Mechanism of Octahedral Substitutions in Nonaqueous Media. Part VIII.[1] Replacement of Chloride by Nucleophiles in *trans*-Chloro(L)bis(ethylenediamine)cobalt(III) Complexes in Methanol

By **Zdravko Bradić, M. Biruš, D. Pavlović, M. Pribanić, and S. Ašperger,*** Department of Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb and Institute 'Rudjer Bošković', Zagreb, Croatia, Yugoslavia

The dependence of the rate of replacement of chloride by thiocyanate, azide, and nitrite in *trans*-$[Co(en)_2LCl]^{n+}$ ion on L (L = NO_2, N_3, CN, Cl, and NCS) is the same in methanol as in water. The rate of replacement of chloride by methoxide in *trans*-$[Co(en)_2LCl]^{n+}$ is faster for L = CN than for L = NO_2, as was the rate of replacement of chloride by hydroxide in base hydrolysis. The effects of L on rates are discussed.

The replacement of chloride by nitrite in *trans*-chlorocyanobis(ethylenediamine)cobalt(III) ion in methanol proceeds with retention of configuration as was shown by preparation of *trans*-cyanonitrobis(ethylenediamine)-cobalt(III) perchlorate.

SINCE the idea[2] of the dichotomy of mechanism of acid hydrolysis of $[Co(en)_2LCl]^{n+}$ complexes, supposedly caused by the electron-donating or -accepting power of L, was put forward in 1956, a great effort was made[3-8] to detect a role for the entering group in solvolyses, anion replacements, and anations. It was generally concluded that there is no support for the duality of mechanism[9-11] for a given leaving group. The role of electron-donating directing ligands is successfully interpreted in terms of ligand-to-metal π-bonding. A final adjudication of the role of electron-accepting directing ligands has not yet been made. As a possible explanation it has been suggested[9] that all the rates of acid hydrolysis for various L can be considered as similar, with the exception of the high rates for L = OH and NH_2 (which are well understood in terms of π-bonding), and the extremely low rate for L = NCS, which then remains as a single case to be explained.

The intention of the present work is to show that the electronic effects of directing ligands, π-donors, and π-acceptors, giving the two-branch curve in aqueous acid hydrolyses[2] of $[Co(en)_2LCl]^{n+}$, are also operating in anion replacements in alcoholic solutions.

Moreover, in base hydrolysis of both *cis*- and *trans*-$[Co(en)_2LCl]^{n+}$ ions the plot of the rate constants against electron-donating ability of L shows that maximum rates occur with ligands of 'medium' electron-donating ability[12] (such as chloride). An analogous situation is now observed in base methanolysis.

RESULTS

Kinetics of Replacement of Chloride by Thiocyanate in trans-$[Co(en)_2LCl]^+$ *Ion in Methanol* (L = NO_2, N_3, CN, Cl *and* NCS).—With L = NO_2, N_3, and CN, acid hydrolysis proceeds with complete retention of configuration[13,14] but with L = Cl and NCS the reaction proceeds with large

---

[1] Part VII, S. Ašperger, M. Flögel, and I. Murati, *J. Chem. Soc.* (*A*), 1969, 569.

[2] S. Ašperger and C. K. Ingold, *J. Chem. Soc.*, 1956, 2862.

[3] C. H. Langford and P. O. Langford, *Inorg. Chem.*, 1963, **2**, 300.

[4] C. H. Langford, *Inorg. Chem.*, 1964, **3**, 228.

[5] C. H. Langford and M. P. Johnson, *J. Amer. Chem. Soc.*, 1964, **86**, 229.

[6] (*a*) S. Ašperger, D. Pavlović, and M. Orhanović, *J. Chem. Soc.*, 1961, 2142; (*b*) S. Ašperger, M. Orhanović, and I. Murati, *ibid.*, 1964, 2969.

[7] M. N. Hughes and M. L. Tobe, *J. Chem. Soc.*, 1965, 1204.

[8] M. L. Tobe, *Rec. Chem. Progr.*, 1966, **27**, 79; *Adv. Chem.*, 1965, **49**, 1, and refs. therein.

[9] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1965, p. 72.

[10] F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, p. 328.

[11] M. L. Tobe, *Inorg. Chem.*, 1968, **7**, 1260.

[12] Ref. 10, p. 181.

