Ultraviolet Spectral Assignments in the Tetracyano Complexes of Platinum, Palladium, and Nickel from Magnetic Circular Dichroism

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Abstract: The magnetic circular dichroism (MCD) of room-temperature aqueous solutions of $Pt(CN)_4^{2-}$, $Ni(CN)_4^{2-}$, and $Pd(CN)_4^{2-}$ have been measured over the region 25–50,000 cm^{-1}. $Pt(CN)_4^{2-}$ and $Ni(CN)_4^{2-}$ each show three distinct, positive A terms in MCD, while the $Pd(CN)_4^{2-}$ MCD is much less clear, reflecting the great overlapping that occurs in the absorption spectrum. It proves essential to explicitly consider spin–orbit coupling, and a model is proposed which accounts semiquantitatively for the A-term patterns in $Pt(CN)_4^{2-}$ and $Ni(CN)_4^{2-}$. The previous interpretation of the $Ni(CN)_4^{2-}$ spectrum is not basically altered, but major changes are made in the $Pt(CN)_4^{2-}$ assignments. Our treatment strongly suggests the d orbital order $b_{2g}(xy) < e_g(xz,yz) \gtrsim a_{1g}(z^2) \ll b_{1g}(x^2 - y^2)$ for $Pt(CN)_4^{2-}$.

The strong absorption bands of the square-planar tetracyanide complexes of d^8 transition metal ions have been the subject of several recent articles.[2–5] We have studied the magnetic circular dichroism (MCD) spectra of $Pt(CN)_4^{2-}$, $Pd(CN)_4^{2-}$, and $Ni(CN)_4^{2-}$ in hopes of clarifying the nature of the excited states involved, a preliminary note on $Ni(CN)_4^{2-}$ having already appeared.[3] The application of MCD to spectroscopic studies has been discussed extensively in a number of previous papers.[6] In the present case, since the ground state is nondegenerate ($^1A_{1g}$), only A or B terms are possible, the A terms (which change sign at the absorption maximum) arising only if the excited state is degenerate, and the B terms (which peak at the absorption maximum) being allowed for both degenerate and nondegenerate transitions. Thus the observation of an A term will constitute unambiguous evidence for a degenerate excited state, and the sign and magnitude of such a term will help considerably in delineating the nature of the transition. The analysis of the A terms observed in the $Pt(CN)_4^{2-}$ and $Ni(CN)_4^{2-}$ MCD spectra will be the central point of this paper.

Experimental Section

All spectra were run in aqueous solutions prepared from recrystallized samples of $K_2M(CN)_4$ (M = Pt, Pd, Ni). The resulting absorption spectra agree well with previously reported data on these ions. MCD spectra were measured in a manner described previously.[7] The results together with the corresponding absorption spectra measured on a Cary 14 are displayed in Figures 1–3. $[\theta]_M$ is the molar ellipticity, defined as in natural optical activity, per unit magnetic field in the direction of the light beam. This sign convention is now used by most workers but is opposite to that used in earlier magnetooptical rotation work. With our convention, the Verdet constant of water is negative.

The MCD data should be accurate to better than ±10% since the signal-to-noise ratio was very favorable and reproducibility and base-line behavior were excellent.

Discussion

The most striking feature of the results is the appearance of three clear, positive A terms for $Pt(CN)_4^{2-}$ (Figure 3) corresponding to the absorption bands at 35,800, 39,200, and 46,100 cm^{-1}. The explanation of this feature lies at the heart of this paper because, while other details are left unsettled, we feel that there is only one reasonable way of accounting for these terms, which in turn leads to a reasonable scheme for interpreting the spectra. The MCD of $Ni(CN)_4^{2-}$ also shows three positive A terms. The one corresponding to the 35,000-cm^{-1} band is barely perceptible but careful measurements under optimum conditions definitely show that the MCD crosses the axis at about 35,200 cm^{-1}. The $Pd(CN)_4^{2-}$ spectrum is clearly a composite of very badly overlapping bands and there are almost no well-resolved features. The same applies for the MCD, and hence our discussion will concentrate mainly on Pt and Ni. We shall assume throughout that the ground-state symmetry of the ions is D_{4h}.

Previous attempts to interpret the absorption spectrum of $Pt(CN)_4^{2-}$ have neglected spin–orbit coupling and have assigned all observed bands to spin-allowed charge-transfer transitions. We have abandoned this approach for several reasons. To begin with, the one-electron spin–orbit coupling constant for the Pt atom is 4060 cm^{-1},[8] so one would expect the spin-forbidden bands to have quite large intensities. Also, our MCD spectrum of $Pt(CN)_4^{2-}$ shows three distinct, positive A terms which indicate, since the ground state is $^1A_{1g}$, that the excited state for three of the four observed bands must be E_u. Without explicitly considering spin–orbit coupling, it is not possible to give a reasonable explanation for all this degeneracy.

The recent Mason–Gray (M–G) assignments (Table I) do *not*, for example, account for the A term we observe for band 3 (Figure 3) since $^1B_{1u}$ is a nondegenerate state. A calculation of A/D for band 2 by standard methods[7] gives $A/D = (i\beta/2)\langle e_g(x)|l_z|e_g(y)\rangle \cong (\beta/2)$ (β= Bohr magneton) when the M–G assignment of $^1A_{1g} \rightarrow$

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[1] Department of Chemistry, University of Sussex, Brighton, Sussex, England.

[2] W. R. Mason, III, and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5721 (1968).

[3] P. J. Stephens, A. J. McCaffery, and P. N. Schatz, *Inorg. Chem.*, **7**, 1923 (1968).

[4] C. Moncuit, *J. Chim. Phys.*, **64** (3), 494 (1967).

[5] H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).

[6] A. J. McCaffery, P. N. Schatz, and P. J. Stephens, *ibid.*, **90**, 5730 (1968), and references therein.

[7] P. N. Schatz, A. J. McCaffery, W. Suëtaka, G. N. Henning, A. B. Ritchie, and P. J. Stephens, *J. Chem. Phys.*, **45**, 722 (1966).

[8] D. S. McClure, *Solid-State Phys.*, **9**, 399 (1959).

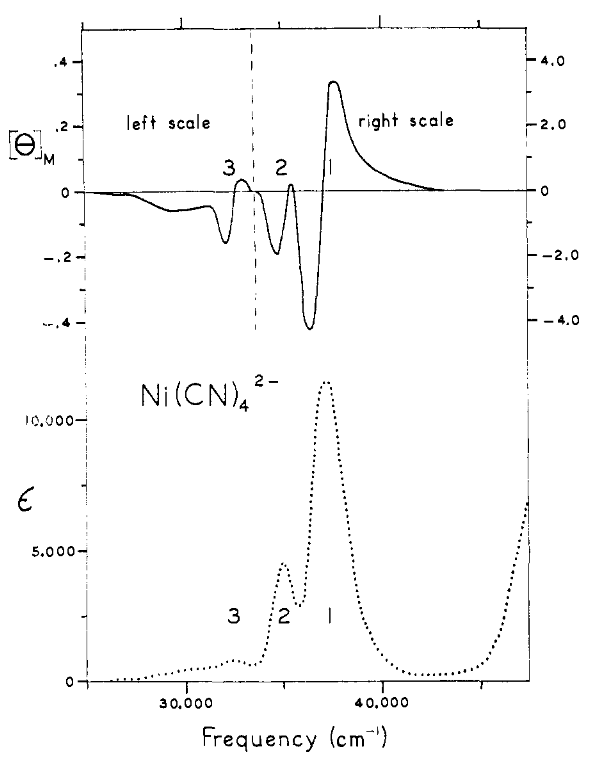

Figure 1. Absorption spectrum and MCD of $Ni(CN)_4^{2-}$ in H_2O. $[\theta]_M$ is the molar ellipticity (defined as in natural optical activity in degrees deciliter decimeter^{-1} mole^{-1}) per gauss in the direction of the light beam. ϵ is the molar extinction coefficient. The numbering of the bands is indicated.

