

Figure 1. Effect of the concentration of methyl acrylate on the visible spectrum of (methyl acrylate)(dipyridyl)nickel in tetrahydrofuran at 23°. Total concentration of the nickel complex is  $2.0 \times 10^{-4} M$ . The concentration ( $M$ ) of the added methyl acrylate is (a) 0, (b)  $2.4 \times 10^{-3}$ , (c)  $16.5 \times 10^{-3}$ , and (d)  $52 \times 10^{-3}$ .

for the green color of the solution, and complex 3 corresponds to the red solution. The visible spectrum of 4 varies with the solvent, indicating solvation of Ni(dipy). The visible spectra of dilute green solutions of 3 in tetrahydrofuran containing different olefins proved identical and Beer's law holds well (except for the maleic anhydride complex). Therefore, we assume complete dissociation of the coordinated olefins in dilute solutions such as we employed for spectroscopic observations. The stability constants obtained spectroscopically are considered to correspond to eq 1 and not to the second step of association of olefins to form Ni(dipy)(olefin)<sub>2</sub>. Among the olefin-coordinated  $\pi$  complexes, Ni(dipy)(MAH)<sub>2</sub> presents an exceptional case; its solution is somewhat reddish, Beer's law is not

Table I. Stability Constants of Olefin-Coordinated Dipyridylnickels

Olefin	Temp, °C	$K \times 10^{-2}$ , l. mol <sup>-1</sup>
Maleic anhydride	22.2	470
	36.1	210
	40.1	170
	46.7	140
Acrolein	26.8	54
	32.5	31
	35.6	23
	42.5	14
Acrylamide	22.4	37
	33.5	16
	39.4	7.4
	45.7	4.9
Acrylonitrile	20.4	13
	30.6	6.0
	36.5	4.9
	41.8	3.5
Methyl vinyl ketone	24.0	6.0
	30.0	4.7
	35.6	3.6
	41.1	2.8
Methyl acrylate	18.3	7.9
	21.2	6.3
	31.8	3.6
	41.6	1.4
Methacrylonitrile	21.9	5.1
	28.8	2.8
	37.9	1.4
	43.3	0.95
Methyl methacrylate	17.3	0.24
	24.6	0.14
	29.2	0.12
	42.4	0.061
Vinyl acetate	30.0	0.0023

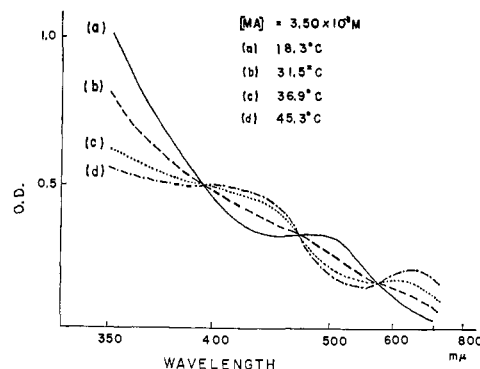


Figure 2. Temperature dependence of the visible spectrum of methyl acrylate complex in tetrahydrofuran. Concentration of methyl acrylate is  $3.5 \times 10^{-3} M$  and that of [Ni(dipy)] is  $8.8 \times 10^{-5} M$ .

obeyed, and the shape of the visible spectrum in tetrahydrofuran changes when the concentration of the complex is increased. This behavior must be associated with the great affinity of maleic anhydride for nickel and the incomplete dissociation of the maleic anhydride complex in solution. The stability constant for the maleic anhydride complex was measured by adding maleic anhydride to a green THF solution containing Ni(dipy)(MVK)<sub>2</sub>, which, from the visible spectrum, can be regarded as completely dissociated to 4 and methyl vinyl ketone in tetrahydrofuran solution.

