Mössbauer Study of Octacyanotungstate Anions

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^{182}W Mössbauer spectra are reported for various W^{IV} and W^{V} octacyanides, including both crystalline materials and frozen solutions. Theoretical interpretation indicates that the quadrupole coupling constants, e^2qQ, in the W^{IV} species arise from partial cancellation of the dominant contribution from the d^2 configuration by effective population of the nominally empty metal d orbitals through ligand→metal σ-bonding. Predictions that e^2qQ should be negative in dodecahedral $[W(CN)_8]^{4-}$, and positive with $|e^2qQ|$ smaller in square-antiprismatic $[W(CN)_8]^{4-}$, have been confirmed experimentally. On this basis $[W(CN)_8]^{4-}$ is assigned a dodecahedral structure in $Li_4[W(CN)_8],nH_2O$ and square-antiprismatic in $Cd_2[W(CN)_8],8H_2O$, and it is inferred that the solid-state structures are retained in frozen solutions of $K_4[W(CN)_8]$ (dodecahedral) and $H_4[W(CN)_8]$ (square antiprismatic). The quadrupole coupling in $[(EtNC)_4W(CN)_4]$ is discussed. In the W^{V} species $e^2qQ \approx 0$, indicating that the above mentioned cancellation is virtually exact in the d^1 configuration, and leading to a crude empirical value of 16 mm s^{-1} for $|e^2qQ|$ due to one d electron. The effect on the W^{IV} coupling constants of distortions from ideal geometry is elucidated. The bonding in $[W(CN)_8]^{n-}$ (n = 3 or 4) appears to be essentially covalent, with the W atom carrying at most a small formal charge.

THE anions $[M(CN)_8]^{n-}$ ($M = Mo$ or W; $n = 3$ or 4) are of considerable spectroscopic and crystallographic interest.[1] X-Ray crystallographic studies have revealed examples of both D_{2d} dodecahedral [2-4] and D_{4d} square-antiprismatic [5-7] co-ordination polyhedra (Figure 1), and the factors determining preference for one or other of these structures seem finely balanced.[1,8-10] Vibrational,[11,12] electronic,[13] e.s.r.,[4,14] and ^{13}C n.m.r.[15] spectra of these systems have all been investigated, sometimes with conflicting interpretations.

In this paper we report experimental and theoretical studies of the ^{182}W Mössbauer spectra of $[W(CN)_8]^{4-}$ and $[W(CN)_8]^{3-}$. The 100·1 keV Mössbauer resonance of ^{182}W is a $2^+ \leftrightarrow 0^+$ transition.† Thus a non-zero electric-field gradient (e.f.g.) [16,17] at the W nucleus

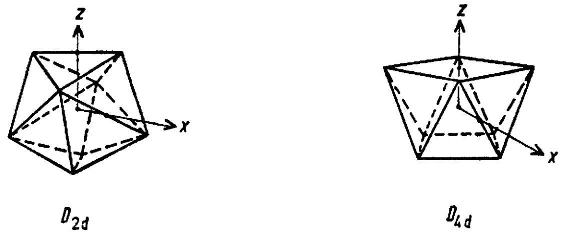

FIGURE 1 The D_{2d} dodecahedron and D_{4d} square antiprism

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† 1 eV ≈ 1·60 × 10^{-19} J.

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will interact with the spectroscopic quadrupole moment Q of the 2^+ nuclear level to give quadrupole splitting of the resonance line. The magnitude and sign of the coupling constant e^2qQ, and the asymmetry parameter η, can all be determined from the observed spectra of powdered samples without recourse to special methods such as Zeeman experiments. Since ^{182}W is a 'deformed' nucleus,[18] the intrinsic quadrupole moment[19] $Q_0 \approx +6{\cdot}4 \times 10^{-28}$ m^2 corresponds to a spectroscopic moment Q of $-1{\cdot}8 \times 10^{-28}$ m^2 for the 2^+ state, with the sign assumed from known systematics of deformed nuclei[18,20] and confirmed by theoretical calculation.[21] Thus ^{182}W is a convenient nuclide for the study of quadrupole interactions. However, an adverse consequence of the nuclear structure of ^{182}W is that the mean-square nuclear radius is virtually the same in both the 0^+ and 2^+ states, with the result that Mössbauer isomer shifts are negligible.[22]