[13] C. K. Poon, *Inorg. Chim. Acta Rev.*, 1970, **4**, 123.

[14] V. Ricevuto and M. L. Tobe, *Inorg. Chem.*, 1970, **9**, 1785. The authors corrected previous report and showed that spontaneous aquation of *trans*-$Co(en)_2N_3X^+$ (X = Cl and Br) takes place with complete retention of configuration.

stereochange.[13] When L = NO_2 the replacement of chloride by thiocyanate ions in methanol proceeds with complete retention of configuration.[6a] Chloride exchange in the *trans*-dichloro-complex takes place with almost complete retention of configuration [15] in methanol, while chloride exchange in dimethylformamide, dimethylacetamide, and dimethyl sulphoxide occurs with considerable change in configuration.[15] When L = NCS the steric course of replacement of chloride by thiocyanate in aqueous solutions could not be determined, since the spectra of *cis*- and *trans*-di-isothiocyanato-complex ions are virtually identical.[16]

When L = CN the steric course of replacement of chloride by thiocyanate in methanol was not determined with certainty, but the steric course of replacement of chloride by nitrite proceeded with complete retention of configuration. Figure 1 shows the absorption spectrum of *trans*-$[Co(en)_2(CN)(NO_2)]^+$ and the spectrum of the product of replacement of chloride by nitrite in *trans*-$[Co(en)_2(CN)Cl]^+$. Spectra are almost identical. The difference in absorption at shorter wavelengths (below 400 nm) is due only to the absorption of nitrite ion present in the reaction mixture. Since the replacement of chloride by nitrite proceeds with retention of configuration it is likely that the replacement of chloride by thiocyanate also goes without stereochange. The rates of replacements of chloride by thiocyanate in trans-$[Co(en)_2LCl]^+$ in methanol for L = NO_2, N_3, CN, and Cl are shown in Figure 2. The replacement rate when L = NCS was also measured but the rate is too slow for presentation in Figure 2.

Table 1 summarizes the kinetic results of replacement of chloride in *trans*-$[Co(en)_2LCl]^+$ ion by 0·05M-thiocyanate in methanol in presence of 0·0014M-perchloric acid. Perchloric acid (70%) was added in this series of measurements to assure that no conjugate base mechanism can operate. The addition of the acid increased water content negligibly (from *ca.* 0·05 to 0·06%). The rate constants for chloride replacements are compared with those of acid hydrolyses.

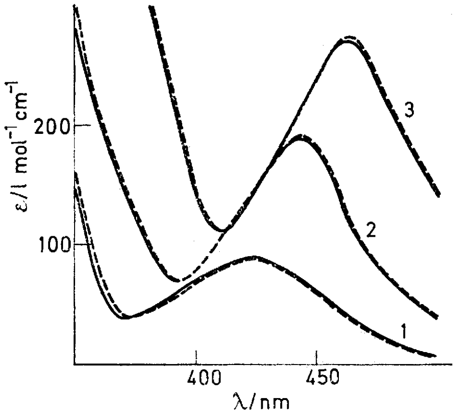

FIGURE 1 Absorption spectra in methanol: 1, of 0·0005M-*trans*-$[Co(en)_2(CN)(NO_2)]ClO_4$ (full line), and of the product of replacement of chloride in 0·0005M-*trans*-$[Co(en)_2(CN)Cl]NO_3$ with 0·02M-$NaNO_2$ in methanol (broken line); 2, of 0·0005M-$[Co(en)_2(CN)(NCS)]ClO_4$ (full line) and of the mixture of 0·0005M-*trans*-$[Co(en)_2(CN)Cl]ClO_4$ and 0·045M-NaSCN in methanol after ten half-lives (broken-line); 3, of 0·0005M-$[Co(en)_2(CN)N_3]ClO_4$ (full line), and of the mixture of 0·0001M-*trans*-$[Co(en)_2(CN)Cl]NO_3$ and 0·01M-NaN_3 in methanol after ten half-lives (broken line)

The rate constants for chloride replacements in Table 1 can be considered to refer to the reactions of the complex–thiocyanate ion pairs, since Figure 2 reveals that at 0·05M-thiocyanate the ion-pair formation is essentially *complete*.