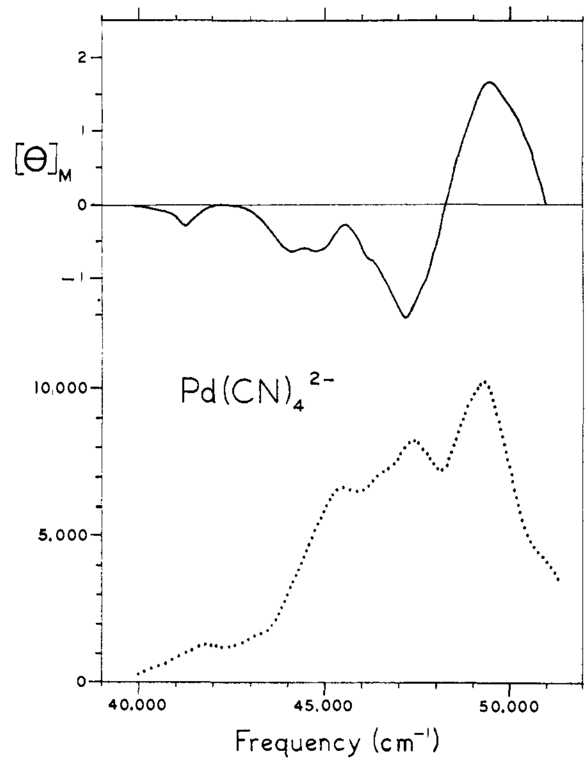

Figure 2. Absorption spectrum and MCD of $Pd(CN)_4^{2-}$ in H_2O. Symbols and units are as in Figure 1.

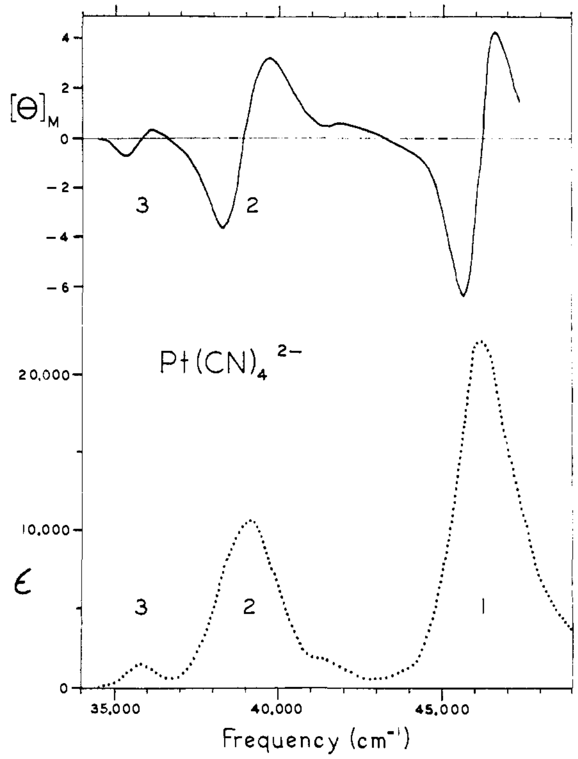

Figure 3. Absorption spectrum and MCD of $Pt(CN)_4^{2-}$ in H_2O. Symbols and units are as in Figure 1.

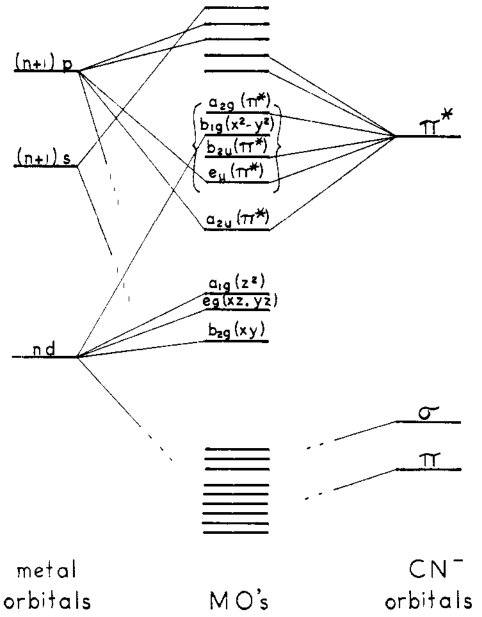

Figure 4. Schematic molecular orbital energy level diagram for $Pt(CN)_4^{2-}$. All molecular orbitals through $a_{1g}(z^2)$ are filled in the ground state. The order of the levels in parentheses and those above are highly uncertain.

$c\,^1E_u[e_g(xz,yz) \rightarrow a_{2u}(\pi^*)]$ is assumed. Here we neglect two-center integrals and approximate $|e_g(x)\rangle$ and $|e_g(y)\rangle$ as d_{yz} and $-d_{xz}$ orbitals.[9] (The notation is that of Figure 4 which gives a schematic MO diagram for $Pt[CN]_4^{2-}$.) This value is somewhat low but the sign is compatible with our MCD data (Table I). The M-G assignment for band 1 as $^1A_{1g} \rightarrow d\,^1E_u[b_{2g}(xy) \rightarrow e_u(\pi^*)]$ gives $A/D = (\beta i/2)\langle e_u(\pi^*)y|l_z|e_u(\pi^*)x\rangle$, where the inte-

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(9) Throughout this paper we use the Griffith conventions, functions, and particularly Tables A16, A17, and A18. (J. S. Griffith, "The Theory of Transition-Metal Ions," Cambridge University Press, Cambridge, England, 1964.)

