relevant spectral features may be analyzed with a neglect of coupled vibrators such as M−C[6]), and both form polynuclear species. Available data on the carbonyls could be used to shed light on the spectra of the cyanides, although such a connection seems not to have been much exploited in the past. In the present work, therefore, we bring together aspects of the two ligands and their complexes which, we believe, will prove

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helpful in the endeavor of a better understanding of the spectra of the complex cyanides. To this end, it is important that the spectra of the cyanides be complete and well-defined. We have, therefore, recorded the infrared and Raman spectra of a variety of octahedral hexacyano anions under standard solution conditions, and the present work is largely devoted to these species.

Experimental Section

Synthesis. All the hexacyanide complexes were purchased from Aldrich and purified by crystallization. The $K_8[Mo_4Se_4(CN)_{12}]$ cluster was kindly provided by Professor T. Hughbanks.[7] The cluster was dissolved in deoxygenated water in an argon-filled glovebox. The burgundy solution showed no visible change with time, and the spectra obtained were reproducible.

Spectra. Raman spectra were recorded by a Raman Jobin-Yvon Spectrophotometer Labram HR 800 using a laser radiation at 633 nm and a 1800 lines/mm grating and selecting a proper confocal hole diameter; the resolution was set between 1 and 4 cm^{-1}. Polarized Raman spectra were obtained with the same instrumental setup after filtering the collected radiation by a polarization filter, oriented parallel or perpendicular to the polarization plane of the incident laser light. The infrared spectra were collected with a Bruker Equinox 55 FT-IR spectrophotometer, using a resolution of 2 cm^{-1} and averaging 32 scans.

Calculations. All the calculations were performed with the Gaussian 03 package.[8] The dipole and quadrupole moments of CO and CN^- species were obtained with single-point coupled cluster calculations, with single and double substitutions from the Hartree−Fock determinant at a specified geometry, with quadruple-ζ Dunning's correlation consistent basis sets augmented with diffuse functions (aug-cc-pvqz). The vibrational, geometrical, and charge data were obtained with the density functional method using Becke's three-parameter hybrid functional with the Lee−Yang−Parr correlation functional. The basis set employed was the 6-31+G-(d,p) for C, N, and O and the LANL2DZ ECP for Fe. All the geometries are optimized. The charges were obtained from a natural bond orbital analysis of the total density. An important check is that the dipole moment calculated for the CO molecule was of the correct sign and, approximately, magnitude (exptl 0.122 D).[9] Improving the basis also improved the agreement with experimental results (calcd 0.125 D).[10] It is difficult to reproduce the experimental value closely. However, the pattern given by our calculations indicates that the differences in dipole moment should be more accurate than the absolute values that we obtain. Comparative calculations on CO, CN^-, and CNH have previously been reported.[11]

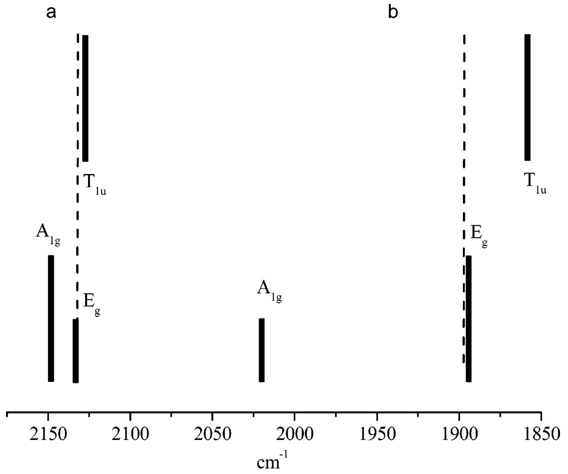

Figure 1. Schematic representation of the infrared (top) and Raman (bottom) spectra of $K_3[Co(CN)_6]$ (a) and $K[V(CO)_6]$ (b).

Results and Discussion

In this section, we give an overview of the current understanding of the vibrational spectra of the octahedral carbonyls and cyanides, introducing our new data or new models at appropriate points. In Figure 1, we show, schematically, the vibrational spectra of the $[Co(CN)_6]^{3-}$ and $[V(CO)_6]^-$ anions in the 2000 cm^{-1} region, all species being in solution. These examples were chosen because they are representative of their analogues and have reasonably similar frequencies and ionic charges as close as possible, thus enabling an adequate comparison and a common presentation. Several points are evident, all of which need either to be understood or to be interpreted.

(1) The cyanide features are at a higher frequency; if the two species were of identical formal charge, the frequency difference would be much greater than that shown in Figure 1. No real explanation has been offered for this. An explanation in terms of force constant difference is circular; one in terms of bonding differences is *post hoc* and lacking in predictive power. We shall offer what we believe is a more fundamental explanation in the present work. We note also that the degeneracy-weighted center of gravity of all features (indicated by the dashed line in the central row of Figure 1) approximately coincides with the E_g frequency, a characteristic on which we shall comment.

(2) The splittings of the cyanide features are smaller than those of the carbonyl, and their infrared intensities are lower.

(3) Although the frequency order $A_{1g} > E_g > T_{1u}$ is common to both sets, the Raman intensity of the A_{1g} feature

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Table 1. Vibrational Data for $[M(CN)_m]^{n-}$ Anions

species	cation	solvent	A_{1g}	E_g	T_{1u}	c of g[a]	spread[b]	ref
$[Cr(CN)_6]^{3-}$	K^+	H_2O	2131	?	2128	2129	3	this work
$[Fe(CN)_6]^{3-}$	K^+	H_2O	2133	2125	2115	2121	18	this work
$[Co(CN)_6]^{3-}$	K^+	H_2O	2148	2133	2127	2132	21	this work
$[V(CN)_6]^{4-}$	K^+	s. s.?	2080	2065	2050	2060	30	11
$[Fe(CN)_6]^{4-}$	K^+	H_2O	2089	2062	2038	2051	51	this work
$[Ru(CN)_6]^{4-}$	K^+	H_2O	2109	2069	2047	2065	52	this work

species	cation	solvent	A_{1g}	B_{1g}	E_u	c of g[a]	spread[b]	ref
$[Ni(CN)_4]^{2-}$	K^+	H_2O	2143.5	2134.5	2123.5	2131	20	14
$[Pd(CN)_4]^{2-}$	K^+	H_2O	2160.5	2146.5	2135.8	2145	25	14
$[Pt(CN)_4]^{2-}$	K^+	H_2O	2168	2148.8	2133.4	2146	35	14

[a] Center-of-gravity frequency, that is, the weighted mean of all frequencies. [b] Difference between the highest and the lowest frequency.

is greater than that of the E_g for the cyanide but lower for the carbonyl. A partial explanation has been offered in the literature, which we complete in the present work.