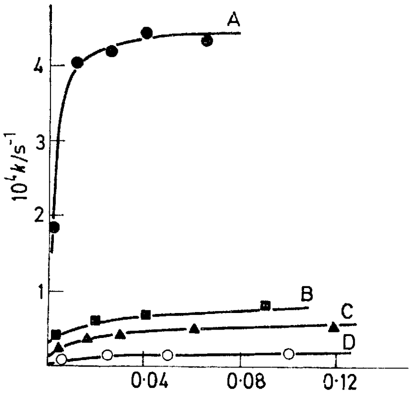

FIGURE 2 Rates of replacement of chloride by thiocyanate in 0·0005M-trans-$[Co(en)_2LCl]^+$ in methanol at 38·6 °C. No addition of perchloric acid: A, L = NO_2; B, L = N_3; C, L = CN; D, L = Cl

Kinetics of Replacement of Chloride by Nitrite and Azide in trans-$[Co(en)_2LCl]^+$ *Ion in Methanol* (L = NO_2, N_3, *and* CN).—The mechanism of replacement of chloride of *trans*-$[Co(en)_2LCl]^+$ ion by nitrite or azide ions is more complex than that by thiocyanate ion, since nitrite and azide are basic reagents (in water [12] pK_a for NO_2^- is 3·4, and for N_3^- is 4·7 at 25 °C) and the replacements can proceed partly *via* the conjugate base mechanism. Acidification of the reaction solution with perchloric acid would reduce the reagent concentration because HNO_2 and HN_3 are weak acids. Figure 3 shows that replacement rates correlate well with reagent basicities. The ion-pair formation constants for the chlorocyano-complex ion with azide, nitrite, and thiocyanate are rather similar (Table 2) so that the differences in ion-pairing cannot account for the differences in replacement rates.

TABLE 1

First order rate constants k_{SCN^-}, of replacements of chloride by 0·05M-thiocyanate in 0·0005M-*trans*-$[Co(en)_2LCl]^+$ ion in methanol in presence of 0·0014M-$HClO_4$ at 38·6 °C, and the rate constants, k_{H_2O}, of acid hydrolysis of the same complexes at 25 °C taken from ref. 10, p. 171

L	$10^4k_{SCN^-}/s^{-1}$	$10^4k_{H_2O}/s^{-1}$
NO_2	5·45	9·8
N_3	0·770	2·2
CN	0·182	0·82
Cl	0·107	0·35
NCS	0·0037	0·0005

Ion-pair formation constants K were determined from equation (1) where $[Y^-]$ is the concentration of the entering

$$\frac{1}{k_{exp}-k_0}=\frac{1}{(k_1-k_0)K[Y^-]}+\frac{1}{k_1-k_0} \qquad (1)$$

---

[15] M. L. Tobe, 'The Steric Course of Octahedral Substitution,' in 'Studies on Chemical Structure and Reactivity,' ed. J. H. Ridd, Methuen, London, 1966, pp. 230 and 231.

[16] F. Basolo, B. D. Stone, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1953, **75**, 819.

nucleophilic reagent, and k_0 and k_1 are the rate constants for the reaction of the free ion and for the rearrangement of the ion-pair, respectively. By plotting $1/(k_{exp} - k_0)$ against $1/[Y^-]$ a good straight line was obtained for each Y^-, and K was determined from the slope.

TABLE 2

Ion-pair formation constants/l mol^{-1} in the replacement of chloride in 0·0001—0·0005M-*trans*-$[Co(en)_2LCl]^+$ by Y^- in methanol at 38·6 °C

L	Y^-		
	SCN^-	NO_2^-	N_3^-
NO_2	700	130	100
CN	70	50	90
N_3	50	20	30

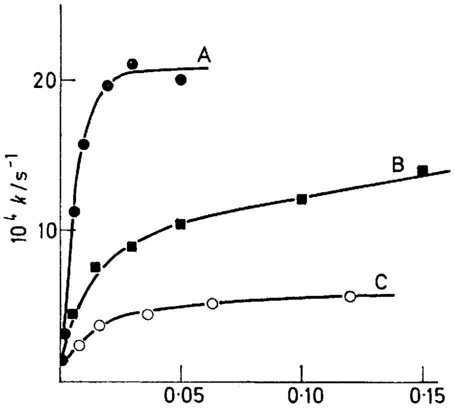

FIGURE 3 Rates of replacements of chloride in 0·0001—0·0005M-*trans*-$[Co(en)_2(CN)Cl]^+$ by A, azide; B, nitrite; and C, thiocyanate in methanol at 38·6 °C

