[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY]

The Infrared Spectrum and Structure of the $[Ni(CN)_4]^{-4}$ Ion[1]

BY MOSTAFA F. AMR EL SAYED[2] AMD RAYMOND K. SHELINE[3]

RECEIVED NOVEMBER 14, 1957

The infrared spectrum of $K_4[Ni(CN)_4]$ has been obtained from 2.5–15 μ. The presence of only one band at 1985 cm.$^{-1}$ agrees with the group theoretical analysis of a tetrahedral structure. A comparison is made of the chemical bonds in the ions $[Ni(CN)_4]^{-2}$ and $[Ni(CN)_4]^{-4}$ in order to explain the low value of the CN frequency in the latter.

Introduction

The structure of $Ni(CO)_4$, in which the four (CO) groups are arranged tetrahedrally around the nickel atom, has been proved by both electron diffraction[4] and spectroscopic means.[5] Since $[Ni(CN)_4]^{-4}$ is isoelectronic with $Ni(CO)_4$, it was predicted[6,7] to have a similar structure. X-Ray analysis has not been carried out for $[Ni(CN)_4]^{-4}$ mainly because of its instability. However, in this investigation, the instability helped to assign the absorption bands by taking the spectrum as a function of time.

Experimental

(a) **Preparation of the Sample.**—$K_4[Ni(CN)_4]$ was prepared by a method described previously,[8] in which $K_2[Ni(CN)_4]$ was reduced by an excess of metallic potassium in a liquid ammonia solution, using a special apparatus to prevent oxidation. After the bulky yellow precipitate was formed, it was washed several times with liquid ammonia, pumped on for several hours, and then swept with dry, oxygen-free nitrogen to free it completely of the liquid ammonia.

(b) **Infrared Spectrum.**—Two major difficulties are encountered in obtaining the spectrum of this complex. The first one is its insolubility in organic solvents; the second one, its instability and its great tendency to oxidize to $K_4[Ni_2(CN)_6]$ and finally to $K_2[Ni(CN)_4]$. However, since the rate of oxidation is greatly reduced in Nujol, these difficulties were overcome by use of the mull technique. The absorption spectrum was taken on a Perkin-Elmer model 21 spectrophotometer using NaCl optics. The spectrophotometer was calibrated by obtaining the spectrum of water vapor in the air and checking the peaks recorded against standard values. These corrections have been applied to the reported values where necessary.

Spectra Analysis

The absorption curves are shown in Fig. 1. Curve (a) is that of a freshly prepared sample. Two strong bands are shown, one with its maximum at 1985 cm.$^{-1}$ and the other at 2135 cm.$^{-1}$. The last band is due to unreduced $K_2[Ni(CN)_4]$ which absorbs strongly at this frequency, as shown from curve (e).

Curve (b) shows the spectrum of another sample left in Nujol for ten hours during which the color changed from yellow to orange. The spectrum given shows the appearance of three new bands at 2128, 2079 and 2055 cm.$^{-1}$, and the reduction of the intensity of the band at 1985 cm.$^{-1}$. The three bands are those of $[Ni_2(CN)_6]^{-4}$, found previously[9] and shown in curve (d). Since $[Ni_2(CN)_6]^{-4}$ is the first oxidation product of $[Ni(CN)_4]^{-4}$, and since it has a very high absorption extinction coefficient in the blue-green region of the visible spectrum,[10] the change of the color of the mull preparation becomes clear and the assignment of the reduced band at 1985 cm.$^{-1}$ to the $[Ni(CN)_4]^{-4}$ ion becomes highly probable.

Curve (c) shows the spectrum of a mull preparation of the sample after it had been left in air until it changed color completely from orange to yellow. Yellow is the characteristic color of $[Ni(CN)_4]^{-2}$,[10] which is the final and most stable oxidation product of $[Ni(CN)_4]^{-4}$. This is clearly shown by the similarity of curves (c) and (e). The disappearance of the other bands in curve (c) strengthens the previous assignment of these bands.

Discussion

From the electron configuration and the energy levels of the nickel atom, one expects the tetrahedral arrangement of the four sp^3 σ bonds around the nickel atom to be the most appropriate one. The vibrational analysis, as obtained from symmetry properties and group theory for the Td point group, has been listed in Table I.