EXPERIMENTS AND RESULTS

All materials were synthesized from $K_4[W(CN)_8],2H_2O$, prepared by the method of Kosińska and Wilczewska-Stasicka.[23] Published procedures were used to obtain $H_4[W(CN)_8],6H_2O$,[24] $K_3[W(CN)_8],H_2O$,[3] $Na_3[W(CN)_8],4H_2O$,[5] and $[Co(NH_3)_6][W(CN)_8]$.[11a] The salts $Cd_2[W(CN)_8],8H_2O$ and $Ag_3[W(CN)_8]$ were obtained by adding Cd^{2+} and Ag^+ to acid solutions of $[W(CN)_8]^{4-}$ and $[W(CN)_8]^{3-}$, respectively; $Li_4[W(CN)_8],nH_2O$ (n is uncertain because the material is deliquescent) was prepared by evaporating, in the dark, the filtrate obtained after mixing solutions of $Ag_4[W(CN)_8]$ and LiCl. All complexes were characterized by C, H, and N microanalyses. In addition X-ray powder photographs of $K_4[W(CN)_8],2H_2O$, $H_4[W(CN)_8],6H_2O$, and $Na_3[W(CN)_8],4H_2O$ were in agreement with published data. The complex $[(EtNC)_4W(CN)_4]$ was kindly provided by Dr. R. V. Parish.

^{182}W Mössbauer quadrupole coupling parameters

Compound	ce^2qQ/E_γ [a] (mm s^{-1})	Line-width [b] (mm s^{-1})	χ^2/degree of freedom	Structure [c]
$K_4[W(CN)_8],2H_2O$	$-16{\cdot}02$	2·49	420/392	dod [2,3]
$K_4[W(CN)_8]$ frozen soln [d]	$-16{\cdot}48$	2·13	418/392	dod [e,12]
$Li_4[W(CN)_8],nH_2O$	$-15{\cdot}90$	2·59	387/392	dod [e]
$H_4[W(CN)_8],6H_2O$	$+12{\cdot}59$	2·81	520/392 [f]	sqa [6]
$H_4[W(CN)_8]$ frozen soln [d]	$+14{\cdot}79$	3·63	371/352	sqa [e]
$Cd_2[W(CN)_8],8H_2O$	$+12{\cdot}80$ ($\eta = 0{\cdot}82$)	3·00	453/390	sqa [e,g]
$K_3[W(CN)_8],H_2O$	*ca.* 0	2·93	450/392	
$Na_3[W(CN)_8],4H_2O$	*ca.* 0	3·20	451/392	sqa [5]
$Ag_3[W(CN)_8]$	*ca.* 0	2·42	385/392	
$[Co(NH_3)_6][W(CN)_8]$	*ca.* 0	2·44	230/191	
$[(EtNC)_4W(CN)_4]$	$-8{\cdot}59$ ($\eta = 0{\cdot}74$)	1·83	169/191	dod [e,h]

[a] All measurements at liquid-helium temperature. Estimated errors are $\pm 0{\cdot}5$ mm s^{-1} for frozen-solution spectra and $\pm 0{\cdot}2$ mm s^{-1} for all other resolved splittings; $\eta \approx 0$ when not given explicitly; c = the velocity of light and E_γ = the transition energy. Upper limit for unresolved quadrupole coupling in single-line spectra is $|ce^2qQ/E_\gamma| = 2$ mm s^{-1}. All centre shifts were zero to within experimental error. [b] Full width at half-height assuming Lorentzian shape. [c] dod = Dodecahedral, sqa = square antiprismatic. [d] 0·5M Aqueous solution + a small amount of glycerol to promote glassification. [e] This work. [f] Thick sample. [g] Ref. 7 reports square-antiprismatic co-ordination in $Cd_2[Mo(CN)_8],2N_2H_4,4H_2O$. [h] Refs. 15 and 33 report dodecahedral co-ordination in $[(MeNC)_4M(CN)_4]$ (M = Mo or W).

The Mössbauer parameters reported in the Table were obtained from spectra of powdered polycrystalline samples recorded at liquid-helium temperature on a conventional constant-acceleration spectrometer with a ^{182}Ta in Ta metal source and a Ge(Li) detector. Sample thicknesses were typically 90 mg cm^{-2} of W; at this thickness saturation effects were noticeable only if the resonance line was not split. The parameters listed in Table 1 were obtained by computer fitting[25] the observed spectra with five Lorentzian lines of equal width and area. Spectra were fitted with η constrained to zero, except in those cases $\{Cd_2[W(CN)_8],8H_2O$ and $[(EtNC)_4W(CN)_4]\}$ where a significantly improved fit was obtained with non-zero η. Examples of the spectra obtained are shown in Figures 2—4.