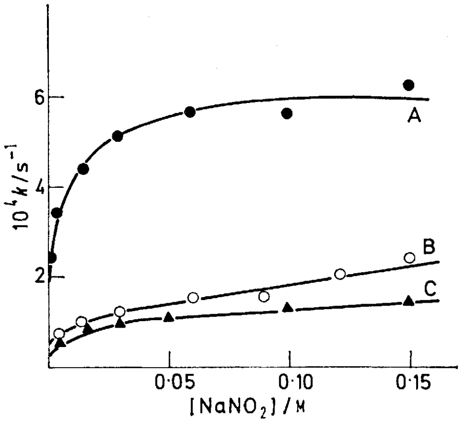

FIGURE 4 Rates of replacement of chloride by nitrite in 0·0005M-*trans*-$[Co(en)_2LCl]^+$ in methanol at 38·6 °C: A, L = NO_2; B, L = N_3; C, L = CN

In spite of the fact that substitution of chloride by nitrite and azide proceeds partly through the conjugate base mechanism, the electronic effects of the directing ligands work in much the same manner as for substitution by thiocyanate (Figure 4). The order of replacement rates for L = NO_2, N_3, and CN is $NO_2 \gg N_3 > CN$ for $Y^- = NCS^-$ and NO_2^-, and $NO_2 \gg CN \geqslant N_3$ for $Y^- = N_3^-$.

Kinetics of Replacement of Chloride by Methoxide in trans-$[Co(en)_2LCl]^{n+}$ *Ion in Methanol* (L = NO_2 *and* CN).—The electronic effects of the directing ligand, as observed in the aqueous base hydrolyses of *cis*- and *trans*-$[Co(en)_2LCl]^{n+}$ ion are seen again in replacement of chloride by methoxide in methanol. The plot of rate constants against electron-donating ability of L for base hydrolyses shows that maximum rates occur with ligands of 'medium' electron-donating ability. The low reactivity of $[Co(en)_2NO_2Cl]^+$ ion to base hydrolyses has been explained in terms of a co-operative π-bonding effect.[17] Table 3 compares the kinetic data in water and methanol.

TABLE 3

Rate constants for base methanolysis at 10 °C (k_{MeO^-}) and for base hydrolyses at 0 °C (k_{OH^-}) for 0·0002—0·0005M-*trans*-$[Co(en)_2LCl]^+$ ion

L	$\frac{k_{MeO^-}}{l\ mol^{-1}\ s^{-1}}$	$\frac{k_{OH^-}}{l\ mol^{-1}\ s^{-1}}$
NO_2	0·18 [a]	0·080 [c]
CN	0·83 [b]	0·13 [c]

[a] Ionic strength was kept constant with $LiClO_4$ at 0·0573M. [b] Ionic strength = 0·0435M. [c] From ref. 10, p. 181.

DISCUSSION

It was found that the electronic effects of the directing ligands observed in aqueous acid and base hydrolyses of $[Co(en)_2LCl]^{n+}$ ion are also observed in anion replacement reactions in methanol. It appears that the effects of L are solvent-independent since analogous L effects were previously observed in dimethylformamide.[3] Moreover the rate of chloride exchange for *trans*-$[Co(en)_2(CN)Cl]^+$ in methanol has been found [18] approximately equal to the rate when L = Cl, but slower than for L = NO_2. Hence there is considerable evidence for the effects of L on the relative order of the rate constants, as originally observed in aqueous acid hydrolyses of *cis*- and *trans*-$[Co(en)_2LCl]^{n+}$ ion, and recently of *trans*-$[Co(cyclam)LCl]^{n+}$ ion.[19,20]

The rate acceleration when L = NO_2 is most probably due to better ligand-to-metal π-bonding in the transition state than in the ground state. The stabilization of the complexes of reduced co-ordination number by π-acceptors has been discussed by Langford and Gray.[9] On the other hand the strong retardation when L = NCS requires better stabilization of the reactants in the ground state than in the transition state. The isocyanate electronic structure $Co-N^+{\equiv}C-S^-$ might more effectively withdraw electrons through its inductive ($-I$) effect in the singly charged ground state than in the doubly charged transition state. ($+I$) effects have been studied [21] and found to be small in these systems, but information on the ($-I$) effect is lacking.

