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Electronic Structure and Spectra of Square-Planar Alkyl Isocyanide Complexes[1]

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Electronic absorption and magnetic circular dichroism (MCD) spectral measurements in acetonitrile are reported for $M(CNR)_4^{n+}$ ($M = Pt(II)$, $R = CH_3, C_2H_5$; $M = Pd(II), Rh(I), Ir(I)$, $R = C_2H_5$) together with some absorption and MCD data for $Pt(CNR)_2(CN)_2$ ($R = C_2H_5$ or $t\text{-}C_4H_9$). These complexes all exhibit intense absorptions in the visible or ultraviolet region which are assigned to metal → ligand (M → L) charge-transfer transitions from the occupied metal d orbitals to the lowest energy π^* CNR orbital (or to both π^* CNR and π^* CN^- in the case of $Pt(CNR)_2(CN)_2$). The M → L spectra are interpreted by means of a model which involves a single π^* CNR acceptor orbital and which includes metal spin–orbit coupling in the M → L excited states. Some spin–orbit calculations are presented for $M(CNC_2H_5)_4^{n+}$ ($M = Pt(II), Pd(II)$, and $Rh(I)$). Spectral assignments are given for each complex and the results are discussed in terms of d-orbital participation in bonding and in terms of the acceptor–donor character of the CNR ligands.

Introduction

Alkyl isocyanide, RNC, ligands are electronically quite similar to CN^-. Both are donor ligands with back-bonding capability *via* empty ligand π^* orbitals and both form complexes which often have similar structures and electronic spectra.[2,3] Square-planar complexes are not exceptional in this regard. Although square-planar cyano complexes have been widely studied,[4,5] there have been few investigations of electronic structure and spectra of comparable alkyl isocyanide complexes. This has probably been a consequence of the lack of good synthetic methods, which have only recently become available.[6] It may be noted that neutral RNC ligands will often stabilize metal ions in lower oxidation states than will anionic CN^- ligands. This feature offers the possibility of extending electronic structural studies to low oxidation states for which cyano complexes are unstable.

In connection with our study of electronic structure and spectra of planar cyano complexes,[4] we have investigated a number of tetrakis(alkyl isocyanide) complexes of ions of the platinum metals of the type $M(CNR)_4^{n+}$ ($M = Pt(II)$, $R = CH_3, C_2H_5$; $M = Pd(II), Rh(I), Ir(I)$, $R = C_2H_5$), and in this paper we report some electronic absorption and magnetic circular dichroism (MCD) measurements. In addition, two bis(alkyl isocyanide)dicyanoplatinum(II) complexes, $Pt(CNC_2H_5)_2(CN)_2$ and $Pt(CN\text{-}t\text{-}C_4H_9)_2(CN)_2$, were prepared and their spectra obtained. The electronic and MCD spectra are interpreted using energy level schemes developed for planar CN^- complexes.[4] These schemes include spin–orbit coupling in metal → ligand (M → L) excited states and involve only the lowest energy π^* RNC orbital in excited configurations. The treatment of spin–orbit coupling follows the approach first suggested by Piepho, Schatz, and McCaffery[7] and used for $Pt(CN)_4^{2-}$.[4,7]

Experimental Section

Preparation of Compounds. Ethyl isocyanide and *tert*-butyl isocyanide ligands were prepared and purified by literature methods[8,9] and were stored in sealed containers below 0° to prevent decomposition or polymerization. We are indebted to Professor P. M. Treichel for a sample of $[Pt(CNCH_3)_4][BF_4]_2$, the synthesis and characterization of which have been published.[6] Triethyloxonium tetrafluoroborate, $[(C_2H_5)_3O][BF_4]$, was obtained from Alfa Inorganics. Unless otherwise noted all other reagents were of reagent grade.

Tetrakis(ethyl isocyanide)platinum(II) Tetrafluoroborate, $[Pt(CNC_2H_5)_4][BF_4]_2$, and Tetrakis(ethyl isocyanide)palladium(II) Tetrafluoroborate, $[Pd(CNC_2H_5)_4][BF_4]_2$. An anhydrous dichloromethane solution of $[(n\text{-}C_4H_9)_4N]_2[M(CN)_4]$ ($M = Pt, Pd$)[10] was treated with a sixfold excess of triethyloxonium tetrafluoroborate and the solution refluxed for 5 hr. The solvent was evaporated, and the residue dissolved in a minimum amount of acetonitrile. After the solution was filtered free of small amounts of insoluble matter, ethyl acetate was added, whereupon a crystalline precipitate was formed. White crystals were collected by filtration, washed with ethyl acetate and anhydrous ether, and dried *in vacuo* at room temperature. *Anal.* Calcd for $[Pt(CNC_2H_5)_4][BF_4]_2$: C, 24.47; H, 3.42; N, 9.51; Pt, 33.12. Found: C, 24.48; H, 3.40; N, 9.32; Pt, 32.98. Calcd for $[Pd(CNC_2H_5)_4][BF_4]_2$: C, 28.81; H, 4.03; N, 11.20; Pd, 21.27. Found: C, 28.57; H, 3.96; N, 11.42; Pd, 21.46.

Tetrakis(ethyl isocyanide)rhodium(I) Perchlorate, $[Rh(CNC_2H_5)_4]ClO_4$. Hydrated rhodium chloride, $RhCl_3 \cdot nH_2O$ (D. F. Goldsmith Chemical and Metal Corp., Evanston, Ill.), was dissolved in absolute ethanol and treated with excess ethyl isocyanide. After refluxing 0.5 hr, the resulting dark solution was cooled to room temperature and filtered to remove insoluble matter. A saturated ethanol solution of ammonium perchlorate was added dropwise until precipitation was complete. The dark blue solid was collected by suction filtration, washed with ice-cold absolute ethanol and anhydrous ether, and dried *in vacuo* at room temperature for about 12 hr. *Anal.* Calcd for $[Rh(CNC_2H_5)_4]ClO_4 \cdot 0.14NH_4ClO_4$: C, 32.79; H, 4.72; N, 13.20. Found: C, 32.87; H, 4.40; N, 13.05.

