

tributed to the steric effect, discussed above, of the two protons attached to the phenyl rings of dqp and *cis* to the two quinolyl nitrogens. The visible spectra provide further evidence in favor of this view.

Electronic Spectra.—The electronic absorption spectra for the complexes are given in Table II. The

TABLE II
ELECTRONIC ABSORPTION SPECTRA

Compound	Medium	${}^5T_{2g} \rightarrow {}^5E_g$, cm^{-1} (ϵ)
Fe(dqp) $_2$ (ClO $_4$) $_2$	Solid	12,000
	Nitromethane	12,000 (20)
Fe(aqp) $_2$ (ClO $_4$) $_2$ ·H $_2$ O	Solid	10,200 sh, 8,000
	Nitrobenzene	10,400 (125), 8400 (135)
Fe(terpy) $_2$ (ClO $_4$) $_2$ ·2H $_2$ O	Nitrobenzene	[27,000 sh (7900), 18,000 (1.15 $\times 10^4$)] ^a

^a Other transitions.

only d-d transition expected in high-spin iron(II) is ${}^5T_{2g} \rightarrow {}^5E_g$, which gives a direct measure of Δ . This band occurs in the region near 10,000 cm^{-1} ²⁵ and may be split by asymmetry or Jahn-Teller distortion.²⁶ The assignment of this band in Fe(dqp) $_2$ (ClO $_4$) $_2$ gives $\Delta = 12,000 \text{ cm}^{-1}$, which is significantly higher than in Fe(H $_2$ O) $_6^{2+}$ ²⁵ but not high enough to spin-pair iron(II). The high-spin-low-spin crossover point in iron(II) is expected to occur at $\Delta \approx 15,000 \text{ cm}^{-1}$.²⁵ The splitting of the ${}^5T_{2g} \rightarrow {}^5E_g$ transition in Fe(aqp) $_2$ (ClO $_4$) $_2$ ·H $_2$ O is attributable to a low symmetry component in this complex, which is to be expected from the nature of the ligand. The lower value of Δ indicated for this complex is also as expected, since oxygen donor atoms generally exert much weaker ligand fields than nitrogens. For this reason, the fact that Fe(aqp) $_2$ (ClO $_4$) $_2$ ·H $_2$ O was found to be high spin is not surprising.

(25) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., London, 1962.

(26) F. A. Cotton and M. D. Meyers, *J. Am. Chem. Soc.*, **82**, 5023 (1960).

The value of Δ can be estimated approximately in low-spin iron(II) complexes from assignment of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, using the relations⁸

$$E({}^1T_1) - E({}^1A_1) = \Delta - C$$

$$E({}^1T_2) - E({}^1A_1) = \Delta + 16B - C$$

Making the usual approximation $C = 4B$, we have

$$\Delta \approx \frac{3}{4}\{E({}^1T_1) - E({}^1A_1)\} + \frac{1}{4}\{E({}^1T_2) - E({}^1A_1)\}$$

Using again the example of the tris(α -diimine)iron(II) of Ito, *et al.*,¹⁵ where the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions were shown to occur at 25,000 cm^{-1} (as a weak shoulder) and at 28,000 cm^{-1} (as a distinct peak), respectively, we obtain $\Delta \sim 26,000 \text{ cm}^{-1}$. Fe(terpy) $_2$ (ClO $_4$) $_2$ ·2H $_2$ O has a spectrum^{18,27} which resembles those of the diimine complexes quite closely. The tail of the 18,000- cm^{-1} charge-transfer band has a slight asymmetry near 24,000 cm^{-1} , and a weak shoulder appears near 27,000 cm^{-1} on a larger charge-transfer band (31,000 cm^{-1}). If these correspond to the two transitions discussed above, then Δ has a value similar to that in the α -diimine complexes; unfortunately, these transitions are poorly resolved, and definite assignments cannot be made at this stage. Perhaps of greater importance is the fact that there is no evidence of these d-d transitions below 18,000 cm^{-1} , suggesting that Δ is at least as high as 18,000 cm^{-1} . The low magnetic susceptibility, showing no sign of the temperature dependence expected and observed near the 5T_2 - 1A_1 crossover,⁷ also indicates that Δ is well above the crossover value of 15,000 cm^{-1} .