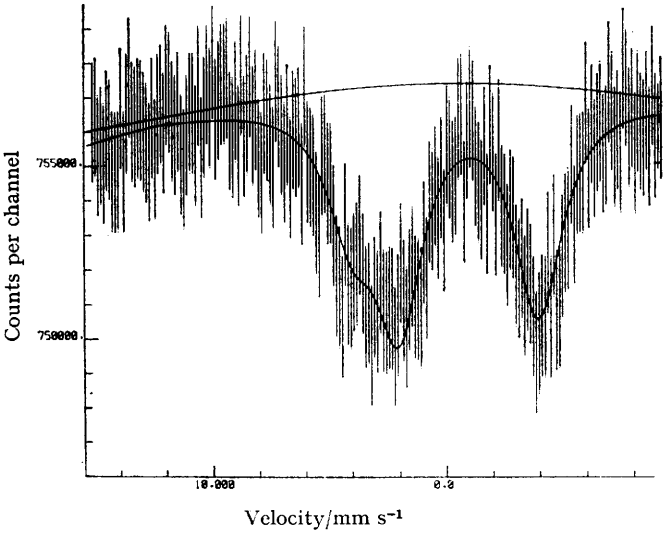

FIGURE 2 Typical ^{182}W Mössbauer spectrum of dodecahedral $[W(CN)_8]^{4-}$ from $Li_4[W(CN)_8],nH_2O$

Coupling Constants in Dodecahedral and Antiprismatic $[W(CN)_8]^{n-}$.—Figure 5 shows schematic molecular-orbital (m.o.) diagrams for both dodecahedral and square-antiprismatic geometries. The ligand-based π-orbitals have been omitted for clarity; they span $2A_1 + 2A_2 + 2B_1 + 2B_2 + 4E$ under D_{2d} and $A_1 + A_2 + B_1 + B_2 + 2E_1 + 2E_2 + 2E_3$ under D_{4d}. Although it is generally agreed that the lowest $5d$-based m.o. is $(d_{x^2-y^2})b_1$ in dodecahedral co-ordination and $(d_{z^2})a_1$ in square-antiprismatic co-ordination, the order given in Figure 5 for the higher

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$5d$-based orbitals is not the only one suggested in the literature.[10,13] This does not affect interpretation of the e.f.g. at W since these higher $5d$-based m.o.s are empty and thermally inaccessible in both the W^{IV} and the W^{V} anions.

One implication of the non-degenerate orbital ground state and large ligand-field splittings {the lowest $d \rightarrow d$ bands in the K^+ salts of $[W(CN)_8]^{4-}$ and $[W(CN)_8]^{3-}$ are at *ca.* 15 000 and over 22 000 cm^{-1}, respectively [13]} is that spin–orbit coupling and, in the W^{IV} d^2 case, interelectronic repulsion, produce relatively small modifications to the simple orbital picture. In agreement with this $[W(CN)_8]^{3-}$ has paramagnetic susceptibility [3] close to the spin-only value and g values [4,14] near to 2.

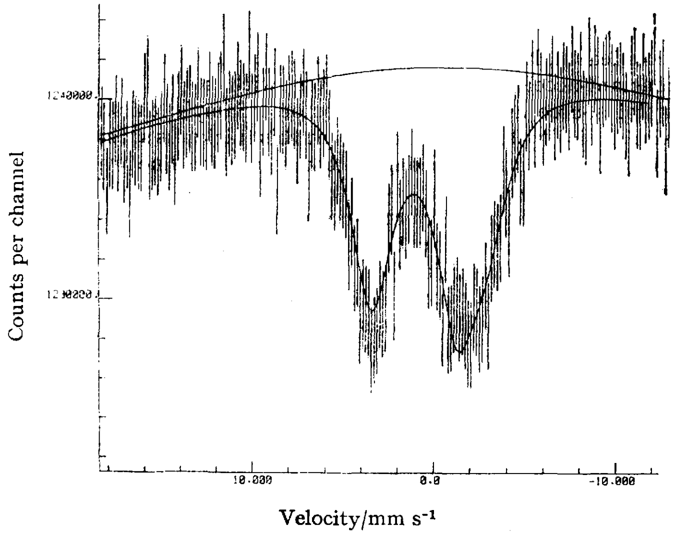

FIGURE 3 Typical ^{182}W Mössbauer spectrum of square-antiprismatic $[W(CN)_8]^{4-}$ from $H_4[W(CN)_8],6H_2O$

