Table III. Rate Parameters and Steric Course of Hydrolysis Reactions[a] of Complexes of the Type [*trans*-$Co(en)_2LCl]^{n+}$

	aquatn				base hydrolysis			
L	10^5k_0, s^{-1}	retention, %	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, cal deg^{-1} mol^{-1}	k_1, M^{-1} s^{-1}	retention, %	$\Delta H^‡$, kcal mol^{-1}	$\Delta S^‡$, cal deg^{-1} mol^{-1}
Cl	3.1	65	27.5	13.1	3200	95	22.6	33.3
Br	4.5	50	24.6	4.1	5300	100	24.3	40.0
OH	160	25[b]	25.6	14.6	0.56	6	22.2	14.8
CN	7.8	100	22.0	−3.4	4.9	100	22.6	20.6
NO_2	98	100	20.9	−2.2	3.7	94	23.8	23.9
NCS	0.005	~40[b]	29.8	7.8	13	26	22.6	22.3
CH_3COO	31	80	26.8	6.7	11	80	22.6	22
N_3	22	80[b]	23.1	2.2				
NH_3	0.037	~90	23.0	−10.8				
CO_3[c]	10	~0	31.1	27.3	0.60	~0	25.2	25.0

[a] Data at 25 °C as given in review by: Edwards, J. O.; Monacelli, F.; Ortaggi, G. *Inorg. Chim. Acta* 1974, *11*, 47. [b] Data from Table I, ref 9. [c] This work.

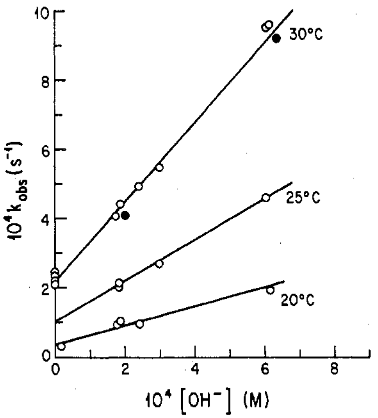
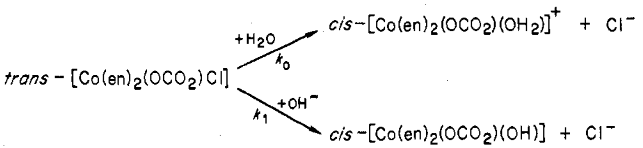


Figure 3. Dependence of k_{obsd} for base hydrolysis of *trans*-$Co(en)_2CO_3Cl$ on hydroxide ion concentration.

are the same within experimental error as the k_{obsd} values obtained at lower pH's at these temperatures as reported above. This is entirely as it should be, since in these "low pH" preliminary experiments, only k_0 is operative. The most reasonable mechanism for the combined hydrolysis process takes the conventional form



(6)

This mechanism accounts for the two-term rate law (eq 5) and also explains the constant limiting rate of reaction within the 7 < pH < 10 range, provided that proton-promoted CO_2 elimination is suppressed by the presence of excess free carbonate.

Most of the previous studies of the base hydrolysis of cobalt(III) complexes of the type *trans*-$[Co(en)_2LCl]^{n+}$ where Cl^- is the released group have yielded kinetics of the form $k_{obsd} = k_1[OH^-]$. However, in these instances the experiments were carried out at pH values exceeding 12, so that the second term of eq 5 swamps out any contribution from the aquation rate k_0. The latter, however, are in many cases available from separate studies at low pH, at least for complexes where L is retained as a ligand even in very acidic solutions. There are also much data relative to the steric course of such reactions, and a selection of the relevant data is given in Table III along with our present findings. For both types of hydrolysis, there is a very large range of rate constants, to a considerable extent determined by variations in the entropies of activation, particularly for base hydrolysis. Retention of geometry is the dominant factor in both aquation and base hydrolysis, and in the former a high degree of retention is in general correlated with lower values of $\Delta S^‡$, as has been previously discussed.[10] The two exceptional species in both types of hydrolysis are the trans OH and trans CO_3 complexes. In aquation, these have low percentages of retention and rather high $\Delta S^‡$ values, although the rate constants at 25 °C are not particularly unusual. In base hydrolysis, they show rather low rate constants and very low percentages of retention, although the temperature variation parameters are not outside the limits exhibited by the other species. The parallelism in the effects of hydroxo and carbonato ligands on the kinetic properties of cobalt(III)–amine complexes has been noted elsewhere. Thus, for example, the rate at 25 °C of trans to cis isomerization of *trans*-$[Co(en)_2(OCO_2)(OH)]$ ($\sim 1 \times 10^{-6}$ s^{-1})[11] is very similar to that reported for *trans*-$[Co(en)_2(OH)_2]^+$ ($\sim 3 \times 10^{-6}$ s^{-1}).[12]

Acknowledgment. The authors gratefully acknowledge financial support from the John D. and Frances H. Larkin Foundation of the State University of New York at Buffalo.

