$$g_\parallel = g_e$$

$$g_\perp = g_e - 6\lambda\alpha^2\beta^2/\Delta E_b$$

We note first that the contribution of the lower lying e_a level is no longer present since this level is now $d_{xy,\,x^2-y^2}$ and is therefore composed entirely of d_{+2} and d_{-2} which do not contribute to g through mixing by the spin-orbit coupling. Furthermore, ΔE_b is expected to be quite large in trigonal-prismatic complexes[21] and α and β, representing covalency, are each expected to be considerably less than one. These factors may combine to make g quite close to g_e and thus produce the observed small anisotropy in g. These arguments rest of course upon the assumption that the ground state in all these complexes is $^2A_1$. This is not an unreasonable conclusion and in fact seems to be the only way to fully understand the epr data. For the V complexes this requires a reversal of metal and ligand levels in going from the dianionic to the neutral species. In other words, the dianion has a roughly l^2d^1 configuration while the neutral complex has a roughly d^1l^0 configuration. This type of reversal does not seem unusual as increasing positive charge will often stabilize metal levels more than ligand levels (*i.e.*, the metal will always bear a larger part of the net positive charge no matter where the electrons are removed from). Thus, the smallness of the g anisotropy is evident. More detailed descriptions of the bonding parameters for these complexes would require unequivocal assignments for $A_\parallel$ and $A_\perp$ values in each case. Furthermore, contribution to g from spin-orbit coupling on the ligands should be considered to understand the small g shifts in each case.

Finally, it is tempting to offer the measurement of $g_\perp$ as a probe for the details of the six-coordinate polyhedron in these and related structures. Thus, should alternate and accurate ways for estimating α, β, λ, and $\langle 1/r^3 \rangle$ become available (either from experiment or theory) then $g_\perp$ could represent a sensitive probe for the value of a^2 and hence for the degree of compression and twisting in trigonal tris(chelate) complexes.[35]

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Registry No. $[(C_6H_5)_4As]_2Mo(mnt)_3$, 25595-41-9; $[(C_6H_5)_4As]_2$-$V(mnt)_3$, 12114-37-3.

[35] After we submitted the current article, a paper appeared reporting a similar study [N. M. Atherton and C. J. Winscom, *Inorg. Chem.*, 12, 283 (1973)]. These workers describe a single crystal study of $[(C_6H_5)_4P]_2V(mnt)_3$ doped in $[(C_6H_5)_4P]_2Mo(mnt)_3$. When averaged to axial symmetry, the g and A values found in their study agree well with ours. The small rhombic anisotropy of g and A which they resolve could be due to lower effective symmetry in their host lattice which was said to be monoclinic. Since the structure of the host is unknown in their case, the identification of g and A tensor components with molecular directions can only be tentative. In point of fact these authors seem unaware of the previous communication[10] of the structure of $[(C_6H_5)_4As]_2Mo(mnt)_3$, the host which we used in the present study. In view of the probable similarity of structure of the two host lattices, it would seem that the $V(mnt)_3{}^{2-}$ anion should occupy similar sites in both cases. In that case $V(mnt)_3{}^{2-}$ should have approximate D_3 symmetry with a small rhombic asymmetry. Thus the assumption by Atherton and Winscom of D_{3h} symmetry for the initial calculations on $V(mnt)_3{}^{2-}$ is at odds with the known structures of both $V(mnt)_3{}^{2-}$ itself[9] and the host, $Mo(mnt)_3{}^{2-}$.[10] This invalid assumption is not mitigated by the subsequent distortion to C_2 symmetry which does not recognize the true nature of the "in between" structures[16] which these compounds adopt. In particular, the e_a–e_b mixing, which we fully discuss in the text, is not considered by Atherton and Winscom. Thus, while the experimental results are in gross agreement in the two studies, the interpretations differ markedly, due to the diverse assumptions of geometric and hence electronic structural parameters.

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A Crystal Field Approach To Pentagonal-Bipyramidal Seven-Coordinate Complexes. Electronic Structure of Heptacyanovanadate(III)

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Crystal field parameters for seven-coordinate pentagonal-bipyramidal complexes have been calculated using a point charge model. These are related to parameters dependent upon energy differences between adjacent metal orbitals. A comparison of the several sets of parameters is made for trigonal- and pentagonal-bipyramidal geometries. The electronic spectrum of the $V(CN)_7{}^{4-}$ ion (symmetry D_{5h}) is interpreted within the context of a strong crystalline field. General trends for the spectra of seven-coordinate D_{5h} complexes are predicted and discussed.