Thus the value of Δ for terpy is very much greater than that of dqp, and this emphasizes the power of the steric effect of the benzo substitution.

(27) R. B. Martin and J. A. Lissfelt, *ibid.*, **78**, 938 (1956).

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Kinetics of Acid Hydrolysis of Chloro(aniline)-, Chloro(*p*-toluidine)- and Chloro(*m*-toluidine)bis(ethylenediamine)cobalt(III) Complexes

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The rates of acid hydrolysis of chloro(aniline)-, chloro(*p*-toluidine)-, and chloro(*m*-toluidine)bis(ethylenediamine)cobalt(III) complexes have been studied at different acid concentrations. Two pathways, one independent and the other dependent upon hydrogen ion concentration, have been detected for the reaction. The rate constants (k_1) of the acid-independent path for the aniline, *p*-toluidine, and *m*-toluidine complexes are 7.01, 6.97, and $6.43 \times 10^{-8} \text{ sec}^{-1}$, respectively, at 50°. The activation energies have been calculated at a particular acidity for the three complexes.

The kinetics of acid hydrolysis of octahedral cobalt(III)-amine complexes have been extensively investigated. If the solution is made sufficiently acidic (pH

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3.0-4.0), these reactions generally become pH independent. However, exceptions are known. Acid hydrolysis of $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ is acid catalyzed² pre-

(2) S. C. Chan, *J. Chem. Soc.*, 2375 (1964).

sumably owing to the protonation of the departing ligand. In the case of a few complexes, in the pH range 3.0–4.0, the observed greater reactivity for acid hydrolysis has been ascribed to partial contribution from the much faster base hydrolysis reaction. Below pH 4.0, however, the concentration of hydroxide ion would be too small to produce sufficient concentration of the conjugate base³ for the base hydrolysis reaction to be kinetically significant. Formation of significant amounts of conjugate base without assistance from hydroxide ions and hence increased rate of hydrolysis in acid media could be due to the shift of the equilibrium



in the forward direction. If $\text{p}K_a$ values of amines are taken to be a measure of the acidity of the NH proton, complexes containing coordinated amines of comparatively low $\text{p}K_a$ values might be expected to react in accordance with eq 1. With this in view, the rates of acid hydrolysis of the complexes *cis*-[Co(en)₂(NH₂C₆H₅)Cl](ClO₄)₂ (I), *cis*-[Co(en)₂(*p*-CH₃C₆H₄NH₂)Cl](NO₃)₂ (II), and *cis*-[Co(en)₂(*m*-CH₃C₆H₄NH₂)Cl](NO₃)₂ (III) have been investigated at different acidities. The effect of substituents in the phenyl ring on the rate of the reaction has also been examined.

Experimental Section

cis-Chloro(aniline)bis(ethylenediamine)cobalt(III) chloride ([Co(en)₂(NH₂C₆H₅)Cl]Cl₂·H₂O), *cis*-chloro(*p*-toluidine)bis(ethylenediamine)cobalt(III) chloride ([Co(en)₂(*p*-CH₃C₆H₄NH₂)Cl]Cl₂), and *cis*-chloro(*m*-toluidine)bis(ethylenediamine)cobalt(III) chloride ([Co(en)₂(*m*-CH₃C₆H₄NH₂)Cl]Cl₂) were prepared as in the literature.⁴ The compounds were recrystallized from aqueous hydrochloric acid before further use.

cis-Chloro(aniline)bis(ethylenediamine)cobalt(III) perchlorate was prepared by dissolving 1 g of the chloride complex in a minimum amount of ice-cold water and adding 60% perchloric acid dropwise. On vigorous stirring, the less soluble perchlorate complex precipitated out. Precipitation with perchloric acid was repeated until no immediate precipitate was obtained on adding silver nitrate. The precipitate was washed with ice-cold water, alcohol, and finally ether and then dried over potassium hydroxide. *Anal.* Calcd for [Co(en)₂(NH₂C₆H₅)Cl](ClO₄)₂: Co, 11.92; Cl (coord), 7.00. Found: Co, 11.77; Cl (coord), 7.05.

