Q[Nd(SDBM)$_4$] chelates in acetone which appear to be highest for any Nd(III) complex in solution reported in the literature.

The nephelauxetic parameter in Sinha's scale[18] was evaluated for the Nd(III) complexes in the three solvents. In general, the bands undergo red shifts with respect to the aquo ion by more than 200 cm^{-1}. The δ values (average for the different J levels) which are in the range 1.2–1.7% do not bear any definite relationship in the compounds with respect to the solvents.

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Registry No. Nd(SDBM)$_3$·H$_2$O, 59654-74-9; [Nd(SDBM)$_4$](morpH), 59654-76-1; [Nd(SDBM)$_4$](pyrrolH), 59654-77-2; [Eu(SDBM)$_4$](pipH), 59654-79-4; Nd(SDBM)$_3$(phen), 58798-42-8; Nd(SDBM)$_3$(bpy), 59654-80-7; Nd(SDBM)$_3$(N-pyO)$_2$, 59654-81-8; [Eu(SDBM)$_4$](morpH), 59654-82-9; [Eu(SDBM)$_4$](pyrrolH), 59654-83-0; Eu(SDBM)$_3$(bpy), 59654-84-1; Eu(SDBM)$_3$(phen), 59654-85-2; Eu(SDBM)$_3$(N-pyO)$_2$, 59654-86-3; Eu(SDBM)$_3$·H$_2$O, 59654-87-4; [Nd(SDBM)$_4$](pipH), 59654-88-5; [Nd(DBM)$_4$](pipH), 56702-55-7.

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The Electronic Structure of Tetrakis(methyl isocyanide)platinum(II). A Model for the Electronic Structure of Strong Ligand Field d^8 D_{4h} Molecules

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In recent years the electrical properties of one-dimensional inorganic[1–6] and organic[5–8] complexes based on partially oxidized tetracyanoplatinate and 7,7,8,8-tetracyano-p-quinodimethane complexes have received considerable attention. The electronic structure of the tetracyanoplatinate(II) anion has been used as a model for calculations and interpretation of the solid state electronic energy band structure for the highly conducting $K_2Pt(CN)_4X_{0.30}\cdot 3H_2O$ (X = Cl, Br) complex[2,9–12] and as a model for d^8 D_{4h} strong ligand field complexes. Several molecular orbital descriptions for $Pt(CN)_4^{2-}$ have appeared recently which differ in the level ordering for the metal d_{z^2}-like molecular orbital[9,10,13–15] which forms the conducting band in the solid.[12] Recent Xα scattered wave molecular orbital calculations suggest that the d orbitals are ordered as d_{xy} (b_{2g}) > d_{xz}, d_{yz} (e_g) > d_{z^2} (a_{1g}) with an unfilled $d_{x^2-y^2}$ (b_{1g}) orbital at much higher energy.[9,10,13] Results of other molecular orbital calculations also place the unfilled $d_{x^2-y^2}$ at higher energy but order the filled d orbitals as d_{z^2} > d_{xz}, d_{yz} > d_{xy}.[14–16] The excited state levels for strong ligand field d^8 D_{4h} platinum complexes are also subject to question.[17]

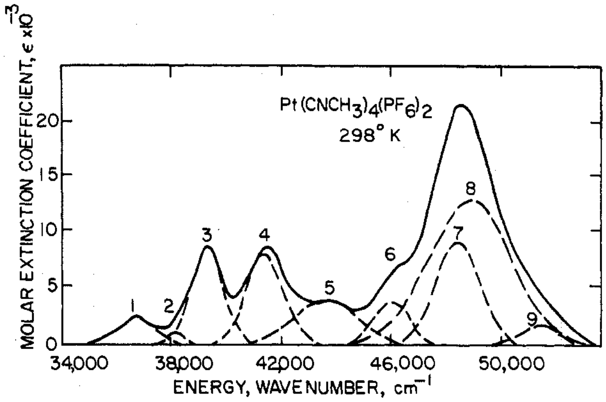

Figure 1. Deconvoluted electronic absorption spectrum of $Pt(CNCH_3)_4(PF_6)_2$ in acetonitrile at room temperature.