Introduction

A single-crystal X-ray diffraction study of potassium heptacyanovandate(III) dihydrate, $K_4V(CN)_7 \cdot 2H_2O$, has shown the $V(CN)_7{}^{4-}$ complex ion to be seven-coordinate with a pentagonal-bipyramidal structure (D_{5h} symmetry).[1] In addition, interest in seven-coordination has manifested itself in the recent appearance of many X-ray crystallographic studies[2] on compounds with this relatively neglected coordination number. While the geometry of many of these has proven to be that of a capped octahedron (C_{3v} symmetry), the most regular of the possible geometries[3] is pentagonal bipyramidal. For these reasons, and in anticipation of more heptacoordinate transition metal complexes of symmetry D_{5h}, a consideration of the electronic structure of pentagonal-bipyramidal complexes has been undertaken. The primary focus here will be on the $V(CN)_7{}^{4-}$

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[3] See E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, 21, 109 (1967), for a description of possible seven-coordinate geometries.

anion. A Ni(II) seven-coordinate structure of C_{3v} geometry has also been described;[4] not surprisingly, its structure in solution is not yet established. Since the V(III) and Ni(II) complexes have d^2 and d^8 configurations, respectively, their crystal field treatments in the same geometry would be similar because of the well-known electron-hole equivalence.

Crystal Field Considerations

For pentagonal-bipyramidal (D_{5h}) symmetry, as shown in Figure 1, the several d orbitals transform like $a_1'(z^2)$, $e_2'(xy, x^2-y^2)$, and $e_1''(xz, yz)$. In the ionic model system of calculation,[5] the crystal field parameters *Ds* and *Dt*, in the commonly accepted convention of Carlin and Piper,[6] are given by

$$\begin{aligned} Ds(D_{5h}) &= \frac{e^2}{14}\left[\frac{4Z_A}{a^3} - \frac{5Z_E}{b^3}\right]\langle r^2\rangle \\ Dt(D_{5h}) &= \frac{e^2}{168}\left[\frac{16Z_A}{a^5} + \frac{15Z_E}{b^5}\right]\langle r^4\rangle \end{aligned} \tag{1}$$

where Z_A and Z_E are the axial and equatorial charges at distances of *a* and *b*, respectively. For a regular pentagonal bipyramid, *e.g.*, $V(CN)_7{}^{4-}$, $a = b$ and $Z_A = Z_E$. *Ds* and *Dt* then reduce to

$$\begin{aligned} Ds(D_{5h}) &= -\frac{Ze^2}{14a^3}\langle r^2\rangle \\ Dt(D_{5h}) &= \frac{31Ze^2}{168a^5}\langle r^4\rangle \end{aligned} \tag{2}$$

It is interesting to contrast eq 1 and 2 with similar expressions for the trigonal bipyramid (D_{3h}) since both geometries give similar d orbital splitting patterns (see Figure 2) and since sufficient work[7-11] has been done to permit an evaluation of these parameters in the five-coordinate system. These are[7,9]

$$\begin{aligned} Ds(D_{3h}) &= \frac{e^2}{14}\left[\frac{4Z_A}{a^3} - \frac{3Z_E}{b^3}\right]\langle r^2\rangle \\ Dt(D_{3h}) &= \frac{e^2}{168}\left[\frac{16Z_A}{a^5} + \frac{9Z_E}{b^5}\right]\langle r^4\rangle \end{aligned} \tag{3}$$

and

$$\begin{aligned} Ds(D_{3h}) &= \frac{Ze^2}{14a^3}\langle r^2\rangle \\ Dt(D_{3h}) &= \frac{25Ze^2}{168a^5}\langle r^4\rangle \end{aligned} \tag{4}$$

The nonvanishing one-electron crystal field (CF) matrix elements for D_{5h} are

$$\begin{aligned} \langle \pm 2 | V_{CF} | \pm 2\rangle &= \langle e_2' | V_{CF} | e_2'\rangle = -2Ds + Dt \\ \langle \pm 1 | V_{CF} | \pm 1\rangle &= \langle e_1'' | V_{CF} | e_1''\rangle = Ds - 4Dt \\ \langle 0 | V_{CF} | 0\rangle &= \langle a_1' | V_{CF} | a_1'\rangle = 2Ds + 6Dt \end{aligned} \tag{5}$$