As long as isosbestic points are clearly observed we can assume the simple equilibrium of eq 1, and the stability constant  $K$  can be determined spectroscopically from the following equation.

$$K = \frac{[\text{Ni(dipy)(olefin)}]}{[\text{Ni(dipy)(solvent)}][\text{olefin}]} = \frac{(x - z)}{(z - y)[\text{olefin}]} \quad (2)$$

In this equation,  $x$ ,  $y$ , and  $z$  correspond respectively to the optical densities in Figure 1. With change of temperature, equilibrium 1 is shifted and the spectral change reflecting the shift can be observed as in Figure 2. The temperature dependence of the stability constants of  $\pi$  complexes of various olefins is shown in Table I and the thermodynamic data are summarized in Table II. Olefins are arranged in Table I in decreasing order of Alfrey-Price's  $e$  value,<sup>11</sup> which is considered to reflect the polarity or electron density of the vinyl group.<sup>12</sup> Tables I and II indicate that the stabilities of type-3 complexes are greater in olefins with strongly electron-withdrawing substituents, *i.e.*, in olefins with larger  $e$  values. This trend is shown in Figure 3, and a linear relation between  $\log K$  at 30° and  $e$  values as expressed by eq 3 was obtained. Clearly an electron-

$$\log K = 2.3e + 0.3 \quad (3)$$

withdrawing substituent reduces the electron density at the double bond and strengthens the bond between the olefin and nickel.

The nature of the bond between an olefin and a transition metal is usually explained by the Dewar-Chatt-Duncanson model in terms of combined  $\sigma$  (olefin  $\rightarrow$  metal) and  $\pi$  (metal  $\rightarrow$  olefin) bondings.<sup>13</sup> The present

(11) J. Brandup and E. H. Immergut, "Polymer Handbook," Interscience, New York, N. Y., 1966, p 341.

(12) The presence of a linear relation between the  $e$  value and Hammett's  $\sigma$  constant is also known: J. Furukawa and T. Tsuruta, *J. Polym. Sci.*, **36**, 257 (1959).

**Table II.** Thermodynamic Data for the Equilibrium of Eq 1 at 300°K

Olefin	$e$ value	$\eta_{1v}^a$	Log $K$	$\Delta F^\circ$ , kcal/mol	$\Delta H^\circ$ , kcal/mol	$\Delta S^\circ$ , eu
Maleic anhydride	2.25		4.52	-6.20	-12.8	-22.0
Acrylamide	1.30		3.31	-4.54	-17.8	-44.2
Acrylonitrile	1.20	0.406	2.82	-3.87	-16.0	-40.5
Methacrylonitrile	0.81	0.431	2.37	-3.25	-14.1	-36.2
Acrolein	0.73	0.315	3.62	-4.92	-19.0	-47.0
Methyl vinyl ketone	0.69	0.448	2.58	-3.54	-13.7	-33.9
Methyl acrylate	0.60	0.453	2.49	-3.42	-13.7	-34.3
Methyl methacrylate	0.40	0.487	1.07	-1.47	-8.7	-24.1
Vinyl acetate	-0.22	0.662	-0.68	0.92		

<sup>a</sup> The energy of the lowest vacant orbital is expressed as  $\alpha - \eta_{1v}\beta$ : T. Kagiya, Y. Sumida, and T. Nakata, *Bull. Chem. Soc. Jap.*, **41**, 2239 (1968).

results suggest that the  $\pi$  bonding between the olefin and nickel is more important for formation of a stable complex. The  $\pi$  bond is formed by an overlap of a filled d orbital of the metal with the antibonding  $\pi$  orbital of the olefin. The closer the original levels are

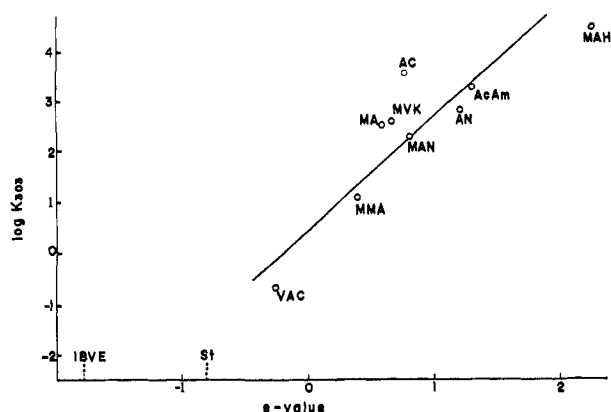


Figure 3. Relation between the stability constants at 30° and  $e$  value of olefins.

