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# Linear Relationships between CN Stretching Frequencies and Polar Substituent Constants of L in $Co(CN)_5L^{3-}$ Complexes

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In the chemistry of pentacyanocobaltate(II), ultraviolet and visible spectroscopies have usually been used to establish the structures of the complexes and to clarify the reaction mechanisms kinetically, but they have scarcely been used to distinguish the organocobalt complexes. In the study to elucidate the reaction mechanism and the novel solvent effect on the selectivity in the hydrogenation of butadiene by pentacyanocobaltate(II),[1] infrared spectroscopy was expected to be useful to observe directly the variation of the intermediates under the reaction condition. In this paper, CN stretching frequencies of various substituted pentacyanocobaltates and some tetracyanocobaltates measured in the aqueous reaction solutions are reported. Also presented here linear relationships between the CN stretching frequencies and polar substituent constants.

## Results and Discussion

CN stretching frequencies of substituted pentacyanocobaltate are given in the Table 1 together with other published data. The complexes in aqueous solutions exhibit single bands in the CN stretching region probably on account of the broadening effect. As shown in Fig. 1, a linear relationship is found between $\Delta\nu_{CN}$ and Taft's $\sigma_I$ function of substituent L. With regard to the organic and hydridic substituents, a much better linear relationship is found with Taft's $\sigma^*$ function as shown in Fig. 2. Similar correlations have been found in substituted metal carbonyls between $\nu_{CO}$ and substituent constants,[2] but the linear relationships reported here are the first for the metal cyano complexes and are noteworthy because L is bound directly to the cobalt atom and the linearity holds in the wide range of L.

In metal cyano complexes, the variation of the CN stretching frequency has been interpreted in terms of the following resonance structures; *i.e.* the larger the contribution of II, the lower the CN stretching frequency.[3,4]

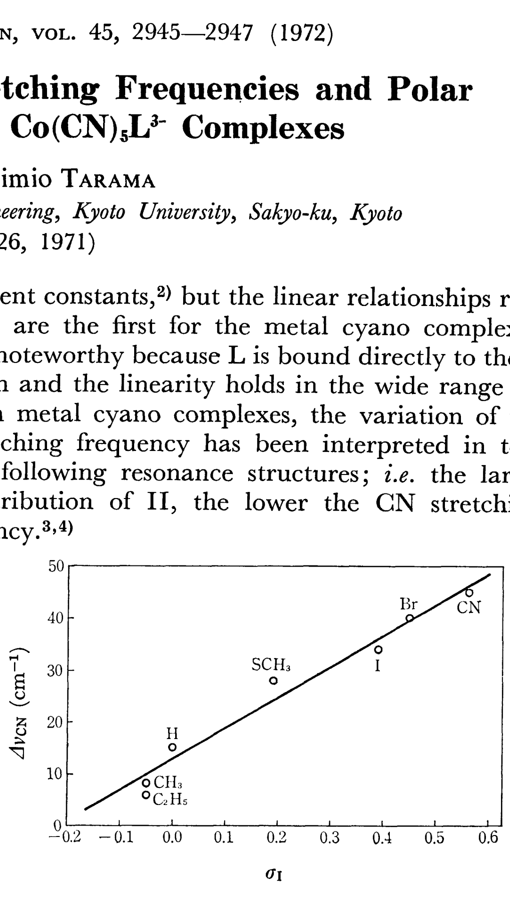

Fig. 1. Plot of $\Delta\nu_{CN}$ *versus* Taft's $\sigma_I$
($\sigma_I$: R. W. Taft, Jr., *et al.*, *J. Amer. Chem. Soc.*, **85**, 709 (1963)).

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[1] K. Tarama and T. Funabiki, This Bulletin, **41**, 1744 (1968); T. Funabiki and K. Tarama, *ibid.*, **44**, 945 (1971); *Tetrahedron Lett.*, **1971**, 1111.

[2] M. Bigorgne, *J. Inorg. Nucl. Chem.*, **26**, 107 (1964); R. Ugo, S. Cenini, and F. Bonati, *Inorg. Chim. Acta*, **1**, 451 (1967); A. A. Ioganson, A. B. Antonova, B. V. Lokshin, N. E. Kolobova, K. N. Anisimov, and A. N. Nesmeyanov, *Izv. Akad. Nauk SSSR, Ser Khim.*, **1969**, 1957 (*Chem. Abstr.*, **72** 26649e (1970)); A. N. Nesmeyanov, K. N. Anisimov, B. V. Lokshin, N. E. Kolobova, and Yu. V. Makarov, *Dokl. Akad. Nauk SSSR*, **176**, 1082 (1967) (*Chem. Abstr.*, **68**, 44365j (1968)); N. Herberhold and H. Brabetz, *Chem. Ber.*, **103**, 3909 (1970).