Tetrakis(ethyl isocyanide)iridium(I) Chloride, $[Ir(CNC_2H_5)_4]Cl$. Excess ethyl isocyanide was slowly added to a dichloromethane solution of $[(n\text{-}C_4H_9)_4N][cis\text{-}Ir(CO)_2Cl_2]$.[11] A dark blue precipitate formed immediately which was separated by suction filtration, washed with ice-cold dichloromethane and anhydrous ether, and dried *in vacuo* overnight. *Anal.* Calcd for $[Ir(CNC_2H_5)_4]Cl$: C, 32.17; H, 4.50; N, 12.51; Cl, 7.91; Ir, 42.90. Found: C, 32.54; H, 4.70; N, 12.27; Cl, 7.52; Ir, 42.97 (by difference).

The perchlorate salt was prepared by the addition of a saturated aqueous ammonium perchlorate solution to a freshly prepared solution of $[Ir(CNC_2H_5)_4]Cl$ in water. The dark blue solid was collected and washed with a few drops of ice water, absolute ethanol, and anhydrous ether. *Anal.* Calcd for $[Ir(CNC_2H_5)_4]ClO_4 \cdot 0.14NH_4ClO_4$: C, 27.24; H, 3.92; N, 10.97. Found: C, 27.16; H, 3.90; N, 10.47.

Dicyanobis(*tert*-butyl isocyanide)platium(II), $Pt(CN\text{-}t\text{-}C_4H_9)_2(CN)_2$. A sixfold excess *tert*-butyl isocyanide was gradually added to a solution of $[(n\text{-}C_4H_9)_4N]_2[PtCl_4]$[10] in dichloromethane. The formation of a dark red precipitate was observed within 5 min, but over a period of 0.5 hr at reflux temperature, a colorless solution was obtained. The solvent was evaporated under reduced pressure at room temperature, and the remaining fluorescent yellow solid was recrystallized from hot acetonitrile. *Anal.* Calcd for $Pt(CN\text{-}t\text{-}C_4H_9)_2(CN)_2$: C, 34.86; H, 4.39; N, 13.55; Pt, 47.19. Found: C, 34.12; H, 4.43; N, 13.56; Pt, 47.25. Conductance (acetonitrile): $\Lambda_M = 10\ \text{cm}^2\ \text{ohm}^{-1}\ \text{mol}^{-1}$.

Dicyanobis(ethyl isocyanide)platium(II), $Pt(CNC_2H_5)_2(CN)_2$. A dichloromethane solution of $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$[9] was treated with a 2:1 stoichiometric amount of triethyloxonium tetrafluoroborate. Following a 4-hr reflux period, the resulting colorless solution was evaporated to dryness on a steam bath giving a crude fluorescent yellow solid. Any remaining triethyloxonium tetrafluoroborate was washed off with excess tetrahydro-2-methylfuran. The remaining solid was washed with benzene. A white fluorescent solid, which was insoluble in benzene, remained after thorough washing. The solid was dried at room temperature *in vacuo*. *Anal.* Calcd for $Pt(CNC_2H_5)_2(CN)_2$: C, 26.89; H, 2.82; N, 15.68; Pt, 54.60. Found:

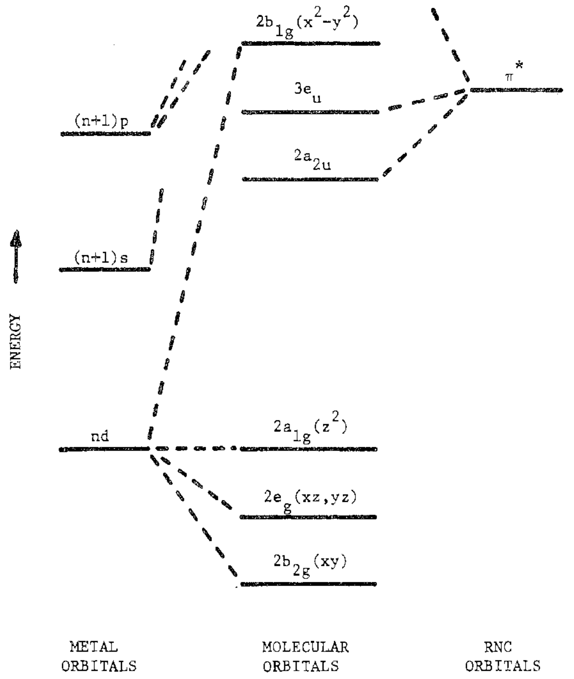

Figure 1. Simplified molecular orbital energy level diagram for $M(CNR)_4{}^{n+}$ complexes.

C, 27.25; H, 2.91; N, 15.41; Pt, 54.48. Conductance (acetonitrile): $\Lambda_M = 6$ cm^2 ohm^{-1} mol^{-1}.

The white compound was also prepared by refluxing a solution of $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$[11] in ethyl iodide for about 2 days. A white solid was obtained on cooling the yellow solution to ice-bath temperature. The absorption spectrum of this product in acetonitrile was identical with that of the product of the preparation described above.

Spectral Measurements. Solutions for absorption and MCD spectra were prepared using spectral grade solvents. Absorption spectra were measured on a Cary 1501 spectrophotometer and MCD measurements were made with a Durrum-Jasco ORD/UV-5 (with CD attachment) equipped with a permanent magnet (field = 10 kG) as described previously.[12] Infrared measurements were made on a Beckman IR 12 spectrophotometer using either Nujol mulls spread on cesium iodide plates or pressed potassium bromide pellets.

Spin-Orbit Calculations. The treatment of spin-orbit interaction in M → L excited states together with the appropriate Hermitian secular determinants is described in our previous paper.[4] As noted there, the approach is the same as taken by Piepho, *et al.*,[7] in the treatment of spin-orbit coupling in the excited states of $Pt(CN)_4{}^{2-}$. Input parameters consisted of energies of the unperturbed M → L singlet or triplet states and a value of the metal spin-orbit coupling constant ζ_{nd}. Successful parameters were those which resulted in a satisfactory fit of excited spin-orbit states to experimental absorption spectra and in addition gave excited states consistent with the MCD *A* and/or *B* terms observed. For example the appearance of an *A* term in the MCD is consistent only with a degenerate state.