(4) A feature not shown in Figure 1 concerns the frequency sequence of modes. For some CN, but not CO, species, the totally symmetric mode is not that with the highest frequency. The examples that we give later are not for $[M(CN)_6]$—but it should be noted that single-crystal Raman studies on the $[Cr(CN)_6]^{3-}$ anion found the A_{1g} mode slightly lower in frequency than the E_g.[12] This may not be relevant; significant differences between solution and solid-state data have been reported for other $M(CN)_6$ species.[13]

(5) Finally, an important and general relationship evident (see the data of Tables 1 and 1SI) is that, when the positive charge increases on a given molecular species, the frequency increases (for both CO and CN).

1. Cyanides and Carbonyls. In Table 1, we give our data for cyanide species, along with some literature data where we have made no study, but the data are complete. In Table 1SI of the Supporting Information are collected all relevant data in the literature concerning the metal carbonyls for which both infrared and Raman spectra have been reported. We highlight the aspect, relevant to octahedral complexes, and common to Tables 1 and 1SI, that the degeneracy-weighted mean frequency of all of the peaks is almost coincident with the E_g frequency, usually slightly lower. This can be interpreted in terms of the expression for the frequency of this mode in a ν(CO/CN)-only model. The effective force constant for the E_g mode is

$$\lambda(E_g) = f - 2k_c + k_t$$

where f is the bond force constant and k_c and k_t are the interaction constants between cis and trans ligands, respectively. That is, the observation is a statement that

$$2k_c \approx k_t$$

The apparently general applicability of this relationship implies that reasonably uniform force constant patterns are to be expected; any apparently discordant force constant pattern should be the subject of suspicion.

There has been a wide variety of explanations for the general characteristics seen in the terminal CN stretching vibrations of cyanide complexes, even a suggestion that the mass of the central metal atom is a factor.[15] A general overview of terminal frequencies, with largely orbital explanations, has been given.[16] In the bonding model, σ donation from C to M depopulates a weakly C−N antibonding orbital, leading to an increase in frequency. The population of π antibonding orbitals decreases the frequency. Although it has been widely invoked, there has been limited quantitative discussion of this model.[17] Jones et al.[14] have related metal−cyanide π bonding to d electron configuration and the C−N force constant, the latter also depending on the metal−cyanide σ bonding. They related both σ and π bonding to the effective nuclear charge on the metal, a suggestion relevant to the present work. Related is the interpretation of the fact that, for instance, $[Fe(CN)_6]^{3-}$ has higher frequencies than the corresponding modes of $[Fe(CN)_6]^{4-}$ in terms of the higher occupancy of the $\pi^*(t_{2g})$ orbitals in the latter.[5] However, Nakamoto has demonstrated that, for first-row M(III) species, the T_{1u} frequency is not dependent on the number of electrons in the t_{2g} orbitals.[20] Although any dependence on the electronic structure of the metal seems small, it must surely be nonzero ($[Ti(CN)_6]^{3-}$ has a surprisingly low t_{1u} frequency,[21] the more surprising in that the center of gravity of the tetracyanoanion of B is above 2120[22]). Jones et al.[14] suggested that the constancy of infrared frequencies for the Cr(III)−Co(III) species indicates a compensation of metal−carbon σ- and π-bonding effects. But not all explanations are solely orbital-based. For the tetracyanides of Zn(II), Cd(II), Hg(II), and Cu(II), the high

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frequency for the latter was related to a high ionicity of the Cu−C bond; we have already mentioned Jones and coworkers' suggestion of the relevance of the effective nuclear charge of the metal. This hint toward an importance of polar effects is mirrored in the work of Bertran et al.,[3] who considered the ν(CN) frequencies observed in the solid state for a series of octahedral hexacyanides to be determined both by the central metal and also by the counterion (a sort of ion-pair effect), although their explanation of the latter was orbital in nature. The importance of "factors (partly electrostatic) that affect the distribution of electron density within the CN^- moiety" has been suggested, with a brief review of electrostatic models (and mention of the Stark effect).[23] The importance of some sort of polar effect is also evident in the earliest attempt to rationalize the spectral data, where cyanide frequencies were regarded as determined by the electronegativity, oxidation state, and coordination number of the central metal.[24] These suggestions of polar effects, which still seem relevant, tend to be more generalizations than explanations. If an explanation for polar effects is to be found, it is in the present work. Our own opinion is that, while there must surely be a connection between the bonding (and antibonding) orbital occupancies and vibrational frequencies, orbital occupancies do not invariantly seem to be the dominant factor.

2. Band Spread. The data in Tables 1 and 1SI show that the spread of the spectral bands of the octahedral species under discussion is much larger for CO complexes than for CN^-. To explain these differences, we have explored what is a potentially significant difference between these ligands, which becomes evident when the isoelectronic sequence CO, CN^-, C_2^{2-} is considered. While there is a large dipole moment change associated with stretching of the bond in CO, this change is identically zero for C_2^{2-}. Interpolating, it seems likely that CN^- is intermediate. In contrast, the stretching of the C−C bond in C_2^{2-} is associated with a quadrupole change. While it is not required by the above argument, it seems possible that the quadrupolar charge movement associated with the bond stretch decreases from C_2^{2-} to CO, in which case there would surely be a corresponding difference between CN^- and CO. To test these hypotheses, some detailed calculations on CO and CN^- have been carried out with the object of assessing the relative importance of dipole and quadrupole moment changes in their stretches. The results are given in Table 2SI.