cis-Chloro(*p*-toluidine)bis(ethylenediamine)cobalt(III) nitrate and *cis*-chloro(*m*-toluidine)bis(ethylenediamine)cobalt(III) nitrate were prepared as above, except that concentrated nitric acid was used as precipitant. *Anal.* Calcd for [Co(en)₂(*p*-CH₃C₆H₄NH₂)Cl](NO₃)₂: Co, 13.23; Cl (coord), 7.96. Found: Co, 13.15; Cl (coord), 7.98. Calcd for [Co(en)₂(*m*-CH₃C₆H₄NH₂)Cl](NO₃)₂: Co, 13.23; Cl (coord), 7.96. Found: Co, 13.18; Cl (coord), 7.92.

For measuring the reaction rates, appropriate solutions were made up in opaque volumetric flasks and thermostated. Measured volumes of solutions were withdrawn at known intervals and chilled in ice-cold acidified acetone–water mixtures.⁵ Chloride ion released by aquation was estimated by potentiometric titration with silver nitrate. A corresponding “blank” titration was also carried out. The kinetics of chloride release was generally followed to about 60% of the total coordinated chloride. Absorption spectra of the complexes and their aquated prod-

ucts were measured with a Hilger-Watts UVISPEK spectrophotometer using matched quartz cells of 1-cm light path.

Results

The apparent first-order rate constants, k_{app} , for release of chloride ions by aquation of complexes I–III were obtained from the slopes of the plots of $\log(V_\infty - V_t)$ vs. time, where V_t is the volume of silver nitrate consumed at the time interval t and V_∞ is the volume calculated for total coordinated chloride. At fixed acid concentration, k_{app} values for all three complexes, which are collected in Table I, decrease slightly with an increase in ionic strength. The reason for this decrease is not clear, except that this might be due to ionic strength effects on the acid–base equilibria (eq 1).

TABLE I
DEPENDENCE OF OBSERVED FIRST-ORDER RATE CONSTANTS FOR CHLORIDE RELEASE ON ADDED NaClO₄ IN AQUEOUS 0.005 M HClO₄ AT 50°

	10 ² [NaClO ₄], M			
	0.00	1.00	2.50	5.00
Complex I	2.00	1.90	1.83	1.72
Complex II	3.14	3.08	2.97	2.87
Complex III	1.58	1.48	1.40	1.30

At fixed ionic strength a considerable increase in rate of chloride release with decrease in the concentration of added acid in the pH range 1.0–3.0 has been observed. The rate constants, however, become acid independent at acidities greater than 0.1 M. The results are collected in Table II. The plots of k_{app} vs. 1/[H⁺] yield straight-line plots with positive intercepts in all three cases.

TABLE II
DEPENDENCE OF OBSERVED FIRST-ORDER RATE CONSTANTS FOR THE APPEARANCE OF CHLORIDE ION ON THE ADDED HClO₄ AT 50° AND $\mu = 0.07$ M

[Complex], mM	[HClO ₄], mM	10 ³ k_{app} , sec ⁻¹
Co(en) ₂ (NH ₂ C ₆ H ₅)Cl ²⁺		
3.52	1.00	6.75
2.98	1.50	5.23
3.32	3.00	2.82
3.00	5.00	1.87
3.12	10.00	1.40
2.89	25.00	0.82
3.00	50.00	0.82
Co(en) ₂ (<i>p</i> -CH ₃ C ₆ H ₄ NH ₂)Cl ²⁺		
3.02	1.00	11.10
3.14	1.50	8.34
2.98	3.00	3.93
2.08	5.00	3.08
2.83	7.50	1.90
3.14	10.00	1.80
Co(en) ₂ (<i>m</i> -CH ₃ C ₆ H ₄ NH ₂)Cl ²⁺		
3.42	1.00	6.52
3.17	1.50	4.50
3.08	3.00	2.52
3.12	5.00	1.68
2.97	7.50	1.34
3.62	10.00	1.20

From the temperature dependence of the rates k_{app} (at 0.005 M perchloric acid), given in Table III, the activation energies have been calculated to be

(3) F. J. Garrick, *Nature*, **139**, 507 (1937); F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1958, pp 124–132.