Results and Discussion

Molecular Orbital Energy Levels. The $M(CNR)_4{}^{n+}$ complexes are all assumed to have D_{4h} symmetry, and the metal and ligand orbitals important in bonding are expected to be analogous to those in the planar $M(CN)_4{}^{n-}$ complexes. Consequently, a molecular orbital energy level diagram for the alkyl isocyanide complexes will be similar to the diagrams previously given for the $M(CN)_4{}^{n-}$ complexes.[10] A simplified version of this diagram, which will be useful for visualizing excited configurations, is given in Figure 1. The highest filled level is $2a_{1g}(z^2)$, and the ground states of the complexes described here, all of which have a d^8-electron configuration, are diamagnetic and are designated $^1A_{1g}$. Excited states which are allowed by dipole selection rules in D_{4h} symmetry are E_u (*x*, *y* polarized) and A_{2u} (*z* polarized). On inclusion of metal spin-orbit coupling, transitions to formally spin-forbidden "triplet" states may gain considerable intensity by admixture of "singlet" states.

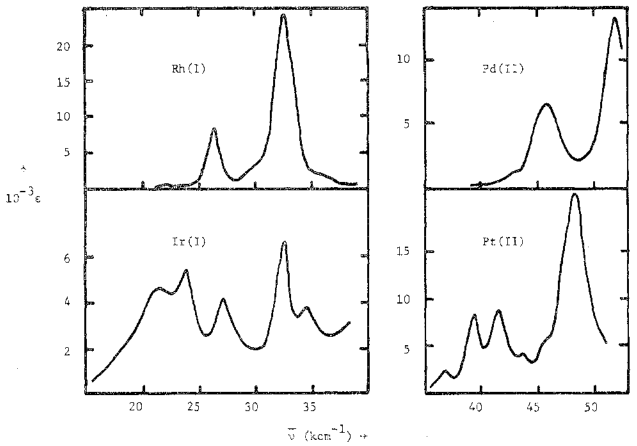

Figure 2. Electronic absorption spectra for $M(CNC_2H_5)_4{}^{n+}$ complexes in acetonitrile solution.

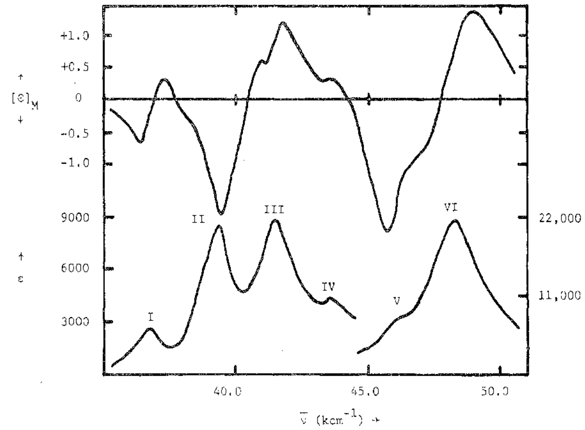

Figure 3. Absorption (lower curve) and MCD (upper curve) spectra for $[Pt(CNC_2H_5)_4][BF_4]_2$ in acetonitrile solution.

Electronic Absorption and MCD Spectra. Electronic absorption spectra for $M(CNC_2H_5)_4{}^{n+}$ complexes in acetonitrile are presented in Figure 2. Some measurements were also made on aqueous solutions of $Pt(CNR)_4{}^{2+}$ (R = CH_3 or C_2H_5), but these solutions were not stable and changes in the spectra were noted after about 0.5 hr. Solutions containing the $Ir(CNC_2H_5)_4{}^+$ ion were particularly sensitive to light. Marked changes in spectra were noted after only short exposure (1–2 min) to light. Consequently measurements were made on fresh solutions prepared in the dark and carefully protected from light. Figures 3–5 present the MCD spectra of $M(CNC_2H_5)_4{}^{n+}$ (M = Pt(II), Pd(II) and Rh(I)) in acetonitrile; MCD data could not be obtained for $Ir(CNC_2H_5)_4{}^+$ because solutions were not sufficiently stable for the time required for measurement. Both *A* and *B* terms are observed in the spectra of the Pt(II) and Rh(I) complexes, but only *B* terms were apparent at energies accessible to measurement for the Pd(II) complex. Not unexpectedly absorption and MCD measurements for $Pt(CNCH_3)_4{}^{2+}$ were nearly identical with those for $Pt(CNC_2H_5)_4{}^{2+}$.

Detailed spectral data and band assignments are collected in Table I, along with spectral data for the $Pt(CNR)_2(CN)_2$ (R = C_2H_5 or *t*-C_4H_9) complexes.

Spectral Assignments. The intense bands in the spectra of the $M(CNR)_4{}^{n+}$ complexes are quite similar to those observed in the square-planar tetracyanometalates[4,10] and are logically assigned as M → L charge-transfer transitions from occupied metal d orbitals to the lowest empty π^* CNR orbital, $2a_{2u}$ in Figure 1. These transitions consist of $^1A_{1g} \rightarrow {}^{1,3}A_{2u}$ $[2a_{1g}(z^2)$

Table I. Spectral Data and Band Assignments

Band	$\bar{\nu}$ (ϵ),[a] kK (M^{-1} cm^{-1})	Obsd MCD term	Excited-state assgnmt	Band	$\bar{\nu}$ (ϵ),[a] kK (M^{-1} cm^{-1})	Obsd MCD term	Excited-state assgnmt
	$[Pt(CNCH_3)_4][BF_4]_2$				$[Pt(CNC_2H_5)_4][BF_4]_2$		
I	36.75 (2080)	$+A$	$E_u(1)$	I	36.70 (2670)	$+A$	$E_u(1)$
II	39.40 (7490)	$+B$	$A_{2u}(1)$	II	39.30 (8550)	$+B$	$A_{2u}(1)$
III	41.60 (7060)	$-B$, $+A$	$E_u(2)$	III	41.45 (8880)	$-B$, $+A$	$E_u(2)$
IV	43.70 (3400)	$-B$?	$E_u(2) + \nu_{CN}$	IV	43.50 (4275)	$-B$?	$E_u(2) + \nu_{CN}$
V	46.50 (6350)[b]	$+B$	$A_{2u}(2)$	V	46.25 (7940)[b]	$+B$	$A_{2u}(2)$
VI	48.70 (18,600)	$+A$	$E_u(4)$	VI	48.25 (22,000)	$+A$	$E_u(4)$
	$[Pd(CNC_2H_5)_4][BF_4]_2$				$[Rh(CNC_2H_5)_4][ClO_4]$		
I	42.80 (1280)[b]	$+B$	$E_u(1)$	I	23.00 (260)	$+B$	$E_u(1)$
II	45.65 (6600)	$+B$	$A_{2u}(1)$	II	26.30 (8400)	$+B$	$A_{2u}(1)$
III	51.65 (13,720)		$E_u(4)$	III	30.00 (3450)[b]	$-B$	$A_{2u}(2)$, $E_u(2)$
	$[Ir(CNC_2H_5)_4][ClO_4]$[c]			IV	32.50 (24,350)	$+A$	$E_u(4)$
I	21.40 (4600)		$E_u(1)$	V	35.50 (2100)[b]	$-A$	$E_u(3)$
II	23.80 (5500)		$A_{2u}(1)$				
III	27.05 (4170)		$E_u(2)$				
IV	32.50 (6670)		$E_u(4)$				
V	34.55 (3850)		$A_{2u}(2)$				

