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High- and Low-Spin Complexes with Similar Ligands. Iron(II) Complexes of Terpyridyl and Its Derivatives[1]

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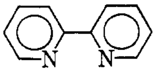
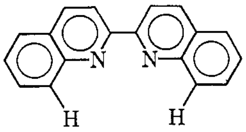
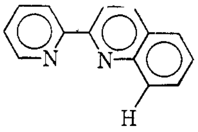
Received July 22, 1968

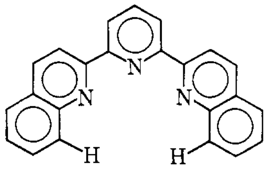
Two new ligands, 2,6-di(2′-quinolyl)pyridine (dqp) and 2-acetyl-6-(2′-quinolyl)pyridine (aqp), have been prepared by the reaction of pyridine-2,6-diacetyl and *o*-aminobenzaldehyde. dqp is a benzo-disubstituted analog of 2,2′,2′′-terpyridyl (terpy), but its bis-chelated ferrous complex is high spin, whereas that of terpy is low spin. This observation and the electronic spectra indicate that dqp is a much weaker ligand ($\Delta \sim 12{,}000$ cm^{-1}) than terpy. These results are interpreted in terms of an increase in the average metal–ligand bond distance as a result of the steric effect of benzo substitution. The bis-chelated ferrous complex of aqp is high spin, as expected.

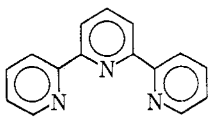

dipy (I)

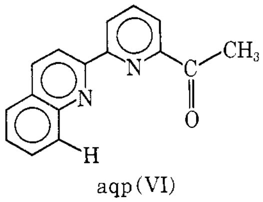

biq (II)


pq (III)

Benzo substitution *cis* to the nitrogen atoms in 2,2′-dipyridyl (dipy) (I) to form 2,2′-biquinolyl (biq) (II) leads to such steric crowding that the metal-chelating properties of the two ligands are very different.[2,3] This steric effect is less drastic in 2-(2′-pyridyl)quinoline (pq) (III), which was obtained by Smirnoff[4] from the reaction of *o*-aminobenzaldehyde with 2-acetylpyridine. The same reaction on 2,6-diacetylpyridine yields 2,6-di(2′-quinolyl)pyridine (dqp) (IV), a benzo-disubstituted 2,2′,2′′-terpyridyl (terpy) (V). An intermediate, 2-acetyl-6-(2′-quinolyl)-pyridine (apq) (VI), is formed in the same reaction.


dqp (IV)


terpy (V)


aqp (VI)

Models show that the hydrogens *cis* to the nitrogens, as shown, should again exert a steric crowding effect when a metal is coordinated to the ligand. It is obvious from a comparison of the metal–ligand bonding angles in complexes of dipy and terpy[5] that the steric effect cannot be as great in dqp as in biq. A likely effect of the increased crowding resulting from benzo substitution is an increase in the metal–ligand distances, which would in turn alter the ligand field strength Δ. In the present nitrogenous chelates, the iron(II) complexes can give a ready test of ligand field strength. Complexes of pq bear considerable resemblance to those of 2-methylphenanthroline but are not very similar to those of dipy.[1,6] The difference between terpy and dqp is even more startling, and we will be concerned mainly with the iron(II) complex of dqp.

Dependence of Ligand Field Strength on the Metal–Ligand Distance

The dependence of the crystal field interaction $V(r)$ on the average metal–ligand distance, a, is given by the relation[7–9]

$$V(r) = e^2Z\langle r^4\rangle f/a^5 = 3\Delta/5$$

Here f is a number depending on the particular point group representation for the complex and is determined from group theory considerations; r relates to the electron distribution and should not be confused with a, though the two are necessarily related to a considerable extent. Ze and e are point charges separated by the distance a.

The transfer of electrons from the t_2 orbital subset to the e subset is expected[10] to increase a and therefore to decrease Δ.[11] This phenomenon has been confirmed experimentally in the case of the $^6A_1$–$^2T_2$ crossover in ferric dithio chelates, where the low-spin species were found, from variable-pressure measurements, to

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[1] Presented in part at the 39th ANZAAS Congress, University of Melbourne, Jan 1967.

