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The Kinetics of Aquation of *cis*-Bispyridinetetraaquachromium(III) Ion

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cis- and *trans*-Bispyridinetetraaquachromium(III) ions were prepared and characterized in solution. The aquation of the *cis*-isomer was studied as a function of acidity and temperature. It aquates to $\text{Cr}(\text{H}_2\text{O})_5\text{py}^{3+}$ ion with no observable isomerization path and the rate law is of the form $-\text{d} \ln [\text{Cr}(\text{H}_2\text{O})_4(\text{py})_2^{3+}]/\text{d}t = (k_{\text{H}_2\text{O}} + k_{\text{OH}}K_a[\text{H}^+]^{-1})/(1 + K_a[\text{H}^+]^{-1})$. The enthalpy (kcal mol^{-1}) and entropy ($\text{cal mol}^{-1} \text{K}^{-1}$) of activation are 25.2 and -4.6 for the aquation of the *cis*- $\text{Cr}(\text{H}_2\text{O})_4(\text{py})_2^{3+}$ ion ($k_{\text{H}_2\text{O}}$ path) and 25.4 and 4.3 for the aquation of the *cis*- $\text{Cr}(\text{H}_2\text{O})_3(\text{OH})(\text{py})_2^{2+}$ ion (k_{OH} path). The standard enthalpy and entropy for the acid dissociation reaction of the *cis*- $\text{Cr}(\text{H}_2\text{O})_4(\text{py})_2^{3+}$ ion are $12.7 \text{ kcal mol}^{-1}$ and $23.2 \text{ cal mol}^{-1} \text{K}^{-1}$. The corresponding constants extrapolated to 25°C have the values $k_{\text{H}_2\text{O}} = 2.0 \times 10^{-7} \text{ s}^{-1}$, $k_{\text{OH}} = 1.23 \times 10^{-5} \text{ s}^{-1}$, and $K_a = 6.0 \times 10^{-5} \text{ M}$.

The hydroxy species is only about 60 times more reactive than the aqua species, which is consistent with the contribution of an associative mechanism in the aquation process of the latter species.

INTRODUCTION

Compounds of stoichiometric composition of bis-pyridinechromium(III) with four other coordination sites occupied by water and hydroxy ligands have been known for a long time¹. They have been used as the starting materials for the preparation of other chromium(III) complexes^{2,3} but no or little work has been done on their additional characterization.

cis- and *trans*-bispyridinetetraaquachromium(III) ions have been recently prepared⁴. We report here on their characterization as well as on the detailed kinetic study of the aquation of the *cis*-isomer as a function of acidity and temperature.

EXPERIMENTAL

Preparation of *cis*- and *trans*- $\text{Cr}(\text{py})_2(\text{H}_2\text{O})_4^{3+}$ Ions in Solution*

Crude $[\text{Cr}(\text{py})_2(\text{H}_2\text{O})_2(\text{OH})_2]\text{Cl}^1$ was treated with 0.1 M HClO_4 to separate the soluble bispyridinechromium(III) from an amount of the insoluble green $\text{Cr}(\text{py})_3\text{Cl}_3$ complex. The solution was used as the source of *cis*- $\text{Cr}(\text{py})_2(\text{H}_2\text{O})_4^{3+}$ and the green solid as the source of the *trans*-isomer. The solution was charged onto and eluted from a Dowex 50w-x8 cation-exchange column with 3 M HClO_4 . Fourteen successive eluents showed a constancy of the uv-visible spectra throughout, a behavior consistent with the isolation of a pure isomer, later characterized as the *cis*-isomer. The eluents stored in dark at -5°C did not change during the time of their use.

* py = pyridine

The solid green $\text{Cr}(\text{py})_3\text{Cl}_3$ was treated in suspension with an excess of mercury(II)perchlorate in 0.1 M HClO_4 until dissolved as a red-violet material. The red-violet species was purified on a cation-exchange column and characterized as $\text{Cr}(\text{py})_3(\text{H}_2\text{O})_3^{3+}$ by its behaviour on the column and by the content of pyridine and chromium(III) which were found in 3 to 1 molar ratio. At 85 °C in 1M HClO_4 this $\text{Cr}(\text{py})_3^{3+}$ species undergoes aquation reaction in a stepwise manner with $k_3 = 3.6 \times 10^{-4} \text{ s}^{-1}$ yielding $\text{Cr}(\text{py})_2^{3+}$ species which in turn aquates with $k_2 = 9.5 \times 10^{-5} \text{ s}^{-1}$ yielding the $\text{Cr}(\text{py})^{3+}$ ion*.

To prepare *trans*- $\text{Cr}(\text{py})_2^{3+}$ an amount of $\text{Cr}(\text{py})_3^{3+}$ was aged in 1 M HClO_4 at 85 °C for 4 hours (7.5 half lives of the reaction involving loss of the first pyridine). It yielded 34% of $\text{Cr}(\text{py})_2^{3+}$ species and 66% of the chromium(III) ions with the lower pyridine contents. The products were separated in a high number of fractions (81) by eluting them from a Dowex 50w-x8 column with increasing concentrations of HClO_4 . A set of fractions (42) showed a constant 2:1 pyridine to chromium ratio and had constant uv-visible spectra consistent with the separation of pure isomer, later characterized as the *trans*- $\text{Cr}(\text{py})_2^{3+}$ isomer. The solution of the isomer stored in dark at -5 °C did not change during the time of their use.

Analytical Methods

Chromium(III) and pyridine contents in the complexes were determined as described previously³, after the decomposition of the complexes in an alkaline medium.