Band	ν (ϵ),[a] kK (M^{-1} cm^{-1})	Obsd MCD term	ν (ϵ),[a] kK (M^{-1} cm^{-1})	Obsd MCD term	Excited-state assgnmt[d]
	$Pt(CNC_2H_5)_2(CN)_2$[e]		$Pt(CN\text{-}t\text{-}C_4H_9)_2(CN)_2$[e]		
I	35.75 (1790)	$+B$	35.75 (2000)	$+B$	$B_{2u}(1)$, $B_{3u}(1)$
II	38.50 (7230)[b]	$+B\}^{f}$	38.25 (8500)[b]	$+B\}^{f}$	$B_{1u}(1)$
III	39.35 (10,000)	$-B\}$	39.25 (11,150)	$-B\}$	$B_{2u}(2)$, $B_{3u}(2)$
IV	41.25 (2500)[b]	$-B$	41.25 (2880)[b]	$-B$	III + ν_{CN} or III + ν_{CNR}
V	46.00 (19,660)	$+B$, $-B$[f]	45.95 (21,450)	$+B$, $-B$[f]	$B_{2u}(4)$, $B_{3u}(4)$, $B_{1u}(4)$

[a] Acetonitrile solution, 24°. [b] Shoulder. [c] Solution photosensitivity precluded MCD measurements. [d] Two sets of states with the same symmetry designations and nearly the same energy are expected, one for transitions to π^* CNR and the other for transitions to π^* CN$^-$; only one set is listed here. [e] Structure assumed to be trans. [f] Pseudo A term.

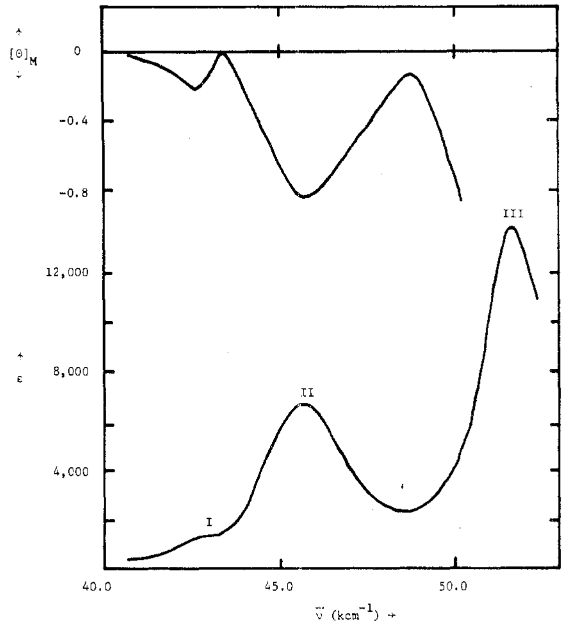

Figure 4. Absorption (lower curve) and MCD (upper curve) spectra for $[Pd(CNC_2H_5)_4][BF_4]_2$ in acetonitrile solution.

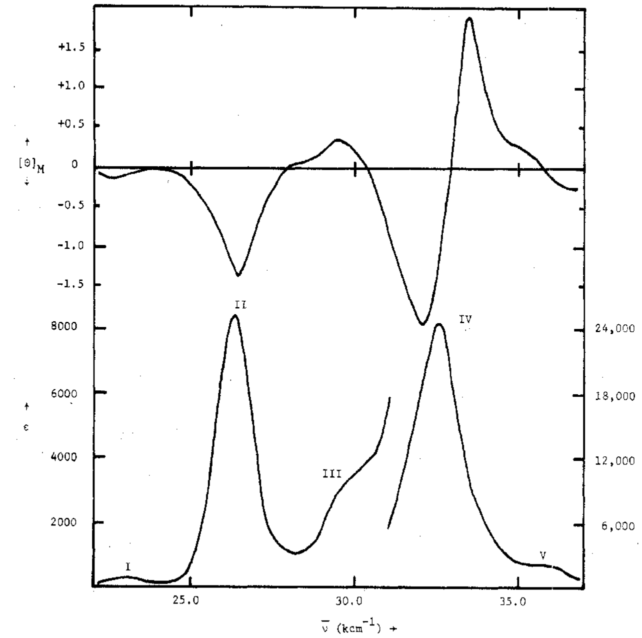

Figure 5. Absorption (lower curves) and MCD (upper curve) spectra for $[Rh(CNC_2H_5)_4][ClO_4]$ in acetonitrile solution.