[2] R. J. Charlton, C. M. Harris, H. R. H. Patil, and N. C. Stephenson, *Inorg. Nucl. Chem. Letters*, **2**, 409 (1966).

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[4] A. P. Smirnoff, *Helv. Chim. Acta*, **4**, 802 (1921).

[5] D. E. C. Corbridge and E. G. Cox, *J. Chem. Soc.*, 594 (1956); C. M. Harris, T. N. Lockyer, and N. C. Stephenson, *Australian J. Chem.*, **19**, 1741 (1966); G. A. Barclay and C. H. L. Kennard, *Nature*, **192**, 425 (1961); W. W. Brandt, F. P. Dwyer, and E. C. Gyarfas, *Chem. Rev.*, **54**, 959 (1954), and references therein.

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occupy a smaller volume than the high-spin species.[12–14] The converse of this situation must hold equally well. Thus, if steric crowding enforces an increase in a, it may result in sufficient decrease in Δ to alter the ground state in an octahedral or pseudo-octahedral complex from low spin ($^1A_1$) in the unstrained form to high spin ($^5T_2$) in the strained form.

For octahedral high-spin d^6 $|t_2{}^4e^2{:}{}^5T_2\rangle$ the expected temperature dependence of the magnetic moment μ_{eff} is given by the relation[7]

$$\mu_{eff}{}^2 = \{56[3x(4 + \gamma)^2 - 4(1 - \gamma/2)^2]e^{-2x} + 5[3x(10 - \gamma)^2 - 20(1 - \gamma/2)^2]e^{x} + 27[x(6 - \gamma)^2 + 12(1 - \gamma/2)^2]e^{3x}\}/\{18x(7e^{-2x} + 5e^{x} + 3e^{3x})\} \quad (1)$$

where $x = \nu/kT$ and ν and γ are coefficients[8,9] in the spin–orbit coupling–magnetic field interaction Hamiltonian

$$\mathcal{H} = \nu\mathbf{L}\cdot\mathbf{S} + \beta(\gamma\mathbf{L} + 2\mathbf{S})\cdot\mathbf{H} \quad (2)$$

To a reasonable approximation, we may equate $\gamma = -1$ and $\nu = \zeta'/4$, where $\zeta' = \alpha\zeta$ is an effective spin–orbit coupling constant, reduced from the free-ion value ($\zeta = 400$ cm^{-1}) by a factor α. Such a reduction would be expected for a number of reasons, the most important of which is t_2-electron delocalization into the ligands. (Delocalization may be further taken into account by allowing $|\gamma|$ to take values less than unity. In this way $|\gamma|$ corresponds to an orbital reduction factor. Equation 1 then reduces to

$$\mu_{eff}{}^2 = \frac{3(49y + 108) + 5(27y - 20)e^{-y/2} + 56(3y - 4)e^{-5y/4}}{2y(3 + 5e^{-y/2} + 7e^{-5y/4})} \quad (3)$$

where $y = \zeta'/kT$.

In the low-spin form, the d electrons are all paired and make no first-order contribution to the magnetic moment. Mixing of the $|t_2{}^6{:}{}^1A_1\rangle$ wave functions with $|t_2{}^5({}^2T_2)e{:}{}^1T_1\rangle$ results in some paramagnetism

$$\chi = \frac{16N\beta^2k}{E(^1T_1) - E(^1A_1)} \quad (4)$$

where k ($\leqslant 1$) is a factor which takes into account the involvement of the d orbitals in the metal–ligand bonding. For example, in a series of low-spin tris(α-diimine)iron(II) ions, the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition has been assigned[15] to a spectral absorption at 25,000 cm^{-1}, so that $\chi = 160k \times 10^{-6}$ cgsu. This is quite small and to a good approximation low-spin d^6 complexes may be said to be diamagnetic.

Experimental Section

Preparations and Analyses. aqp and dqp.—Freshly prepared *o*-aminobenzaldehyde[16] (6 mmol) dissolved in 50 ml of ethanol was added to a solution of 2,6-diacetylpyridine (3 mmol) in ethanol (25 ml). After the addition of 7 ml of 1 *N* NaOH, the mixture was refluxed for 30 min. Fractional crystallization from benzene yielded dqp, mp 214–215°, and aqp, mp 141–142°. *Anal.* Calcd for dqp, $C_{23}H_{15}N_3$: C, 82.9; H, 4.5; N, 12.6. Found: C, 83.0; H, 4.7; N, 12.6. Calcd for aqp, $C_{16}H_{12}N_2O$: C, 77.4; H, 4.9; N, 11.3. Found: C, 78.1; H, 4.8; N, 10.6.

