CONTRIBUTION FROM THE RAYMOND KIRK CHEMICAL LABORATORY,
POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN, NEW YORK 11201

Spectrophotometric Study of the Equilibrium Dissociation of Bis(terpyridine)cobalt(II) in Acid Medium

BY JAGDISH PRASAD AND NORMAN C. PETERSON

Received December 26, 1968

The equilibrium constants for the reactions

$$\mathrm{Co(terpy)_2^{2+}} + 2\mathrm{H^+} \overset{K_1}{=} \mathrm{Co(terpy)^{2+}} + \mathrm{(terpy)H_2^{2+}} \qquad \text{(A)}$$

and

$$\mathrm{Co(terpy)^{2+}} + 2\mathrm{H^+} \overset{K_2}{=} \mathrm{Co^{2+}} + \mathrm{(terpy)H_2^{2+}} \qquad \text{(B)}$$

were obtained by spectroscopic observation of $\mathrm{Co(terpy)_2^{2+}}$ ion. Values obtained for these constants are 0.082 ± 0.001 and 0.032 ± 0.002 M^{-1}, respectively, at 25° and $\mu = 0.24$. Thermodynamic parameters for reaction A are $\Delta H_1° = 4.7 \pm 0.3$ kcal mol^{-1} and $\Delta S_1° = 11 \pm 1$ cal deg^{-1} mol^{-1} and for reaction B are $\Delta H_2° = 14.5 \pm 0.9$ kcal mol^{-1} and $\Delta S_2° = 42 \pm 3$ cal deg^{-1} mol^{-1}. The absorptivity of the complex $\mathrm{Co(terpy)_2^{2+}}$ is 1374 ± 3 at 505 mμ and 1581 ± 3 at 445 mμ. Results were computed from absorption measurements by a nonlinear least-squares calculation.

Introduction

Recently, there has been a growing interest in the chemistry of the tridentate ligand 2,2′,2″-terpyridine (terpy) and its metal complexes. This ligand readily forms stable complexes with transition metals. In the visible region the ligand does not absorb at wavelengths longer than 390 mμ while its bis complexes absorb strongly in this region. The bis cobalt complex of this ligand has a high extinction coefficient in the visible region and obeys Beer's law. This study was undertaken because of the incomplete data available in the literature.[1-7] The ligand is a diacid base and both dissociation constants have been reported previously.[8] These values taken together with the equilibrium constants determined in this work can be used to obtain the formation constants of the complex ions.

Experimental Section

2,2′,2″-Terpyridine was obtained from the G. F. Smith Chemical Co. and was recrystallized from a 40–60° cut of petroleum ether. An insoluble liquid was separated. The once-crystallized substance was further recrystallized from aqueous methanol at 0° in an ice bath. Pale yellow crystals (mp 84–86°) were obtained. Cobalt bromide free of iron and nickel was obtained from the G. F. Smith Chemical Co. Other chemicals were of ACS reagent grade and were used as such.

Bis(terpyridine)cobalt(II) Bromide.—This was synthesized by the method of Burstall and Morgan.[9] The fine, deep brown crystals were washed twice with carbon tetrachloride to remove excess ligand and were dried over sulfuric acid. Two samples synthesized independently were analyzed. *Anal.* Calcd for $\mathrm{C_{30}H_{22}N_6CoBr_2H_2O}$: C, 51.2; H, 3.2; N, 11.9; Co, 8.4; Br, 22.7; $\mathrm{H_2O}$, 2.6. Found for sample I: C, 50.8; H, 3.3; N, 11.9; Co, 8.4; Br, 22.6; $\mathrm{H_2O}$, 2.3. Found for sample II: C, 50.4; H, 3.4; N, 11.7; Co, 8.2; Br, 22.5.

Mono(terpyridine)cobalt(II) Bromide.—This was prepared by adopting the procedure of Hogg and Wilkins[5] for the bis complex. The grass green powder was washed with spectral quality carbon tetrachloride and dried over concentrated sulfuric acid under vacuum. *Anal.* Calcd for $\mathrm{C_{15}H_{11}N_3CoBr_2}$: C, 39.8; H, 2.45; N, 9.29; Co, 13.05; Br, 35.5. Found: C, 39.6; H, 2.8; N, 8.9; Co, 13.2; Br, 36.3. The analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