→ 2a$_{2u}$], $^1A_{1g}$ → $^{1,3}E_u$ [2e$_g$(xz, yz) → 2a$_{2u}$], and $^1A_{1g}$ → $^{1,3}B_{1u}$ [2b$_{2g}$(xy) → 2a$_{2u}$]. Consistent with this assignment, the characteristic blue shift in the spectra between isoelectronic complexes is observed as the metal oxidation state is increased. Figure 2 shows that the spectrum of $Pd(CNC_2H_5)_4^{2+}$ or $Pt(CNC_2H_5)_4^{2+}$ is blue shifted by approximately 15 kK compared to isoelectronic $Rh(CNC_2H_5)_4^+$ or $Ir(CNC_2H_5)_4^+$, respectively. Further, Figure 2 shows a greater number of bands and higher relative intensities of some of the low-energy bands for the third-row complexes compared to those of the second row. These differences may be offered as an indication of an increase in the importance of metal spin–orbit coupling in the heavier complexes since spin–orbit effects will give rise to excited-state energy splitting and allow spin-forbidden transitions to gain intensity. Free-ion spin–orbit coupling constants range from ~1200–1600 cm^{-1} for Rh(I) and Pd(II) to over 4000 cm^{-1} for Ir(I) and Pt(II).[13] In the case of Pt(II), a successful interpretation of M → L charge-transfer spectra in cyano and cyanoamine complexes required the detailed consideration of spin–orbit coupling in M → L excited states.[4] Therefore some spin–orbit calculations were performed for the

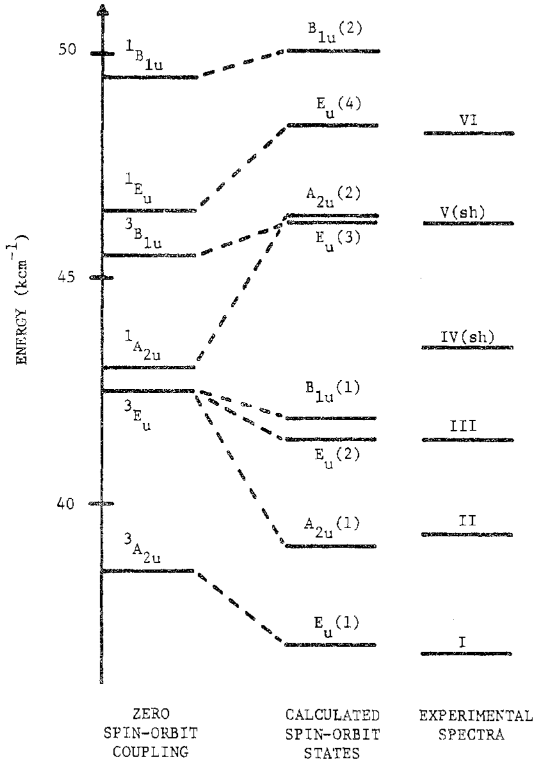

Figure 6. Spin-orbit states for $Pt(CNC_2H_5)_4^{2+}$. Input parameters for the calculated states (in kK): $\zeta = 3.0$; $^1B_{1u}$, 49.5; $^3B_{1u}$, 45.5; ^1E_u, 46.5; ^3E_u, 42.5; $^1A_{2u}$, 43.0; $^3A_{2u}$, 38.5. Experimental absorption spectral data for acetonitrile solution.

$M(CNC_2H_5)_4^{n+}$ (M = Rh(I), Pd(II), and Pt(II)) complexes. Following the treatment of Piepho, *et al.*,[7] for $Pt(CN)_4^{2-}$, only the lowest energy π^* CNR acceptor orbital was used in excited configurations. Calculated energies of the spin-orbit states are plotted in Figures 6–8, together with the experimental spectra; successful input parameters are given in the figure captions. Calculated spin-orbit energies and mixing coefficients are collected in Table II.[14] These results served as a guide to formulating the band assignments for the M → L spectra given in Table I. These assignments will be briefly discussed for each complex.

$Pt(CNC_2H_5)_4^{2+}$. Calculated spin-orbit energies for $Pt(CNC_2H_5)_4^{2+}$ are given in Figure 6. The results are quite similar to those for $Pt(CN)_4^{2-}$,[4,7] and the pattern of assignments, therefore, will also be similar. Band I is assigned to $E_u(1)$, derived mainly from $^3A_{2u}$. The positive *A* term in the MCD is predicted for a transition to this state.[4,7] The low intensity is rationalized from the small amount of singlet character (3.2% ^1E_u) predicted by the mixing coefficients (Table II[14]). Band II is ascribed to $A_{2u}(1)$, while band III is assigned to $E_u(2)$. The MCD is interpreted as having a positive *B* term for band II and a negative *B* term together with a smaller positive *A* term for band III. This latter feature is not very clear in the MCD, but the dip in the positive part of the curve near the energy of band III can be taken as resulting from the negative portion of the positive *A* term. If this interpretation is correct, then band II and band III are analogous to the 38.5-kK band in $Pt(CN)_4^{2-}$ which shows a strong positive *A* term ascribed to a positive *A* term and a positive pseudo *A* term (two overlapping *B* terms of opposite sign arising from adjacent states close in energy).[4] In the case of $Pt(CNC_2H_5)_4^{2+}$ instead of a pseudo *A* term, two separate *B* terms of opposite sign are observed because of a greater energy separation between the $A_{2u}(1)$ and $E_u(2)$ states. Nevertheless the lower energy *B* term is expected to be positive and the higher energy one negative (the signs of the MCD

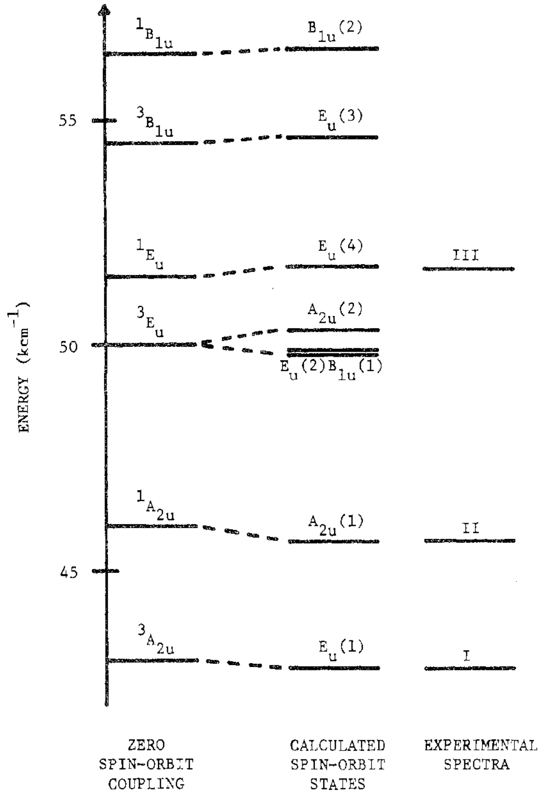

Figure 7. Spin-orbit states for $Pd(CNC_2H_5)_4^{2+}$. Input parameters for the calculated states (in kK): $\zeta = 1.0$; $^1B_{1u}$, 56.5; $^3B_{1u}$, 54.5; ^1E_u, 51.5; ^3E_u, 50.0; $^1A_{2u}$, 46.0; $^3A_{2u}$, 43.0. Experimental absorption spectral data for acetonitrile solution.