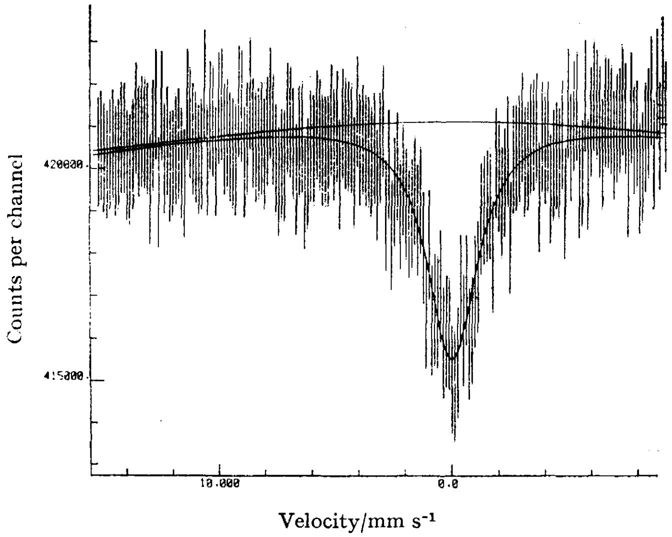

FIGURE 4 Typical ^{182}W Mössbauer spectrum of $[W(CN)_8]^{3-}$ from $K_3[W(CN)_8],H_2O$

The e.f.g. at W will be interpreted in terms of effective population [17,26] of the metal $5d$ atomic orbitals (a.o.s). This neglects smaller metal $6p$ and lattice contributions. The influence of π-bonding will not be considered explicitly, because first the extent to which it modifies the wave functions is unclear [15] and secondly, since the π-orbitals span all irreducible representations of D_{2d} or D_{4d}, there is no symmetry constraint and a distinct possibility that any modification of effective populations may be largely isotropic. The lowest $5d$-based m.o. contains one electron in $[W(CN)_8]^{3-}$ and two in $[W(CN)_8]^{4-}$. These electrons give a positive contribution to eq in dodecahedral symmetry and a negative contribution in square antiprismatic. The symmetry species given in Figure 5 show that in the dodecahedron $(d_{x^2-y^2})b_1$ is a non-bonding $d_{x^2-y^2}$ a.o. if π-bonding is neglected, whereas $(d_{z^2})a_1$ in the antiprism may involve both the metal $6s$ a.o. and the ligand σ-orbitals, implying greater deviation from pure $5d$ a.o. character in the latter case. [Note, however, that in the d^2 W^{IV} anion mixing of the filled $(d_{z^2})a_1$ with the filled ligand σ-orbitals will not affect the e.f.g. in the Cotton–Harris approximation.[17]] Unless the extent of π-bonding is very different in the two geometries, the magnitude of the e.f.g. set up by the 'd' electrons will be smaller in square-antiprismatic co-ordination. The four nominally empty higher $5d$ a.o.s can participate in the filled ligand-based σ-m.o.s. In both geometries effective population of these $5d$ a.o.s gives a contribution to the e.f.g. which opposes the contribution from the occupied $5d$-based m.o. This 'σ-orbital' contribution increases with increasing covalency.

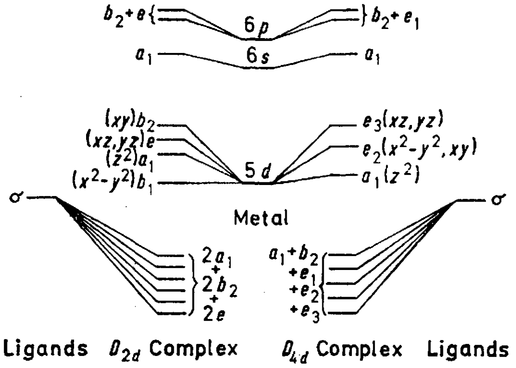

FIGURE 5 Schematic diagram of valence m.o. levels in dodecahedral and square-antiprismatic octacyanotungstate anions