The bis complex was also characterized by its spectra. It showed peaks in the visible region at 552.5, 505, and 445 mμ. The corresponding log ϵ values were 2.74, 3.15, and 3.19, respectively, where ϵ is the molar extinction coefficient. Many typical bands were observed in the uv region consistent with other work. Fresh solutions were prepared daily under nitrogen atmosphere to avoid air oxidation. Solutions of $\mathrm{Co(terpy)^{2+}}$ were prepared at 0°. For the formation of bis complex from the mono complex, solutions were prepared in a 25-ml volumetric flask, leaving just sufficient space for the aliquots of $\mathrm{Co(terpy)^{2+}}$ stock solution. These solutions were then brought to the required temperature until equilibrium was reached. Observations were made after 3–4 hr. On keeping a solution of the bis complex (3.2×10^{-4} M) for 24 hr the absorption changed typically 2.2–2.6%. A Cary Model 14 double-beam recording spectrophotometer fitted with a water-jacketed cell compartment was used for absorption measurements. The cell compartment was completely flushed with nitrogen before recording spectra. The ionic strength was held constant at 0.24 M using NaCl and HCl. The perchlorate salt of the complex was insoluble. Absorption measurements were made at 505 and 445 mμ. These were chosen as the most suitable wavelengths for study because Beer's law is obeyed in the range 10^3–10^5 M and the extinction coefficients are high (1374 and 1581) and free of interference. Matched 10-, 1-, and 0.1-cm quartz cells were used. The absorbances reported are given corrected to 1 cm. Temperature control of the cell was ±0.05°.

Treatment of Data

Measurements of the absorption spectra of solutions of the cobalt(II)–terpyridine complex ion in acid were made at various concentrations at 15.6, 25.2, 27.2, and

---

[1] M. L. Moss and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, **15**, 74 (1943).

[2] W. W. Brandt and J. P. Wright, *J. Am. Chem. Soc.*, **76**, 3082 (1954).

[3] B. Martin and L. A. Lissfelt, *ibid.*, **78**, 938 (1956).

[4] K. Nakamoto, *J. Phys. Chem.*, **64**, 1420 (1960).

[5] R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 341 (1962).

[6] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 622 (1966).

[7] R. Farina, R. Hogg, and R. G. Wilkins, *ibid.*, **7**, 170 (1968).

[8] P. O'D. Offenhartz, P. George, and G. P. Haight, Jr., *J. Phys. Chem.*, **67**, 116 (1963).

[9] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1649 (1937).

34.6°. Assuming that only $Co(terpy)_2^{2+}$ ion absorbs at 505 mμ, we have

$$A = \epsilon b[Co(terpy)_2^{2+}] \qquad (1)$$

where A is the absorption due to $Co(terpy)_2^{2+}$ complex ion and b is the path length of the cell. It was discovered that a plot of C/A *vs.* H_t^2/C was linear with some curvature at small values of the abscissa as shown in Figure 1, where H_t is the total hydrogen ion concentration and C is the total concentration of $Co(terpy)_2^{2+}$.

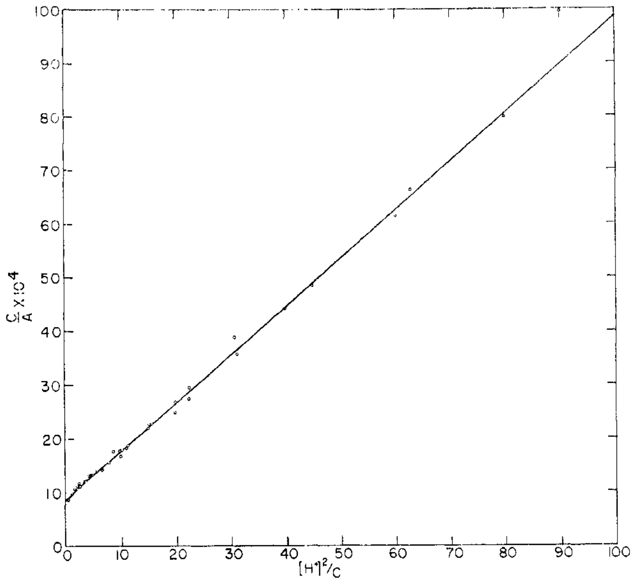


Figure 1.—Graph showing the relationship of C/A *vs.* $(H_t)^2/C$ for observations of absorbance, A, of $Co(terpy)_2^{2+}$ in acid at 27.2°. C is the concentration of added $Co(terpy)_2^{2+}$.