Fe(dqp)$_2$(ClO$_4$)$_2$.—A solution of dqp (2 mmol) and iron(II) perchlorate hexahydrate (1 mmol) in acetone was refluxed for a few minutes and allowed to cool. The dark red precipitate was filtered off and washed with benzene. *Anal.* Calcd for $C_{46}H_{30}N_6O_8Cl_2Fe$: C, 59.9; H, 3.3; N, 9.1; Fe, 6.1. Found: C, 59.9; H, 3.6; N, 8.6; Fe, 6.2.

Fe(aqp)$_2$(ClO$_4$)$_2$·H$_2$O.—The pale red compound was prepared in a manner similar to the above. *Anal.* Calcd for $C_{32}H_{26}N_4O_{11}Cl_2Fe$: C, 49.9; H, 3.4; N, 7.3; Fe, 7.3. Found: C, 50.1; H, 3.4; N, 7.3; Fe, 7.4.

Fe(terpy)$_2$(ClO$_4$)$_2$·2H$_2$O.—This compound was prepared by literature methods.[17,18] The violet compound was recrystallized twice from aqueous ethanol. *Anal.* Calcd for $C_{30}H_{26}N_6O_{10}Cl_2Fe$: C, 47.6; H, 3.5; N, 11.1; Fe, 7.3. Found: C, 47.6; H, 3.5; N, 10.8; Fe, 7.4.

Magnetic Measurements.—Molar magnetic susceptibilities, χ_M, were determined on a cryostat-controlled Gouy balance,[3,19] calibrated with HgCo(SCN)$_4$. Magnetic moments were calculated from

$$\mu_{eff} = \sqrt{8.00\chi_M T}$$

Spectral Measurements.—Infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer using Nujol and hexachlorobutadiene mulls on sodium chloride plates. Near-infrared and visible spectra were obtained with a Carl Zeiss PMQII spectrophotometer equipped with matched 1-cm silica cells. The diffuse reflectance spectra were measured using the Carl Zeiss RA3 reflectance attachment and magnesium oxide as the reference.

Electrical Conductivity Measurements.—These were made using a Philips conductivity bridge (GM4144) with cells of Type PR9512/01.

Analyses.—The carbon, hydrogen, and nitrogen analyses were carried out in the microanalytical laboratory under the direction of Dr. E. Challen. Iron analyses were carried out spectrophotometrically with 1,10-phenanthroline.

Results and Discussion

Electrical Conductivity.—The molecular conductivity of Fe(aqp)$_2$(ClO$_4$)$_2$·H$_2$O (9.9×10^{-4} *M* in nitrobenzene at 25°) is 55.4 ohm^{-1} mol^{-1} cm^{-1} and is indicative of a bi-univalent electrolyte.[20] Fe(dqp)$_2$(ClO$_4$)$_2$ is very poorly soluble in nitrobenzene, but in nitromethane it functions as a 1:2 electrolyte,[20] and its conductivity in this solvent (4.6×10^{-4} *M* at 25°) was found to be 201 ohm^{-1} mol^{-1} cm^{-1}.

Infrared Spectra.—Iron(II), in both high- and low-spin states, obtains greater ligand field stabilization from octahedral symmetry than from tetrahedral, so that a coordination number of 6 is preferred except with a few highly polarizable ligands such as Cl$^-$. For this reason and from their structural formulas, the ligands dqp and aqp are expected to function as tridentates, provided that the anion is not coordinated to the metal; ClO$_4{}^-$ was chosen as the anion since per-

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[19] S. J. Gruber, C. M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem.*, **30**, 1805 (1968).