Of particular interest are the dipole and quadrupole changes consequent on bond length changes (vibrations). The calculations indicate that the dipole moment change associated with stretching of the CN bond is an order of magnitude smaller than that for CO. This is surely related to the weakness of infrared active ν(CN) features relative to ν(CO) in their transition metal complexes and to the order of magnitude differences in the frequency spreads in Tables 1 and 1SI (they would be consistent with the suggestion that the splittings observed for complex species have a significant dipole−dipole component).[25]

The spread of the spectral bands is also a function of the charge on the species; an increase in negative charge is to be associated with an increase of spread (the spread also seems to depend to a smaller extent on the transition metal series). This feature indicates that the greater the negative charge, and so, usually, the physically larger the species, the greater the absolute magnitude of the vibrational interaction constants. In turn, this presumably indicates that closer proximity to the metal atom has a damping effect; that is, the vibrational interactions contain a significant component, which is through-space rather than through-electron density. That is, we believe that this is yet another phenomenon which is a consequence of the dipole−dipole nature of the vibrational coupling between ligands. For the carbonyls, support for a through-space explanation comes from the fact that, when crystalline, hexacarbonyls can exhibit factor group coupling.[26] The band multiplicity associated with factor group effects must surely be through-space because they result from intermolecular vibrational coupling. It is, therefore, probably unwise to attempt a solely orbital interpretation of intramolecular CO−CO vibrational interaction constants; a dipole−dipole model might be as appropriate. There seems to be no corresponding report in the literature for hexacyanides (although the factor group method has been used for them, no factor group splittings have been reported). This difference between the carbonyls and cyanides surely lies in the different magnitudes of the dipole moment changes associated with their bond stretching vibrations together with the greater separation between cyanide anions consequent upon the incorporation of cations in the lattice.

3. Relative Raman Intensities. A difference noted above between the octahedral hexacarbonyls and hexacyanides lies in the pattern of their Raman intensities. For the carbonyls, the A_{1g} band is weaker than the E_g; the opposite is true for the cyanides. Such a statement depends on the correct assignment of the Raman spectra; the only Raman polarization data in the literature on hexacyanides are rather old, and so, we have made new measurements with state-of-art equipment. An example of our spectra is given in Figure 2, and our Raman intensity data are given in Table 3SI.

Whereas for the hexacarbonyls the relative intensities of the A_{1g} and E_g bands seem to change little with species with the same charge, there is a significant variation for the hexacyanides. Nonetheless, a consistent picture emerges when the data are analyzed by expressing the observed molecular tensors as a sum of bond-derived polarizability tensors. This analysis gives the ratio of the components parallel and perpendicular to the bond axis (b and a, respectively).[27] The analysis involves a quadratic equation

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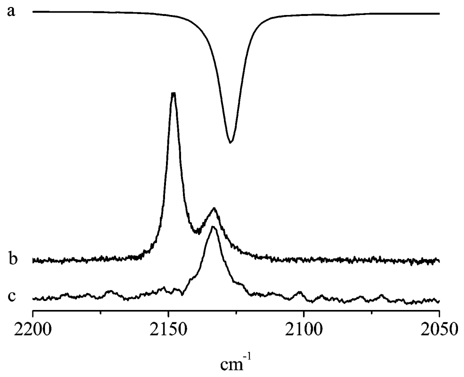

Figure 2. Infrared (a) and Raman, unpolarized (b) and polarized (c), spectra of $K_3[Co(CN)_6]$, recorded in a water solution.

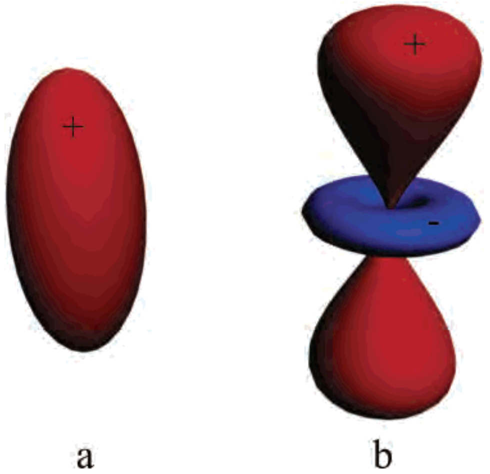

Figure 3. Pictorial representation of the general shape of the bond-derived polarizability tensors in $M(CY)_6$ species: (a) Y = N and (b) Y = O.

and so gives two ratio values for each species. As with the carbonyls, we have chosen those which are most similar. That is, we have assumed that the derived polarizability components of the cyanide ligand should be as transferable as is consistent with the data. In the event, all correspond to the positive value of the square root.

For the cyanides, the a and b components are of the same sign, although for species of the same charge, their ratio varies considerably (Table 3SI). The fact that the components are the same sign means that the CN^- bond-derived polarizability tensors are cigar-shaped; the difference in ratio means that some are plumper than others. In contrast (Figure 3), the CO bond-derived polarizabilities have a shape akin to that of a d_{z^2} orbital, the ratio of the two lobes being approximately 4:−1 (for the hexacarbonyls, it is the cancellation which results when these bond components are added in phase in the A_{1g} mode which means that this band is weaker than the E_g).[28] All of these arguments are summarized, pictorially, in Figures 4 and 5.

An important point of this analysis is that it enables us to conclude that the A_{1g} feature will, in zeroth order, be the most intense Raman feature in the terminal ν(CN) region. The fact that it is of the highest Raman intensity and, usually, at the highest frequency should serve to identify it unambiguously. Nonetheless, particularly in cases where it is part of an unexpected frequency pattern, discussed in the next section, confirmation by polarization measurements is desirable.