TABLE I

VIBRATIONS OF $[Ni(CN)_4]^{-4}$ ION (TETRAHEDRAL, Td)

Type	Activity	Skeletal vibrations	Designation	Non-skeletal vibrations	Designation
A_1	R.	1	ν_1	1	ν_2
A_2	I.a.	0	..	0	..
E	R.	1	ν_3	1	ν_4
F_1	I.a.	0	..	1	ν_5
F_2	I.R.,R.	2	ν_6–ν_7	2	ν_8–ν_9

By a method described in a previous work,[11] it was found that, of the two non-skeletal triply degenerate infrared active vibrations, one is a stretching mode and the other is a bending fundamental. This is in agreement with the observed single absorption band in the NaCl region.

A similar analysis for a square planar structure (D_{4h} point group) was not carried out since its formation is energetically unfavorable; that is, because in order to form such a structure one has to promote two electrons to one of the 4p orbitals to form dsp^2 hybrid orbitals.

---

(1) This investigation was supported by a research grant from the office of Ordnance Research, U. S. Army, under contract No. DA-01-009-ORD-461.

(2) From portions of a thesis to be submitted by M. F. A. E. to the graduate school of Florida State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Institute for Theoretical Physics, Blegdamsvej 17, Copenhagen, Denmark.

(4) L. O. Brockway and P. C. Cross, *J. Chem. Phys.*, **3**, 828 (1935).

(5) P. C. Cross, *ibid.*, **6**, 525 (1938).

(6) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," Interscience Publishers Inc., New York, N. Y., 1950, p. 379.

(7) R. S. Nyholm, *Chem. Revs.*, **53**, 303 (1953).

(8) J. W. Easter and W. M. Burgess, THIS JOURNAL, **64**, 1187 (1942).

(9) M. F. A. El-Sayed and R. K. Sheline, *ibid.*, **78**, 702 (1956).

(10) M. F. A. El-Sayed and R. K. Sheline, unpublished results.

(11) J. W. Cable, R. S. Nyholm and R. K. Sheline, THIS JOURNAL, **76**, 3373 (1954).

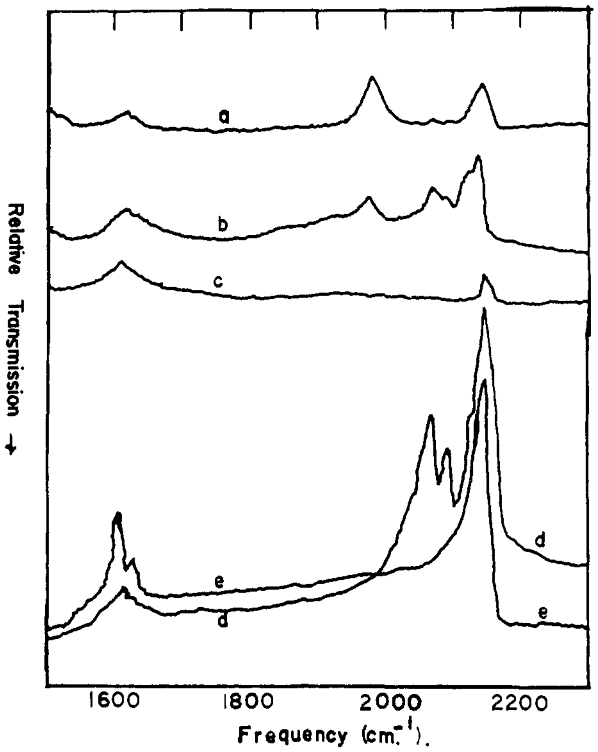


Fig. 1.—Analysis of the $[Ni(CN)_4]^{-4}$ spectrum: a, b and c are the spectra of $[Ni(CN)_4]^{-4}$ taken at different periods of time; d, the spectrum of $[Ni_2(CN)_6]^{-4}$; e, the spectrum of $[Ni(CN)_4]^{-2}$. These curves have different base lines. The relatively weak absorption shown in all the curves at the 1600 cm.$^{-1}$ region is due to either NH_3 impurity or H_2O of crystallization of $[Ni(CN)_4]^{-2}$.[9]