in energy, the more stable is the  $\pi$  complex and the stronger is the interaction between the olefin and the metal.<sup>14</sup> In the previous paper<sup>8</sup> we estimated the energy levels of the highest occupied orbitals of **1** and **4** to lie at about  $-6.5$  eV with reference to the energy of the free electron. On the other hand, the energy levels of the lowest antibonding orbitals of olefins can be estimated from the ionization potentials<sup>15</sup> and  $\pi \rightarrow \pi^*$  excitation energies<sup>16</sup> of the olefins. Some examples of the energy levels of the  $\pi^*$  orbitals are  $-4.5$  eV for acrylonitrile,  $-4.0$  eV for methyl vinyl ketone, and  $-3.0$  eV for ethylene. Recently Kagiya and coworkers calculated the energies of the lowest vacant orbitals ( $\epsilon_{1v} = \alpha - \eta_{1v}\beta$ ) of various olefins.<sup>17</sup> Figure 4 shows that there is a roughly linear relation between the logarithms of the stability constants of the olefin-nickel complexes and the energies of the  $\pi^*$  orbitals of

(13) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, C79 (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(14) L. I. Schiff, "Quantum Mechanics," McGraw-Hill, New York, N. Y., 1955; A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961.

(15) (a) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952); (b) K. Watanabe, *ibid.*, **26**, 542 (1957); (c) A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **82**, 4123 (1960).

(16) M. J. Kamlet, "Organic Electronic Spectral Data," Interscience, New York, N. Y., 1946.

(17) T. Kagiya, Y. Sumida, and T. Nakata, *Bull. Chem. Soc. Jap.*, **41**, 2239 (1968).

olefins. The coefficient  $\eta_{1v}$  is included in Table II. A similar plot of the energy of the highest occupied orbitals of various olefins vs. log  $K$  indicates the absence of the relationship in Figure 4. These results strongly suggest that "back-bonding" between the filled d orbital and the  $\pi^*$  orbital of the olefin plays a decisive role in the formation of a stable complex between the olefin and nickel.

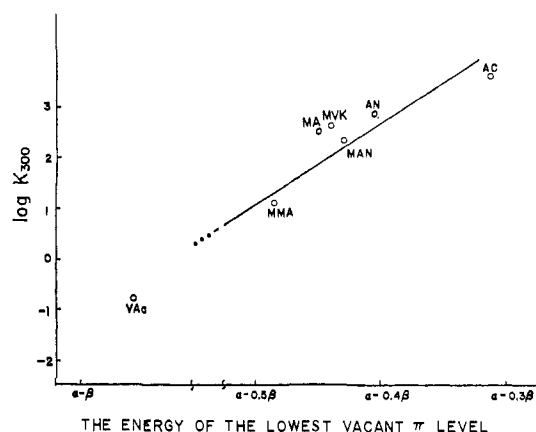


Figure 4. Relation between the stability constants  $K$  at 27° and the energies of the lowest vacant  $\pi^*$  levels of olefins.

As we reported in our previous paper,<sup>8</sup> the interactions of olefins with nickel cause blue shifts of the charge-transfer bands. The charge-transfer bands were interpreted as due to electronic excitation from the highest filled d orbital of nickel to the lowest antibonding orbitals of the dipyriddy ligand. The blue shifts of the charge-transfer bands in olefin-nickel complexes can be explained by the lowering of the energy of the highest filled d orbital due to the withdrawal of electrons in the orbital by  $\pi$ -acceptor ligands.<sup>18</sup> Therefore, greater blue shifts are expected for olefin-nickel complexes with higher stability constants. The positions of the lower frequency charge-transfer bands<sup>8</sup> are 22,800 (AN), 22,450 (AC), 21,500 (MAN), 20,500 (MVK, MA), and 19,200  $\text{cm}^{-1}$  (MMA). This order agrees roughly with the order of the stability constants of the olefin-nickel complexes:  $AC > AN > MVK > MA > MAN > MMA$ .

**$\pi$ -Complex Formation between  $R_2Ni(\text{dipy})$  and Olefins.** Dialkyl(dipyriddy)nickel (**1**) forms unstable complexes of the type  $R_2Ni(\text{dipy})(\text{olefin})$  (**2**) with

(18) H. B. Gray and C. J. Ballhausen, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1964.