---

[17] Ref. 10, p. 186.

[18] G. Semerano, G. Schiavon, G. Paradisi, and E. Campi, Summary of the paper presented at International Conference on Co-ordination Chemistry, Sept., 1967, Tokyo.

[19] C. K. Poon and M. L. Tobe, *J. Chem. Soc.* (*A*), 1967, 2069.

[20] K. S. Mok and C. K. Poon, *Inorg. Chem.*, 1971, **10**, 225; K. S. Mok, C. K. Poon, and H. W. Tong, *J.C.S. Dalton*, 1972, 1701.

[21] F. Basolo, J. G. Bergmann, R. E. Mecker, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1956, **78**, 2676.

If the same intermediates are formed in all solvents due to the effects of the directing group then the difference in steric course can be explained by assuming that in aqueous acid hydrolysis water enters from all sides of the trigonal bipyramid (*e.g.*, L = Cl) yielding the *cis*- and *trans*-products. In methanolic solutions, the decreased dielectric constant and increased Coulomb repulsion between charged entering group and directing groups could possibly yield entirely *trans*-product. This suggestion is supported: (1) by our earlier observation[22] that *cis*-$[Co(en)_2(H_2O)Cl]^{2+}$ reacts with chloride or bromide in methanol giving *trans*-dihalogeno-complex ion quantitatively; and (2) that *trans*-dichloro-complex reacts with azide in methanol giving *ca.* 95% *trans*-azidochloro-complex[23] with the positive $\Delta S^{\ddagger}$ in agreement with values previously assigned to the trigonal bipyramidal configuration.

EXPERIMENTAL

Preparations.—*trans*-Dichlorobis(ethylenediamine)cobalt(III) chloride and *trans*-chloronitrobis(ethylenediamine)cobalt(III) nitrate were prepared as described previously.[22] *trans*-Diazidobis(ethylenediamine)cobalt(III) perchlorate was prepared as described[24] and characterized by its spectra.[25] *trans*-Azidochlorobis(ethylenediamine)cobalt(III) perchlorate was prepared as recently recommended[26] and characterized by its spectra.[14] *trans*-Chlorocyanobis(ethylenediamine)cobalt(III) chloride monohydrate was prepared as described[27,28] and characterized by its spectra.[27] The proof that the complex is the *trans*-isomer was given when the *cis*-isomer was prepared.[29] The perchlorate and the nitrate salts of the complex were also prepared as described.[27] *trans*-Chloroisothiocyanatobis(ethylenediamine)cobalt(III) thiocyanate was prepared as described[30] and characterized by its spectra.[31]

trans-Cyanonitrobis(ethylenediamine)cobalt(III) perchlorate was prepared by dissolving *trans*-$[Co(en)_2(CN)Cl]Cl,H_2O$ (1 g) in the minimum of water at *ca.* 70 °C. The solution was filtered and a concentrated solution of sodium nitrite (1·5 g) was added to the filtrate. The solution was kept at 70 °C for 1 h and then solid sodium perchlorate was added, causing a yellow precipitate. The solution was cooled in an ice-bath, and the crystalls were filtered off, washed with a little cold water, and methanol, and recrystallised from water with added sodium perchlorate. The crystalline $[Co(en)_2(CN)(NO_2)]ClO_4$ was washed again with water, methanol, and ether and dried *in vacuo* over $CaCl_2$ (Found: C, 17·0; H, 4·5; N, 24·1; Co, 16·9. Calc. for $C_5H_{16}ClCoN_6O_6$: C, 17·13; H, 4·59; N, 23·97; Co, 16·81%). The i.r. spectra of the complex showed a single peak at 894 cm^{-1} indicating *trans*-configuration.[32] There is also a strong absorption band at 1609 cm^{-1}, as expected for *trans*-bis(ethylenediamine)complexes.[33]