4. Unexpected Frequency Patterns. One important way in which the cyanides differ from the carbonyls is in the band at the highest frequency. For carbonyls, no matter the geometry, we know of no exception to the rule that it corresponds to a totally symmetric mode. While the same is possibly true of $[M(CN)_6]$ species, it is not true for all high-symmetry cyanide anions and may also be untrue for some low-symmetry species. We will explore a high-symmetry problem shortly, but it is convenient to prelude it by a discussion of a simple species which has been well-documented in the literature, although our conclusions differ from those of the original authors.

4.a. A Simple $M(CN)_3$ System. The infrared and Raman spectra of *fac*-Co(aepn)$(CN)_3$ [aepn = N-(2-aminoethyl)-1,3-propanediamine] have been reported for solid samples.[29] Although the space group is $P2_1/c$ (with $Z = 4$), and so contains centers of inversion, the infrared and Raman ν(CN) peaks coincide. One may be confident that factor group effects are negligible and that, therefore, the spectra are, essentially, those of the isolated molecules subject only to site splitting. The $(CN)_3$ groups show almost perfect C_{3v} symmetry (C−N bond lengths identical to 0.01 Å, bond angles to 2°). However, the aepn ligand reduces the molecular symmetry to C_s. A parallel with a species such as (butadiene)Fe$(CO)_3$ is evident.[30] In the latter, the effect of the butadiene is manifest by a relatively small splitting of the degenerate E mode of the carbonyl ligands, and we confidently anticipate an analogous pattern for *fac*-Co(aepn)$(CN)_3$, because the intermolecular site effects (C_1) are scarcely likely to overwhelm the intramolecular. The spectra of the cyanide complex show a doublet of peaks at high frequencies and a single peak at lower frequencies. The obvious interpretation is of a split high-frequency E and low-frequency A_1. This interpretation requires that the totally symmetric mode be at the lowest frequency, not the highest, a situation apparently without precedent. Not surprisingly, the original authors preferred an alternative interpretation. However, the high-symmetry species to which we now turn is composed of $M(CN)_3$ units. These units are so well-separated that it is difficult to conceive that novel and dominant phenomena arise from interactions between them. Any such phenomenon must be inherent in the $M(CN)_3$ components themselves—and that in which we are interested requires that it be possible that the totally symmetric, A_1, combination has a frequency lower than that of the degenerate E modes in $M(CN)_3$.[31]

4.b. Pseudo-Cubic Clusters $M_4E_4(CN)_{12}$. The structure of the pseudo-cubic clusters $M_4E_4(CN)_{12}$ is well-known.[33,34]

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[28] Although there are clear differences between the CO and CN^- ligands, they may, nonetheless, share a common pattern. This is that the b/a ratio becomes more positive with an increasing positive (or decreasing negative) charge on the species.

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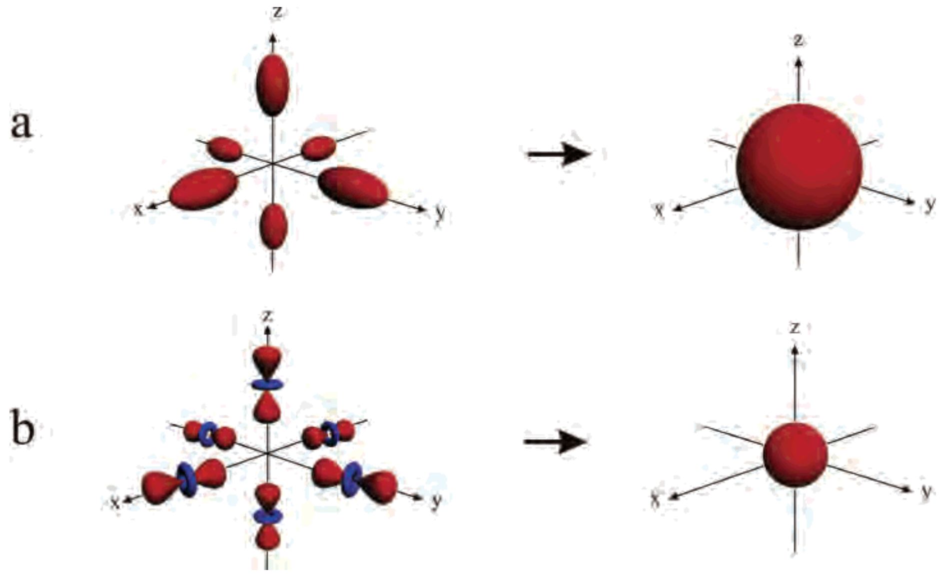

Figure 4. Pictorial representation of the general shape of the molecular bond-derived polarizability tensors for the ν(CN) (a) and ν(CO) (b) A_{1g} modes, derived from their bond components.

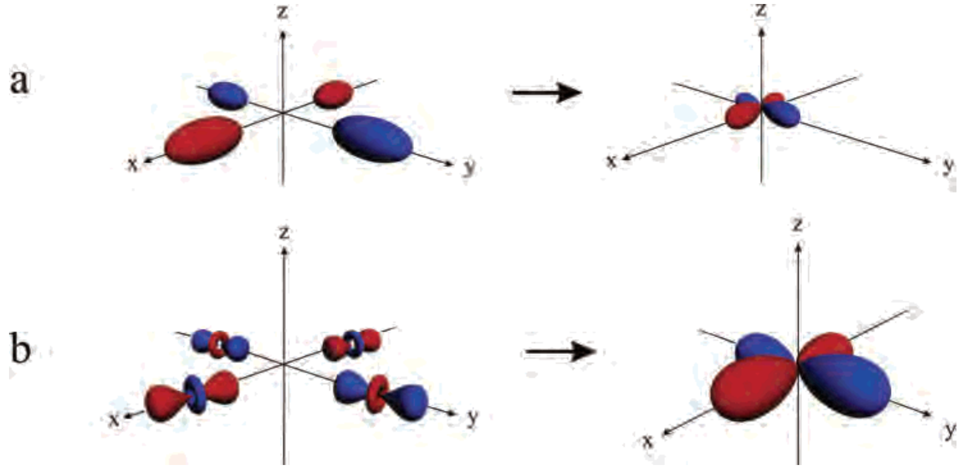

Figure 5. Pictorial representation of the general shape of the molecular bond-derived polarizability tensors for the ν(CN) (a) and ν(CO) (b) E_g modes, derived from their bond components.