Table I. Experimental Absorption and Faraday Parameters of $Pt(CN)_4^{2-}$ and $Ni(CN)_4^{2-}$

					Assignment	
ν_{max} (10^3 cm^{-1})	ϵ_{max}[a]	D[b]	A/D[c] (gaussian)	A/D[d] (moments)	Mason-Gray[e] $^1A_{1g} \rightarrow$	This paper $A_{1g} \rightarrow$
			$Pt(CN)_4^{2-}$			
35.8 (band 3)	1,480	0.521[f]	0.373	0.438[i]	$^1B_{1u}[d_{xy} \rightarrow a_{2u}(\pi^*)]$	E_u3 $\{B_{1u}2$
39.2 (band 2)	10,700	6.221[f]	0.960	0.956[i]	$c\,^1E_u[d_{xz,yz} \rightarrow a_{2u}(\pi^*)]$	E_u2, $A_{2u}2$
(41.3)	~(1,900)				$^1A_{2u}[d_{z^2} \rightarrow a_{2u}(\pi^*)]$	[l]
46.1 (band 1)	22,100	10.52[f]	0.419	0.485[i]	$d\,^1E_u[d_{xy} \rightarrow e_u(\pi^*)]$	$A_{2u}1$, E_u1, $B_{1u}1$
			$Ni(CN)_4^{2-}$			
(30.5)	~(460)				$^1A_{2g}[d_{xy} \rightarrow d_{x^2-y^2}]$	A_{2g}, E_u4
32.4 (band 3)	760	[g]	[h]		$^1B_{1u}[d_{xy} \rightarrow a_{2u}(\pi^*)]$	$B_{1u}2$, E_u3
35.0 (band 2)	4,500	1.450[f]	[i]	[j]	$^1A_{2u}[d_{z^2} \rightarrow a_{2u}(\pi^*)]$	$A_{2u}2$, E_u2, $B_{1u}1$
37.2 (band 1)	11,400	5.672[f]	0.819	1.174	$c\,^1E_u[d_{xz,yz} \rightarrow a_{2u}(\pi^*)]$	$A_{2u}1$, E_u1
50.5[k]	23,000[k]				$d\,^1E_u[d_{xy} \rightarrow e_u(\pi^*)]$	Same

[a] Molar extinction coefficient. [b] Dipole strength in units of square debye. $D = (9.183 \times 10^{-3}/\nu_0)\int\epsilon\, d\nu$. [c] A/D in units of Bohr magneton. [d] For a discussion of the method of moments, see P. J. Stephens, *Chem. Phys. Letters*, **2**, 241 (1968). [e] Reference 2. [f] From gaussian fit of absorption spectrum. [g] Overlapping too severe to permit reliable value. [h] $A \sim 0.054\ D^2\ \beta$. This is a rough value based on a gaussian fit. [i] $\bar{\nu}$ (footnote *d*) approximated as ν_{max}. [j] Estimate not possible. [k] Data from ref 2. [l] See text.

gral cannot be easily approximated since $|e_u(\pi^*)x\rangle$ is, for example, a molecular orbital constructed from carbon and nitrogen $2p_x$, $2p_y$, $2p_z$, and 2s orbitals and the platinum $6p_x$ orbital. There are numerous one-center contributions to A/D of both signs and varying magnitudes and, in addition, some rather important two-center terms. Our calculations indicate, however, that A/D is probably positive with a magnitude $\lesssim(^1/_6)\beta$. The actual value would, of course, depend on the exact form of the eigenvector for $|e_u(\pi^*)\rangle$. The M-G assignment for band 1 would therefore appear to predict the correct sign for A/D but with a considerably smaller magnitude than is observed experimentally (Table I); but still, the M-G assignments leave us with no explanation for the A term we observe in the MCD for band 3.

Still neglecting spin-orbit coupling, a third A term might perhaps be accounted for by (1) metal-to-ligand (M → L) transitions involving the nonbonding orbital $b_{2u}(\pi^*)$, the only ungerade ligand orbital aside from $e_u(\pi^*)$ and $a_{2u}(\pi^*)$ conceivably in range; (2) the other ^1E_u transition to $e_u(\pi^*)$, $^1A_{1g} \rightarrow {}^1E_u[a_{1g}(z^2) \rightarrow e_u(\pi^*)]$; (3) ligand-to-metal (L → M) transitions; (4) d-d transitions; (5) changes in geometry in the excited state; (6) overlapping B terms. We shall argue that none of these possibilities can account reasonably for the presence of three positive A terms.

The first two are easily eliminated. For an M → L transition $^1A_{1g} \rightarrow {}^1E_u[e_g(xz,yz) \rightarrow b_{2u}(\pi^*)]$, we calculate $A/D = (-\beta i/2)\langle e_g(x)|l_z|e_g(y)\rangle \cong (-\beta/2)$, while all A terms observed are positive. The $^1A_{1g} \rightarrow {}^1E_u[a_{1g}(z^2) \rightarrow e_u(\pi^*)]$ transition gives $A/D = (-\beta i/2)\langle e_u(\pi^*)y|l_z|e_u(\pi^*)x\rangle$, which is opposite in sign but equal in magnitude to the A/D value calculated for $^1A_{1g} \rightarrow {}^1E_u[b_{2g}(xy) \rightarrow e_u(\pi^*)]$. Obviously then, *both* of these transitions cannot give rise to positive A terms.

L → M transitions are ruled out by the observation[10] that $Au(CN)_4^-$ shows no absorption maxima below 54,000 cm^{-1}. Since L → M transitions typically decrease in energy as the oxidation number increases, such transitions for $Pt(CN)_4^{2-}$ should surely be at energies above 54,000 cm^{-1}, *i.e.*, well beyond our range of observation.

The ligand field (d-d) bands in $Pt(CN)_4^{2-}$ are expected at very high energy, overlapping or lying beyond the charge-transfer bands.[2] The only singlet d-d transition which is degenerate is $^1A_{1g} \rightarrow {}^1E_g[e_g \rightarrow b_{1g}]$. However, an A term arising from this parity-forbidden transition would not be expected to have anything like the intensity of the A terms in bands 1 and 2. If band 3 were assigned to this transition and the order of d orbitals $b_{1g} \gg b_{2g} > e_g \gtrsim a_{1g}$ were assumed, one would expect the $b_{2g} \rightarrow b_{1g}$ (d-d) transition at lower energy where no bands are observed. Other orders for the d orbitals such as that in Figure 4 would remove this difficulty but would lead to problems for band 1 since $^1A_{1g} \rightarrow {}^1E_u[a_{1g} \rightarrow e_u(\pi^*)]$ probably has a small *negative* A/D value. (The sign of an A term from $^1A_{1g} \rightarrow {}^1E_g[e_g \rightarrow b_{1g}]$ would be determined by the symmetry of the vibrations making the transition allowed.)

Excited-state distortions from D_{4h} to D_{2d} or C_{4v} remove inversion symmetry without splitting the degeneracy of E states. However, this does not result in sign changes for the A terms calculated on the basis of D_{4h} symmetry for the charge-transfer transitions previously considered, and hence introduces no new qualitative features. Such distortions would be expected to increase the intensity of the d-d transitions and, in particular, the intensity of a $^1A_{1g} \rightarrow {}^1E_g$ transition and any A term associated with it. However, we assume that such effects cannot increase the intensity into the range of bands 1 and 2.

B terms arise from the mixing by the magnetic field of each unperturbed state with all other unperturbed states connected by a magnetic transition dipole. The magnitude of the contribution to a B term is inversely proportional to the energy difference of the states which are mixed. Thus, since $Ni(CN)_4^{2-}$, $Pt(CN)_4^{2-}$, and $Pd(CN)_4^{2-}$ have no states close in energy to the ground state, B terms should arise principally from the mixing of neighboring excited states. Such mixing is allowed in D_{4h} only between two E_u states, or between an E_u and an A_{2u} state. Thus no B terms would be expected for a $^1A_{1g} \rightarrow {}^1B_{1u}$ transition to a first approximation. When an A_{2u} state is close to an E_u state, one might wonder if overlapping B terms could give the appearance of an additional A term. It is easy to show that if a $B(^1A_{1g} \rightarrow {}^1A_{2u})$ term which results principally from the mixing of a neighboring ^1E_u state by the magnetic field has one sign, then a $B(^1A_{1g} \rightarrow {}^1E_u)$ term from the mixing in of the same $^1A_{2u}$ state will have the same magnitude but opposite sign. As the two states get close in energy, the

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[10] W. R. Mason, III, and H. B. Gray, *Inorg. Chem.*, 7, 55 (1968).