Isothiocyanatocyanobis(ethylenediamine)cobalt(III) perchlorate was prepared from *trans*-$[Co(en)_2(CN)Cl]Cl,H_2O$ and sodium thiocyanate following in principle the procedure described for the preparation of the *trans*-cyanonitro-complex with the only difference that *trans*-$[Co(en)_2(CN)(NCS)]SCN$ precipitated spontaneously. The crystals were filtered off and converted into the perchlorate salt $[Co(en)_2(CN)(NCS)]ClO_4$ (Found: C, 19·6; H, 4·4; N, 23·5. Calc. for $C_6H_{16}ClCoN_6O_4S$: C, 19·87; H, 4·45; N, 23·17%). The i.r. spectra showed a single band at 1589 cm^{-1} suggesting *trans*-configuration,[33] but there was a band at 894 and a band at 870 cm^{-1}. Whereas a single peak in this region would indicate a *trans*-configuration[32] a split peak does not necessarily indicate a *cis*-configuration.[27] Figure 1 shows the absorption spectra of the complex. Spectra are virtually identical with that of the mixture of *trans*-$[Co(en)_2(CN)Cl]ClO_4$ and NaSCN in methanol after ten half-lives, which also suggests that the complex has the *trans*-configuration.

Azidocyanobis(ethylenediamine)cobalt(III) perchlorate $[Co(en)_2(CN)(N_3)]ClO_4$ was prepared from *trans*-$[Co(en)_2(CN)Cl]Cl,H_2O$ and sodium azide following the procedure for the preparation of the *trans*-cyanonitro-complex (Found: C, 17·2; H, 4·9; N, 32·45; Co, 16·8. Calc. for $C_5H_{16}ClCoN_8O_4$: C, 17·33; H, 4·65; N, 32·33; Co, 17·00%). Figure 1 shows the absorption spectra of the complex. Spectra are identical with those of the mixture of trans-$[Co(en)_2(CN)Cl]ClO_4$ and NaN_3 in methanol after ten half-lives, which suggests that the complex has a *trans*-configuration. The i.r. spectra appeared complicated and could not be used for identification of stereoconfiguration.

Absolute methanol was prepared by Lund and Bjerrum's method.[34] Merck's analytical grade absolute methanol containing 0·05% water was also used. The purity of alcohol was checked by its conductivity because it could contain alkali.

Sodium methoxide was prepared by dissolving pure sodium in methanol. The concentration of methoxide was determined by titration with potassium hydrogen phthalate. All other chemicals were of analytical grade.

TABLE 4

Wavelengths λ/nm used in kinetic measurements

Complex *trans*-$[Co(en)_2LCl]^+$	Reagent			
	SCN^-	NO_2^-	N_3^-	MeO^-
L = NO_2	475	435; 500	485	340
CN	445	410	312	312
N_3	528	480	540	
NCS	510			
Cl	540			

Spectrophotometry.—Light absorption measurements in the visible and u.v. regions were made with a Cary 16K spectrophotometer, and i.r. measurements with a Perkin-Elmer 457 grating spectrophotometer by use of KBr pellets.

Kinetics.—Kinetics were followed spectrophotometrically

---

[22] S. Ašperger and M. Flögel, *J. Chem. Soc.* (*A*), 1968, 769.

[23] Unpublished results from this laboratory.

[24] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Inorg. Chem.*, 1967, **6**, 1807.

[25] P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 1960, 4812.

[26] K. W. Hicks, D. L. Toppen, and R. G. Linck, *Inorg. Chem.*, 1972, **11**, 310.

[27] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 966.

[28] I. B. Baranovskii and A. V. Babaeva, *Zhur. neorg. Khim.*, 1964, **9**, 2163.

[29] K. Ohkawa, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Japan*, 1966, **39**, 1715.

[30] A. Werner, *Annalen*, 1912, **386**, 133.

[31] D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 1953, 2680.

[32] M. E. Baldwin, *J. Chem. Soc.*, 1960, 4369.

[33] P. E. Merritt and S. E. Wiberley, *J. Phys. Chem.*, 1955, **59**, 55.

[34] H. Lund and J. Bjerrum, *Ber.*, 1931, **64**, 210.

in a thermostatted cell compartment at 38·6 ± 0·05 °C and at 10·0 ± 0·1 °C, and 10 mm quartz cells. The solutions of the complex and of the reagents in methanol *were separately* thermally equilibrated in a water thermostat (±0·02 °C), and then quickly mixed and transferred to the thermally equilibrated cell compartment. The kinetics of the reactions were followed at the wavelength where the absorption change is at its maximum or large (Table 4).

We thank Dr. W. L. Reynolds for discussions.

[3/553 *Received*, 15*th March*, 1973]