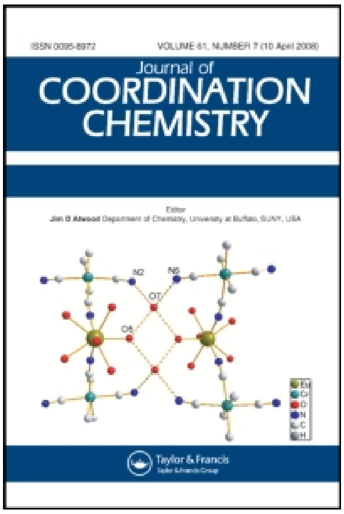

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ELECTRONIC STRUCTURES OF DICYANONICKEL(II) COMPLEXES WITH TRIMETHYLPHOSPHINE

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Contribution from the Laboratoire de Chimie Minérale et Structurale, Institut de Chimie, 1, rue Blaise-Pascal, 67-Strasbourg, France, and Contribution No. 4673 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91109.

We have recently reported[3] the unusual temperature dependence of the ligand-field spectra of some trigonal-bipyramidal complexes. On cooling solutions of several low-spin compounds containing nickel(II), palladium(II), and platinum(II), the lowest energy band ν_1, which is asymmetric or split at 295°K, was found to increase markedly in extinction coefficient and become more symmetrical. By contrast, the asymmetric band ν_1 found in the electronic spectra of the corresponding solid complexes shows little change on lowering the temperature. In the light of these results, it is worthwhile measuring the effect of temperature on the electronic spectra of compounds such as $[NiX_2\{P(CH_3)_3\}_3]$ (X = Cl, Br, I, CN) which contain simple monodentate ligands. In this note, we consider spectral properties of $[Ni(CN)_2\{P(CH_3)_3\}_1]$ and also the related four-coordinate cyano-phosphine $[Ni(CN)_2\{P(CH_3)_3\}_2]$. The preparation of both compounds has been reported by Jensen and Dahl[4] but spectroscopic and magnetic properties were not considered in that communication.

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EXPERIMENTAL SECTION

Preparation of the Compounds

Trimethylphosphine, $P(CH_3)_3$, was prepared as described by Jensen, *et al.*[5], and was collected and stored as the silver iodide complex. The phosphine was regenerated on heating this complex in a nitrogen atmosphere.

Dicyanobis(trimethylphosphine)nickel(II), $[Ni(CN)_2\{P(CH_3)_3\}_2]$ and dicyanotris(trimethylphosphine)nickel(II), $[Ni(CN)_2\{P(CH_3)_3\}_3]$, were prepared and recrystallized by the methods of Jensen and Dahl.[4] *Anal.* $[Ni(CN)_2\{P(CH_3)_3\}_2]$, Calcd for $C_8H_{18}N_2NiP_2$: C, 36.55; H, 6.90; N, 10.64. Found: C, 36.17; H, 6.72; N, 10.49%. *Anal.* $[Ni(CN)_2\{P(CH_3)_3\}_3]$, Calcd for $C_{11}H_{27}N_2NiP_3$: C, 38.97; H, 8.03; N, 8.25. Found: C, 39.12; H, 8.26; N, 8.29%.

Physical Measurements

Infrared spectra were obtained with a Beckman IR 11 grating spectrophotometer using Nujol mulls between potassium bromide plates. Raman spectra were recorded on a Coderg spectrometer equipped with a helium-neon OIP laser.

Solution electronic spectra were measured on a Cary 14 spectrophotometer, using 1 cm silica cells and EPA solvent (a 5:5:2 mixture of diethyl ether, isopentane, and ethanol; all three solvents were Fluka spectroquality). For measurements at 77°K, the silica cells were held in a low temperature dewar. The solid complexes were supported in thin films of polyvinyl acetate (Rhodopas) for spectral examination.

Magnetic susceptibilities were determined with a Faraday balance, equipped with a Setaram MTB 10-8 micro balance and an Alpha electromagnet. At least three measurements were averaged for each compound at 298°K, and the observed susceptibilities were corrected for diamagnetic components.

Molecular weights were determined in biphenyl using a Buchi melting point apparatus. Dipole moments in benzene were obtained using a W.T.W. DM 01 instrument.