Table II. Electronic States Arising from One-Electron Excitations to the Ligand $a_{2u}(\pi^*)$ Orbital from the Occupied d Orbitals[a]

Excitation	Single group state (no spin–orbit coupling)	Double group state[b] (spin–orbit coupling)
$a_{1g}(z^2) \rightarrow a_{2u}(\pi^*)$	$^1A_{2u}$	A_{2u}
	$(^3A_{2u})$	(A_{1u}), E_u
$e_g(xz,yz) \rightarrow a_{2u}(\pi^*)$	^1E_u	E_u
	(^3E_u)	(A_{1u}), A_{2u}, (B_{1u}), (B_{2u}), E_u
$b_{2g}(xy) \rightarrow a_{2u}(\pi^*)$	$(^1B_{1u})$	(B_{1u})
	$(^3B_{1u})$	(B_{2u}), E_u

[a] States to which transitions from the $^1A_{1g}$ ground state are forbidden by symmetry are in parentheses. [b] Double group states are distinguished from single group states by the absence of a left superscript.

B terms do approach the form of an *A* term.[11] But in D_{4h} no *new* *A* terms will arise in this way, because the D_{4h} symmetry requires that at least one of any two states mixing to give a *B* term be of E_u symmetry, and E_u states, of course, give *A* terms by themselves. However, when $A_{1g} \rightarrow E_u$ and $A_{1g} \rightarrow A_{2u}$ transitions overlap and so are separated in energy by an amount of the order of their band widths, the magnitude of the "pseudo" *A* term formed by the overlapping *B* terms can be of the same order of magnitude as that of the *A* term arising from the $A_{1g} \rightarrow E_u$ transition. This will be discussed in greater detail later in this paper.

Even if we had been able to account for our three positive *A* terms by one of the six possibilities discussed above, we would still have been troubled by the absence of bands in the $Pt(CN)_4{}^{2-}$ absorption spectra below about 34,000 cm^{-1}. If band 3 represents a transition to a singlet state, there clearly are lower energy transitions possible to triplet states. With the high value of the one-electron spin–orbit coupling constant ζ_{5d} for Pt(II), these bands should be observable in the absorption spectrum.

Let us now consider in some detail the consequences of spin–orbit coupling with application first to Pt(II) where ζ_{5d} is somewhere in the range 3000–4000 cm^{-1}.[8,12] We shall first consider M → L transitions to $a_{2u}(\pi^*)$, which in $Pt(CN)_4{}^{2-}$ is almost certainly the lowest lying empty orbital. Table II shows the states arising from the (M → L) transitions. The key point is that with spin–orbit coupling, four E_u states arise which will mix, and each resulting state will give rise to an *A* term; each $A_{1g} \rightarrow E_u$ transition will become electric dipole allowed in proportion to the amount of ^1E_u character the E_u eigenvector contains. When spin–orbit coupling is neglected, only one allowed transition, $^1A_{1g} \rightarrow {}^1E_u[e_g \rightarrow a_{2u}(\pi^*)]$, can produce an *A* term. Likewise, the $A_{2u}(^3E_u)$ and $A_{2u}(^1A_{2u})$ states and the $B_{1u}(^3E_u)$ and $B_{1u}(^1B_{1u})$ states will mix under spin–orbit coupling, but these states are nondegenerate, and so do not directly give rise to *A* terms. Since $^1A_{1g} \rightarrow {}^1B_{1u}$ transitions are dipole forbidden, the $^1B_{1u}$ absorptions would be expected to be of much lower intensity than the $^1A_{2u}$ or ^1E_u absorptions.

The wave functions for the mixed E_u states will be of the general form

$$|E_ui\rangle = a_i|E_u(^1E_u)\rangle + b_i|E_u(^3A_{2u})\rangle + c_i|E_u(^3E_u)\rangle + d_i|E_u(^3B_{1u})\rangle \quad (1)$$

The coefficients have been determined (Table III) by diagonalizing the spin–orbit coupling matrix after approximating the MO's by pure d functions and supplying the parameters ζ, *X*, *Y*, and *Z*. Here ζ is the one-electron (d) spin–orbit coupling constant and $X \equiv (^1E_u - {}^3A_{2u})$, $Y \equiv (^3A_{2u} - {}^3E_u)$, and $Z \equiv (^3E_u - {}^3B_{1u})$ are the energy differences in the absence of spin–orbit coupling. The upper triangle of the resulting hermitian secular determinant is shown in (2). The spin–orbit

$$\begin{vmatrix} -E + X + Y + Z & \frac{i\sqrt{3}}{2}\zeta & \frac{i}{2}\zeta & \frac{i}{2}\zeta \\ & -E + Y + Z & \frac{\sqrt{3}}{2}\zeta & 0 \\ & & -E + Z & -\frac{1}{2}\zeta \\ & & & -E \end{vmatrix} = 0 \quad (2)$$

coupling matrix elements needed here reduce to one-electron matrix elements of the type $\langle a|l_\gamma|b\rangle$, where l_γ is the *x*, *y*, or *z* component of the angular momentum operator and $|a\rangle$ and $|b\rangle$ are molecular orbitals which are largely metal d in character. Thus, in this case, it seems reasonable to approximate the orbitals as pure d functions and then reduce ζ from its free ion value to account for ligand orbital mixing. In all our calculations ζ was therefore scaled down somewhat arbitrarily to 0.85 of the published free ion value.

Making the same approximations, the A_{2u} and B_{1u} matrices can be determined. Here $Y(A_{2u}) \equiv (^1A_{2u} - {}^3E_u)$ and $Y(B_{1u}) \equiv (^1B_{1u} - {}^3E_u)$ must be chosen and the resulting eigenvectors are $|A_{2u}i\rangle = e_i|A_{2u}(^1A_{2u})\rangle + f_i|A_{2u}(^3E_u)\rangle$ (Table III) and $|B_{1u}i\rangle = g_i|B_{1u}(^1B_{1u})\rangle + h_i|B_{1u}(^3E_u)\rangle$.

The eigenvalues of the E_u spin–orbit coupling matrix give us the predicted relative positions of the four $A_{1g} \rightarrow E_ui$ bands. From the E_ui eigenvectors the *A* term for each $A_{1g} \rightarrow E_ui$ transition can be calculated as

$$A_i \cong \frac{\beta}{2}\{|a_i|^2 + 2|b_i|^2 + |c_i|^2 - 2|d_i|^2\}|a_i|^2|D_E|^2 \quad (3)$$

where $|D_E|^2 = |\langle ^1A_{1g}||m||^1E_u\rangle|^2$ is the dipole strength in units of square debyes for the pure $^1A_{1g} \rightarrow {}^1E_u$ transition, and $\langle ^1A_{1g}||m||^1E_u\rangle$ is the indicated reduced matrix element.[13]

Our approach has been to ascertain, first, whether sensible values of the parameters (ζ, *X*, *Y*, *Z*, $Y(A_{2u})$, $Y(B_{1u})$) exist which can account at least semiquantitatively for the observed absorption and MCD spectra,

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(11) P. J. Stephens, private communication.