This result strongly suggests that the main reaction being observed is

$$Co(terpy)_2^{2+} + 2H^+ \overset{K_1}{=} Co(terpy)^{2+} + (terpy)H_2^{2+} \qquad (2)$$

After making use of the equilibrium constant expression, combining, and rearranging eq 1 gave

$$\frac{C}{A} = \frac{2}{\epsilon} + \frac{K_1(H^+)^2}{\epsilon C} + \frac{A}{\epsilon^2 C} \qquad (3)$$

which agrees with our observed results if we assume that the last term, A/ϵ^2C, is negligible and (H^+) is taken as H_t. Approximate values for the equilibrium constant K_1 and ϵ calculated from the slope and intercept of the straight line (Figure 1) are $\simeq 0.21\ M^{-1}$ and $\simeq 2300$, and it is evident that the last term in eq 3 is small.

Detailed analysis of the results requires that the influence of two additional acid–base equilibria on the main reaction be considered

$$(terpy)H_2^{2+} \overset{K_3}{=} (terpy)H^+ + H^+ \qquad (4)$$

$$(terpy)H^+ \overset{K_4}{=} terpy + H^+ \qquad (5)$$

Offenhartz, *et al.*,[8] have measured K_3 and K_4. Their reported values are $pK_3 = 4.7$ and $pK_4 = 3.3$ at 25°. The further dissociation of the $Co(terpy)^{2+}$ was also included

$$Co(terpy)^{2+} + 2H^+ \overset{K_2}{=} Co^{2+} + (terpy)H_2^{2+} \qquad (6)$$

Assuming that the system is completely defined by reactions 2, 4, 5, and 6, we obtained stoichiometric equations

$$C = [Co^{2+}] + [Co(terpy)^{2+}] + [Co(terpy)_2^{2+}] \qquad (7)$$

$$H_t = [H^+] + [(terpy)H^+] + 2[(terpy)H_2^{2+}] \qquad (8)$$

$$2C = [terpy] + [(terpy)H^+] + [(terpy)H_2^{2+}] + [Co(terpy)^{2+}] + 2[Co(terpy)_2^{2+}] \qquad (9)$$

Eliminating [terpy], $[(terpy)H^+]$, and $[Co(terpy)^{2+}]$ using the equilibrium constant expressions and rearranging the equations gave the following three nonlinear equations in three unknowns which can be solved simultaneously

$$C = [Co(terpy)_2^{2+}]\{1 + (K_1(H^+)^2/[(terpy)H_2^{2+}]) + (K_1K_2(H^+)^4/[(terpy)H_2^{2+}]^2)\} \qquad (10)$$

$$H_t = [H^+] + 2[(terpy)H_2^{2+}] + (K_3[(terpy)H_2^{2+}]/[H^+]) \qquad (11)$$

$$2C = [Co(terpy)_2^{2+}]\{2 + (K_1(H^+)^2/[(terpy)H_2^{2+}])\} + [(terpy)H_2^{2+}]\{1 + (K_3/(H^+)) + (K_3K_4/(H^+)^2)\} \qquad (12)$$

Equations 10–12 were solved numerically using trial values of the K's by means of an algorithm of nested interations.[10]

At the wavelengths used, only two species contribute to the absorbance; mainly $Co(terpy)_2^{2+}$ and $Co(terpy)^{2+}$ slightly. Least-squares analysis using these data revealed that K_1 was fairly well established, but K_2 and ϵ were not precisely determined. Observations of the absorbance of $Co(terpy)_2^{2+}$ without acid were included to constrain ϵ to an acceptable value, and the calculated values were obtained from eq 1 for those observations. Absorbance measurements on solutions of $Co(terpy)^{2+}$ without added acid were included to improve the accuracy of determination of K_2. The equilibrium expressions for these solutions were solved in closed form.

A least-squares calculation was carried out to obtain the $\Delta H°$ and $\Delta S°$ for reactions 2 and 6. The least-squares values of the parameters were taken as those which minimize the quantity $\Phi = \Sigma_i(A_i - A_{calcd})^2$ with respect to variation of the parameters, where A_i is the measured absorbance and A_{calcd} was computed in the following way. For solutions of $Co(terpy)_2^{2+}$ without acid, A_{calcd} was computed by eq 1, using a different ϵ for each wavelength. For solutions of $Co(terpy)_2^{2+}$ in acid, eq 13 was used, where the concentrations were computed by solving eq 10–12 as described above. Equation 13 was also applied to solutions of

$$A_{calcd} = \epsilon_1[Co(terpy)_2^{2+}] + \epsilon_2[Co(terpy)^{2+}] \qquad (13)$$

$Co(terpy)^{2+}$ in the absence of acid, but the concentrations of the two species were computed exactly based on reactions 2 and 6. The absorptivity ϵ_2 of $Co(terpy)^{2+}$ was taken as 19 at 445 and 505 mμ.[5] This was not adjusted.