(4) J. C. Bailar and L. B. Clapp, *J. Am. Chem. Soc.*, **67**, 171 (1945).

(5) D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 2680 (1953).

TABLE III
DEPENDENCE OF OBSERVED FIRST-ORDER RATE CONSTANTS
FOR THE CHLORIDE RELEASE ON TEMPERATURE
IN 0.005 M AQUEOUS PERCHLORIC ACID

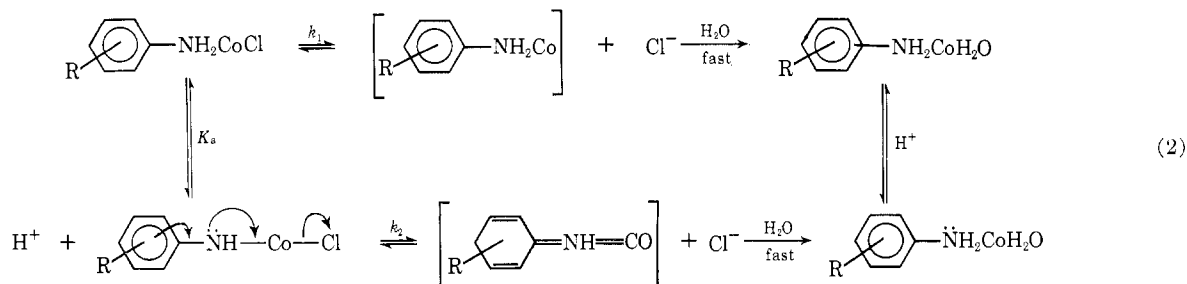
Temp, °C	k_{app} , sec ⁻¹	E , kcal/mol
Co(en) ₂ (NH ₂ C ₆ H ₅)Cl ²⁺		
40.5	5.9×10^{-6}	27.0
50.0	1.87×10^{-5}	
60.8	1.00×10^{-4}	
Co(en) ₂ (<i>p</i> -CH ₃ C ₆ H ₄ NH ₂)Cl ²⁺		
40.5	4.85×10^{-6}	32.0
50.0	3.08×10^{-5}	
61.0	1.75×10^{-4}	
Co(en) ₂ (<i>m</i> -CH ₃ C ₆ H ₄ NH ₂)Cl ²⁺		
40.0	4.37×10^{-6}	30.0
50.0	1.68×10^{-5}	
60.0	7.98×10^{-5}	

27.0, 32.0, and 30.0 kcal/mol for complexes I–III, respectively.

The representative absorption spectrum of complex I consists of two bands with peaks at 340 and 520 mμ, the first band being the more intense. In the aquated product the absorption maximum of the second band (ligand field) appears at 506 mμ, showing the expected shift to shorter wavelength.

Discussion

From the nature of acid dependence of the rate of chloride release for complexes I–III, it might be inferred that the reaction proceeds through two simultaneous paths: (i) an acid-independent dissociative path and (ii) an acid-dependent conjugate base path. The reaction scheme shown in eq 2 yields the rate expres-



sion

$$k_{app} = k_1 + \frac{k_2 K_a}{[\text{H}^+]} \quad (3)$$

which is consistent with the rate being acid independent at high acid concentration ($k_{app} \rightarrow k_1$). Values of k_1 and $k_2 K_a$ have been calculated by the least-squares⁶ method using the experimental data. These are collected in Table IV.