(12) D. S. Martin, M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, 4, 1682 (1965).

(13) M. Tinkham, "Group Theory and Quantum Mechanics," McGraw-Hill Book Co., Inc., New York, N. Y., 1964.

Table III. Mixing Coefficients for Eigenvectors Associated with the Parameters of Figures 5 and 6

	E_ui mixing coefficients					$A_{2u}i$ mixing coefficients	
	a_i $E_u(^1E_u)$	b_i $E_u(^3A_{2u})$	c_i $E_u(^3E_u)$	d_i $E_u(^3B_{1u})$		e_i $A_{2u}(^1A_{2u})$	f_i $A_{2u}(^3E_u)$
Pt					Pt		
E_u1	0.798	−0.425i	−0.314i	−0.289i	$A_{2u}1$	0.775	0.632i
E_u2	−0.584	−0.384i	−0.586i	−0.411i	$A_{2u}2$	0.632	−0.775i
E_u3	0.148	0.785i	−0.593i	−0.099i			
E_u4	−0.006	0.236i	0.454i	−0.859i			
Ni					Ni		
E_u1	0.986	−0.102i	−0.125i	−0.033i	$A_{2u}1$	0.768	0.641i
E_u2	−0.137	−0.146i	−0.978i	0.065i	$A_{2u}2$	0.641	−0.768i
E_u3	−0.082	−0.984i	0.157i	−0.011i			
E_u4	−0.041	0.005i	−0.061i	−0.997i			

and second, whether these parameters have some degree of uniqueness.

Figures 5 and 6 show schematically parameters which put A terms at the observed frequencies and lead to reasonable dipole strengths for bands 1, 2, and 3 in $Pt(CN)_4^{2-}$ and $Ni(CN)_4^{2-}$. These parameters predict that band 1 and band 2 in both the $Ni(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$ absorption spectra are composite $A_{1g} \rightarrow A_{2u}i + E_ui$ bands. Here we have the situation described earlier in this paper where overlapping B terms can give rise to substantial "pseudo"-A terms. The experimentally measured quantity $[A/D]_i$ should for these bands be compared with the sum of the A_i and the "pseudo" A_i terms divided by the sum of the dipole strengths for the $A_{1g} \rightarrow A_{2u}i$ and $A_{1g} \rightarrow E_ui$ transitions.

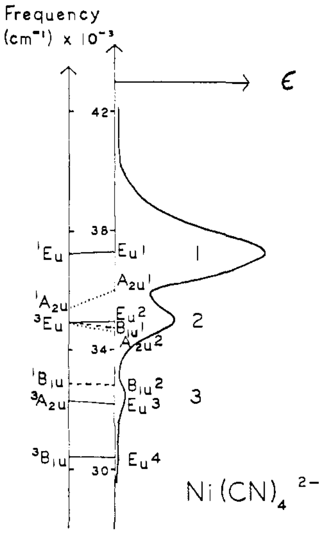

Figure 5. Proposed energy level scheme for $Ni(CN)_4^{2-}$. On the left are the states in the absence of spin-orbit coupling. To the right are the double group states when spin-orbit coupling is included (ζ_{3d} = 530 cm^{-1}). The lines indicate the main contribution to each double-group state. On the extreme right, a sketch of the absorption spectrum is provided with the bands numbered as in Figure 1. The parameters used are in cm^{-1} (see text for definitions): $X = 4900$, $Y = -2600$, $Z = 4500$, $Y(A_{2u}) = 500$, $Y(B_{1u}) = -3000$.

The magnitude of such a pseudo-A term formed by overlapping B terms can be estimated if several approximations are made. We assume that by far the largest contribution will arise from the mixing by the magnetic field of the nearly coincident E_ui and $A_{2u}i$ states of the composite band ($A_{1g} \rightarrow A_{2u}i + E_ui$) and, therefore, that we can ignore other states in our calculation. Magnetic dipole matrix elements are approximated by assuming pure d functions for $|e_g\rangle$, $|a_{1g}\rangle$, and $b_{2g}\rangle$ as in the calculation of A_i above. To obtain an upper limit,[11] we now asume that the two transitions actually coincide in energy, and the expression for the pseudo-A term (A_i'(max)) becomes

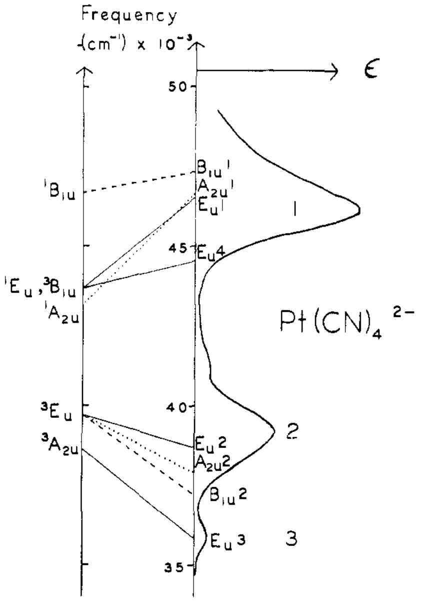

Figure 6. Proposed energy level scheme for $Pt(CN)_4^{2-}$. On the left are the states in the absence of spin-orbit coupling. To the right are the double group states when spin-orbit coupling is included (ζ_{5d} = 3500 cm^{-1}). The lines indicate the main contribution to each double group state. On the extreme right, a sketch of the absorption spectrum is provided with the bands numbered as in Figure 3. The parameters used are in cm^{-1} (see text for definitions): $X = 5000$, $Y = -1000$, $Z = -4000$, $Y(A_{2u}) = 3500$, $Y(B_{1u}) = 7000$.

$$\begin{aligned} A_i'(\max) \cong -\beta i\{|a_i|^2|e_i|^2\langle {}^1A_{2u}|\mu|{}^1E_u\rangle + {} \\ e_if_i^*a_i^*[b_i\langle A_{2u}({}^3E_u)|\mu|E_u({}^3A_{2u})\rangle + {} \\ d_i\langle A_{2u}({}^3E_u)|\mu|E_u({}^3B_{1u})]\}\langle {}^1A_{1g}|m|{}^1A_{2u}\rangle \times {} \\ \langle {}^1A_{1g}|m|{}^1E_u\rangle^* \end{aligned} \tag{4}$$

Letting $D_A = \langle {}^1A_{1g}|m|{}^1A_{2u}\rangle$ and $D_E = \langle {}^1A_{1g}|m|{}^1E_u\rangle$, this gives

$$\begin{aligned} A_i'(\max) \cong \beta\{|a_i|^2|e_i|^2(-\sqrt{6}) + {} \\ e_if_i^*a_i^*(b_i\sqrt{3} + d_i)\}D_E^*D_A \end{aligned} \tag{5}$$