The above analysis of the e.f.g. at W can be roughly quantified as follows. Since both D_{2d} and D_{4d} symmetries require $\eta = 0$, the e.f.g. is characterised by the single quantity [16,17] in equation (1), where the sum

$$eq = \langle \sum_i e_i r_i^{-3}(3\cos^2\theta_i - 1) \rangle \qquad (1)$$

is over all particles (electrons and other nuclei) with charges e_i and co-ordinates r_i, and the origin is at the W nucleus with O_Z parallel to the principal symmetry axis. If attention is restricted to the e.f.g. arising from the $5d$ a.o.s, with an effective population n_d assigned to the lowest $5d$ a.o. and an average effective population $\bar{n}_\sigma$ to each of the other four d orbitals,* then equation (1) becomes (2) where the + sign applies for the dodecahedron and − for the antiprism, R_d is the Sternheimer factor, and n_d will,

$$eq_d = \pm\tfrac{4}{7}e(1 - R_d)\langle r^{-3}\rangle_d(n_d - \bar{n}_\sigma) \qquad (2)$$

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* More precisely, $\bar{n}_\sigma = n_{z^2} + \frac{1}{2}(n_{xz} + n_{yz}) - n_{xy}$ for the dodecahedron, and for the antiprism $\bar{n}_\sigma = (n_{x^2-y^2} + n_{xy}) - \frac{1}{2}(n_{xz} + n_{yz})$.

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by the arguments above, be smaller in the antiprism. The quadrupole coupling constants, ce^2qQ/E_γ, listed in the Table, are in agreement with this interpretation. Remembering that Q is predicted to be negative, it is seen that the signs of ce^2qQ/E_γ observed for known dodecahedral [2,3] $K_4[W(CN)_8],2H_2O$ and known square-antiprismatic [6] $H_4[W(CN)_8],6H_2O$ are in agreement with equation (2) if $n_d > \bar{n}_\sigma$. Alternatively, since $n_d > \bar{n}_\sigma$ would certainly be anticipated for the d^2 anions, these data can be regarded as confirming the nuclear-theory prediction of sgn$\{Q\}$. Notice also that $|ce^2qQ/E_\gamma|$ is slightly less in $H_4[W(CN)_8],6H_2O$ as predicted.

Clearly (compare Figures 2 and 3) ^{182}W Mössbauer spectroscopy provides a convenient method for distinguishing the dodecahedral and square-antiprismatic configurations of $[W(CN)_8]^{4-}$. In the Table the structural assignments for $Li_4[W(CN)_8],nH_2O$ and $Cd_2[W(CN)_8],8H_2O$ are made on this basis. (The large η observed in the latter salt is discussed below.) The frozen-solution data in the Table suggest that in both $K_4[W(CN)_8]$ and $H_4[W(CN)_8]$ the solid-state geometry is retained in solution, in agreement with more recent studies [12] of the vibrational spectra of $K_4[M(CN)_8]$ (M = W or Mo), but contrary to earlier suggestions.[11] Mössbauer studies on frozen solutions of $[W(CN)_8]^{4-}$ salts at various concentrations and pH values might be helpful in elucidating the factors which determine the stereochemistry of the $[W(CN)_8]^{4-}$ ion. None of the $[W(CN)_8]^{3-}$ anions in the Table showed resolvable quadrupole splitting (Figure 4), suggesting that in the d^1 anions n_d and $\bar{n}_\sigma$ [equation (2)] approximately cancel. This is consistent with the high degree of covalency expected in cyanide complexes of third-row transition elements.

Consider, as a crude first approximation, a 'rigid-orbital model' in which the m.o. wave functions are unchanged on removing a d electron from $[W(CN)_8]^{4-}$ to get $[W(CN)_8]^{3-}$. Then $\bar{n}_\sigma$ will be the same in both oxidation states, and n_d may be written 2κ in the former and κ in the latter, where κ is an orbital-reduction factor [27] for the lowest d orbital. The absence of observable quadrupole splitting in $[W(CN)_8]^{3-}$ indicates that, ignoring small differences between dodecahedral and antiprismatic geometries, $\kappa \approx \bar{n}_\sigma$. Thus applying equation (2) to dodecahedral $[W(CN)_8]^{4-}$ we obtain (3). With [28] $(1 - R_d) =$

$$\kappa\left|\tfrac{4}{7}ce^2(1 - R_d)\langle r^{-3}\rangle_d Q/E_\gamma\right| \approx 16 \text{ mm s}^{-1} \qquad (3)$$