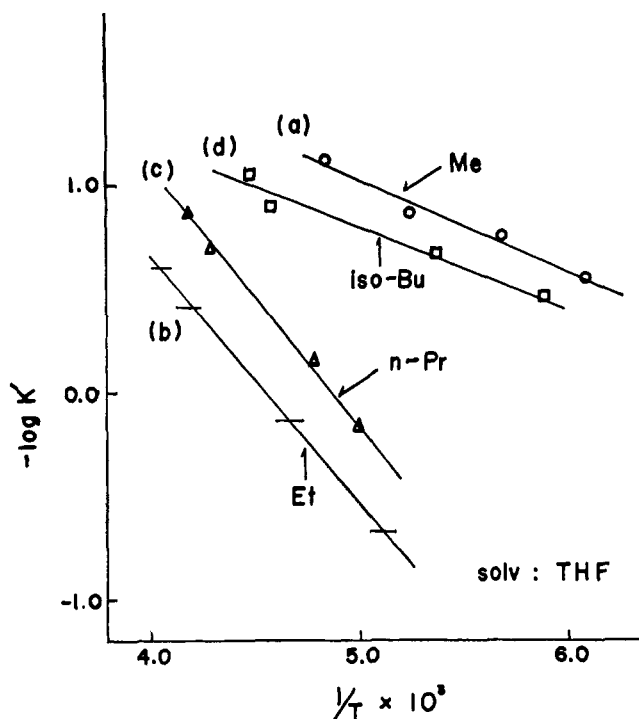
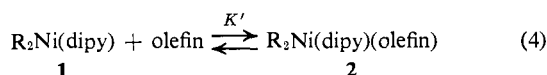


Figure 5. Temperature dependence of stability constants,  $K' = [\text{R}_2\text{Ni}(\text{dipy})(\text{olefin})]/[\text{R}_2\text{Ni}(\text{dipy})][\text{olefin}]$ . Olefin = acrylonitrile.

acrylonitrile and acrolein.<sup>8,9</sup> The color of **2** in the solid state is orange, but a dilute solution of **2** in tetrahydrofuran or diethyl ether at  $-78^\circ$  is green. Since no gas evolution is observed on dissolution of **2** in tetrahydrofuran, fission of the alkyl–nickel bonds is not taking place and the green color is considered to be due to **1**. The green solution turns to orange on addition of an olefin at low temperature. The behavior of the complex in solution suggests the presence of an equilibrium such as



where  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, i\text{-C}_4\text{H}_9$ ; olefin = acrylonitrile, acrolein.

$$K' = [\text{R}_2\text{Ni}(\text{dipy})(\text{olefin})]/[\text{R}_2\text{Ni}(\text{dipy})][\text{olefin}] \quad (5)$$

Since **2** is stable only at low temperature where we could not accurately observe the spectra of solutions, the precise determination of the stability constants was not feasible. Therefore, we estimated the stability constants from visual observations of the solution's color (see the Experimental Section). The temperature dependence of the stability constants is shown in Figure 5, and  $\log K'$  and thermodynamic data at  $200^\circ\text{K}$  are summarized in Table III.

Table III. Thermodynamic Data for the Equilibrium of Eq 4 at  $200^\circ\text{K}$

R	Olefin	Log $K'$	$\Delta F^\circ$ , kcal/mol	$\Delta H^\circ$ , kcal/mol	$\Delta S^\circ$ , eu
$\text{CH}_3$	Acrylonitrile	-1.03	0.95	-2.15	-15.5
$\text{C}_2\text{H}_5$	Acrylonitrile	0.54	-0.50	-4.55	-20.3
$n\text{-C}_3\text{H}_7$	Acrylonitrile	0.16	-0.15	-4.90	-23.8
$i\text{-C}_4\text{H}_9$	Acrylonitrile	-0.80	0.74	-1.67	-12.1
$\text{C}_2\text{H}_5$	Acrolein	0.27	-0.25	-5.60	-26.8

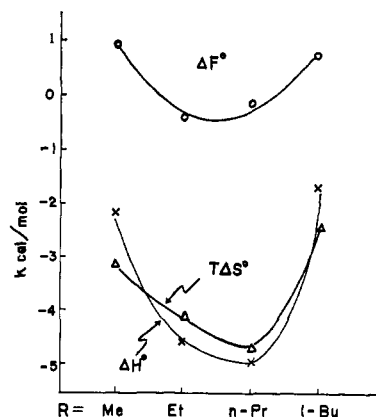


Figure 6. Influence of the alkyl group of  $\text{R}_2\text{Ni}(\text{dipy})$  on the stability of  $\text{R}_2\text{Ni}(\text{dipy})(\text{AN})$ .