Registry No. *trans*-$Co(en)_2(OCO_2)Cl$, 72827-35-1; *trans*-$Co(en)_2(OH_2)Cl^{2+}$, 14403-92-0; *trans*-$Co(en)_2(CO_3)(OH)$, 55658-81-6; *cis*-$Co(en)_2(CO_3)(OH)$, 26368-79-6; *trans*-$[Co(en)_2(OH)Cl]Cl$, 20941-80-4.

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Contribution from the Department of Chemistry and Physical Chemistry, University of Belgrade, 11001 Beograd, Yugoslavia

Significance of Nephelauxetic Effect in the Interpretation of Cobalt-59 Nuclear Magnetic Resonance Frequencies of Cobalt(III) Complex Compounds

N. Juranić

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Due to second-order paramagnetism, which arises from the orbital angular momentum induced by mixing of low-lying paramagnetic states of the cobalt(III) ion under the influence of a magnetic field, one can expect a linear relationship between ^{59}Co resonant frequencies and the longest wavelength d–d transition in octahedral cobalt(III) complexes.[1,2]

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Table I. Energies of d-d Electron Transitions,[2,4,8-12] the Nephelauxetic Ratio,[8-12] and the Magnetogyric Ratio[2-6] of Selected Cobalt(III) Complexes with Octahedral Ligand Field Symmetry

type	complex	$\Delta E(^1A_{1g} \rightarrow {}^1T_{1g})^{-1}$, nm	$\Delta E(^1A_{1g} \rightarrow {}^1T_{2g})^{-1}$, nm	β_{35}	γ, MHz T^{-1}
CoO_6	$[Co(C_2O_4)_3]^{3-}$	605	424	0.48	10.237
	$[Co(CO_3)_3]^{3-}$	645	444	0.49	10.248
CoN_6	$[Co(NH_3)_6]^{3+}$	475	340	0.56	10.188
	$[Co(en)_3]^{3+}$	465	338	0.54	10.178
CoC_6	$[Co(CN)_6]^{3-}$	311	257	0.41	10.106
CoS_6	$[Co(S_2P(OC_2H_5)_2)_3]$	735	526	0.37	10.196
	$[Co(S_2COC_2H_5)_3]$	617	481	0.29	10.169
	$[Co(S_2CNH_2)_3]$	637	483	0.32	10.179
CoP_6	$[Co(P(OCH_3)_3)_6]^{3+}$	345	303	0.25	10.103
	$[Co(P(OCH_3)CCH_3)_6]^{3+}$	300	261	0.31	10.093
$CoSe_6$	$[Co(Se_2CN(CH_3)_2)_3]$	667	500	0.30	10.174

Application of ligand field theory to the magnetic shielding of the cobalt nucleus in octahedral cobalt(III) complexes gives the following expression for ^{59}Co resonant frequencies:[1-4]

$$\nu = \nu_0(1 - \sigma^d - \sigma^p) = \nu_0(1 - \sigma^d) + 32\nu_0\beta^2\langle r^{-3}\rangle k'^2(\Delta E^{-1}) \tag{1}$$

where β is the Bohr magneton, r is the distance of d electrons from cobalt nucleus, k' is the orbital reduction factor, and E is the energy of the d–d transition $^1A_{1g} \rightarrow {}^1T_{1g}$. On the basis of this equation, one expects that the correlation between the ^{59}Co resonance frequency and the longest wavelength d–d transition displays a linear relationship, with intercept equal to $\nu_0(1 - \sigma^d)$ and direction coefficient given by $32\nu_0\beta^2\langle r^{-3}\rangle k'^2$. While substantial variation of the diamagnetic shielding term (σ^d) (and consequently the intercept value) is not likely,[2] variation of the slope due to covalent-bonding effects is quite expected.[4,5]

The corresponding correlation is well established for complexes containing first-row-element ligators[2,3] (Figure 1a). Data for complexes containing sulfur, selenium, and arsenic chelates deviate from the first-row-ligator correlation line. It was suggested that another linear correlation, of the same origin, exists for second-row ligators[4,5] (Figure 1b). However, recently obtained data for cobalt(III) complexes with phosphorus as the ligating atom point to the existence of a linear correlation for second-row ligators, which do not have an intercept in common with the line for first-row ligators[6] (Figure 1c). The difference between intercepts of the first- and second-row ligators is very large and corresponds to the difference in the diamagnetic shelding constant which is as large as 0.005, while a reasonable estimation of the diamagnetic shielding constant value[2] gives $\sigma^d = 0.0021$. Therefore, it is probable that one or both of these correlations are accidental.