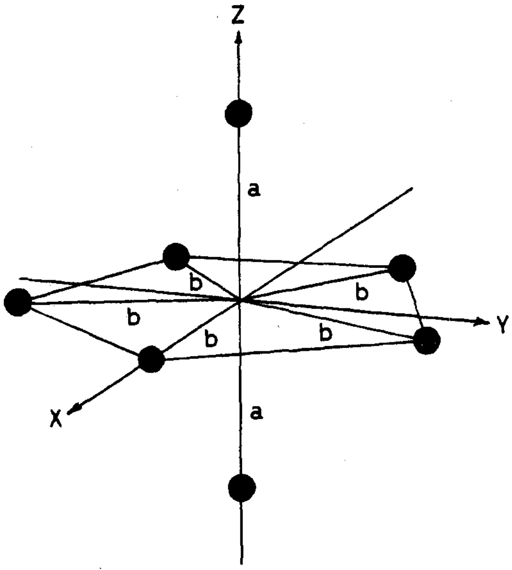

Figure 1. Pentagonal-bipyramidal coordination sphere.

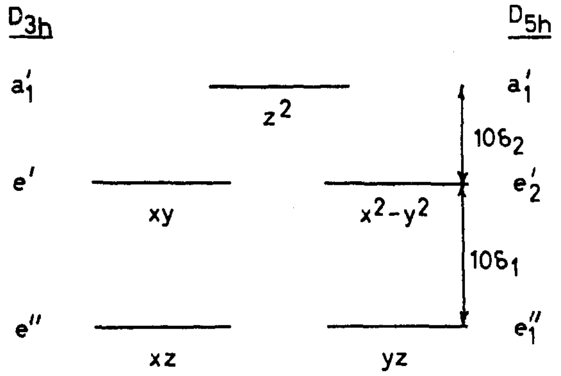

Figure 2. d orbital splitting diagram for pentagonal- and trigonal-bipyramidal geometries.

A comparison of eq 1 and 3 reveals the anticipated result that the only difference in crystal field parameters arises from the additional equatorial ligands in the D_{5h} case. From eq 3 and 4

$$\begin{aligned} Ds(D_{5h}) &= -Ds(D_{3h}) \\ Dt(D_{5h}) &= \frac{31}{25}Dt(D_{3h}) \end{aligned} \tag{6}$$

That is, the addition of two equatorial ligands has changed the sign of *Ds* and increased *Dt* by approximately 20% relative to trigonal-bipyramidal geometry. Some crystal field parameters for the d^2 D_{3h} VX_3L_2 complexes (X = Cl, Br) have been presented by Wood[9] who determined average *Ds* and *Dt* values of 480 and 1395 cm^{-1}, respectively, for L = $N(CH_3)_3$. Deriving *Ds* and *Dt* values for $V(CN)_7{}^{4-}$ from these results will not be straightforward because of the larger crystal field strength of CN^- and because of the nonequivalence of the axial and equatorial ligands in the D_{3h} case.

Since $V(CN)_7{}^{4-}$ is the first authenticated example of a true D_{5h} seven-coordinate complex ion containing d electrons, a brief discussion of the relative energies of the d orbitals is warranted. For D_{5h}, the z^2 orbital points directly at the two axial ligands and interacts with the five equatorial ligands *via* the z^2 "doughnut" (see Figure 1); this is predicted to be the strongest interaction and thus a_1' is placed highest in energy. The *xz* and *yz* orbitals are

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not oriented directly at any of the ligands; ligand-orbital repulsion should be at a minimum, and e_1'' is placed lowest in energy. Although the xy and $x^2 - y^2$ orbitals do interact strongly with the equatorial ligands, the ligand-z^2 interaction should be stronger; thus, e_2' is placed between a_1' and e_1''. It is conceivable that e_2' is above a_1', and, in fact, their relative ordering will likely depend on the particular compound under consideration. While our main concern is with $V(CN)_7^{4-}$, the discussion to be presented here is equally valid for D_{5h} complexes of the type MX_5L_2 (X = equatorial ligand; L = axial ligand) in which the relative positions of X and L in the spectrochemical series could play a role in determining the ordering of a_1' and e_2'. When L is a stronger field ligand than X, then $a_1' > e_2'$ is expected; conversely, $e_2' > a_1'$ is possible when X is *much* stronger than L. For $V(CN)_7^{4-}$ in which the axial and equatorial bond lengths are equal,[1] we predict $a_1' > e_2' > e_1''$, as indicated in Figure 2.