[3] M. F. A. El-Sayed and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **6**, 187 (1958).

[4] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley-Interscience, New York, (1969).

Table 1. CN Stretching frequencies of substituted pentacyanocobaltate $Co(CN)_5L^{3-}$

| $Co(CN)_5L^{3-}$ L | $\nu_{CN}$(obs.) $cm^{-1}$ | $\Delta\nu_{CN}$ $cm^{-1}$ | $\nu_{CN}$(in literatures) $cm^{-1}$ |
|---|---|---|---|
| None or $H_2O$ | 2082 | 0 | 2095, 2136;[a] 2083;[b] 2093, 2127;[c] 2080;[d] |
| $(CH_3)_2CH-$ | 2087 | 5 | |
| $CH_3CH_2CH_2-$ | 2088 | 6 | 2084;[e] |
| $CH_3CH_2-$ | 2088 | 6 | 2085;[e] 2094±3;[f] |
| $CH_3-$ | 2090 | 8 | 2087;[e] 2094±3;[f] |
| $(CH_3)_2C=CH-CH_2-$ | 2090 | 8 | 2092;[e] |
| $CH_3-CH=CH-CH_2-$ | 2091 | 9 | 2092;[e] |
| $CH_2=CH-CH_2-$ | 2094 | 12 | 2092;[e] |
| $C_6H_5CH_2-$ | 2094 | 12 | 2092;[e] 2093±3;[f] |
| H- | 2097 | 15 | 2113;[g] 2098;[b] 2090, 2115, 2127, 2145;[c] |
| RS- ($R=CH_3$, $C_2H_5$, $C_6H_5CH_2$) | 2110 | 28 | |
| I- | 2116 | 34 | 2117;[h] |
| Br- | 2122 | 40 | 2125;[h] |
| CN- | 2127 | 45 | 2126, 2129, 2143;[i] 2134;[h] 2128;[j] 2120;[d] |

a), i) W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, **1959**, 2757, b), h) J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, **87**, 5361 (1965); c) G. Pregaglia *et al.*, *Discuss. Faraday Soc.*, **46**, 110 (1968); d) J. Halpern and M. Pribanic, *J. Amer. Chem. Soc.*, **93**, 96 (1971); e) J. Kwiatek and J. K. Seyler, *J. Organometal. Chem.*, **3**, 421 (1965); f) J. Halpern and J.P. Maher, *J. Amer. Chem. Soc.*, **86**, 2311 (1965); g) R. S. G. Banks and J. M. Pratt, *Chem. Commun.* **1965**, 776; j) L. H. Jones, *Inorg. Chem.*, **2**, 277 (1963); [(a), (b), (d), and (j) were observed in aqueous solution.]

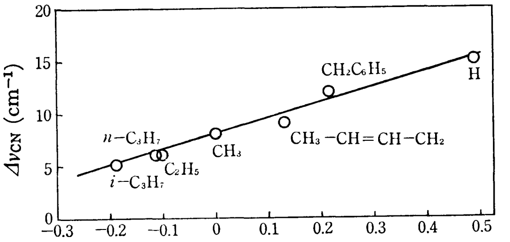

Fig. 2. Plot of $\Delta\nu_{CN}$ *versus* Taft's $\sigma^*$.
($\sigma^*$: R. W. Taft, Jr., in M. S. Newman: "Steric Effects in Organic Chemistry," John Wiley & Sons, Inc., New York (1956)).

$$\underset{\text{I}}{\text{M-C}\equiv\text{N:}} \longleftrightarrow \underset{\text{II}}{\overset{+}{\text{M}}=\text{C}=\overset{-}{\underset{\cdot\cdot}{\text{N}}}\text{:}} \qquad (1)$$

According to El-Sayed and Sheline,[3] the CN stretching frequencies of cyano complexes depend on: (i) the electronegativity, (ii) the oxidation state, and (iii) the coordination number of the metal. The variation of the CN stretching frequency in the substituted pentacyanocobaltates is related to (ii), but the concept of the oxidation state of the metal atom does not seem to be enough to explain the linear variation of the CN stretching frequency with polar substituent constants. The results are explained as follows. From the correlation of $\sigma_I$ or $\sigma^*$ value with the inductive electron-withdrawing power of the substituent L, it is reasonable to suppose that the net charge density on the substituent L increases with the increasing $\sigma_I$ or $\sigma^*$ value, which, consequently, decreases the contribution of structure II in Eq. (1). Thus, in the case of the complexes such as $Co(CN)_6{}^{3-}$ and $Co(CN)_5X^{3-}$ (X=halogen), the net charge density on the substituents must be large, and the contribution of the structure II must be small. This is supported by the fact that the linearity holds for $Co(CN)_6{}^{3-}$, because the linear relationship in Fig. 1 holds when there is little back donating of electron from the cobalt atom to the substituent L. In these complexes the oxidation state of Co(III) seems appropriate as proposed. On the other hand, in the case of alkyl complexes, the net charge density on the alkyl groups must be small or nil. The small $\Delta\nu_{CN}$ values suggest that Co(II) may be preferable to Co(III) although Co(III) has been proposed for these complexes. This difference in the net charge density on the substituent may be connected with the difference in the type of fission of the Co–L bond. In the former complexes, the Co–L bond is split heterolytically[5] and in the latter homolytically. From this point of view, it would be interesting to study the type of fission of the Co–SR bond in $Co(CN)_5SR^{3-}$, because it is assumed from the CN stretching frequency in Table 1 that the net charge density on SR and the contribution of structure II in Eq. (1) are intermediate between the above two groups of complexes.