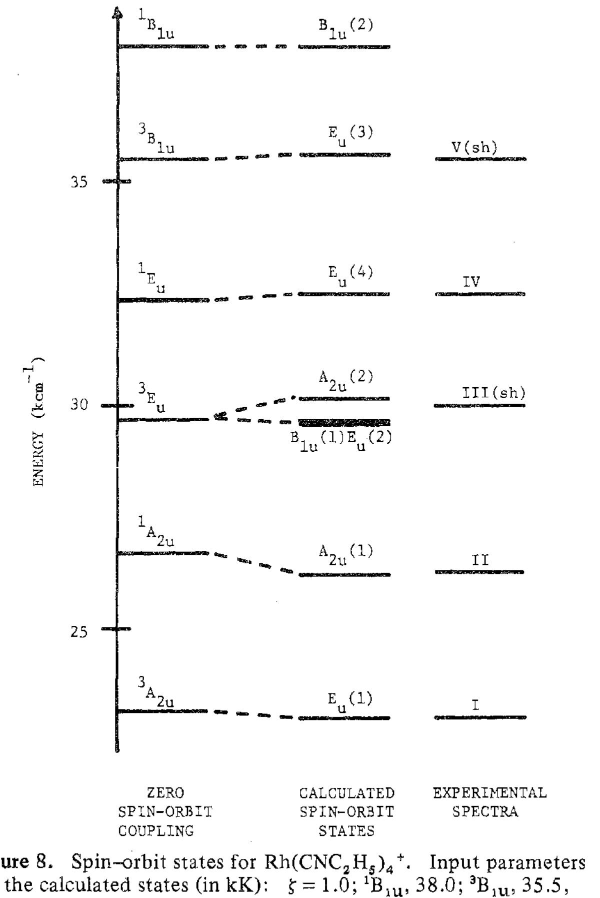

Figure 8. Spin-orbit states for $Rh(CNC_2H_5)_4^+$. Input parameters for the calculated states (in kK): $\zeta = 1.0$; $^1B_{1u}$, 38.0; $^3B_{1u}$, 35.5, ^1E_u, 32.4; ^3E_u, 29.7; $^1A_{2u}$, 26.7; $^3A_{2u}$, 23.4. Experimental absorption spectral data for acetonitrile solution.

spectra being negative and positive, respectively) if the major interaction in the presence of the magnetic field is between $A_{2u}(1)$ and $E_u(2)$. The interaction of $A_{2u}(i)$ and $E_u(i)$ states has been discussed more fully elsewhere.[4,7]

Bands V and VI are assigned to $A_{2u}(2)$ and $E_u(4)$, respectively. The MCD shows a positive *B* term for band V though it is overlapping with the positive *A* term for band VI. There is undoubtedly interaction between these states in the presence of the magnetic field as described above for $A_{2u}(1)$ and $E_u(2)$, and the interaction is expected to give a positive *B* term for $A_{2u}(2)$ and a negative *B* term for $E_u(4)$. The *A* term predicted for $E_u(4)$ is expected to be positive, in agreement with experiment.

Band IV is not accounted for in the spin–orbit model. The energy of this band 2050 cm^{-1} higher than band III suggests an assignment to an excited ligand vibrational state built on $E_u(2)$; a similar assignment was suggested for a corresponding band at 41.5 kK for $Pt(CN)_4{}^{2-}$. A ligand field transition assignment for band IV is considered unlikely since ligand field bands in CNR complexes, like CN^- complexes, are expected to be above 50 kK for Pt(II).[4,10] The assignments for $Pt(CNCH_3)_4{}^{2+}$ are analogous to those for $Pt(CNC_2H_5)_4{}^{2+}$.

$Ir(CNC_2H_5)_4{}^+$. As noted above the solutions of $Ir(CNC_2H_5)_4{}^+$ were highly photosensitive, and in spite of precautions, noticeable intensity changes in the spectra were observed in only a short time after solution preparation. Consequently the spectral data for this complex are less precise and did not warrant a detailed spin–orbit calculation. Since the spin–orbit coupling constant for Ir(I) is similar to that for Pt(II), the band assignments are expected to be substantially the same as for $Pt(CNC_2H_5)_4{}^{2+}$. Therefore the assignments given in Table I were made by comparison with the platinum complex.

$Pd(CNC_2H_5)_4{}^{2+}$ and $Rh(CNC_2H_5)_4{}^+$. Since the spin–orbit coupling constants for Pd(II) and Rh(I) are smaller than for Pt(II) and Ir(I), the calculated spin–orbit states are very nearly the same as the unperturbed singlet and triplet states, as shown in Figure 7 for $Pd(CNC_2H_5)_4{}^{2+}$ and Figure 8 for $Rh(CNC_2H_5)_4{}^+$. The lowest energy band, band I, in both complexes, which is mainly $^3A_{2u}$ and derives its intensity from the spin–orbit mixing with ^1E_u, is relatively less intense, consistent with the lower spin–orbit coupling.

Band II in both the Pd(II) complex and the Rh(I) complex is assigned to $A_{2u}(1)$ which is mainly $^1A_{2u}$. The MCD very clearly shows *B* terms for both complexes, consistent with this assignment. Band IV for $Rh(CNC_2H_5)_4{}^+$ shows a positive *A* term in the MCD and therefore is assigned to $E_u(4)$ which is mainly ^1E_u. Band III, then, is assigned to the states arising from ^3E_u. Band V in the $Rh(CNC_2H_5)_4{}^+$ spectra is a weak, but quite distinct, shoulder on the high-energy side of band IV. The $E_u(3)$ state arising from $^3B_{1u}$ is placed near this energy. It has been pointed out that the *A* term expected for a transition to this state is predicted to be negative.[4,7] The MCD in the region of band V is weak but shows a distinct negative *A* term, therefore supporting this assignment.