According to reaction scheme (2) the acid dependence of chloride release from the amine complexes would depend upon the pK_a values of the coordinated amines. However, the magnitude of k_2 would depend upon the π -bonding ability of the amido base. In view of the very rapid reaction of the hydroxide ion with these

TABLE IV
RATE CONSTANTS AT 50°

Complex	$10^3 k_1$, sec ⁻¹	$10^3 K_a k_2$, mol sec ⁻¹
I	7.01	6.27
II	6.97	10.67
III	6.43	6.10

complexes, it was not possible to obtain reliable values of pK_a and hence k_2 of any of these complexes experimentally. Basolo, *et al.*,⁷ have estimated that the pK_a of Co(en)₂NH₃Cl²⁺ is certainly greater than 15. Examination of the pK_a values of a series of amines (Table V) shows that the pK_a of aniline decreases to 4.58 as compared to 9.24 for that of ammonia, owing to the electron-withdrawing phenyl group as the substituent.

TABLE V^a
ACID DISSOCIATION CONSTANTS OF AMINES (RNH₂)
IN WATER AT 25°

	R					
	H	CH ₃	C ₂ H ₅	C ₆ H ₅	<i>m</i> -CH ₃ C ₆ H ₄	<i>p</i> -CH ₃ C ₆ H ₄
pK_a	9.24	10.64	10.63	4.58	4.68	5.09

^a A. I. Vogel, "A Textbook of Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1964, p 1168.

In view of the above considerations, as a reasonable estimate, a pK_a value⁸ of greater than 10 may be assigned to the complex Co(en)₂(NH₂C₆H₅)Cl²⁺. The *m*-toluidine and the *p*-toluidine complexes would be expected to have pK_a values of the same order as that of the aniline complex. The pK_a values of these aromatic amine complexes, being considerably lower than that of the corresponding ammonia complex, are expected to produce kinetically significant concentration

of the amido bases even in acid media, particularly at relatively higher temperatures (50°), thus increasing the contribution of the conjugate base path toward chloride release. Using this estimated value of $pK_a > 10$ for these aromatic amine complexes, k_2 is found to be of the order of 10^8 sec⁻¹, $k_2 K_a$ being of the order of 10^8 mol sec⁻¹ for these complexes. Since k_2 is the rate constant for the S_N1 dissociation of the conjugate bases of the complexes, this order appears to be quite reasonable.

The effect of substituting a methyl group in the phenyl ring on the rate of chloride release (k_1) may now be examined (see Table IV). Since the inductive effect cannot be suitably transmitted to the cobalt atom through the fully protonated nitrogen atom, the

(6) T. B. Crumpler and J. H. Yoe, "Chemical Computations and Errors," John Wiley & Sons, Inc., New York, N. Y., 1940, p 217.

(7) F. Basolo and R. G. Pearson, *J. Am. Chem. Soc.*, **78**, 4878 (1956).

(8) The authors are thankful to a referee for this suggestion.

acid-independent k_1 values of the three complexes should be equal. For the aniline and *p*-toluidine complexes this is found to be the case. The slightly lower k_1 value of the *m*-toluidine complex might be due to a steric or some other unknown factor. Substituent effects are expected to be more significantly reflected in the k_2 values of these complexes, since the nature and position of the substituent in the phenyl ring would make the Co-N π bond less or more effective. Higher k_2K_a values for the chloro-*p*-toluidine complex might be the result of higher k_2 values, which might again be due to the *para*-orienting effect of the methyl group. However, with the approximately estimated values of k_2 this aspect need not be discussed further.

While this work was in progress, the aquation rate of chloro(aniline)bis(ethylenediamine)cobalt(III) chloride was reported by Jones, *et al.*⁹ The rate of chloride

(9) M. M. Jones, N. K. Chawla, and D. G. Lambert, *J. Am. Chem. Soc.*, **89**, 557 (1967).

release was followed by them conductometrically presumably in the absence of added acid. The rate constant for chloride release at 40° was reported to be $2.1 \times 10^{-4} \text{ sec}^{-1}$. In the absence of acid with the perchlorate salt we obtained a rate constant of $1.8 \times 10^{-4} \text{ sec}^{-1}$ at 40°. With the aged aquo complex they reported to have observed very slow release of aniline with the formation of the diaquo complex. With the chloro complexes under acid conditions up to about 60% reaction (chloride release) no aniline release could be detected by us. In view of the similarity in the method of preparation and on analogy with the ir findings of Baldwin¹⁰ with a number of similar ethylenediamine complexes, we prefer the *cis* configuration for these arylamine complexes though all attempts to isolate the other isomer have proved unsuccessful.