According to eq 1, a linear correlation between the ^{59}Co resonance frequencies and longest wavelength d–d transition should be expected only for a series of complexes in which d orbitals are affected by ligators in a similar way. An investigation into the extent of covalent bonding, extension, and deformation of d orbitals may be achieved on the basis of the nephelauxetic ratio (β_{35})[8,9] of complexes under consideration. Moreover, it may be expected that d-electron delocalization is manifested by a uniform decrease of the parameters β_{35} and k'^7 as well as of $\langle r^{-3}\rangle$. Consequently, the slope $32\beta^2\langle r^{-3}\rangle k'^2$ should vary directly with the nephelauxetic ratio β_{35}. On this basis it is doubtful whether the data for complexes with first-row ligators (or second-row ligators) have to fit the same correlation line (see Table I).

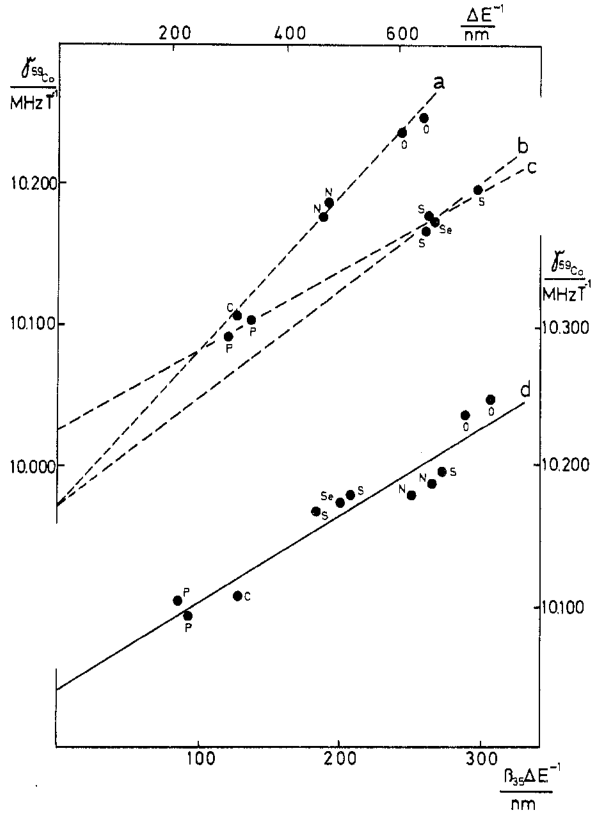

Figure 1. Correlation of ^{59}Co magnetogyric ratio with the longest wavelength d–d transition (a–c) and with the longest wavelength d–d transition value reduced by the nephelauxetic ratio (d). For easier comparison of the results of different authors, the magnetogyric ratios, instead of frequencies, are plotted. In this case eq 1 takes the following form: $\gamma = \gamma_0(1 - \sigma^d - \sigma^p)$.

One should, of course, be aware that various regions of the wave functions of d electrons are of different importance for the expectation values of β_{35}, k', and $\langle r^{-3}\rangle$. Nevertheless, the corrected slope, given by $32\beta^2\langle r^{-3}\rangle k'^2/\beta_{35}$, appears to be reasonably insensitive to delocalization effects. This conclusion follows from Figure 1d, where ^{59}Co magnetogyric ratios of all the complex compounds considered (Table I) are correlated with $\beta_{35}/\Delta E$. Such a correlation may be quite general. There is no ambiguity of the intercept value, which gives $\gamma_0 = 10.060$ MHz T^{-1}. This number may be used as the improved vlaue of the magnetogyric ratio of the cobalt nucleus. It is interesting

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to note that from the slope it follows that $32\beta^2\langle r^{-3}\rangle k'^2/\beta_{35} = 615\ \mathrm{cm}^{-1}$, which is very close to the theoretical value of the slope which corresponds to localized free-ion d orbitals,[3] i.e., $32\beta^2\langle r^{-3}\rangle = 620\ \mathrm{cm}^{-1}$.

The suggested correlation seems very promising. However, theoretical relations between parameters β_{35}, k', and $\langle r^{-3}\rangle$ should be carried out in order to elucidate the fundamental nature of such a correlation.

Correspondence

Magnetic Susceptibility of Porphyrins

Sir:

In view of the active interest in magnetic properties of metalloporphyrins it is important to know accurately the diamagnetism of the porphyrin moiety. Most researchers use either Pascal's constants[1] or one of four published porphyrin magnetic susceptibility values (Table I).[2-4] With use of Pascal's constants the calculated diamagnetism for protoporphyrin IX dimethyl ester is -346×10^{-6} (cgs emu/mol units are used throughout) which is considerably smaller than the experimental values,[2] but the calculated value for H_2TPP (-365×10^{-6}) is similar to one experimental value reported in the literature,[3] leaving considerable uncertainty concerning the "constitutive correction" for the porphyrin ring. Application of Pascal's constants to correct for the substituents in H_2T-piv-PP[4] yields -467×10^{-6} for H_2TPP which is substantially different from the earlier value.[2] The questions raised by these comparisons and diamagnetic susceptibility measurements in our laboratory led to an interlaboratory comparison, the results of which we report here.