$Pt(CNR)_2(CN)_2$. The bis(alkyl isocyanide)dicyano complexes also exhibit intense M → L charge-transfer bands, similar in pattern to those of $Pt(CN)_4{}^{2-}$.[4] In fact, except for band II, the distinct shoulder on the low-energy side of band III, the absorption spectra of $Pt(CNR)_2(CN)_2$ are nearly identical with that of $Pt(CN)_4{}^{2-}$. The MCD spectra are also quite similar, but apparent *A* terms for bands II and III and for band V of the bis complexes must be ascribed to pseudo *A* terms because there will be no strictly degenerate levels in the lower symmetry of these complexes.

Although the structure of the bis complexes is not known, it is likely that the *tert*-butyl isocyanide complex is trans, since a cis geometry would offer severe ligand repulsions. The remarkable similarity between the spectral data (Table I) of $Pt(CN\text{-}t\text{-}C_4H_9)_2(CN)_2$ and $Pt(CNC_2H_5)_2(CN)_2$ suggests the complexes have the same structure. The infrared spectra of both complexes show a single RNC and a single CN^- C–N stretching frequency, consistent with a trans geometry. Therefore the electronic spectra were assigned assuming both complexes are trans (D_{2h} symmetry). The excited states appropriate for the D_{2h} trans geometry have been given previously.[4] The close correspondence between the spectra of the bis complexes and $Pt(CN)_4{}^{2-}$ indicates that the π^* CN^- and π^* CNR acceptor orbitals are at nearly the same energy. Consequently, the M → L transitions to the two types of ligands are virtually coincident and indistinguishable. The band assignments for the $Pt(CNR)_2(CN)_2$ complexes were made by comparison with $Pt(CN)_4{}^{2-}$.

Bonding and Electronic Structure in Planar Alkyl Isocyanide Complexes. The characteristically similar pattern of M → L charge-transfer transitions observed for $M(CNR)_4{}^{n+}$ and $Pt(CNR)_2(CN)_2$ and the similarity of this pattern to that observed[4] for $Pt(CN)_4{}^{2-}$ suggests common features for the origin and terminus of the transitions. The success of the spin–orbit model used here for the interpretation and assignment of the $M(CNR)_4{}^{n+}$ spectra and previously[4] for $Pt(CN)_4{}^{2-}$ and various cyanoamineplatinum(II) complexes indicates that to a good approximation the M → L excited states involve a single low-energy π^* ligand acceptor orbital in excited configurations, *viz.*, $2a_{2u}$ (or its counterpart in lower symmetry complexes). Therefore the marked similarity in the spectra originates from a similarity in placement of the occupied metal d orbitals from which the M → L transitions originate. If electron repulsion differences in M → L excited states of the same spin multiplicity are assumed to be small, then the energy ordering of the excited states can be used to determine the relative energies of the occupied metal d orbitals. The order of singlet (or triplet) excited states for the $M(CNR)_4{}^{n+}$ complexes indicated by the successful input parameters in Figures 6–8 is $^1B_{1u}(d_{xy} \rightarrow 2a_{2u}) > {}^1E_1(d_{xz}d_{yz} \rightarrow 2a_{2u}) > {}^1A_{2u}(d_{z^2} \rightarrow 2a_{2u})$ and therefore indicates the order $d_{z^2} > d_{xz}d_{yz} > d_{xy}$. Essentially the same order is indicated for $Pt(CNR)_2(CN)_2$, except the $d_{xz}d_{yz}$ degeneracy is expected to be lifted. This order of occupied d orbitals was also found for $Pt(CN)_4{}^{2-}$, where it was concluded that the d_{z^2} orbital was nearly nonbonding.[4] The d_{z^2} orbital in the RNC complexes is also expected to be nearly nonbonding or only very weakly σ antibonding, since the RNC ligands are weaker σ donors than CN^-. Thus, the stabilization of the d_π orbitals (d_{xz}, d_{yz}, and d_{xy}) relative to d_{z^2} is consistent with the participation of these orbitals in M → L π bonding. The degree of stabilization of the d_π levels compared to that of d_{z^2} (the occupied d-orbital splitting, assuming a nearly nonbonding d_{z^2}) is somewhat larger in the RNC complexes than in $Pt(CN)_4{}^{2-}$ and several cyanoamineplatinum(II) complexes. Based on energy differences between appropriate excited states ($^1A_{2u}$ and ^1E_u or $^1B_{1u}$ in $Pt(CN)_4{}^{2-}$, for example) and ignoring electron repulsion differences, the maximum d_π orbital stabilization relative to d_{z^2} was estimated to be no larger than 5–7 kK for $Pt(CN)_4{}^{2-}$ and the cyanoamineplatinum(II) complexes.[4] Comparable estimates of the maximum d_π orbital stabilization for the $M(CNR)_4{}^{n+}$ complexes range from ~7 kK for Pt(II) and Ir(I) to 10–13 kK for Pd(II) and Rh(I). This suggests a slightly higher degree of M → L π bonding for RNC compared to that for CN^-, which is not surprising since the neutral RNC ligand is believed to be a stronger π acid than the anionic CN^- ligand. The stronger π-acid character of RNC may also be responsible for the small but definite (1–3 kK) blue shift in corresponding M → L charge-transfer bands in $Pt(CNR)_4{}^{2+}$ compared to that in $Pt(CN)_4{}^{2-}$ (band I, for example, the lowest energy band in both complexes is at 35.5 kK for $Pt(CN)_4{}^{2-}$ [4] but at 36.7

Table III. Infrared Spectral Data for Some Square-Planar Cyanide and Alkyl Isocyanide Complexes

Compd	$\bar{\nu}_{CN}$- (CN$^-$), cm^{-1}	$\bar{\nu}_{CN}$- (CNR), cm^{-1}	Matrix
$[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$	2128		Nujol
$[Pt(CNCH_3)_4][BF_4]_2$		2308	KBr
$[Pt(CNC_2H_5)_4][BF_4]_2$		2280	KBr
$[Pd(CNC_2H_5)_4][BF_4]_2$		2280	KBr
$[Rh(CNC_2H_5)_4][ClO_4]$		2250	KBr
$[Ir(CNC_2H_5)_4][ClO_4]$		2240	KBr
$[Pt(CNC_2H_5)_4][Pt(CN)_4]^a$	2138	2290	KBr
$[Pt(CN\text{-}t\text{-}C_4H_9)_4][Pt(CN)_4]^a$	2132	2280	Nujol
$Pt(CNC_2H_5)_2(CN)_2$	2162	2285	KBr
$Pt(CN\text{-}t\text{-}C_4H_9)_2(CN)_2$	2178	2270	KBr

[a] Data from ref 15.

kK for $Pt(CNC_2H_5)_4^{2+}$, both in acetonitrile solution). The lack of resolution of separate M → L_{CN^-} and M → L_{CNR} transitions in the spectra of the $Pt(CNR)_2(CN)_2$ complexes indicate the π^* CN^- orbitals must be very close in energy. Consequently, the blue shift is likely due to slightly greater metal orbital stability in $Pt(CNR)_4^{2+}$ resulting from a greater positive charge on the metal than in $Pt(CN)_4^{2-}$.