With regard to $Co(CN)_5H^{3-}$, which is the active complex in the hydrogenation reactions, the oxidation state of Co(I),[6] Co(II),[7] and Co(III)[8] have been proposed. Figure 1 indicates that the net charge density on the hydrogen atom may be only slightly larger than that on the alkyl substituents. This is consistent with the low basicity of the complex[9] and the homolytic fission of the Co–H bond in the catalytic hydrogenation. Thus, Co(II) seems most preferable for this complex. The linear relationships in Figs. 1 and 2 may be used to estimate the approximate sub-

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5) R. Grassi, A. Haim, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 237 (1967).

6) G. A. Mills, S. Weller, and A. Wheeler, *J. Phys. Chem.*, **63**, 403 (1959).

7) L. Simandi and F. Nagy, *Acta Chim. Acad. Sci. Hung.*, **46**, 101 (1965); M. G. Burnett, P. J. Connolly, and C. Kemball, *J. Chem. Soc.*, *A*, **1967**, 800.

8) N. K. King and M. E. Winfield, *J. Amer. Chem. Soc.*, **83**, 3366 (1961).

9) J. Halpern and L-Y. Wong, *ibid.*, **90**, 6665 (1968).

stituent constant: $\sigma^*(-CH_2CH{=}CH_2)=0.26$, $\sigma^*(-CH_2CHC{=}(CH_3)_2)=0.0$.

The CN stretching frequencies of $\pi$-allyl- and *syn*-$\pi$-(1-methylallyl)-tetracyanocobaltates were observed at 2102 and 2098 cm$^{-1}$, respectively.[10] They are higher than those of $\sigma$-allyl- and $\sigma$-but-2-enyl-pentacyanocobaltates, which is consistent with the postulate that an increase in the coordination number results in the decrease in the CN stretching frequency.[11]

## Experimental

Aqueous solutions of the complexes with a cobalt concentration of 0.2M were prepared at 0°C. In all experiments, the $CoCl_2$ solution was added to the KCN solution, and organic substances were added to the KCN solution before the addition of the $CoCl_2$ solution. The complexes were prepared either by the reaction of $Co(CN)_5{}^{3-}$ with alkyl halides and mercaptans, or by the reaction of $Co(CN)_5H^{3-}$ with conjugated dienes. In the reaction with alkyl halide, rapid transformation of $Co(CN)_5X^{3-}$ to $Co(CN)_5OH_2{}^{2-}$ was observed.[5] In the reaction with mercaptans, two distinct bands corresponding to $Co(CN)_5SR^{3-}$ and $Co(CN)_5H^{3-}$ were observed, demonstrating the proposed mechanism for this reaction,[12] and that was confirmed by the observation of the single band of $Co(CN)_5SR^{3-}$ in the reaction with dialkyldisulfides. $Co(CN)_6{}^{3-}$ was prepared by the method described by Benedetti-Pichler.[13]

Formations and structures of the organocobalt complexes were confirmed by the NMR spectra of the reaction solution as reported earlier in the case of $\sigma$-but-2-enyl and *syn*-$\pi$-(1-methylallyl) complexes.[10]

Samples in small polyethylene envelopes were placed between two plates of rock salt, and the infrared spectra were recorded on a JASCO DS-403G spectrophotometer in the 2000—2200 cm$^{-1}$ region. Frequencies were accurate to within ±1 cm$^{-1}$.

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10) T. Funabiki and K. Tarama, *Chem. Commun.*, **1971**, 1177. Values of $\nu_{CN}$ are corrected in this paper.

11) L. H. Jones and R. A. Penneman, *J. Chem. Phys.*, **22**, 965 (1954); R. A. Penneman and L. H. Jones, *ibid.*, **24**, 293 (1956); *J. Inorg. Nucl. Chem.*, **20**, 19 (1961).

12) T. Mizuta and T. Kwan, *Nippon Kagaku Zasshi*, **87**, 825 (1966).

13) Benedetti-Pichler, *Z. Anal. Chem.*, **70**, 258 (1927).