Experimental Section. The porphyrins were prepared and purified as previously described.[5] In each case the final purification steps involved chromatography on Baker 0537 alumina by using chloroform as eluant followed by recrystallization. A commerical (Strem Chemicals) sample of H_2TPP was also used. Magnetic susceptibility measurements in Denver, CO, were made on a Bruker BM4 Faraday balance with a 1-μg sensitivity Sartorius balance. The product $H(\mathrm{d}H/\mathrm{d}s)$ ranged from 2×10^6 to $10 \times 10^6\ \mathrm{G}^2\ \mathrm{cm}^{-1}$. Magnetic susceptibility measurements by Professor I. A. Cohen were made with an Ainsworth Faraday balance with 1-μg sensitivity and a central magnetic field of about 7 kG. $HgCo(SCN)_4$ was used as the primary standard, with $\chi_g = 16.2 \times 10^{-6}\ \mathrm{cm}^3\ \mathrm{g}^{-1}$ at 20 °C,[6] and $Ni(en)_3S_2O_3$[7] was used as secondary standard to calibrate the technique.

Table I. Literature Values for the Magnetic Susceptibility of Porphyrins

compd	susceptibility ($\times 10^6$)	ref
protoporphyrin IX dimethyl ester	−585	2
mesoporphyrin IX dimethyl ester	−595	2
tetraphenylporphyrin (H_2TPP)	−386	3
tetrakis(pivaloylphenyl)porphyrin	−690	4

Table II. Magnetic Susceptibility of Porphyrins

	susceptibility ($\times 10^6$)		
compd[a]	av[b]	extrapd[c]	cor to H_2TPP[d]
H_2-*p*-MeTPP	−658	−765	−718
	−620	−711	−644
	−583	−718	−671
	−721[e]		
H_2-*o*-MeTPP	−638	−724	−677
	−602	−745	−698
H_2-*i*-PrTPP	−751	−846	−704
	−719	−861	−719
H_2TPP	−595	−720	
	−549	−731	
	−572[f]	−627	
	−524[f]	−633	
	−396[e,f]		

[a] Abbreviations used: H_2-*p*-MeTPP, tetrakis(*p*-methylphenyl)porphyrin; H_2TPP, tetraphenylporphyrin; H_2-*o*-MeTPP, tetrakis(*o*-methylphenyl)porphyrin; H_2-*i*-PrTPP, tetrakis(*p*-isopropylphenyl)porphyrin. [b] Values measured at four or five field strengths were averaged, ignoring the field dependence. [c] Value obtained by least-squares extrapolation to infinite field strength. [d] The correction involved use of Pascal's constants to account for differences in ring substituents. [e] Measurement by Professor I. A. Cohen at 7 kG. [f] Commercial sample.

Results and Discussion. The magnetic susceptibility measurements of free–base porphyrins were all found to be dependent on the magnetic field strength. The Faraday method measurements can validly be corrected for ferromagnetic impurities by extrapolating to infinite field.[8] The Faraday measurement data obtained in Denver, CO, have been corrected for field dependence in this way. Table II presents the magnetic susceptibilities for several porphyrins and the values for H_2TPP obtained from them by Pascal's constant calculations. The susceptibility values extrapolated to infinite field are strikingly different from the average values. Also the slope of the χ vs. reciprocal of field strength plot differed for different aliquants of the same bulk sample of porphyrin. The data implied an adventitious ferromagnetic impurity. Energy-dispersive X-ray fluorescence measurements demonstrated the presence of Fe in the H_2-*i*-PrTPP and H_2TPP samples (only these two were tested). The commercial H_2TPP sample contained more Fe than the purified H_2-*i*-PrTPP sample. It is possible that the Fe is in the ferromagnetic impurity. It should be noted that only a very small amount of ferromagnetic impurity is needed to cause the results observed, since the field dependence amounted to less than about 20-μg difference from the value that would have been expected for each measurement if there had been no ferromagnetic impurity. However such small differences have a large impact on the final values since the weight changes due to diamagnetism are so small (e.g. less than about 0.2 mg in the Faraday measurements).

We judge that the "best" value to use for the magnetic susceptibility of H_2TPP is the average of the extrapolated values from the Faraday measurements, corrected for substituents by using Pascal's constants (the commercial sample

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