The low value of the C≡N frequency in $[Ni(CN)_4]^{-4}$ as compared with that in $[Ni(CN)_4]^{-2}$ can be explained semiquantitatively on the basis of Pauling's principle of electrical neutrality.[12] Assuming values of 1.6 and 2.5 for the electronegativities of nickel and carbon, respectively, it follows from the correlation between electronegativity and per cent. ionic character[13] that the metal carbon bond is about 20% ionic and that the single bond in

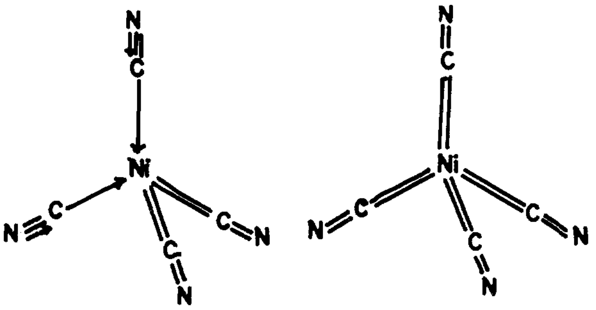
$$M + :\overset{-}{C}{\equiv}N: \longrightarrow \overset{-0.8}{M}{-}C{\equiv}N:$$

imparts a charge of −0.8, while the metal carbon double bond

$$M: + :C = \overset{..\,-}{N}: \quad \overset{+0.4}{M}: :C: :\overset{..\,-}{N}:$$

imparts a charge of +0.4 to the metal atom.

For the sake of comparison of $[Ni(CN)_4]^{-2}$ and $[Ni(CN)_4]^{-4}$, the relative contributions of only the two extreme resonating forms, *i.e.*, the pure single bonded form and the pure double bonded form for the Ni–C bond will be calculated. Since the principle of electrical neutrality requires that the charge on the metal atom be zero, the summation of the contribution of each resonating form multiplied by the charge of its central atom should be equal to zero. Therefore, the following equation holds for $[Ni(CN)_4]^{-2}$



I II

Fig. 2.—Possible resonating structures of $[Ni(CN)_4]^{-4}$.

$$(-0.8 \times 4 + 2)X - (0.4 \times 4 + 2)(1 - X) = 0$$

where +2 is the oxidation number of the central Ni atom; X is the contribution of the pure single bonded form, and $(1 - X)$ is the contribution of the pure double bonded form. Solving this equation gives $X = {}^3/_4$. Thus the relative proportions of the contribution of the single to the double-bonded NiC structures is 3:1; that is, the Ni–C bond must be thought of as a resonance hybrid made up of three single and one double Ni–C bonds. Therefore, the NiC bond order is 1.25. Consequently the C–N bond order is 2.75.

A similar calculation for $[Ni(CN)_4]^{-4}$, where the oxidation number of the central atom is zero, gives a value of ${}^1/_3$ for X. Therefore, the average Ni–C bond order is 1.67 and, as a result, the average C–N bond order is 2.33.

If it is assumed that the Ni–C bond strength in the two ions under comparison is given by the product of the bond order and the σ-hybrid bond strength, then the Ni–C bond strength in the two ions is approximately the same. That is because the Ni–C bond strength in $[Ni(CN)_4]^{-2}$ would be the product of 1.25 (the bond order) and 2.694 (the σ-bond strength for a dsp^2 hybrid) for 3.36. In $[Ni(CN)_4]^{-4}$ this product would be 1.67 (the bond order) times 2.0 (the bond strength for an sp^3 hybrid), namely, 3.34. Then the CN frequency should depend only on the CN bond order, since the σ-bonds in the CN groups are sp carbon hybrids in both cases and the CN groups are attached to bonds of the same strength in both ions. The fact that the CN bond order in $[Ni(CN)_4]^{-4}$ is on the double-bonded side, whereas in $[Ni(CN)_4]^{-2}$ it is on the triple-bonded side, now explains the observed difference in the positions of their CN frequencies. Two reasonable resonating forms for $[Ni(CN)_4]^{-4}$, similar to those proposed for $Ni(CO)_4$,[14] are shown in Fig. 2.

TALLAHASSEE, FLORIDA

---

(12) L. Pauling, *J. Chem. Soc.*, 1461 (1948).

(13) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 70.

(14) J. W. Cable and R. K. Sheline, *Chem. Revs.*, **56**, 1 (1956).