The schematic figure is illustrated in the Supporting Information (Figure 1SI).

Under T_d idealized symmetry, the ν(CN)'s span the modes A_1 (R) + E (R) + T_1 (- -) + $2T_2$ (ir, R) (in parentheses, the infrared and Raman activities). This species consists of four $M(CN)_3$ units interconnected by face-bridging E atoms; the CN groups of different $M(CN)_3$ units are surely well-insulated, vibrationally, from each other [the coupling between $M(CN)_3$ units being largely through-space]. There have been several reports of the vibrational spectra of these species, but no common pattern has emerged. In some, the totally symmetric mode has been reported as lying below the highest frequency band. However, it is possible to find points of criticism of all of these reports: the report of frequencies but not of spectra, the use of solid samples, and the absence of polarized Raman spectra. In this situation, we have performed new measurements on the $[Mo_4Se_4(CN)_{12}]^{8-}$ anion. Infrared and Raman spectra were obtained from the same aqueous solution along with polarized Raman data. The spectra obtained are presented in Figure 6.

They are quite unambiguous; the strongly infrared active T_2 mode is some 15 cm^{-1} above the highest frequency Raman-active feature. The latter is the most intense Raman feature and is confirmed as associated with the totally symmetric mode by the polarized Raman spectrum, where it is absent. Having established that the A_1 feature may not be at the highest frequency, it is appropriate to review the literature data and the assignments that they contain. This is done in Figure 7.

As we have already indicated, there is no clear pattern, and certainly, it is hazardous to generalize with such a limited

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(31) Another system in which the totally symmetric ν(CN) band may be at a lower frequency (to judge by relative Raman intensities) is in *fac*$[Fe(CN)_3(CO)_3]^-$, although an evident coupling between CN and CO vibrators clouds the conclusion.[32]

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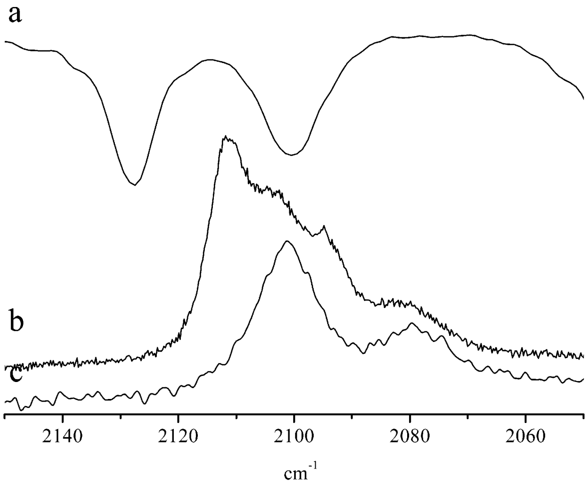

Figure 6. Infrared (a) and Raman, unpolarized (b) and polarized (c), spectra of $K_8[Mo_4Se_4(CN)_{12}]$, recorded in a water solution.

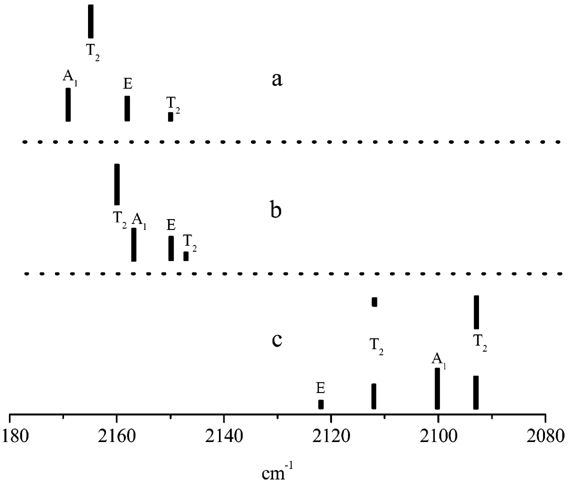

Figure 7. Schematic representation of the infrared (top) and Raman (bottom) spectra of $K_4[Re_4S_4(CN)_{12}]$ (a),[33] $K_4[Re_4Se_4(CN)_{12}]$ (b),[33] and $K_8[Mo_4S_4(CN)_{12}]$ (c).[34]

number of examples. However, it seems that intense infrared and Raman features move together. So, in $[Mo_4S_4(CN)_{12}]^{8-}$, where the A_1 is at the lowest frequency of all of the examples, so too is the most intense infrared band. In this context, $[Mo_4Se_4(CN)_{12}]^{8-}$ may be seen as something of an intermediate case, where infrared intensity is moving from the higher- to the lower-frequency, T_2, infrared band. If, indeed, there is a common pattern linking the A_1 and T_2, then this is entirely consistent with the discussion above. The A_1 mode in C_{3v} symmetry is the parent of $A_1 + T_2$ modes in T_d. The most evident indicator of the presence of a lower-frequency A_1 (C_{3v}) mode would be the failure of corresponding to the A_1 (T_d) to have the highest frequency.

Inevitably, associated with the unusual frequency patterns go abnormal force constant data. Indeed, for the species $[Mo_4S_4(CN)_{12}]^{8-}$, for which a detailed normal coordinate analysis was carried out,[34] the CN modes were excluded, notwithstanding the fact that they show significant splittings. The reason is clear; to include them would lead to interaction constants quite different from analogous data reported in the literature. We believe that this exclusion was correct because an assumption inherent in all normal coordinate analyses is that there be no mode-specific (vide infra) interactions. So, the weighted sum of all splittings resulting from the presence of an interaction constant in an analysis is zero. There is no such cancellation when a mode-specific term is present,[35] and this we believe to be the case for at least some $[M_4E_4(CN)_{12}]$ species. Clearly, the problem with these molecules lies in the A_1 mode; there exists some mechanism by which it is stabilized, while the other modes are much less evidently affected. As we have indicated above, we believe that the problem also exists for some $M(CN)_3$ species, and it is to these that we turn for our explanation; they are the basic component of all $[M_4E_4(CN)_{12}]$ molecules.