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TABLE I

MAGNETIC DATA

					$Fe(dqp)_2(ClO_4)_2$					
Temp, °K	85.2	103.9	147.3	153.1	174.6	209.2	227.1	256.4	312.5	341.5
χ_M, cgsu	40,308	32,301	22,394	22,181	19,240	16,352	14,925	12,946	10,476	9532
μ_{eff}, BM	5.27	5.22	5.19	5.27	5.25	5.31	5.29	5.25	5.24	5.24
					$Fe(aqp)_2(ClO_4)_2 \cdot H_2O$					
Temp, °K	80.0	109.5	133.9	163.5	192.1	224.2	255.9	308.2	338.7	
χ_M, cgsu	47,616	34,417	27,982	22,446	18,975	16,181	14,108	11,479	10,371	
μ_{eff}, BM	5.43	5.45	5.46	5.44	5.45	5.46	5.47	5.45	5.45	
					$Fe(terpy)_2(ClO_4)_2 \cdot 2H_2O$					
Temp, °K	92.0	110.5	138.5	175.2	215.1	262.0	305.0			
χ_M, cgsu	102	156	142	120	149	135	120			

chlorate is generally ionic in complexes and only rarely coordinated. The infrared spectra of the complexes in the perchlorate region reveal the presence of ionic perchlorate (T_d symmetry) only.[21] The ν_3 (T_2) bands were observed as the typical broad maxima at 1075 cm^{-1} in $Fe(dqp)_2(ClO_4)_2$ and at 1080 cm^{-1} in $Fe(aqp)_2(ClO_4)_2 \cdot H_2O$. The weak ν_1 (A_1) absorption occurs at 935 cm^{-1} in $Fe(aqp)_2(ClO_4)_2 \cdot H_2O$ but could not be uniquely assigned in $Fe(dqp)_2(ClO_4)_2$. The ligand aqp has a carbonyl stretch at 1690 cm^{-1}. In $Fe(aqp)_2(ClO_4)_2 \cdot H_2O$ the C=O stretch appears at 1650 cm^{-1}. This shift to lower energy is in keeping with coordination of the carbonyl group to the metal.

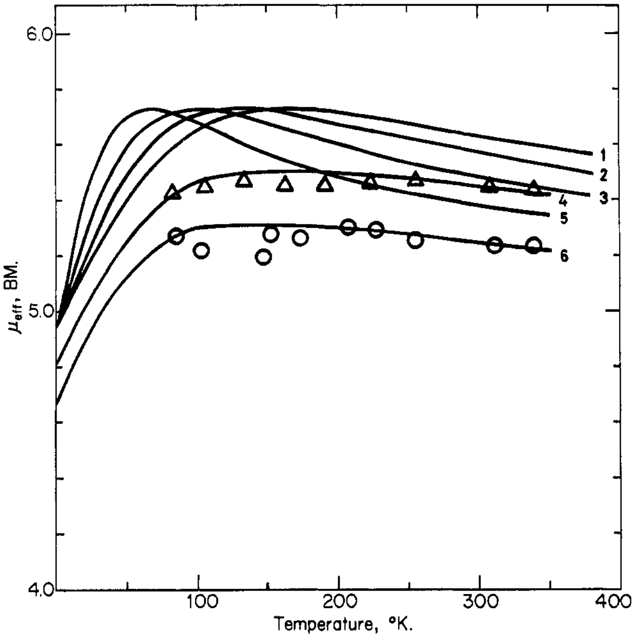

Figure 1.—Dependence of magnetic moments μ_{eff} in high-spin iron(II) upon temperature. Curves 1–6 are calculated from eq 1 using the following values of γ and ζ' ($=4\nu$): (1) $\gamma = -1$, $\zeta' = 400$ cm^{-1}; (2) $\gamma = -1$, $\zeta' = 320$ cm^{-1}; (3) $\gamma = -1$, $\zeta' = 240$ cm^{-1}; (4) $\gamma = -0.8$, $\zeta' = 320$ cm^{-1}; (5) $\gamma = -1$, $\zeta' = 160$ cm^{-1}; (6) $\gamma = -0.6$, $\zeta' = 280$ cm^{-1}. The experimental points are shown as triangles for $Fe(aqp)_2(ClO_4)_2 \cdot H_2O$ and as circles for $Fe(dqp)_2(ClO_4)_2$.