RESULTS AND DISCUSSION

The Five-Coordinate Complex: $[Ni(CN)_2\{P(CH_3)_3\}_3]$

The compound $[Ni(CN)_2\ P(CH_3)_3\ _3]$ can be obtained as a red-orange crystalline solid and it has a molecular weight of 319 (calculated 339) in biphenyl. The solid complex slowly loses $P(CH_3)_3$ at room temperature and, after several days, converts to the four-coordinate complex $[Ni(CN)_2\{P(CH_3)_3\}_2]$. The five-coordinate compound dissolves readily in dichloromethane, ethanol, acetonitrile, and benzene to give orange solutions. These solutions are stable, but

TABLE I.
Electronic absorption spectral data

	Solution,[a] $\bar{\nu}_{max}$ (kcm^{-1})		Solid State,[b] $\bar{\nu}_{max}$(kcm^{-1})	
Compound	295°K	77°K	295°K	77°K
$[\mathrm{Ni(CN)_2\{P(CH_3)_3\}_3}]$[c]	–	23.3 sh (4000)	–	23.4 sh
	25.6 (4200)	25.6 (6100)	25.7	25.7
	41.4 (8000)	41.4 (10,000)	41.4	41.4
$[\mathrm{Ni(CN)_2\{P(CH_3)_3\}_2}]$	29.8 (900)	30.8 sh (1500)	30.3	30.3
	33.2 sh (4300)	33.4 (5000)	–	33.3
	34.5 (6000)	35.1 sh (4200)	34.6	34.6
	40.8 (35,000)	41.3 (28,500)	40.5	40.5
	42.5 (8000)			

[a] In EPA solution; molar extinction coefficients (l. mol^{-1} cm^{-1}) in parentheses.
[b] In a polyvinyl acetate support.
[c] Solution spectra measured in the presence of excess phosphine.

excess phosphine is required to prevent the dissociation:

$$[\mathrm{Ni(CN)_2\{P(CH_3)_3\}_3}] \rightleftharpoons [\mathrm{Ni(CN)_2\{P(CH_3)_3\}_2}] \quad \mathrm{P(CH_3)_3} \tag{1}$$

Magnetic measurements give an effective moment of $\mu_{eff} = 0.65$ B.M consistent with a low-spin d^8 five-coordinate compound showing a small temperature-independent paramagnetism. This result eliminates the possibility of an equimolecular mixture of $[\mathrm{Ni(CN)_2\{P(CH_3)_3\}_2}]$ (square-planar or tetrahedral) and $[\mathrm{Ni(CN)_2\{P(CH_3)_3\}_4}]$ being present in the solid state.

Five-coordinate complexes may exist in idealized trigonal-bipyramidal (TBP) and square-pyramidal (SPY) geometries.[6] Both low-spin d^8 forms, however, are unstable with respect to certain vibrations (E′ for D_{3h} and B_1 for C_{4v} symmetries) and intermediate structures may be favored due to this second-order Jahn-Teller effect[7]; lattice or solvent interactions can also be important. Stalick and Ibers[8] have determined the molecular structures of the five-coordinate compounds $[\mathrm{Ni(CN)_2\{PC_6H_5(OC_2H_5)_2\}_3}]$ and $[\mathrm{Ni(CN)_2\{PC_6H_5(CH_3)_2\}_3}]$. Both complexes are distorted from TBP towards SPY geometry, with the former having a structure intermediate between the two idealized stereochemistries.

The infrared and Raman spectra of both solid $[\mathrm{Ni(CN)_2\{P(CH_3)_3\}_3}]$ and its dichloromethane solution only exhibit one band assignable to a cyanide stretch, at 2100 cm^{-1} (ir) and 2116 cm^{-1} (Raman). These measurements indicate theoretically that this complex has a *trans*-TBP geometry both in the solid state and when dissolved in dichloromethane, but unfortunately the spectra are rather insensitive to distortions from D_{3h} symmetry. Thus the distorted TBP compounds $[\mathrm{Ni(CN)_2\{PC_6H_5(R)_2\}_3}]$($\mathrm{R = OC_2H_5,\ CH_3}$) both show only one ir band in the cyanide stretching region.[9,10] The low value (0.27 D) of the dipole moment of $[\mathrm{Ni(CN)_2\{P(CH_3)_3\}_3}]$ in benzene, however, indicates that the two cyanides are nearly *trans*.

The electronic spectra of $[\mathrm{Ni(CN)_2\{P(CH_3)_3\}_3}]$ have been measured at 295 and 77°K, both in EPA solution (with excess $\mathrm{P(CH_3)_3}$) and in the solid state; the data are summarized in Table I. An advantage of using trimethylphosphine as a ligand is that the first internal transition is at high energy (*ca.* 50 kcm^{-1}) resulting in a simple spectrum up to 45 kcm^{-1}.