The K's are $K_i = \exp[(\Delta S°_i/R) - (\Delta H°_i/RT)]$, where $\Delta S°_i$ and $\Delta H°_i$ are taken as thermodynamic parameters for eq 2 and 6, and literature values for reactions 4 and 5 were taken as[8] $\Delta H_3 = 6.8$ kcal/mol^{-1}, $\Delta H_4 = 0.7$ kcal/mol^{-1}, $\Delta S_3 = 8.0$ cal deg^{-1} mol^{-1}, and $\Delta S_4 = -19.0$ cal deg^{-1} mol^{-1}.

The least-squares normal equations are nonlinear in

---

(10) S. H. Storey and F. VanZeggeren, *Can. J. Chem. Eng.*, **45**, 323 (1967).

Table I

Observed and Predicted Absorbance Under Various Conditions of Temperature and Concentration[a]

			Absorbance (505 mμ)				Absorbance (445 mμ, H_t = 0.0)	
10^5C, M	H_t, M	Temp, °C	A_i	A_{calcd}	10^5C_M, M	Temp, °C	A_i	A_{calcd}
32.0	0.01	15.6	0.392	0.384	100	22.2	0.423	0.430
32.0	0.03	15.6	0.295	0.285	60	22.2	0.240	0.243
32.0	0.05	15.6	0.230	0.230	30	22.2	0.114	0.129
32.0	0.02	25.2	0.350	0.336	128	27.2	0.604	0.592
32.0	0.04	25.2	0.262	0.260	96	27.2	0.450	0.441
32.0	0.06	25.2	0.190	0.199	64	27.2	0.300	0.300
87.9	0.0	27.2	1.220	1.210	32	27.2	0.142	0.147
52.7	0.0	27.2	0.705	0.714	16	27.2	0.080	0.074
37.6	0.0	27.2	0.520	0.518	12	27.2	0.058	0.054
23.9	0.0	27.2	0.322	0.329	100	34.6	0.497	0.497
96.0	0.04	27.2	0.970	0.970	60	34.6	0.305	0.299
60	0.04	27.2	0.519	0.514	30	34.6	0.114	0.129
36	0.04	27.2	0.275	0.276	87.9[b]	27.2	1.400	1.389
24	0.03	27.2	0.197	0.193	52.7[b]	27.2	0.825	0.834
24	0.06	27.2	0.109	0.105	37.6[b]	27.2	0.590	0.595
8	0.03	27.2	0.044	0.043	23.9[b]	27.2	0.368	0.374
8	0.05	27.2	0.022	0.021	12.6[b]	27.2	0.190	0.198
32	0.01	34.6	0.344	0.358	5.0[b]	27.2	0.080	0.080
32	0.03	34.6	0.254	0.252				
32	0.05	34.6	0.180	0.172				

[a] Every third observation is listed. C, C_M, and H_t are the tota lconcentrations of $Co(terpy)_2^{2+}$, $Co(terpy)^{2+}$, and hydrogen ion added, respectively. [b] The bis complex without acid at 445 mμ and 27.2°.

the parameters and the minimization of Φ was done by an interative algorithm for nonlinear least-squares calculations[11,12] starting from initial guesses for the parameters. The least-squares program was used with analytical derivatives of A_i with respect to each of the parameters, *i.e.*, $\partial A/\partial\epsilon$, $\partial A/\partial(\Delta S)$, and $\partial A/\partial(\Delta H)$. The six parameters were adjusted simultaneously using all 108 observations. Good agreement between the observed and predicted absorbance was obtained. Typical results are shown in Table I.

Results

Thermodynamic parameters for reactions 2 and 6 are listed in Table II at 25°. The thermodynamic parameters for the reaction of terpyridine with acid are those reported for ionic strength[8] $\mu = 0.01$ M and it is expected that the correction to ionic strength 0.24 M used in this work will be reflected in small systematic errors in the thermodynamic parameters found for reactions 2 and 6. The formation constants and the associated thermodynamic parameters will be affected directly by the terpyridine–acid thermodynamic data. However, the quantities log (K_1/K_2), $\Delta S_1 - \Delta S_2$, and $\Delta H_1 - \Delta H_2$ are insensitive to errors in the terpyridine–acid data. The thermodynamics of the formation reactions are given in Table III, together with data for cobalt(II) complexes of other ligands for comparison.