Magnetism.—The magnetic results are given in Table I. $Fe(dqp)_2(ClO_4)_2$ and $Fe(aqp)_2(ClO_4)_2 \cdot H_2O$ are high spin, and their magnetic properties are compared in Figure 1 with some sample plots of μ_{eff} against T, calculated from eq 1. It is apparent that eq 3 ($\gamma = -1$) represents the results poorly for all values of ζ'. The results are reasonably represented by eq 1 when $\gamma = -0.8$ and $\zeta' = 340$ cm^{-1} for $Fe(aqp)_2(ClO_4)_2 \cdot H_2O$ and when $\gamma = -0.6$ and $\zeta' = 280$ cm^{-1} for $Fe(dqp)_2(ClO_4)_2$. The lower values of $|\gamma|$ and ζ' in the dqp complex indicate a greater degree of t_2-electron delocalization into dqp than into aqp. With its extra aromatic rings dqp in fact offers greater scope for such delocalization than aqp, and this good agreement with expectations suggests that electron delocalization is the major factor affecting the magnitude of μ_{eff}. Distortion from the assumed octahedral symmetry can also affect μ_{eff} and can be taken into account by adding a distortion term $L_z^2\delta$ to the Hamiltonian (eq 2) and considering, for example, an octahedral complex with tetragonal distortion. Calculations of this type have been made in some situations,[22-24] but fairly detailed structural information, such as single-crystal X-ray data, would be desirable in order to decide whether the distortion is important here. Calculations show that if the number of parameters is increased in this way, then the results can be fitted for various values of δ and for a range of γ and ζ' values centered about those given above. Such fits are physically not very meaningful, but they serve to indicate that the values of ζ' and $|\gamma|$ quoted above are only approximate. Moreover, there are yet other factors which may have at least a slight influence on μ_{eff}, such as anisotropy of bonding to the ligands and the effects of the anions and of the lattice itself.

$Fe(terpy)_2(ClO_4)_2$ is low spin and exhibits a very low temperature-independent magnetic susceptibility of about 130 × 10^{-6} cgsu. From eq 4 we now have $E(^1T_1) - E(^1A_1) \sim 30{,}000k$ cm^{-1}, and if this quantity is of the order of 25,000 cm^{-1}, then $k \sim 0.8$, a reasonable magnitude.

On the basis of the evidence, we conclude that $Fe(terpy)_2^{2+}$ and $Fe(dqp)_2^{2+}$ have essentially the same structure, yet the former is high spin and the latter is low spin. This dramatic change in magnetic properties on slight modification of the ligand can only be at-

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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 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 $\Delta = 12{,}000$ cm^{-1}, which is significantly higher than in $Fe(H_2O)_6{}^{2+}$ [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 $\Delta \approx 15{,}000$ cm^{-1}.[25] The splitting of the ${}^5T_{2g} \rightarrow {}^5E_g$ transition in $Fe(aqp)_2(ClO_4)_2 \cdot H_2O$ 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 $Fe(aqp)_2(ClO_4)_2 \cdot H_2O$ was found to be high spin is not surprising.

TABLE II

ELECTRONIC ABSORPTION SPECTRA

Compound	Medium	${}^5T_{2g} \rightarrow {}^5E_g$, cm^{-1} ($\epsilon$)
$Fe(dqp)_2(ClO_4)_2$	Solid	12,000
	Nitromethane	12,000 (20)
$Fe(aqp)_2(ClO_4)_2 \cdot H_2O$	Solid	10,200 sh, 8,000
	Nitrobenzene	10,400 (125), 8400 (135)
$Fe(terpy)_2(ClO_4)_2 \cdot 2H_2O$	Nitrobenzene	[27,000 sh (7900), 18,000 (1.15×10^4)][a]

[a] Other transitions.

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 relations[8]

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

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

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

$$\Delta \approx {}^3/_4\{E({}^1T_1) - E({}^1A_1)\} + {}^1/_4\{E({}^1T_2) - E({}^1A_1)\}$$

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 $\Delta \sim 26{,}000$ cm^{-1}. $Fe(terpy)_2(ClO_4)_2 \cdot 2H_2O$ 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.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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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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Received April 29, 1968

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 $\times 10^{-6}$ 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 3.0–4.0), these reactions generally become pH independent. However, exceptions are known. Acid hydrolysis of $Co(NH_3)_5F^{2+}$ is acid catalyzed[2] pre-

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