A_i'(max) and A_i can be calculated in units of $D_E^*D_A\beta$

Table IV. Theoretically Calculated Values of D_i, A_i, and A_i'(max) Using the Parameters of Figures 5 and 6 and the Eigenvectors of Table III[a]

	D_i (for $A_{1g} \rightarrow A_{2u}i$ and $A_{1g} \rightarrow E_ui$ only)	A_i ($A_{1g} \rightarrow E_ui$)	A_i'(max) ($-D_E^*D_A$ is positive)
$Pt(CN)_4^{2-}$			
1	$0.64\lvert D_E\rvert^2 + 0.60\lvert D_A\rvert^2$	$0.30\lvert D_E\rvert^2$	$1.44\ (-D_E^*D_A)$
2	$0.34\lvert D_E\rvert^2 + 0.40\lvert D_A\rvert^2$	$0.11\lvert D_E\rvert^2$	$0.73\ (-D_E^*D_A)$
3	$0.022\lvert D_E\rvert^2$	$0.018\lvert D_E\rvert^2$	0
4	$0.00004\lvert D_E\rvert^{2}$[b]	$-0.00002\lvert D_E\rvert^2$	$-0.0031\ (-D_E^*D_A)$[c]
$Ni(CN)_4^{2-}$			
1	$0.97\lvert D_E\rvert^2 + 0.59\lvert D_A\rvert^2$	$0.49\lvert D_E\rvert^2$	$1.55\ (-D_E^*D_A)$
2	$0.019\lvert D_E\rvert^2 + 0.41\lvert D_A\rvert^2$	$0.0095\lvert D_E\rvert^2$	$0.029\ (-D_E^*D_A)$
3	$0.0068\lvert D_E\rvert^2$	$0.0067\lvert D_E\rvert^2$	0
4	$0.0017\lvert D_E\rvert^2$	$0.0017\lvert D_E\rvert^2$	0

[a] $D_E = \langle ^1A_{1g}\|m\|^1E_u\rangle$ and $D_A = \langle ^1A_{1g}\|m\|^1A_{2u}\rangle$. [b] This is for $A_{1g} \rightarrow E_u4$ only. E_u1 overlaps E_u4 (see Figure 6). [c] This is for $A_{2u}1$–E_u4 mixing only.

and $|D_E|^2\beta$, respectively, for a given set of eigenvectors, $|E_ui\rangle$ and $|A_{2u}i\rangle$. The total dipole strength D_i of the combined $A_{1g} \rightarrow A_{2u}i$ and $A_{1g} \rightarrow E_ui$ transition may also be estimated

$$D_i = |a_i|^2|D_E|^2 + |e_i|^2|D_A|^2 \tag{6}$$

While the sign of A_i is independent of the sign of D_E and D_A, the sign of A_i'(max) is not, but we can determine the sign, if not the magnitude, of $D_E^*D_A$ quite easily.

$$\begin{aligned} D_E^*D_A &= \langle ^1A_{1g}\|m\|^1E_u\rangle^*\langle ^1A_{1g}\|m\|^1A_{2u}\rangle \\ &= -(2\sqrt{2})\langle a_{1g}|m_z|a_{2u}(\pi^*)\rangle\langle -e_gy|m_x|a_{2u}(\pi^*)\rangle \\ &= -(2\sqrt{2})\langle d_{z^2}|m_z|a_{2u}(\pi^*)\rangle\langle d_{zx}|m_x|a_{2u}(\pi^*)\rangle \end{aligned} \tag{7}$$

In the last step we have approximated $|a_{1g}\rangle$ and $-|e_gy\rangle$ as pure d functions. MO calculations by the extended Hückel method on $Pt(CN)_4^{2-}$ show that[14]

$$|a_{2u}(\pi^*)\rangle = n\,6p_z(Pt)\rangle + r\sum_{i=1}^{4}\{|2p_{z_i}(C)\rangle - s|2p_{z_i}(N)\rangle\} \tag{8}$$

where n, r, and s are all positive with s close to one, and z is perpendicular to the molecular plane. The integrals over the angular coordinates, θ and φ, for all terms containing $|6p_z(Pt)\rangle$ and $|2p_{z_i}(C)\rangle$ are positive, and since s is close to one and multicenter integrals of this sort fall off quickly with distance, the negative contributions from the $-s|2p_{z_i}(N)\rangle$ terms will be small. Thus $D_E^*D_A$ will surely be *negative*. It therefore follows from eq 5 that A_i'(max) will be positive if the quantity $\{|a_i|^2|e_i|^2\sqrt{6} - e_if_i^*a_i^*(b_i\sqrt{3} + d_i)\}$ is positive.

In Table IV, values of D_i, A_i, and A_i'(max) are given for the parameters shown in Figures 5 and 6, and the associated $A_{2u}i$ and E_ui eigenvectors (Table III). It must be emphasized here that A_i'(max) is the *upper limit* for the pseudo-*A* term, and so the actual pseudo-*A* contribution to the experimental *A* term might be up to a factor of 10 smaller than this. If for purposes of estimation we assume[15] that $D_E = -D_A$ ($D_E^*D_A$ is negative) and normalize D_i to the scale of the observed values, it is possible to compare (Table V) calculated values of $(A_i + A_i'(\text{max}))/D_i$ and relative D_i with the equivalent observed values. We expect *A*/*D* values calculated in this manner for bands 1 and 2 to be larger than the experimental values, since we have used the *upper limit* of the pseudo-*A* contribution. In addition, theoretical *A*/*D* values will be high if there are other overlapping transitions which contribute to the experimental dipole strength but not to the experimental *A* or pseudo-*A* terms.

Table V. Comparison of Theoretical and Observed Parameters[a] for $Pt(CN)_4^{2-}$ and $Ni(CN)_4^{2-}$ ($D_E = -D_A$ and D_i is normalized to the scale of the observed values for comparison purposes)

	D_i theoretical (assuming $A_{1g} \rightarrow A_{2u}i$ and $A_{1g} \rightarrow E_ui$ only)	D[b] exptl	Upper limit for *A*/*D* theoretical = $\dfrac{A_i + A_i'(\text{max})}{D_i}$	*A*/*D* exptl
		$Pt(CN)_4^{2-}$		
1	10.49	10.5	1.40	0.419[b]
2	6.26	6.22	1.15	0.956[c]
3	0.19	0.52	0.79	0.438[c]
4	0.0003[d]		−0.0025[e]	
		$Ni(CN)_4^{2-}$		
1	5.46	5.67	1.31	0.819[b]
2	1.51	1.45	0.09	*f*
3	0.024	*g*	0.98[h]	*i*
4	0.006	*g*	−0.99[h]	*j*

[a] When both the moment and gaussian-fit data are available, we have chosen the value which we feel to be most reliable. In principle, the moment method (P. J. Stephens, *Chem. Phys. Letters*, **2**, 241 (1968)) is always preferable because it requires no assumptions regarding band shape. However, it is not applicable (for individual bands) if serious overlapping occurs. In that case, we use gaussian fits. We have found for quite a wide range of data that *A* terms extracted from gaussian fits usually agree quite well with those obtained by the method of moments. This is not true for the damped oscillator model band shape. We shall discuss this matter in some detail in a future paper. [b] By gaussian fit. [c] By method of moments: see Stephens, footnote *a*. [d] This is for $A_{1g} \rightarrow E_u4$ only. E_u1 overlaps E_u4 (see Figure 6). [e] D_i is that for $A_{1g} \rightarrow E_u1 + A_{2u}1 + E_u4$. [f] Estimate not possible. [g] Overlapping too severe to permit reliable value. [h] This is high as D_i used in the calculation was for $A_{1g} \rightarrow A_{2u}i + E_ui$ only. [i] $A \sim 0.054\ D^2\ \beta$. This is a rough value based on a gaussian fit. [j] *B* term only in MCD.