Although Ds and Dt have theoretical significance in a simple point-charge model, in practice their explicit evaluation commonly leads to values which may differ greatly from those determined experimentally.[6] As is generally done in the determination of $10Dq$ for octahedral complexes, we choose to evaluate D_{5h} crystal field parameters spectroscopically. Therefore, it seems more appropriate to select a set of parameters directly related to energy differences between adjacent metal orbitals and thus to spectroscopic studies than to use Ds and Dt. The parameters $10\delta_1$ and $10\delta_2$, as shown in Figure 2, have been chosen. Using the center-of-gravity rule the one-electron matrix elements become

$$\begin{aligned} \langle e_2'|V_{CF}|e_2'\rangle &= 4\delta_1 - 2\delta_2 \\ \langle e_1''|V_{CF}|e_1''\rangle &= -6\delta_1 - 2\delta_2 \\ \langle a_1'|V_{CF}|a_1'\rangle &= 4\delta_1 + 8\delta_2 \end{aligned} \tag{7}$$

Relationships between Ds and Dt and δ_1 and δ_2 are given by

$$\begin{aligned} 7Ds &= 10\delta_2 - 10\delta_1 \\ 7Dt &= 6\delta_2 + 8\delta_1 \\ 10\delta_2 &= 4Ds + 5Dt \\ 10\delta_1 &= -3Ds + 5Dt \end{aligned} \tag{8}$$

It should be emphasized that any such choice of crystal field parameters is arbitrary; in a recent crystal field approach to ferrocene, the orbital energies were used as the parameters.[12] The sign of δ_2 will be negative for compounds in which the level ordering $e_2' > a_1' > e_1''$ occurs.

By substituting eq 6 into eq 8 we see that for $10\delta_1(D_{3h}) = -3Ds + 5Dt$, the *value* of $10\delta_1(D_{5h})$ will *increase* to *ca.* $3Ds + 6Dt$ for the same ligand. In evaluating the change in $10\delta_2$, one must take account of the actual values of Ds and Dt before deciding whether it will increase or decrease; in light of most observed values of Ds and Dt,[9,10] $10\delta_2(D_{5h})$ should generally be smaller than $10\delta_2(D_{3h})$. That $10\delta_1/10\delta_2$ will be larger for D_{5h} than D_{3h} is implicit in the earlier qualitative discussion concerning the relative energies of the d orbitals. For $V(CN)_7^{4-}$, it is likely that $10\delta_1$ will be considerably larger than in the $VX_3(N(CH_3)_3)_2$ complexes; the ligand field bands are also predicted to be higher in energy and more closely spaced for $V(CN)_7^{4-}$.

A complete crystal field calculation (neglecting spin-orbit coupling) is available which is appropriate for the d^2 pentagonal-bipyramidal case. This is the treatment of nickelocene (d^8) in an axial ($D_{\infty h}$) ligand field by Pavlik, Cerny, and Maxova.[13] The same workers' treatment of d^3,d^7 sandwich complexes[14] would be appropriate for the $Mo(CN)_7^{4-}$ complex if it is indeed of D_{5h} symmetry.[15] Ligand field calculations for ferrocene[12] could be applied to d^4,d^6 pentagonal-bipyramidal systems.

The results of the d^2 $D_{\infty h}$ calculation[13] for the strong-field case are presented in Table I, which may be derived from ref 13 by noting that the irreducible representations A_{1g}, A_{2g}, E_{1g}, E_{2g}, E_{3g}, and E_{4g} (notation of ref 13 for $D_{\infty h}$) correlate with A_1', A_2', E_1'', E_2', E_2'', and E_1', respectively, in D_{5h}; also, the sign of Ds must be changed and the parameters Ds and Dt converted to δ_1 and δ_2 by use of eq 8. For the d^8 electronic configuration, the signs of the crystal field parameters must be inverted.