The room temperature spectrum of the complex in dichloromethane (with excess phosphine) is identical to that obtained in EPA solvent. Assuming D_{3h} symmetry, the lowest energy asymmetric band (ν_1) can be assigned to the orbitally allowed ${}^1A'_1 \rightarrow {}^1E'$ ($e'd_{x^2-y^2}$, $d_{xy} \rightarrow a'_1d_{z^2}$) transition. The forbidden transition, ${}^1A'_1 \rightarrow {}^1E''(e''$ d_{xz}, $d_{yz} \rightarrow a'_1d_{z^2}$) is too weak to be observed, even at 77°K. On cooling, the assymmetric band ν_1 becomes more symmetrical and increases in extinction coefficient but by contrast with measurements on the compounds[3] $[\mathrm{Ni(CN)_2\{PC_6H_5(R)_2\}_3}]$ ($\mathrm{R = CH_3,\ OC_2H_5}$), the two components ν'_1 and ν''_1 contributing to ν_1 become somewhat better resolved at 77°K, with the lower energy component ν'_1 appearing as a significant shoulder. A similar spectral change with temperature is found in the solid state (see Table I). The fact that the two components ν'_1 and ν''_1 do not approach one another on lowering the temperature, i.e. $\Delta\bar{\nu}_1$ ($=\bar{\nu}_1{}'' - \bar{\nu}_1{}'$) remains approximately constant, implies that the asymmetry of ν_1 is due to a permanent ground state distortion from D_{3h} to C_{2v} both in the solid *and* solution state. There is no obvious explanation as to why $\Delta\bar{\nu}_1$ should remain approximately constant on cooling a solution containing $[Ni(CN)_2(PR_3)_3]$ ($PR_3 = P(CH_3)_3$) but when $PR_3 = PC_6H_5(CH_3)_2$ or $PC_6H_5(OC_2H_5)_2$, $\Delta\bar{\nu}_1$ decreases with temperature (due to dynamic Jahn-Teller distortion of the $^1E'$ excited state or a temperature dependent distortion of the ground state).

If excess trimethylphosphine is not present in solution, the electronic spectrum of $[Ni(CN)_2\{P(CH_3)_3\}_3]$ shows an additional band at 34.5 kcm^{-1} indicating the formation of the corresponding *bis*(phosphine) (*vide infra*) owing to partial dissociation according to Eqn. 1. When excess trimethylphosphine is added, this band disappears. A similar effect was noted previously[10] on adding $P(C_6H_5)(CH_3)_2$ to a solution of the complex $[Ni(CN)_2\{PC_6H_5(CH_3)_2\}_3]$. It is possible that the shoulder found by Chastain *et al.*[9] at 33.3 kcm^{-1} in the spectrum of $[Ni(CN)_2\{PC_6H_5(OC_2H_5)_2\}_3]$ is due to the presence of a small amount of $[Ni(CN)_2\{PC_6H_5(OC_2H_5)_2\}_2]$; this shoulder was assigned to a Ni → CN(π^*) transition. We consider, therefore, that the 41.4 kcm^{-1} band in the spectrum of $[Ni(CN)_2\{P(CH_3)_3\}_3]$ is due to the charge-transfer transition Ni → CN(π^*) ($e' \rightarrow e'$).

The Four-Coordinate Complex $[Ni(CN)_2\{P(CH_3)_3\}_2]$

This compound can be isolated as a yellow crystalline powder with a molecular weight of 243 (calculated 263) in biphenyl, and is stable both in the solid state and solution (dichloromethane, benzene, EPA). Addition of excess $P(CH_3)_3$ results in the formation of the red-orange triphosphine complex considered above. Magnetic susceptibility measurements on the complex $[Ni(CN)_2\{P(CH_3)_3\}_2]$ yield $\mu_{eff} = 0.37$ B.M., consistent with a low-spin d^8 square-planar structure. In addition, the presence of only one band in the cyanide stretch region of the infrared (2110 cm^{-1}) and Raman (2118 cm^{-1}; polarized) solid spectra implies a *trans* geometry for the molecule.[11]

The solid state (295 and 77°K) and solution (295°K) electronic spectra of $[Ni(CN)_2\{P(CH_3)_3\}_2]$ are similar, as shown in Table I. They have features reminiscent of the square-planar $[Ni(CN)_4]^{2-}$ anion,[12] except for the increase in band intensity which is characteristic of phosphine complexes.[6b] The lowest energy band can be assigned to one or more of the spin-allowed d–d transitions in D_{2h} symmetry. Similar transitions appear in the 29-30 kcm^{-1} region of the spectra of $[Ni(CN)_2\{PC_6H_5(C_2H_5)_2\}_2]$ (ref. 13) and $[Ni(CN)_2\{P(C_6H_5)_2OC_2H_5\}_2]$ (ref. 9). The next three bands at 33.2, 34.5, and 40.8 kcm^{-1} are presumably due to Ni → CN(π^*) transitions.

The EPA solution spectrum of $[Ni(CN)_2\{P(CH_3)_3\}]$ at 77°K is different from that at 295°K, especially with respect to extinction coefficients, indicating a temperature dependent *cis-trans*-equilibrium. Characterization of the isomerization of $[Ni(CN)_2\{P(CH_3)_3\}_2]$ in solution by nmr and other spectral methods will be published separately.[14]

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