Discussion

Evidently $K_2 < K_1$ for the formation of cobalt(II)–terpyridine complexes as reported for the other neutral ligands in Table III, contrary to the order found from kinetic data, although strict comparison with the kinetic results is not possible because of variations in ionic strength and temperature.

Table II

Thermodynamic Parameters for Reactions 2 and 6 at μ = 0.24 M[a]

Reaction	$K_{25°}$, M^{-1}	$\Delta H°$, kcal mol^{-1}	$\Delta S°$, cal deg^{-1} mol^{-1}	Absorptivity of $Co(terpy)_2^{2+}$
2	0.082 ± 0.001[b]	4.7 ± 0.3	11 ± 1	ϵ^{505} 1374 ± 3 ϵ^{445} 1581 ± 3
6	0.032 ± 0.002[b]	14.5 ± 0.9	42 ± 3	

[a] Uncertainties given are estimates of the standard errors from the least-squares calculation. [b] Standard errors in K estimated from data at a single temperature are smaller than estimated from errors in $\Delta H°$ and $\Delta S°$.

The major influence on ΔH of chelation is thought to arise from steric and electrostatic repulsions between ligand groups in the complex.[13] The terpy system has an unusually large ΔH_1 reflecting very small steric interactions in the complex relative to the ligand. The smaller ΔH_2 suggests additional steric interaction between the two ring systems. The bipy system is similar, in contrast to the en and den systems.

For systems with the same number and size of chelate rings, the important entropy effects of chelation are thought to be due to changes in solvation on complex formation and arrangement of chelate rings.[13] In the terpy system, the arrangement of rings is severely limited[14] and thus solvation effects are likely dominating. Other smaller effects are differences in configurational entropies of the ligand in the chelate relative to the uncoordinated ligands. For the cobalt(II)–terpy system changes in spin multiplicity[15,16] can also contribute enthalpy and entropy effects. We speculate that the spin-multiplicity effects are small and that changes in solvation are the dominating contribution to entropies of formation.

---

(11) D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963).

(12) D. W. Marquardt, IBM Share Library Distribution No. 309401 NONLIN-2.

(13) A. E. Martell, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C. 1967, p 272.

(14) F. W. B. Einstein and B. R. Penfold, *Acta Cryst.*, **20**, 924 (1966).

(15) R. Farina and R. G. Wilkins, *Inorg. Chem.*, **7**, 514 (1968).

(16) J. S. Judge, Ph.D. Dissertation, Syracuse University, 1967.

TABLE III

THERMODYNAMIC DATA FOR THE FORMATION OF VARIOUS Co(II) COMPLEXES OF NEUTRAL LIGANDS (ΔG, KCAL MOL^{-1} AT 25°; ΔH, KCAL MOL^{-1}; ΔS, CAL DEG^{-1} MOL^{-1})

$$Co^{2+} + L = CoL^{2+}$$

$$CoL^{2+} + L = CoL_2^{2+}$$

	L				
	$3NH_3$[c]	den[d]	terpy[b]	en[e]	bipy[f]
$-\Delta G_1$	6.16	10.9	12.95 ± 0.04 (11.5)[a]	8.1	8.1
$-\Delta G_2$	6.08	8.0	12.42 ± 0.01 (13.5)[a]	6.4	7.2
$-\Delta G_3$	...	...	...	4.1	6.4
$-\Delta H_1$	5.26	8.15	22 ± 0.9 (10.7)[a]	6.9	8.2
$-\Delta H_2$	7.74	10.25	12.2 ± 0.3	7.1	7.0
$-\Delta H_3$	...	...	...	8.2	6.1
ΔS_1	2.9	9.0	−30 ± 3	+4.0	−0.35
ΔS_2	−5.54	−7.5	0 ± 1	−2.0	0.7
ΔS_3	...	...	...	−13.8	1.05

[a] From kinetic data of Holyer, *et al.*;[6] ΔG_2 given at 5°. [b] Computed from data in Table I (this work) and terpy data.[8] [c] M. Chatelet, *J. Chim Phys.*, **59,** 2365 (1937); J. Bjerrum, "Metal Ammine Formation in Solution," Thesis, 1941, reprinted by P. Haase and Son, Copenhagen, Denmark, 1957, p 187. [d] den = diethylenetriamine: M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 2994 (1961). [e] en = ethylenediamine: M. Ciampolini, P. Paoletti, and L. Sacconi, *Nature*, **186,** 880 (1960); *J. Chem. Soc.*, 4553 (1958). [f] bipy = 2,2′-bipyridine: G. Anderegg, *Helv. Chim. Acta*, **46,** 2397, 2813 (1963).