Electronic Spectrum of $V(CN)_7^{4-}$

The cyanide complex of V(III) has been the subject of several electronic spectral investigations. Reflectance measurements on the solid reveal absorptions at *ca.* 22,200 and 28,300 cm^{-1} in what is expected to be the d-d region;[16,17] transitions at 36,400 cm^{-1} and beyond were observed by Bennett and Nicholls.[17] We too have observed these bands in KBr disks and Nujol mulls of $K_4V(CN)_7 \cdot 2H_2O$. Perumareddi, *et al.*,[18] recorded the spectrum in aqueous solution and found absorptions at 14,700 (5.7), 18,870 (7.5), 22,200 (27), and 28,600 cm^{-1} (50) (extinction coefficients in parentheses); they were unable to rationalize their data in terms of an octahedral V(III) complex. Alexander and Gray[19] reported similar data and for an octahedral complex deduced values for $10Dq$, B, and C of 23,500, 375, and 2700 cm^{-1}, respectively. However, the band *ca.* 19,000 cm^{-1} was not resolved in either work and was inferred only by Gaussian analysis. The 14,700-cm^{-1} transition has been ascribed[17] to a $VO(CN)_5^{3-}$ impurity, and we concur in this assignment. Since $V(CN)_7^{4-}$ disproportionates in aqueous solution[17] and $V(CN)_6^{4-}$ has absorptions in the same region as the V(III) species, the definitive spectrum in water is not apparent. Neither $VO(CN)_5^{3-}$ nor $V(CN)_6^{4-}$ have bands in the 19,000-cm^{-1} region and so this absorption may indeed belong to $V(CN)_7^{4-}$. To check this assumption, the electronic spectrum of a genuine sample of $K_4V(CN)_7 \cdot 2H_2O$[1] in a Nujol mull was recorded at liquid nitrogen temperature.[20] A weak shoulder was clearly apparent and centered at *ca.* 20,600 cm^{-1}, thus validating the Gaussian analyses of the aqueous spectra.[18,19] From the low-temperature work, by visually subtracting out contributions due to overlapping bands, we place the positions of the three bands at 20,600, 22,800, and 28,600 cm^{-1}. A thorough search of the spectral range between 4000 and 19,000 cm^{-1} revealed no absorptions that could be ascribed to electronic excitations of $V(CN)_7^{4-}$

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(20) The low-temperature spectrum was recorded on a Cary Model 14 spectrophotometer with a quartz dewar designed for immersion of samples into liquid nitrogen.

Band Assignments for $V(CN)_7{}^{4-}$

The $V(CN)_7{}^{4-}$ ion has two unpaired electrons;[17] the ground state configuration is $(e_1'')^2$ and the electronic ground state is $^3A_2'$. By a consideration of Table I and the observed spectrum, all but the one-electron excitations should be at high energy (>38,000 cm^{-1}) and buried under the more intense charge-transfer bands. The possible one-electron transitions and their energies in the strong-field limit are summarized in Table II; singlets arising from the $(e_1'')(e_2')$ and $(e_1'')(a_1')$ configurations are neglected since transitions to those states are expected to be buried under the spin-allowed bands. None of the possible transitions are symmetry allowed.

The three observed transitions are assigned as $^3A_2' \rightarrow {}^3E_2''$, $^3A_2' \rightarrow {}^3E_1''[(e_1'')(e_2')]$, and $^3A_2' \rightarrow {}^3E_1''[(e_1'')(a_1')]$ in order of increasing energy. Ligand field parameters are calculated to be $B = 367$ cm^{-1}, $10\delta_1 = 21{,}700$ cm^{-1}, and $10\delta_2 = 4700$ cm^{-1}. The low-energy side of the 22,800-cm^{-1} band is, in fact, quite broad and may contain another buried band out as far as *ca.* 17,000 cm^{-1}. The $^3A_2' \rightarrow {}^1A_1'$ transition is predicted to be somewhere in this region. Were the three observed transitions assigned as $^3A_2' \rightarrow {}^1A_1'$, $^3A_2' \rightarrow {}^3E_2''$, and $^3A_2' \rightarrow {}^3E_1''$ $[(e_1'')(e_2')]$ in order of increasing energy, then the calculated value of B would be 967 cm^{-1} which is *above* the free ion value of 862 cm^{-1} [21] and thus unacceptable. The calculated B value of 367 cm^{-1} is reasonable in light of Orgel's comment that shielding effects should be particularly important in highly charged ions with few d electrons.[22]

Assuming that the $^3A_2' \rightarrow {}^1A_1'$ transition is indeed buried under the broad shoulder at 20,000 cm^{-1}, $^3A_2' \rightarrow {}^1E_2'$ is predicted to be at 8000–10,000 cm^{-1}. We have not observed this band but it should be quite weak because of the low spin-orbit coupling constant of V^{3+} (217 cm^{-1} in the free ion)[23] and because it will be *ca.* 10,000 cm^{-1} from the nearest spin-allowed band from which it could steal some intensity. Spin-forbidden bands for the D_{3h} VX_3L_2 complexes[9] are either uncertain or not observed.