Table I. The Electronic Absorption Spectral Parameters for $Pt(CNCH_3)_4(PF_6)_2$[a]

Band	Wavenumber, $\lambda_{\max}$, cm^{-1}	Molar extinction ϵ, l./(mol cm)[b]	Oscillator strength[c]
1	36 730	2360	0.015
2	38 165	955	0.0028
3	39 320	8310	0.042
4	41 435	7890	0.048
5	43 635	3830	0.039
6	46 085	3850	0.021
7	48 460	9110	0.064
8	48 920	12800	0.169
9	51 490	1540	0.010

[a] The hexafluorophosphate anion does not exhibit an absorption below 52 000 cm^{-1}. [b] In acetonitrile. [c] Energy maxima accurate to ±10 cm^{-1}, ϵ and f accurate to ±10%. Oscillator strengths calculated by $f = 4.32 \times 10^{-9} F \int \epsilon \, d\nu$, $F = 9n/(n^2 + 2)^2 = 0.843$: A. Rubinowicz, *Rep. Prog. Phys.*, **12**, 233 (1948–1949).

In order to understand more fully the properties of these highly conducting complexes we have previously investigated the electronic absorption spectra of $Pt(CN)_4^{2-}$,[17] and now report our results for $Pt(CNCH_3)_4^{2+}$,[18] **1**, and a unified state diagram for both complexes.

Results and Discussion

Using computer curve resolving techniques,[17] the room temperature acetonitrile solution spectrum of **1**[19] was deconvoluted into nine Gaussian components (Figure 1, Table I) corresponding to a minimum number of bands to achieve the best fit. This spectrum resembles the deconvoluted absorption spectrum of the tetracyanoplatinate anion, **2**,[17,20] and since the spectrum of **1** is better resolved than **2** it may also serve as a useful model for understanding the electronic structure of d^8 D_{4h} square-planar complexes with strong field ligands.[21] The nine Gaussian bands for **1** are blue shifted with respect to the bands of similar oscillator strength for **2**, due in part to the 4+ charge difference which stabilizes the system

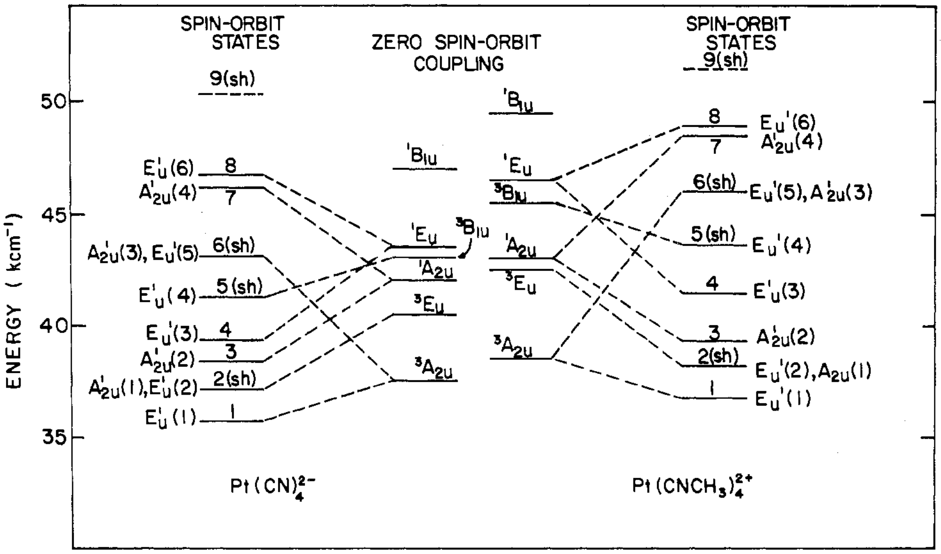

Figure 2. State diagrams consistent with the observed electronic absorption bands and MCD for both $Pt(CNCH_3)_4{}^{2+}$ and $Pt(CN)_4{}^{2-}$. The zero spin-orbit coupling values for the $Pt(CN)_4{}^{2-}$ and $Pt(CNCH_3)_4{}^{2+}$ were taken from the literature[15,16] while (sh) refers to a shoulder in observed spectra which has been deconvoluted into a distinct band.

by lowering the energies of filled molecular orbitals to a greater extent than the empty molecular orbitals.