The large differences in ΔH for the two steps are almost completely compensated by changes in ΔS, as observed in a number of other systems.[13]

Acknowledgment.—This work was supported by PHS Research Grant No. AM 10946-03 from the National Institute of Arthritic and Metabolic Diseases.

CONTRIBUTION FROM THE CENTRO CHIMICA E TECHNOLOGIA COMPOSTI METALLORGANICI ELEMENTI DI TRANSIZIONE DEL C.N.R., FACOLTÀ DI CHIMICA INDUSTRIALE, BOLOGNA, ITALY

Novel Complexes of Rhodium and Iridium with Electronegative Olefins

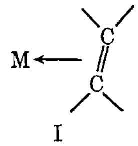
BY PAOLO UGUAGLIATI, GIULIO DEGANELLO, LUIGI BUSETTO, AND UMBERTO BELLUCO

Received January 17, 1969

$[Rh(CO)_2Cl]_2$ undergoes halogen bridge splitting by triphenylphosphine to give *trans*-$RhCl(CO)_2(P(C_6H_5)_3)$. Tetracyanoethylene (TCNE) forms a 1:1 adduct with this substrate, of the formula $RhCl(CO)_2(P(C_6H_5)_3)(TCNE)$ (*cis*-dicarbonyl). *cis*-$RhCl(CO)_2(L)$ (L = pyridine, *p*-toluidine) forms adducts with TCNE and fumaronitrile (FMN) of the type $RhCl(CO)_2(L)$(TCNE or FMN) (*trans*-dicarbonyl). $IrCl(N_2)(P(C_6H_5)_3)_2$ reacts with TCNE to give $[IrCl(P(C_6H_5)_3)_2(TCNE)]$ and with FMN to give both $IrCl(N_2)(P(C_6H_5)_3)_2(FMN)$ and $IrCl(P(C_6H_5)_3)_2(FMN)$. In all these adducts the cyanoolefins are bonded to the metal through the olefinic bond. By the action of 1,2-bis(diphenylphosphino)ethane (diphos), $RhCl(CO)_2(L)(TCNE)$ is converted to $[Rh(L)(diphos)(TCNE)]Cl$ whereas $RhCl(CO)_2(L)(FMN)$ gives $[Rh(diphos)(CO)_2]Cl$. Infrared spectra, bonding modes, and reactivity are discussed.

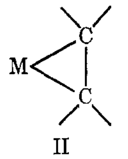
Introduction

Cyanoolefins display a remarkable electrophilic character[1,2] which also manifests itself when the cyanoolefin is coordinated to a transition metal ion.[3-5] The extent of such electron-withdrawing ability, as is deduced from the carbonyl stretching frequency in adducts of the type $IrCl(CO)(P(C_6H_5)_3)_2$(Lewis acid),[5] is intermediate between the SO_2 and BF_3 groups for tetracyanoethylene and fumaronitrile. This peculiar property has recently provoked speculations as to the modes of bonding of cyanoolefins in a metal complex.[6-9] The arguments center around the following alternative configurations for these complexes; M is (initially) a d^8 metal ion. The origin of this dual interpretation lies in the fact that it is impossible to define a coordination number for the central metal even when the



I

conventional metal–olefin structure



II

three-membered, metallocyclopropane ring

---

[1] T. L. Cairns and B. C. McKusick, *Angew. Chem.*, **73,** 520 (1961).

[2] K. Vasudevan and V. Ramakrishnan, *Rev. Pure Appl. Chem.*, **17,** 95 (1967).

[3] W. H. Baddley, *J. Am. Chem. Soc.*, **88,** 4545 (1966).

[4] W. H. Baddley, *ibid.*, **90,** 3705 (1968).

[5] R. N. Scott, D. F. Shriver, and L. Vaska, *ibid.*, **90,** 1079 (1968).

[6] P. Fitton and J. E. McKeon, *Chem. Commun.*, 4 (1968).

[7] W. H. Baddley, *Inorg. Chim. Acta Rev.*, **2,** 5 (1968).

[8] J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **89,** 844 (1967).

[9] J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968).