The results of this rough calculation are encouraging. Signs and approximate magnitudes of all *A* terms and relative dipole strengths are in reasonable agreement with experiment. The assignment of band 1 in $Ni(CN)_4^{2-}$ and band 2 in $Pt(CN)_4^{2-}$ as composite $A_{1g} \rightarrow A_{2u}i + E_ui$ bands and the resulting pseudo-*A* term contribution to *A* explains the high *A*/*D* and extremely low *B* values observed experimentally for these bands. If only "true" *A* terms are considered, *A*/*D* values calculated for these bands for all reasonable parameters are consistently too low by a factor of 2 or more (Table IV).

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(14) D. D. Shillady, private communication.

(15) The results are quite insensitive to this assumption. For example, if we assume $D_E = -2D_A$, the magnitudes of *A* for band 3 in both Pt and Ni improve slightly, but other results are basically unchanged.

Values of *X*, *Y*, and *Z* which reproduced our band separations and *A* term signs for Pt $(CN)_4^{2-}$ placed the $E_u(^3B_{1u})$ state within approximately ±500 cm^{-1} of the $E_u(^1E_u)$ state and placed the $E_u(^3A_{2u})$ and $E_u(^3E_u)$ states less than 2000 cm^{-1} apart, but quite definitely put the latter pair about 3000 cm^{-1} lower in energy than the former pair. The actual order of the $E_u(^3A_{2u})$ and E_u (^3E_u) states was found significant in that the chosen order gave much better magnitudes for the *A* terms and allowed the A_{2u} states to be placed more reasonably. As can be seen from Tables IV and V, our parameters predict *A* terms of the correct signs and relative orders of magnitude for bands 1, 2, and 3. A fourth *A* term is predicted at 44,290 cm^{-1} but of such low intensity that it would not be expected to be seen experimentally, since it falls under the *A* term for band 1. We have also indicated reasonable positions for the B_{1u} and A_{2u} states in Figure 6. $A_{2u}2$ might correspond to the peak M-G observed at 38,400 cm^{-1} in EPA at 77°K.[2] We calculate the intensity ratio $A_{2u}1/A_{2u}2$ as about 3/2 and that for $B_{1u}1/B_{1u}2$ as about 14/1. Since the $A_{1g} \rightarrow B_{1u}$ transition is orbitally forbidden, the intensity of even the $B_{1u}1$ band should be low.

Values of *X*, *Y*, and *Z* outside of the range suggested above were unable to predict three positive *A* terms of the correct orders of magnitude without predicting a fourth negative *A* term of considerable intensity. In particular, if an order of the d orbitals such as that assumed by M-G is used,[2] a negative *A* term of easily measurable intensity is predicted to fall below 32,000 cm^{-1} for all values of *X*, *Y*, and *Z* which assign positive *A* terms of correct orders of magnitude to bands 1, 2, and 3. Our *X*, *Y*, and *Z* parameters, therefore, have implications as to the order of the $e_g(xz,yz)$, $a_{1g}(z^2)$, and $b_{2g}(xy)$ molecular orbitals. Clearly, the position of the $E_u(^3B_{1u})$ state in Figure 6 implies that the $b_{2g}(xy)$ orbital is below the $a_{1g}(z^2)$ and $e_g(xz,yz)$ orbitals with the order $b_{1g} >>> a_{1g}(z^2) \gtrsim e_g(xz,yz) > b_{2g}(xy)$ most likely. The order of the $a_{1g}(z^2)$ and $e_g(xz,yz)$ orbitals cannot, however, be specified with certainty. Previously there has been no really sound experimental evidence in the literature supporting a particular order of the d orbitals for $Pt(CN)_4^{2-}$. In fact, the orbital orders suggested in the past were either based on assignments of the $Pt(CN)_4^{2-}$ spectrum which we believe our MCD data have contradicted, or were chosen by analogy to the orders found for $PtCl_4^{2-}$. Since Cl^- and CN^- act quite differently as ligands in metal complexes, drawing conclusions for $Pt(CN)_4^{2-}$ from results for $PtCl_4^{2-}$ is risky. There have been a number of studies of the polarized crystal spectrum of $Pt(CN)_4^{2-}$, but the bands observed differ widely in nature and energy from those found in solution, presumably due to strong Pt-Pt interactions. We were, therefore, not able to make use of these studies.

The simplicity of the $Pt(CN)_4^{2-}$ absorption and MCD spectra lead us to conclude that what we see is largely due to transitions to the $a_{2u}(\pi^*)$ orbital. We have not, however, assigned the shoulder at 41,300 cm^{-1} in the $Pt(CN)_4^{2-}$ absorption spectrum or the corresponding *B* term in the MCD. This might be the lowest energy ligand field transition, $^1A_{1g} \rightarrow {}^1B_{1g}[a_{1g}(z^2) \rightarrow b_{1g}(x^2 - y^2)]$, though the intensity is somewhat high for a d-d transition. However, such a transition could gain significant intensity under a vibronic perturbation by admixture from the nearby E_u states. Intensity could also be gained if the excited state were distorted from D_{4h} symmetry as discussed previously. Alternatively, the shoulder at 41,300 cm^{-1} and the corresponding *B* term in the MCD could be assigned to an $A_{1g} \rightarrow A_{2u}$ transition with the A_{2u} state a mixture derived principally from $A_{2u}(^3E_u[a_{1g} \rightarrow e_u(\pi^*)])$ or $A_{2u}(^3E_u[e_g \rightarrow b_{2u}(\pi^*)])$, $A_{2u}(^1A_{2u}[a_{1g} \rightarrow a_{2u}(\pi^*)])$, and $A_{2u}(^3E_u[e_g \rightarrow a_{2u}(\pi^*)])$. An E_u transition arising largely from the triplet M → L transitions to $e_u(\pi^*)$ with an extremely small *A* term might also fall in this region. Spin-orbit coupling will mix states arising from transitions to $e_u(\pi^*)$ (but not $b_{2u}(\pi^*)$) with those arising from transitions to $a_{2u}(\pi^*)$, if the two states have the same symmetry and if the transitions originate from the same molecular orbital. This mixing should be small since here the spin-orbit coupling matrix elements which determine the mixing coefficients of the states reduce to matrix elements of the type $\langle e_u(\pi^*)\gamma|H_{so}|a_{2u}(\pi^*)\rangle$, where $|e_u(\pi^*)\rangle$ and $|a_{2u}(\pi^*)\rangle$ are molecular orbitals constructed largely from ligand orbitals with only small contributions from the platinum 6p orbitals. Of the many one- and two-center integrals over atomic orbitals to which this matrix element reduces, only the term $\langle 6p_\gamma|\zeta_{6p}\mathbf{l}\cdot\mathbf{s}|6p_z\rangle$ where γ is *x* or *y* will be large, and this term is weighted by small mixing coefficients. Ligand-ligand terms may be neglected to a good approximation since the relevant one-electron spin-orbit coupling constants for nitrogen and carbon are at least an order of magnitude smaller than that for platinum 5d or 6p electrons. Furthermore all two-center terms are negligible.[16] Thus, although E_u states or A_{2u} states arising from transitions to $e_u(\pi^*)$ (but not $b_{2u}(\pi^*)$) would perturb the states calculated earlier assuming no interaction, really major changes in our calculated band positions would not be expected.