State diagrams for **1** and **2** involving transitions between the three filled d orbitals[22] and the states arising from the a_{2u} and e_u ligand orbitals are shown in Figure 2. The assignments are consistent with the observed absorption intensities and reported magnetic circular dichroism (MCD) data for both **1** and **2**.[14-16] Energy levels for zero spin-orbit coupling have been reported previously.[15,16] The ordering of the d levels is assumed to be $d_{x^2-y^2} >> d_{z^2} > d_{xz}, d_{yz} > d_{xy}$ in agreement with Piepho et al.[14] and Isci and Mason.[15,16] The ordering of the low-lying unoccupied molecular orbitals is assumed to be $a_{2u} < e_u < b_{1g}$, and there is general agreement that the lowest π^* orbital is the a_{2u}.[9-11,13-16] The ordering of the e_u and b_{1g} orbitals is also consistent with that reported previously.[14,16] The state diagrams are based upon energy, spin, and symmetry considerations, which lead to identical transitions and states for both **1** and **2**, for which spin-forbidden singlet–triplet transitions are assigned to the observed bands of lower oscillator strength. The transitions are presented in Table II along with orbital assignments and excited states. Primes on symmetry labels signify that spin–orbital splitting has been considered.

Bands 1–4 are assigned as transitions between the a_{1g} d orbital and the lowest singlet and triplet a_{2u} and e_u excited states.[23] The lowest energy absorption (band 1) is assigned to $E_u'(1)$ derived mainly from $^3A_{2u}$, in agreement with the assignments of Piepho et al.[14] and Isci and Mason.[15,16] Band 2, previously unreported, is assigned to $E_u'(2)$, $A_{2u}'(1)$ derived principally from ^3E_u. This corresponds to an orbital transition to the $^3e_u\pi^*$ ligand orbital, a departure from previous spectral assignments. The intensity of this band is very weak (Table I) which is consistent with the singlet–triplet assignment. Band 3 is ascribed to $A_{2u}'(2)$ derived mainly from $^1A_{2u}$, which is in agreement with the spin–orbit excited state assignments of Piepho et al.[14] and Isci and Mason,[15,16] although their transitions are derived principally from the ^3E_u. Band 4 is assigned to $E_u'(3)$ derived from ^1E_u, which departs from previous assignments[14-16] involving the $a_{2u}\pi^*$ ligand.

Band 5 is assigned to $E_u'(4)$ corresponding to a $b_{2g} \rightarrow {}^3a_{2u}$ transition. The singlet–triplet transition is consistent with the lower oscillator strength for band 5 as compared to bands 3 and 4 (Table I). Previous theoretical calculations have failed to account for transitions corresponding to this band. Band 6 has a relatively small oscillator strength (Table I), and thus is predicted to be a singlet–triplet transition. The assignment for this band is $E_u'(5)$, $A_{2u}'(3)$, corresponding to $e_g \rightarrow {}^3e_u$. Bands 7 and 8 are intense absorptions assigned as $A_{2u}'(4)$ derived from $e_g \rightarrow {}^1e_u$, and $E_u'(6)$ corresponding to $b_{2g} \rightarrow {}^1e_u$ transitions, respectively. Both bands are symmetry and spin allowed. Band 9 is weak and predicted to be $E_u'(7)$, $A_{2u}'(5)$ derived from either $b_{2g} \rightarrow {}^3e_u$ or $e_g \rightarrow {}^3e_u$ transitions. Band 9 may also be assigned to an $a_{1g} \rightarrow b_{1g}$ d–d transition; however, the intensity seems too large to warrant this assignment, and MCD data are not available to aid in the assignment. Our experimental results[18] place the e_g d levels at 6700 and 5500 cm⁻¹ and the b_{2g} levels at 7920 and 6080 cm⁻¹ below the a_{1g} d levels for **1** and **2**, respectively. This is in good agreement with d–d splitting data previously published for d^8 D_{4h} complexes.[21]