The electronic spectrum of a d^1 pentagonal-bipyramidal complex has been recorded in μ-oxalato-bis(oxalato)hexaaquodititanium(III) tetrahydrate in which each titanium(III) has two axial water ligands and five equatorial ligands consisting of one water molecule, two oxygens of a bridging oxalate, and two oxygens of a nonbridging oxalate.[24] Transitions at 9400 and 12,300 cm^{-1} may be assigned as $^2E_1'' \rightarrow {}^2E_2'$ and $^2E_1'' \rightarrow {}^2A_1'$. Making the reasonable assumptions that all oxygens in the titanium(III) complex will have the same effective ligand field strength and that the overall crystal field splitting $10\delta_1 + 10\delta_2$ should be nearly the same for Ti(III) and V(III), then it is seen that CN^- has approximately doubled the overall splitting relative to oxygen ligands; it is noted that $10Dq$ of $Cr(CN)_6{}^{3-}$ is ~1.5 times that of $Cr(OH_2)_6{}^{3+}$.

Pertinent crystal field splitting parameters for selected bipyramidal complexes (two pentagonal and one trigonal) are collected in Table III. Values of Ds for the seven-coordinate complexes are negative as predicted by the ionic model. Also, the relative values of $10\delta_1$ and $10\delta_2$ for D_{5h} relative to D_{3h} are as expected. No clear statement can apparently be made about the relative sizes of $10\delta_1 + 10\delta_2$ for the two different geometries. Since Ds and Dt are expected to increase as the crystal field strength of the ligands increases, then from eq 2 and 8 it is apparent that $10\delta_1/10\delta_2$ as well as $10\delta_1 + 10\delta_2$ will increase as stronger field ligands are introduced into the pentagonal bipyramid.

Table I. Strong-Field Energies[a] for the d^2 Configuration in a Pentagonal-Bipyramidal (D_{5h}) Environment

Configuration	Crystal-field energy	State	Coulombic energy[b]
$(a_1')^2$	$8\delta_1 + 16\delta_2$	$^1A_1'$	$4B + 3C$
$(e_2')(a_1')$	$8\delta_1 + 6\delta_2$	$^1E_2'$	$2C$
		$^3E_2'$	$-8B$
$(e_2')^2$	$8\delta_1 - 4\delta_2$	$^1A_1'$	$4B + 4C$
		$^1E_1'$	$4B + 2C$
		$^3A_2'$	$4B$
$(e_1'')(a_1')$	$-2\delta_1 + 6\delta_2$	$^1E_1''$	$3B + 2C$
		$^3E_1''$	B
$(e_1'')(e_2')$	$-2\delta_1 - 4\delta_2$	$^1E_2''$	$4B + 2C$
		$^1E_1''$	$-2B + 2C$
		$^3E_1''$	$-2B$
		$^3E_2''$	$-8B$
$(e_1'')^2$	$-12\delta_1 - 4\delta_2$	$^1A_1'$	$7B + 4C$
		$^1E_2'$	$B + 2C$
		$^3A_2'$	$-5B$

[a] In descending energy. [b] In terms of the Racah parameters; the common additive parameter A has been omitted for all states.

Table II. Possible One-Electron d–d Transitions for a Strong-Field d^2 Pentagonal-Bipyramidal Complex

State	Energy[a]
$^1E_2'[(e_1'')^2]$	$6B + 2C$
$^1A_1'[(e_1'')^2]$	$12B + 4C$
$^3E_2''[(e_1'')(e_2')]$	$10\delta_1 - 3B$
$^3E_1''[(e_1'')(e_2')]$	$10\delta_1 + 3B$
$^3E_1''[(e_1'')(a_1')]$	$10\delta_1 + 10\delta_2 + 6B$

[a] Relative to the $^3A_2'$ ground state.

Table III. Ligand Field Splitting Parameters for Selected Bipyramidal Complexes (in cm^{-1})

	$V(CN)_7{}^{4-}$ [a]	$Ti_2(oxalate)_3(H_2O)_{10}$ [b]	$VCl_3(N(CH_3)_3)_2$ [c]
$10\delta_1$	21,700	9400	5930
$10\delta_2$	4700	2900	9010
$10\delta_1 + 10\delta_2$	26,400	12,300	14,940
$10\delta_1/10\delta_2$	4.6	3.2	0.66
Ds	−2430	−930	440
Dt	2880	1320	1450

[a] This work. [b] From ref 24. [c] From ref 9.

Hopefully, more seven-coordinate systems with simple ligands (*i.e.*, monodentate) will be obtained in the future, and a comparison with $V(CN)_7{}^{4-}$ will be possible to further test the ideas presented in this paper.

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Registry No. $K_4V(CN)_7$, 33041-87-1.

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