(10) M. E. Baldwin, *J. Chem. Soc.*, 4369 (1960).

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Complexes of 2,2'-Azopyridine with Iron(II), Cobalt(II), Nickel(II), Copper(I), and Copper(II). An Infrared Study

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Vibrational spectroscopy in both the conventional and far-infrared regions, electronic spectroscopy, and magnetism are used to characterize a series of coordination complexes of 2,2'-azopyridine. Complexes of the title ions with ligand to metal ratios of 3:1, 2:1, or 1:2 are described. The nickel(II) and iron(II) derivatives are six-coordinate, while both six-coordinate and four-coordinate tetrahedral complexes of cobalt(II) and copper are reported. Evidence is presented indicative of a very strong interaction between the spin-paired iron(II) atom and the ligand.

Metal complexes involving the aza group are frequently intensely colored and find extensive use as dyestuffs. Much has been published² concerning these dyestuffs, which often involve large complicated aza ligands. Few fundamental papers dealing with simple aza ligands have appeared, although some interest has been shown recently.³ A short note⁴ on 2,2'-azopyridine appeared during this investigation.

Highly colored complexes are also formed by diimine ligands with oxidizable metal ions, and it is of interest to compare the two systems N=C—C=N in the diimines and N=C—N=N—C=N in the aza ligands. We have therefore investigated the complexes formed by 2,2'-azopyridine (L) and salts of metals of the first transition series.

The ligand 2,2'-azopyridine is capable, in principle, of several modes of coordination. Those shown as I–IV are the most likely; there is no evidence for coordination as in V. The ligand cannot function as a tridentate without considerable angular strain. We find that three coordination modes occur: series a, coordination mode I—L(CuCl)₂, L(CuI)₂, L(CuCl₂)₂, and L(CoCl₂)₂; series b, coordination mode II—ML₂(NCS)₂ (M = Fe, Co, Ni), CoL₂X₂ (X = Cl, Br), and NiL₃(ClO₄)₂. The binuclear complex L(Cu(O₂CCH₃)₂)₂ is thought to involve mode IV.

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(2) P. Pfeiffer, Th. Hesse, H. Pützner, W. Scholland, and H. Thielert, *J. Prakt. Chem.*, **149**, 217 (1937); H. Zollinger, "Chemie der Azofarbstoffe," Birkhäuser Verlag, Basel, Switzerland, 1958, Chapter 13, and references therein; W. F. Breech and H. D. K. Drew, *J. Chem. Soc.*, 608 (1940); W. J. Geary, G. Nickless, and F. H. Pollard, *Anal. Chim. Acta*, **26**, 575 (1962); **27**, 71 (1962); I. M. Klotz and W. C. Loh-Ming, *J. Am. Chem. Soc.*, **75**, 4159 (1953).

(3) N. Campbell, A. W. Henderson, and D. Taylor, *J. Chem. Soc.*, 1281 (1953); R. F. Heck, *J. Am. Chem. Soc.*, **90**, 313 (1968); G. W. Parshall, *ibid.*, **89**, 1822 (1967); M. M. Bagga, P. L. Pauson, F. J. Preston, and R. I. Reed, *Chem. Commun.*, 543 (1965); J. Kleiman and M. Dubeck, *J. Am. Chem. Soc.*, **85**, 1544 (1963); P. E. Baikie and O. S. Mills, *Chem. Commun.*, 707 (1966); R. P. Bennett, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., 1968, No. M183; R. G. Denning and J. Thatcher, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., 1968, No. M199.

(4) P. J. Beadle and R. Grzeskowiak, *Inorg. Nucl. Chem. Letters*, **3**, 245 (1967).