Table II. Transitions and Excited States Derived from $d \rightarrow a_{2u}$ and $d \rightarrow e_u$ Charge Transfer Spectra for $Pt(CNCH_3)_4{}^{2+}$ and $Pt(CN)_4{}^{2-}$

Band	One-electron transition	Excited state symmetry[a]
1	$a_{1g}(d_{z^2}) \rightarrow {}^3a_{2u}$	$E_u'(1)(^3A_{2u})$
2	$a_{1g}(d_{z^2}) \rightarrow {}^3e_u$	$E_u'(2)(^3E_u)$ $A_{2u}'(1)(^3E_u)$
3	$a_{1g}(d_{z^2}) \rightarrow {}^1a_{2u}$	$A_{2u}'(2)(^1A_{2u})$
4	$a_{1g}(d_{z^2}) \rightarrow {}^1e_u$	$E_u'(3)(^1E_u)$
5	$b_{2g}(d_{xy}) \rightarrow {}^3a_{2u}$	$E_u'(4)(^3B_{1u})$
6	$e_g(d_{xz}, d_{yz}) \rightarrow {}^3e_u$	$E_u'(5)(^3A_{2u})(^3A_{1u})$ $(^3B_{2u})(^3B_{1u})$ $A_{2u}'(3)(^3A_{1u})$
7	$e_g(d_{xz}, d_{yz}) \rightarrow {}^1e_u$	$A_{2u}'(4)(^1A_{2u})$
8	$b_{2g}(d_{xy}) \rightarrow {}^1e_u$	$E_u'(6)(^1E_u)$
9	$e_g(d_{xz}, d_{yz}) \rightarrow {}^3e_u$ or	$E_u'(7)(^3A_{2u})(^3A_{1u})$ $(^3B_{2u})(^3B_{1u})$ $A_{2u}'(5)(^3A_{1u})$
	$b_{2g}(d_{xy}) \rightarrow {}^3e_u$ or	$E_u'(7)(^3E_u)$ $A_{2u}'(5)(^3E_u)$
	$a_{1g}(d_{z^2}) \rightarrow b_{1g}\ (d_{x^2-y^2})$	

[a] Primes on symmetry labels indicate spin-orbit states.

These assignments are a departure from those predicted by theoretical calculations based on the $d \rightarrow a_{2u}$ transition model.[9,10,14,15] They are of course based on assumptions regarding the d orbital and π^* ligand orbital ordering. Assignments based upon the d orbital levels previously proposed[9,10,13] with the π^* ligand ordering used here do not correctly predict the experimentally observed intensities and MCD data. Attempts have been made to determine the energy splittings for the three d metal orbitals using ESCA[24] for the isolated tetracyanoplatinate(II) ions in $(Bu_4N)_2Pt(CN)_4$ in the solid state.[17] The results were not useful since a single broad band was observed which could not be deconvoluted into the expected three d levels.

The striking correspondence between the electronic spectra of **1** and **2** suggests in principle that **2** could become partially oxidized to form a highly conducting one-dimensional complex. The dipositive charge on the ion would make $Pt(CNCH_3)_4^{2+}$ more difficult to oxidize with respect to $Pt(CN)_4^{2-}$; however, a number of similar dications have been oxidized by halogen.[25-27] Bromine oxidation of **1**, in contrast to results for **2**, results in the formation of $Pt^{II}(CNCH_3)_3Br^+$,[18,28] presumably through an unstable Pt^{IV} intermediate, with no evidence for the formation of a partially oxidized phase of a stable Pt^{IV} complex. Furthermore, several platinum(IV) isocyanide complexes have been reported to be unstable with respect to dealkylation.[27] Thus, the electronic structure of an isolated complex cannot be used to predict the ability of the ion to undergo partial oxidation.