1·4 and $\langle r^{-3}\rangle_d = 11$ bohr^{-3} (an average of calculated values [29,30] for free W^{4+} and W^{5+}) equation (3) gives $\kappa = 0{\cdot}35$, while for $\langle r^{-3}\rangle_d = 8$ bohr^{-3} (an average of calculated values [30,31] for free neutral W) $\kappa = 0{\cdot}48$.* Possible contributions to these estimates of κ include π-bonding, metal $6p$ and lattice e.f.g.s, and changes in radial wave functions on binding the W atom into a compound. Although each of these factors will vary, there is some evidence that 16 mm s^{-1} may be used as a typical empirical value for the 'quadrupole coupling due to one d electron' in other molecular tungsten compounds,[32] notably $[WCl_6]^-$. Certainly the above analysis indicates that the W atom in $[W(CN)_8]^{n-}$ cannot usefully be regarded as $W^{(8-n)+}$, but in reality carries only a small formal charge.

Coupling Constant in $[(EtNC)_4W(CN)_4]$.—The coupling constant observed for $[(EtNC)_4W(CN)_4]$ (Table) adds support to the interpretation given above. By analogy with the known [15,33] structure of $[(MeNC)_4M(CN)_4]$ (M = Mo or W), this complex presumably has dodecahedral co-ordination of W, with CN^- on the A sites (Hoard and Silverton's notation [8]) and EtNC on the B sites. The A and B sites form distinct equivalent sets under D_{2d}, so that D_{2d} symmetry is retained for ideal co-ordination geometry. Since [34] EtNC is less effective as a σ-donor than CN^- (compare also the partial-field-gradient parameters [35] for CN^- and EtNC bound to low-spin Fe^{II}), electron density at the (more equatorial) B sites will be reduced, the main effect being to decrease d_{xy} participation in the b_2 σ-m.o.s. Thus e^2qQ is shifted to more positive, *i.e.* less negative, values. The relatively large shift of *ca.* 7·4 mm s^{-1} [*ca.* 6·7 mm s^{-1} after correction (see below) for non-zero η] observed for the modest change in ligand clearly indicates that the observed splittings arise from cancellation of two larger contributions.

Distortions from Ideal Geometry.—Discussion so far has been in terms of the ideal dodecahedral and square-antiprismatic geometries. However, both $Cd_2[W(CN)_8],8H_2O$ and $[(EtNC)_4W(CN)_4]$ have large η values indicative of distortions from ideal geometry. Also, it seems [4] that difficulties in the interpretation of e.s.r. data on the d^1 anions can only be resolved if such distortions are taken into account. Consider any continuous distortion of dodecahedral $[W(CN)_8]^{4-}$ into the antiprismatic structure. Since the e.f.g. changes sign on passing from one geometry to the other, the distortion path must pass through at least one point at which either the e.f.g. vanishes or $\eta = 1$ (see Appendix). The large η values observed in $Cd_2[W(CN)_8],8H_2O$ and $[(EtNC)_4W(CN)_4]$ are indicative of distortion paths passing through $\eta = 1$.

On a criterion of minimum atomic movement, the most likely distortion path involves moving the ligands along great circles in such a way as to make one of the antiprism C_2 axes into the S_4 axis of the dodecahedron.[36] All intermediate steps have D_2 symmetry with the principal directions of the e.f.g. tensor fixed. By noting that in D_2 symmetry the only symmetry-allowed mixing of d orbitals is between d_{z^2} and $d_{x^2-y^2}$, the d orbitals can be written in dodecahedral principal axes (*i.e.* O_Z along the C_2 axis of the antiprism shown as O_X in Figure 1) as in equations (4)—(8) with $\pi/2 \leqslant \alpha \leqslant 2\pi/3$, the endpoints $\alpha = \pi/2$ and $2\pi/3$ corresponding to the dodecahedron and square antiprism, respectively. At $\alpha = 2\pi/3$ the d_i in equations (4)—(8) look unfamiliar because of the choice of axes. Note that α is a measure of electronic distortion and not a geometrical parameter; an explicit relation between α

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* 1 bohr ≈ 5·29 × 10^{-11} m.