For $Ni(CN)_4^{2-}$ *X* and *Y* could be chosen easily since the small spin-orbit coupling produces little change in the band positions (see Figure 5). Reversing the order of $E_u(^3A_{2u})$ and $E_u(^3E_u)$ would be unreasonable because this would leave no significant energy difference between the $^1A_{2u}$ and $^3A_{2u}$ states. We calculate the intensity ratio $A_{2u}1/A_{2u}2$ to be about 3/2, while the $B_{1u}2$ state has ~50 times the singlet character of the $B_{1u}1$ state. $A_{2u}1$ might correspond to the peak M-G observed at 36,000 cm^{-1} in EPA at 77°K.[2]

We assign band 2 as the composite $A_{1g} \rightarrow E_u2 + A_{2u}2 + B_{1u}1$, but since the spin-orbit coupling is small, the intensity is overwhelmingly contributed by $A_{2u}2$. The experimental *A* term is clearly positive, but we are unable to estimate its value, even roughly. Similarly, we assign the band 3 region as the composite $A_{1g} \rightarrow E_u3 + B_{1u}2$. Our justification for assuming that band 3 arises partially from the orbitally forbidden $^1A_{1g} \rightarrow {}^1B_{1u}$ transition is that its intensity seems too large to result from an $A_{1g} \rightarrow E_u3$ transition alone but too small to be that of a fully allowed charge-transfer transition. We are able to estimate the *A* term for band 3 by a gaussian fit with the result $A = 0.054\ D^2\beta$. Unfortunately, because of severe overlapping, there is no possibility of estimating a corresponding *D* value. However, if we compare this experimental *A* value with the theoretical one, $(0.98\ D^2)(0.024\ \beta) \sim 0.024\ D^2\beta$, we note that the agreement is quite reasonable.

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(16) A. A. Misetich and T. Buch, *J. Chem. Phys.*, 41, 2524 (1964).

The value of Z and the position of the $E_u(^3B_{1u})$ state could not be specified precisely. Since band 3 appears to be partially $^1B_{1u}$, Z should be chosen to place $E_u(^3B_{1u})$ somewhere below 31,000 cm^{-1}. In fact, values of Z that place it higher in energy with one exception[17] do not lead to reasonable agreement with our MCD data. We have chosen Z to be 4500 cm^{-1} which places E_u4 at approximately 30,500 cm^{-1}. The relatively weak negative A term associated with this transition is not observed in the MCD, and we suggest that it is obscured by B terms observed in this region.

As in the case of $Pt(CN)_4^{2-}$, spin-orbit coupling will mix states arising from transitions to $e_u(\pi^*)$ (but not $b_{2u}(\pi^*)$) with those derived from transitions to $a_{2u}(\pi^*)$. This would be expected to perturb somewhat the results we have calculated above.

The outstanding feature of the $Pd(CN)_4^{2-}$ absorption spectrum (Figure 2) is its obscurity. In this case, spin-orbit coupling is large enough to give significant intensity to "spin-forbidden" bands. The complexity of the spectrum results perhaps from the lack of composite bands such as those found (by our interpretation) in the $Pt(CN)_4^{2-}$ spectrum. Alternatively (or in addition), the $e_u(\pi^*)$ or $b_{2u}(\pi^*)$ orbitals might be closer in energy to the $a_{2u}(\pi^*)$ orbital than in either $Pt(CN)_4^{2-}$ or $Ni(CN)_4^{2-}$. The rather clear dips in the MCD spectrum at about 41,700 and 45,300 cm^{-1}, which are not mirrored in absorption, are suggestive of the presence of substantial A terms among the overlapping bands. These could be respectively the E_u2 and E_u1 bands which show up clearly in Pt and Ni. In fact, their estimated energy separation and relative magnitudes are consistent with calculations using ζ_{4d} = 1250 cm^{-1} (0.85 of the free ion value). We do not feel it worthwhile at this point to make assignments of the numerous bands in the $Pd(CN)_4^{2-}$ spectrum since no unique interpretation is possible with even the order of the d orbitals so much in doubt. This ion should be an excellent candidate for future study by MCD at low temperature.

Conclusions

The outstanding feature of the MCD spectra of $Pt(CN)_4^{2-}$ and $Ni(CN)_4^{2-}$ is the occurrence of three positive A terms in each, and we have argued that the only reasonable explanation for this lies in the mixing of the E_u states under spin-orbit coupling. A simple model using this idea accounts for the observed results semiquantitatively. In $Ni(CN)_4^{2-}$, spin-orbit coupling accounts for the small A terms in bands 2 and 3, but the basic interpretation of the absorption spectrum given previously[2,3,5] is unchanged. However, for $Pt(CN)_4^{2-}$, substantial changes in the previous assignments are required by the MCD data, the most important of which is the reassignment of the intense band at 46,100 cm^{-1}. In $Pd(CN)_4^{2-}$, the MCD gives some hints regarding the assignments, but the problem of overlapping bands is very severe, and definitive assignments seem impossible at present. It is clear that all of the spectral interpretations would benefit greatly from low-temperature MCD studies, and we hope to be able to report such work in the future. More generally, we feel that the present work demonstrates once again the great power of MCD spectroscopy in clarifying the interpretation of basic features of electronic absorption spectra.

Acknowledgments. We thank Dr. P. J. Stephens for several extremely helpful suggestions regarding interpretation of the MCD data. We are indebted to Mr. D. D. Shillady for performing an extended Hückel calculation on $Pt(CN)_4^{2-}$ and for his comments thereon. One of us (S. B. P.) acknowledges support under an NDEA fellowship. This work was supported by the National Science Foundation.

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(17) If the parameters of Figure 5 are changed to place $E_u(^3B_{1u}) \approx E_u(^3E_u)$, reasonable agreement with the MCD data is possible since the calculated A term for E_u2 (assuming a large pseudo-A contribution also) could swamp the negative A term of E_u4. With such parameters, both E_u2 and E_u4 would lie under band 2, but E_u1, E_u3, $A_{2u}1$, and $A_{2u}2$ would remain much as before. The $^1B_{1u}$ state would then lie much higher than is suggested in Figure 5, and band 3 would be assigned partially to a d–d transition to account for its total intensity. Although this would lead to an order for the d orbitals closer to that of $Pt(CN)_4^{2-}$, it seems a less attractive interpretation since there is no experimental evidence supporting the assignment of band 3 as a ligand field transition.