As we reported in the preceding paper,<sup>8</sup> adducts of type **2** were isolable in the cases of  $(\text{C}_2\text{H}_5)_2\text{Ni}(\text{dipy})$  and  $(\text{C}_3\text{H}_7)_2\text{Ni}(\text{dipy})$  with acrylonitrile but not for  $(\text{CH}_3)_2\text{Ni}(\text{dipy})$ . The reason will be clear from the following discussion on the stability of **2**.

The stability of the dialkylnickel complex with acrylonitrile is influenced by the kind of alkyl groups attached to nickel, as indicated in Figure 6. The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  derived from the stability constants of **2** decrease from the methyl through ethyl to *n*-propyl complexes and increase again in the isobutyl complex. As we reported in the preceding paper,<sup>8</sup> the energy levels of the highest occupied d orbitals ( $\epsilon_{\text{ho}}$ ) of  $\text{R}_2\text{Ni}(\text{dipy})$  are influenced by the inductive effect of the alkyl groups attached to nickel in the order  $\epsilon_{\text{ho}}(i\text{-C}_4\text{H}_9) > \epsilon_{\text{ho}}(n\text{-C}_3\text{H}_7) > \epsilon_{\text{ho}}(\text{C}_2\text{H}_5) > \epsilon_{\text{ho}}(\text{CH}_3)$ . If the energy difference between  $\epsilon_{\text{ho}}$  of nickel and the  $\pi^*$  level of the olefin were the sole factor determining the interaction between the olefin and  $\text{R}_2\text{Ni}(\text{dipy})$ , a stable complex would be expected for the alkyl complex with the higher  $\epsilon_{\text{ho}}$ . The expectation of this trend is fulfilled for the methyl, ethyl, and propyl complexes, but a significant deviation is observed for the isobutyl complex. The deviation can be attributed to the great steric interaction between the bulky isobutyl groups attached to nickel and the coordinating acrylonitrile ligand in the  $\pi$  bond between nickel and acrylonitrile.

**A Relation between the Stability Constants and Reaction Rates of  $\text{R}_2\text{Ni}(\text{dipy})$  and Olefins.** As we noted in the previous papers,<sup>8,10</sup> the reaction between  $\text{R}_2\text{Ni}(\text{dipy})$  and an olefin takes place at a lower temperature and at a greater rate when the olefin has a stronger electron-withdrawing substituent. Based on the knowledge of the stabilities of the olefin-coordinated  $\pi$  complexes, we can now discuss the relationship between the reaction rates and the stability constants.

From a kinetic study of the reaction of  $\text{R}_2\text{Ni}(\text{dipy})$  with olefins<sup>8</sup> and the isolation of type-**2** complexes<sup>8,9</sup> we concluded that the reactions proceed through an intermediate of type **2**. The activation energies required to break the alkyl–nickel bonds will be lower as the olefins combine more strongly with  $\text{R}_2\text{Ni}(\text{dipy})$ , and a parallel relation is expected between the stability constants of  $\text{R}_2\text{Ni}(\text{dipy})(\text{olefin})$  and the reaction rates of  $\text{R}_2\text{Ni}(\text{dipy})$  with the olefins at room temperature. Unfortunately, the stability constants of **2** are available only for the acrylonitrile and acrolein complexes, but a

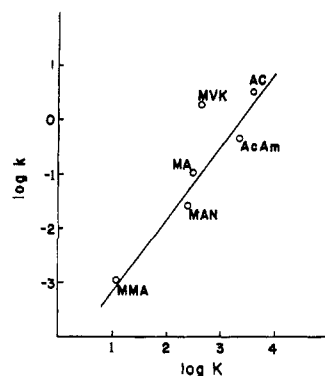


Figure 7. Relation between the stability constants  $K$  and the specific rate constants  $k$  of the reactions of  $R_2Ni(dipy)$  with olefins at  $30^\circ$ .

series of stability constants was obtained for the dealkylated olefin complexes of type 3. Since the nature of the  $\pi$  bond between the olefin and nickel is considered not to differ significantly between 2 and 3, stability constants of type-3 complexes may be used in place of those of 2. Figure 7 indicates that a linear relation exists between the logarithms of stability constants of 3 and the rate constants<sup>8</sup> for reactions of 1 with olefins at room temperature. This result gives additional support for the proposed reaction mechanism of  $R_2Ni(dipy)$  and olefins.<sup>8</sup> The same trend is also found in the polymerization of vinyl monomers by dialkylbis(dipyridyl)iron.<sup>10</sup> The detailed discussion of the polymerization mechanism will be reported separately.