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[36] A. J. Smith, personal communication.

and geometrical parameters describing the distortion will not be required here, although it is assumed that this relation is continuous and monotonic.

$$d_1 = d_{z^2} \cos \alpha + d_{x^2-y^2} \sin \alpha \tag{4}$$

$$d_2 = -d_{z^2} \sin \alpha + d_{x^2-y^2} \cos \alpha \tag{5}$$

$$d_3 = d_{xy} \tag{6}$$

$$d_4 = d_{yz} \tag{7}$$

$$d_5 = d_{xz} \tag{8}$$

If, as seems likely in $[\mathrm{W(CN)_8}]^{4-}$, all excited orbitals remain thermally inaccessible throughout the distortion, then the e.f.g. may be calculated at the level of approximation used above by assigning an effective population n_d to d_1, and average effective populations $\bar{n}_\sigma$ to d_2, d_3, d_4, and d_5. The components $V_{\alpha\beta}$ of the e.f.g. tensor are then given by equations (9) and (10), with $(n_d - \bar{n}_\sigma)$ decreasing on

$$V_{\alpha\beta} = (1 - R_d)(n_d - \bar{n}_\sigma)\langle d_1|v_{\alpha\beta}|d_1\rangle \tag{9}$$

where

$$v_{\alpha\beta} = -er^{-5}(3x_\alpha x_\beta - r^2\delta_{\alpha\beta}) \tag{10}$$

passing from the dodecahedron to the antiprism. An e.f.g. of this form has been considered previously.[37] Since the labelling of the principal axes according to the convention [16] $|V_{zz}| \geqslant |V_{yy}| \geqslant |V_{xx}|$ will vary with α, it is convenient to use the symmetrized parameters [38] S_{02} $[= -\frac{3}{4}e^2q^2(1 + \frac{1}{3}\eta^2)]$ and S_{03} $[= \frac{1}{4}e^3q^3(1 - \eta^2)]$. For the e.f.g. given by equation (9) [37] we obtain (11) and (12). In the range

$$S_{02} = -(12/49)[e(n_d - \bar{n}_\sigma)\langle r^{-3}\rangle_d(1 - R_d)]^2 \tag{11}$$

$$S_{03} = -(16/343)[e(n_d - \bar{n}_\sigma)\langle r^{-3}\rangle_d(1 - R_d)]^3 (4 \cos^2 2\alpha - 3) \cos 2\alpha \tag{12}$$

$\pi/2 \leqslant \alpha \leqslant 2\pi/3$, S_{03} has exactly one zero (at $\alpha = 7\pi/12$) and since $q \neq 0$ (because $S_{02} \neq 0$) this zero must correspond to $\eta = 1$. Note also that S_{02} varies with distortion only through the change in $(n_d - \bar{n}_\sigma)$. However, since $e^2qQ = 2eQ[-S_{02}/(3 + \eta^2)]^{\frac{1}{2}}$, the non-zero η value will cause e^2qQ to have a weak additional variation with distortion. Thus for $[\mathrm{(EtNC)_4W(CN)_4}]$ the quantity $-8{\cdot}59[1 + \frac{1}{3}(0{\cdot}74)^2]^{\frac{1}{2}} = -9{\cdot}34$ mm s^{-1} is a better measure of the change in $(n_d - \bar{n}_\sigma)$ on substituting EtNC for $\mathrm{CN^-}$ at the B sites of the dodecahedron.

The above arguments suggest that Mössbauer experiments on distorted $[\mathrm{W(CN)_8}]^{4-}$ anions will unambiguously characterize them as dodecahedron-like ($eq > 0$) or square-antiprism-like ($eq < 0$).

APPENDIX

The result cited in the above discussion of distortions from ideal geometry may be proved as follows. Suppose a particular distortion path is characterized by parameters $\{\alpha_1, \alpha_2, \ldots\} = \boldsymbol{\alpha}$ and that the e.f.g. tensor $\boldsymbol{V}$ is a continuous function of $\boldsymbol{\alpha}$. This implies that the symmetrized parameters [38] S_{02} and, in particular, S_{03} are continuous functions of $\boldsymbol{\alpha}$. Now if the distortion path joins two ideal geometries in which the e.f.g. has opposite signs, then S_{03}, which has the same sign as eq, must vanish at least once on the path. At the zeros of S_{03}, $q^3(1 - \eta^2) = 0$ which has the solutions $q = 0$ (*i.e.* $\boldsymbol{V} = 0$) or $\eta = 1$. Thus if a distortion path leads to a change in the sign of the e.f.g., there is at least one point where either $\boldsymbol{V} = 0$ or $\eta = 1$.

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