The stabilization of the $d\pi$ orbitals, and consequently their participation in M → L bonding, appears to be somewhat greater for Rh(I) and Pd(II) than for Pt(II) or Ir(I). Thus, ^1E_u or $^1B_{1u}$ (or the corresponding triplet states) is *relatively* higher in energy compared to $^1A_{2u}$ (or $^3A_{2u}$) in the second-row complexes than for the third-row complexes. This is likely due to a more favorable $4d\pi$–$L\pi^*$ overlap than $5d\pi$–$L\pi^*$. More puzzling, however, is the indication of very little difference in the relative energies of the d_{z^2} and the $d\pi$ orbitals between Rh(I) and Pd(II); the same appears true for Ir(I) and Pt(II) as judged from the similarity between the relative energies of corresponding M → L transitions. This feature may reflect nearly compensating changes in σ bonding (affecting the energy of the nearly nonbonding d_{z^2} level) and π bonding (affecting the energy of the $d\pi$ levels). The $d\pi$ orbitals are expected to become more contracted and less favorable for π bonding as the metal oxidation state is increased from I to II, but at the same time σ bonding to the metal will be favored by a higher charge on the metal. More than a qualitative consideration of such effects, however, is probably not warranted due to lack of detailed information about electron repulsion differences.

Finally, the effects of changes in M → L bonding can be seen in shifts in the C–N stretching frequencies of CN^- and CNR in the infrared spectra. Some $\bar{\nu}_{CN}(CN^-)$ and $\bar{\nu}_{CN}(CNR)$ frequencies for the several related complexes are collected in Table III. For example, there is a significant increase in $\bar{\nu}_{CN}(CNR)$ in $M(CNR)_4^{n+}$ as the metal oxidation state is increased. This increase is interpreted as reflecting a decrease in M → L bonding as the charge on the metal is raised. There is also a significant increase in $\bar{\nu}_{CN}(CN^-)$ between $Pt(CN)_4^{2-}$ and the $Pt(CNR)_2(CN)_2$ complexes, which can also be explained in terms of an increase in metal charge as CN^- ligands are replaced by the stronger π-acid CNR ligands. An increase in $\bar{\nu}_{CN}(CNR)$ between $Pt(CNR)_2(CN)_2$ and $Pt(CNR)_4^{2+}$ is also expected for the same reason, but the changes in $\bar{\nu}_{CN}$-(CNR) between $Pt(CNR)_4^{2+}$ and $Pt(CNR)_2(CN)_2$ are much smaller.

Registry No. $[Pt(CNCH_3)_4][BF_4]_2$, 33989-89-8; $[Pt(CNC_2H_5)_4][BF_4]_2$, 53993-09-2; $[Pd(CNC_2H_5)_4][BF_4]_2$, 53993-11-6; $[Rh(CNC_2H_5)_4][ClO_4]$, 53993-13-8; $[Ir(CNC_2H_5)_4][ClO_4]$, 53993-15-0; $Pt(CNC_2H_5)_2(CN)_2$, 53993-16-1; $Pt(CN\text{-}t\text{-}C_4H_9)_2(CN)_2$, 53993-17-2; $[(n\text{-}C_4H_9)_4N]_2[Pt(CN)_4]$, 21518-40-1; $[(n\text{-}C_4H_9)_4N]_2[Pd(CN)_4]$, 21518-39-8; $[(C_2H_5)_3O][BF_4]$, 368-39-8; $[Ir(CNC_2H_5)_4]Cl$, 53993-18-3; $[(n\text{-}C_4H_9)_4N][cis\text{-}Ir(CO)_2Cl_2]$, 53993-19-4.

Supplementary Material Available. A listing of calculated spin–orbit eigenvalues and mixing coefficients, Table II, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number AIC40390C.

References and Notes

(1) Abstracted in part from the Ph.D. dissertation of H. Isci, Northern Illinois University, 1974; presented in part at the XVIth International Conference on Coordination Chemistry, Dublin, Ireland, Aug 1974.

(2) See for example L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," Wiley-Interscience, New York, N. Y., 1969.

(3) A. C. Sarapu and R. F. Fonske, *Inorg. Chem.* **11**, 3021 (1972).

(4) H. Isci and W. R. Mason, *Inorg. Chem.*, preceding paper and references cited therein.

(5) C. D. Cowman, C. J. Ballhausen, and H. B. Gray, *J. Amer. Chem. Soc.*, **95**, 7873 (1973).

(6) P. M. Treichel, W. J. Kuebel, and R. W. Hess, *J. Amer. Chem. Soc.*, **93**, 5424 (1971), and references therein.

(7) S. B. Piepho, P. N. Schatz, and A. J. McCaffery, *J. Amer. Chem. Soc.*, **91**, 5994 (1969).

(8) H. L. Jackson and R. C. Makusick, "Organic Synthesis," Vol. IV, R. Rabjohn, Ed., Wiley, New York, N. Y., 1963, p 438.

(9) J. Casanova, N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, **31**, 3473 (1966).

(10) W. R. Mason and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5721 (1968).

(11) D. Forster, *Inorg. Nucl. Chem. Lett.*, **5**, 433 (1969).

(12) W. R. Mason, *J. Amer. Chem. Soc.*, **95**, 3573 (1973).

(13) J. S. Griffith, "The Theory of Transition-Metal Ions," Cambridge University Press, Cambridge, England, 1964 p 438.

(14) Supplementary material.

(15) H. Isci and W. R. Mason, *Inorg. Chem.*, **13**, 1175 (1974).