Table 2. Atomic Charges, ν(CN) Frequencies, and Their Shifts Consequent upon Protonation Calculated for CO, CN, and CN^-

species	q_C	q_X	q_H	ν_{CX} cm^{-1}	effect of H^+
CO	0.514	−0.514		2202	
CN	0.414	−0.414		2151	
CN^-	−0.228	−0.722		2124	
HCO^+	0.814	−0.154	0.340	2261	+59
HCN^+	0.514	0.152	0.335	1917	−234
HCN	0.073	−0.314	0.241	2203[a]	+52

[a] See ref 38.

4.c. Quadrupole−Quadrupole Coupling. In contrast to the dipole moments, the quadrupole moment changes consequent on bond stretching are an order of magnitude greater for CN^- than those for CO (see Table 2). That is, for the cyanides, ligand−ligand-derived quadrupole interactions are approximately 4 orders of magnitude more important, relative to the dipole−dipole, than in the carbonyls. Similarly, ligand-derived quadrupole−metal-derived quadrupole interactions are approximately 2 orders of magnitude more important.

Quadrupole−quadrupole coupling, then, offers a possible explanation for phenomena found for the CN ligand but not the CO. There are several mechanisms by which quadrupolar interactions could lower the frequency of a totally symmetric mode (for convenience, denoted A_1), and we shall describe, in qualitative terms, two limiting cases. These two cases are not mutually exclusive, so some combination might well be more appropriate; equally, they are not the only possibilities.[36]

Figure 8 shows a quadrupole−quadrupole interaction between ligand and metal transition quadrupoles. It is to be emphasized that the diagram shows charge displacements so that overlapping + and − lobes represent a charge-compensating situation. It is to be noted that, although charge migrations occur, there is little, if any, overall charge displacement. Such an interaction would explain a decrease in A_1 frequency by the introduction of a NC−M stabilizing mechanism which acts solely on the A_1 mode. Clearly, the

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(35) The term "mode-specific" will only be applicable to high-symmetry species such as those which are the topic of the present discussion. With a descent in symmetry, any such "mode-specific" energy term may contribute to modes of more than one symmetry, those that correlate with the high-symmetry species. In such cases, it will become easier to accommodate the effects of such an energy term within a normal coordinate analysis. However, distorted parameters would result, lacking any real meaning.

(36) One such is ligand quadrupole−metal dipole. We have not included this because it would involve a charge displacement, which is scarcely likely to lead to a stablilization of the A_1 mode.

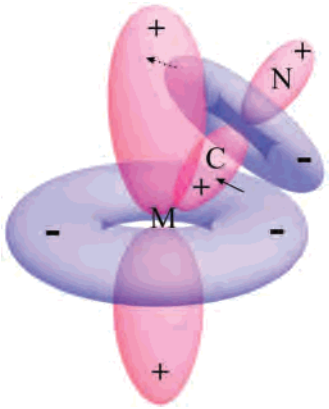

Figure 8. Schematic diagram of a possible metal–CN derived-quadrupole coupling in the A_1 mode of the (local C_{3v}) $M(CN)_3$ unit in $M_4E_4(CN)_{12}$. For clarity, only one CN group is shown. It is to be emphasized that *charge* displacements are shown, so that red (charge decrease) adjacent to blue (charge increase) represents a stable situation. The arrows indicate charge movements.

mechanism would involve rather large and diffuse quadrupolar electron distributions, requiring the involvement of excited states, particularly at the metal center. These excited states will be very sensitive to the identity of M and those of the other ligands attached to it, offering an explanation for the very different spectral patterns reported for $[M_4E_4(CN)_{12}]$ species. Experimentally, these sensitivities could be used in a search for examples of this mechanism (and could perhaps be found in the data outlined at the beginning of this section). There would also be a sensitivity to the C–M–C bond angle.

Figure 9 shows a rather different limiting possibility. The transition dipole and quadrupolar charge displacements on a CN group are shown. If the transition displacements are of appropriate matching amplitudes and phases, then there can be effectively zero charge displacement associated with the C atom. In the absence of the contribution from the quadrupole, the charge displacement associated with the C atom would be nonzero and identical for each C. The intervention of the quadrupole has reduced a repulsive interaction, lowering the frequency of the A_1 mode. Experimentally, this mechanism will show little sensitivity to M and its associated ligands, although there will be a dependence on the C–M–C bond angle. It should be noted that both of the two mechanisms that we have suggested are mode-specific, hence, the reference to mode-specific interactions in section 4.b.

5. The Effect of Charge on Frequencies. The most important and general relationship evident in the data of Table 1 seems to be that of the dependence of the cyanide frequency on the charge on the metal atom to which it is bonded. When the positive charge increases, the frequency increases (for both CO and CN). Relatively simple electrostatics seem to be of importance. There is nothing novel in the general idea, although it does not seem to have been considered as of possible general importance in the vibrational spectroscopy of classical coordination complexes. To put this into context, we note that the increase in the center-of-gravity frequency moving from $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$ is some 70 cm^{-1} (Table 1SI indicates that the frequency change for the octahedral carbonyls consequent upon a change in charge of unity is ca. 108 cm^{-1}). Relevant is the work of Bauschlicher,[37] who computationally studied the effect of a small applied electric field on the vibrational frequencies of CN and CN^-. He found that the effects were of comparable magnitudes but in opposite directions. We have investigated this aspect by computationally assessing the effect of a positive charge (a proton) on the vibrational frequencies of CN^-, CN, and CO when the proton is attached to the carbon atom. Our calculations have the advantage that comparison with experimental results is possible. The results are given in Table 2.