Both **1** and **2** have similar electronic structures but only the cyano complex has been partially oxidized. Strong band formation must occur in a solid in order to achieve partial oxidation and a metallic state. The formation of such a solid cannot be predicted on the basis of the symmetry and ordering of the electronic structure of the isolated building block of the solid. In order to achieve strong overlap of the d_{z^2}-like wave functions to form a band, the d_{z^2} orbital needs a large spatial extension. This is facilitated by the d^8 third-row transition metals. However, the 4+ charge difference should diminish the overlap of the a_{1g} wave functions between adjacent $Pt(CNCH_3)_4^{2+}$ ions, relative to the overlap of wave functions for those $Pt(CN)_4^{2-}$ ions, thereby decreasing the probability of formation of one-dimensional complexes. These observations are qualitatively borne out by noting[1,4] that the only highly conducting transition metal one-dimensional complexes are based on $5d^8$ Ir^I and Pt^{II} anions.[29-31]

Registry No. $Pt(CNCH_3)_4(PF_6)_2$, 38317-61-2.

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(19) Low-temperature glasses, i.e., EPA and 9:1 $MeOH:H_2O$, alter the spectra presumably through reaction with the alcohol.

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(29) Since only a handful of highly conducting one-dimensional complexes have been reported, it is hoped that these comments will stimulate work to find examples of highly conducting complexes based on cations and of nonthird-row transition metals.

(30) Highly conducting $Hg_{2.86}AsF_6$ which contains an infinite chain of $Hg^{+0.35}$ atoms has been characterized. The mercury atoms are ligand free and the complexes exhibit isotropic conductivity: I. D. Brown, B. D. Cutforth, C. G. Davies, R. J. Gillespie, P. R. Ireland, and J. E. Vekris, *Can. J. Chem.*, **52**, 791 (1974); B. D. Cutforth, W. R. Datars, R. J. Gillespie, and A. Van Schyndel, *Adv. Chem. Ser.*, **No. 150**, 56 (1976).

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Perfluoro(alkylsilanes). 3. Fluorine–Fluorine Coupling Constants in Perfluoro(alkylsilanes) and Related Molecules

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Coupling constants between fluorine atoms in linear and cyclic fluorocarbons and their derivatives have been the subject of numerous investigations in the past 15 years. However, the path to understanding theoretical principles and recognizing molecular parameters which are most influential in determining magnitudes of such couplings has often not been a smooth one. Early workers[3,4] formulated correlations between $^3J_{FF}$ in fluoroethanes with substituent electronegativity without consideration of the relative signs of the coupling constants or of relative free energies of the various rotational conformers. Lack of recognition of magnetic nonequivalence in CF_2 groups[5] and controversy over "through space" interactions[6] have also retarded progress in this area to some extent.

More recently, a variety of workers have demonstrated the marked sensitivity of F–F couplings to stereochemical disposition, both in cyclic and acyclic systems. Long-range couplings have been more widely reported, and theoretical calculations of F–F couplings which include orbital and spin dipolar terms have appeared.[6b,c]

Perfluoroalkanes would seem to be reasonable prototypes for studies of F–F coupling constants; however, the high symmetry of these species can lead to highly complex spin systems. A good illustration is n-C_4F_{10}: the spin system was initially incorrectly assigned.[5] Harris and Woodman[7] subsequently analyzed the spectrum as an $[AA'X_3]_2$ system. The spectrum is of such complexity that, even with the use of ^{13}C satellite spectra as an aid to analysis, definitive values of all the F–F couplings in the molecule could not be obtained.