## Experimental Section

**I. Materials.** All materials were prepared, purified, and stored as described in our previous papers.<sup>8,19</sup>

**II. Spectral Measurement.** Ultraviolet and visible spectra were recorded on a Shimadzu Type SV-50A spectrometer. The complexes and solvents were transferred to the cell under nitrogen and in some cases the solvent and the olefin were distilled into the cell *in vacuo*, but no significant differences were observed between the two procedures.

**1. Determination of the Stability Constants of  $Ni(dipy)(olefin)$ .** The temperature of the cell was maintained within  $0.3^\circ$  by circulating thermostated water around the cell. Green solutions obtained by dissolving  $Ni(dipy)(olefin)_n$  in tetrahydrofuran in the absence of extra olefin were checked to see if Beer's law was obeyed. Measured amounts of the olefin were added to the green solution and the spectral change was recorded.

**2. Determination of the Stability Constants of  $R_2Ni(dipy)(olefin)$  at Low Temperatures.** A tetrahydrofuran solution containing  $R_2Ni(dipy)$  and a measured amount of olefin was first kept at  $-110^\circ$  and then gradually warmed to room temperature. The color of the solution is orange at very low temperature, indicating the formation of  $R_2Ni(dipy)(olefin)$ , and changes at higher temperature to dark green, indicating the dissociation of the coordinated olefin. The complete change of color is observed over a range of about  $5^\circ$ . During this change the solution should pass the point where the concentration of  $R_2Ni(dipy)(olefin)$  is equal to that of  $R_2Ni(dipy)$ . Since the spectra of  $R_2Ni(dipy)$  and  $R_2Ni(dipy)(olefin)$  are similar to those of  $Ni(dipy)(solvent)$  and  $Ni(dipy)(olefin)$ , respectively, one can prepare a solution containing equimolar amounts of  $Ni(dipy)(olefin)$  and  $Ni(dipy)(solvent)$  at room temperature and take the color of the solution as that of a solution containing equal amounts  $R_2Ni(dipy)(olefin)$  and  $R_2Ni(dipy)$  at low temperature. After some training one can observe this equilibrium point with a precision of  $\pm 1^\circ$ . The experiments were carried out with varying amounts of olefin in solution and the stability constants  $K'$  were calculated from eq 5.

(19) (a) A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Amer. Chem. Soc.*, **87**, 4652 (1965); (b) *ibid.*, **90**, 1878 (1968).

## Electronic Structures of Thiocyanatopentacyanocobaltate(III) and Related Complexes

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**Abstract:** Electronic absorption spectra of the complex series  $K_3[Co(CN)_5X]$  ( $X = SCN^-, NCS^-, N_3^-,$  and  $NCSe^-$ ) in aqueous solution are assigned in terms of a molecular orbital scheme derived from the energy levels of thiocyanate and  $M(CN)_5^{3-}$ . These assignments are supported by spectra of  $[(n-C_4H_9)_3N]_3[Co(CN)_5X]$  ( $X = -NCS^-, N_3^-,$  and  $-NCSe^-$ ) in low-temperature glasses. The nature of the bonding interactions between the metal ion and the triatomic ligand is discussed. The spectra do not provide any evidence for the participation of  $\pi$ -acceptor orbitals of the triatomic ligand in this bonding.

It has been established that the mode of bonding of thiocyanate to transition metals is subject to a variety of influences, some of which have their origin in intramolecular electronic effects.<sup>1-3</sup> In an effort to sort out certain of the important bonding interactions between metal ions and thiocyanate, we have chosen a

(1) A. Turco and C. Pecile, *Nature (London)*, **191**, 66 (1961).  
 (2) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).  
 (3) J. L. Burmeister, *Coord. Chem. Rev.*, **1**, 205 (1966); **3**, 225 (1968).

model system in which analogous complexes containing N-bonded and S-bonded thiocyanate, as well as azide and selenocyanate, can be investigated. Specifically, the complexes we have studied are the acidopentacyanometalates of cobalt(III) and iron(III). Our attention was originally drawn to this series by the reported preparation<sup>4</sup> of  $K_3[Co(CN)_5SCN]$ , which is an unusual complex in that it contains a first-row metal

(4) J. L. Burmeister, *Inorg. Chem.*, **3**, 919 (1964).