This table shows that our results agree with the conclusions of Bauschlicher. The frequency of HCO^+ is greater than that of CO, whereas that of HCN^+ is less than that of CN. On the other hand, the frequency of HCN is above that of CN^-.[39] The fact that our results are in general accord with both experimental and other theoretical data gives us confidence in the additional calculations that we have performed (vide infra).

The fact that HCN has a higher frequency than CN^- in Table 2 suggests that the increase observed for the ν(CN) frequency of terminal cyanides with an increase in formal charge on the metal may be attributed a simple origin. It could be the consequence of the presence of an adjacent (additional) positive charge, operating through the depopulation of a weakly antibonding highest occupied molecular orbital. The q_H data show that the protons are located in the σ lone pairs on the carbon to which they are attached and so may be regarded as substituting for a metal atom which has no d orbitals. It has to be recognized that in introducing protons in these calculations we are also extending our basis set. To investigate this aspect further, we have carried out a second set of calculations which mimic those above but without the extension of the orbital basis set which they contain. They thus explore the possibility that even σ bonding is not essential to the behavior observed. In these calculations, a (variable) positive charge was placed in fixed locations, at 1.5 and at 2.0 Å from the C atom in CN^- (and, in parallel calculations, from the C atom in CO; data in Table 5SI). The geometry was optimized (this corresponds to the relaxation step, to be discussed below) and the ν(CN)—or υ(CO)—frequency calculated. In each case, the calculated frequency is strongly dependent on the value of the positive charge, which was up to ca. +1.5; for both species, the change in frequency, always an increase, was up to 300 cm^{-1}, the charge-frequency relationships showing little curvature (Figure 10). These calculations on model systems seem to be relevant to the real systems. Small charge variations at a site which is a M–C bond length away from the C atom lead to frequency changes entirely comparable to (or larger than) those observed experimentally. To invoke σ or π effects without prior discussion of charge variations is surely to

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(37) Bauschlicher, C. W. *Int. J. Quantum Chem.* **1997**, *61*, 859–863.
(38) Lee, T. J.; Rendell, A. P. *Chem. Phys. Lett.* **1991**, *177*, 491–497.
(39) Our calculated frequency for HCN is above that observed experimentally,[38] but it is of the nature of the calculations that frequency changes will be more accurate than absolute frequencies.

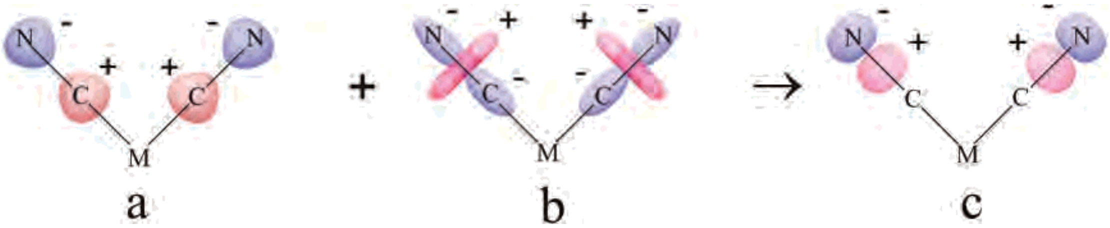

Figure 9. Schematic diagram of a fortuitous cancellation between charge displacements associated with the derived dipole and derived quadrupole associated with a CN stretch in a M(CN)$_2$ unit. The derived-dipole-only case is shown in part a. The accumulation of charge near the C atom is to be noted; these accumulations will be in phase in the A$_1$ mode and so have a destabilizing influence. Part b shows the derived quadrupole. Part c is a sum of parts a and b in which the charge changes at the C atom in parts a and b fortuitously cancel. The destabilization associated with the dipole-only case no longer exists.

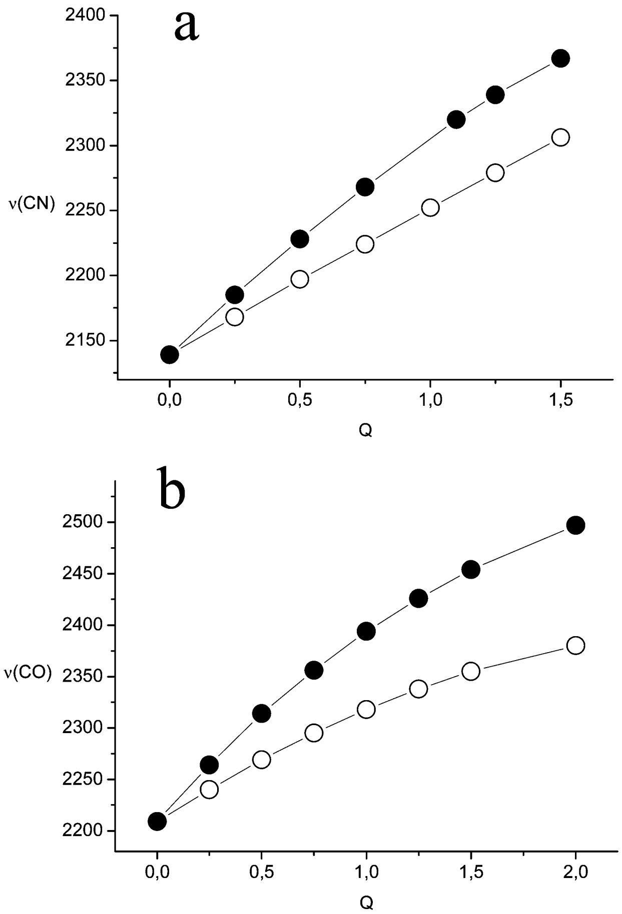

Figure 10. Calculated effect of a variable positive charge placed 1.5 Å (closed circle) or 2.0 Å (open circle) from the C atom on the stretching frequency of (a) CN$^-$ and (b) CO.

ignore an important, and perhaps dominant, effect. Jones et al. have already pointed out that a change in effective nuclear charge on the metal will have σ or π bonding consequences.[14] We note, however, that a charge dependence is clear (cf. $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$, whereas an orbital dependence is not). Most $[M(CN)_6]^{3-}$ species exhibit rather similar infrared ν(CN) frequencies, independent of M, its d-orbital occupancy, and its transition series. Safest, of course, would be to discuss σ and π effects in the context of a series of related compounds, and this, almost invariably, has been the basis for such discussions in the literature. The present work perhaps offers an understanding of why this pattern has arisen.

5.a. The Internal Stark Effect. The model that arises from these calculations is basically an electrostatic one. The electrostatic field generated between the negative charge on the cyanide anion and the positive charge on the cation to which the carbon atom is attached is of key importance. However, this electrostatic component is only the first step. The second is the readjustment of the electron density in the molecule to a new equilibrium distribution. There is a parallel between this model and the vibrational Stark effect. In the vibrational Stark effect, an externally applied electric field causes the electron density in a molecule to adjust to a new equilibrium. The frequency change consequent on this adjustment is the observable.[40] The vibrational Stark effect has been of particular interest in biological species, where the change in frequency of a vibrator such as CN has been used to give an indication of the local field that it experiences.[41] It has also found application in studies in which simple species are absorbed on a metal or ionic crystal surface, located at an interface or matrix-isolated.[42] The internal electric field of our model would surely lead to a larger effect. Encouragingly, the experimental results seem quite well modeled in terms of magnitude by our data. It therefore seems appropriate to give the name "Internal Vibrational Stark Effect" (IVSE) to our model.[43]

Put simply, the suggestion is that the value of the center of gravity ν(CN) observed in a simple complex is, in large measure, determined by the effective charge on the cation to which the carbon is attached. It may be that these frequencies could be used as an indicator of such charges. We note, in particular, that in introducing protons in Table 2 we are not introducing any p or d orbitals. Correspondingly, in our model, neither bonding nor antibonding π orbitals are essential for an explanation of ν(CN) frequency shifts in cyanide complexes. These conclusions are strongly supported by the calculations we have reported in the previous section, calculations in which it is a charge, not a proton, which is added adjacent to the ligand.

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(40) For a recent theoretical study, see Martí, J.; Luis, J. P.; Duran, M. *Mol. Phys.* **2000**, *98*, 513−520.

(41) Brewer, S. H.; Franzen, S. *J. Chem. Phys.* **2003**, *119*, 851−858.

(42) Franzen, S. *J. Am. Chem. Soc.* **2002**, *124*, 13271−13281. (b) Spitzer, R. C.; Sievers, A. J.; Silsbee, R. H. *J. Opt. Soc. Am. B* **1992**, *9*, 978−981. (c) Lambert, D. K.; Poppe, G. P. M.; Wijers, C. M. J. *J. Chem. Phys.* **1995**, *103*, 6206−6216. (d) Wang, H.; Tobin, R. G.; Lambert, D. K.; Fisher, G. B.; DiMaggio, C. L. *J. Chem. Phys.* **1995**, *103*, 2711−2718. (e) Wasileski, S. A.; Koper, M. T. M.; Weaver, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 2796−2805.

(43) A difference to be noted is that the vibrational Stark effect later requires both positive and negative charges for the creation of the field, whereas for the IVSE, only a positive charge is involved.

Conclusions

In this contribution, we have presented new experimental and theoretical data which help to define the areas of similarity and difference between the vibrational spectra of octahedral carbonyls and cyanides. Whereas the vibrational spectra of the former are generally well-understood, be they simple or cluster species, those of the latter are not. Our hope is that the present work will provide a foundation for the better understanding of the cyanides. In particular, we have indicated the importance of Raman data wherever these can be obtained. They enable discussions of center-of-gravity frequencies, and these surely offer more potential insight than do simple infrared data. It would also be useful to have more Raman intensity measurements because they seem more sensitive to the electronic structure than do frequency data. We have indicated the general form to be expected for the bond-derived polarizability tensor of a terminal cyanide group. This general form may be used to obtain, qualitatively, the tensor sum appropriate to each mode of an individual species, enabling relative band intensities to be used in making assignments for species more complicated than hexacyanides. Although we have focused on the A_{1g} mode, it is possible that for some cyanide species these predictions could also be helpful in the assignment of other features. We have also pointed out the relatively large quadrupole moment change associated with C−N stretching vibrations and to the possibility that they may have spectral importance, offering an explanation for some apparently obscure frequency patterns. If, indeed, quadrupolar effects are important, there is no reason that they should be of relevance only to cyanide complexes.

Finally, we have suggested a simple electrostatic model for interpreting relative frequencies in complexes containing terminal cyanide ligands. This is based on the electric field generated between the negative charge on the cyanide anion and the positive charge on the cation to which it is attached. This is not to say that it is akin to the crystal field model, a model which is recognized as having severe limitations for the species under discussion. Rather, it is an internal molecular counterpart of the vibrational Stark effect, the latter describing the frequency shifts that arise when an electric field is applied to a species. We have therefore suggested that it might be called the Internal Vibrational Stark Effect model. We have made an assessment of this model through the use of degenerate perturbation theory calculations, and these will be reported elsewhere.

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Supporting Information Available: Vibrational data for $M(CO)_6$ species (Table 1SI); the calculated dipole and quadrupole moments of CN^- and CO (Table 2SI); the relative Raman intensities of the octahedral hexacarbonyls and hexacyanides (Table 3SI); the bond populations for CO, CN, and CN^- and protonated species (Table 4SI); the calculated values of the ν(CN/CO) when a variable positive charge is placed at a fixed distance from C (Table 5SI); and the schematic diagram of the structure of $M_4E_4(CN)_{12}$ complexes (Figure 1SI). This material is available free of charge via the Internet at http://pubs.acs.org.

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