Kinetic Measurements

The spectrophotometric determination of the kinetics of *cis*- $\text{Cr}(\text{py})_2^{3+}$ aquation was technically performed as described previously^{3,5}. A Cary 17 or a Beckman DU-2 instrument was used. At 232.2 nm the molar absorptivities ($\text{M}^{-1} \text{ cm}^{-1}$) were as follows: 3.3×10^3 for *cis*- $\text{Cr}(\text{py})_2^{3+}$, 2.25×10^3 for *trans*- $\text{Cr}(\text{py})_2^{3+}$, 1.05×10^3 for

TABLE I

d-d Absorption Band Characteristics of Bisaminetetraaquachromium(III) Complexes in 0.1 M to 3.0 M HClO_4

Amine	λ_{max} nm ($\epsilon, \text{M}^{-1} \text{ cm}^{-1}$)	λ_{min}	λ_{max}	λ_{min}
bipyridyl ^a	529 (27.2)	465 (10.7)	442 (31.2)	(sh)
<i>cis</i> -bispyridine	533 (25.9)	458 (8.15)	393 (35.6)	347 (9.5)
<i>trans</i> -bispyridine	536 (23.4)	454 (6.0)	392 (24.6)	351 (7.8)

^a R. Marčec and M. Orhanović, *J.C.S. Dalton* (1975) 319.

TABLE II

Uv Absorption Spectral Characteristics of Bispyridinetetraaquachromium(III) Complexes in 10^{-2} to 3 M HClO_4

Bispyridine	λ_{max} nm ($\epsilon, \text{M}^{-1} \text{ cm}^{-1}$)	λ_{min}	λ_{max}	λ_{min}
<i>cis</i> -	259 (6.85×10^3)	238 (2.15×10^3)	213 (2.05×10^4)	208 (2.0×10^4)
<i>trans</i> -	260 (6.16×10^3)	237 (1.32×10^3)	215, sh (9.25×10^3)	—

* Hereafter water ligands will be omitted from the formulas.

the mixture of $\text{Crpy}^{3+} + \text{Hpy}^+$ and the same value for the mixture of $\text{Cr}^{3+} + 2\text{Hpy}^+$. The absorptivities of the reaction components at 213 and 250 nm are presented in Table II and in reference 3. The ionic strength was kept constant at 1 M adjusted with NaClO_4 .

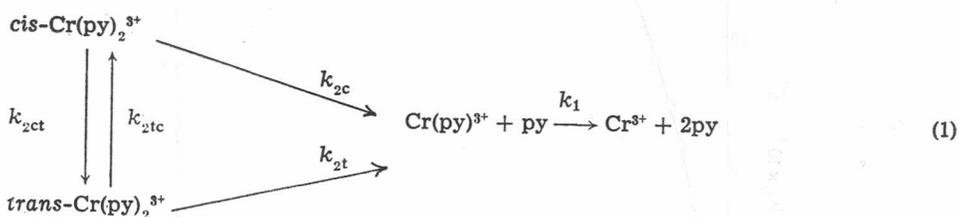
RESULTS AND DISCUSSION

Characterization of *cis*- and *trans*- $\text{Cr}(\text{py})_2^{3+}$

The two isomers were characterized by the stoichiometric composition, by their relative visible-uv spectral characteristics and the behavior on a cation-exchange column. The visible absorption maxima and minima are given in Table I. A higher absorption in the visible region of the *cis*-isomer, with the area under the first two d-d transition bands being 31% greater than that of the *trans*-isomer, was used as one of the indications of the relative configurations of the isomers. This indication is strongly supported by the relative behavior of the isomers on a cation exchange column. An equimolar amount of the *cis*- and *trans*-isomer was eluted from a Dowex 50w-x8 column with 1.5 M HClO_4 . Although no complete separation was achieved, their relative amounts in the successive eluents systematically changed from a pure *trans*- at the beginning to an almost pure *cis*-isomer at the end of elution, the usual observation for isomers of the $\text{MA}_4\text{B}_2^{3+}$ type. Here as well as in the preparative experiments, relative isomeric purity was determined by the use of the great difference in the uv absorption of the *trans*- and *cis*- $\text{Cr}(\text{py})_2^{3+}$ ions in the 200–220 nm region, Table II. There is no proof, of course, that the absolute isomeric purity was achieved.

Kinetics of Aquation of *cis*- $\text{Cr}(\text{py})_2^{3+}$

Preliminary experiments in 1 M HClO_4 showed that *cis*- $\text{Cr}(\text{py})_2^{3+}$ aquated in a stepwise manner, by forming the $\text{Cr}(\text{py})^{3+}$ ion as an aquation product³. In the possible reaction scheme (1):



the aquation of $\text{Cr}(\text{py})^{3+}$ by the k_1 paths was previously studied in details³. An estimate of k_{2t} in 1 M HClO_4 at 85 °C was also made⁴.

The aquation of *cis*- $\text{Cr}(\text{py})_2^{3+}$ was followed spectrophotometrically at 213, 250 and 232.2 nm. At 232.2 nm, the isosbestic point of the mixtures of $\text{Crpy}^{3+} + \text{Hpy}^+$ and $\text{Cr}^{3+} + 2\text{Hpy}^+$, the standard plot of the first order reaction gave a straight line for four half lives of the *cis*- $\text{Cr}(\text{py})_2^{3+}$ aquation. Since *trans*- $\text{Cr}(\text{py})_2^{3+}$ aquates at a different rate and has different absorption from that of the *cis*- $\text{Cr}(\text{py})_2^{3+}$ ion and the products, the linearity of the plots is taken as an evidence of the lack of the isomerization (the k_{2ct} path) in the aquation process of *cis*- $\text{Cr}(\text{py})_2^{3+}$. This evidence is supported by the kinetic measurements

at 213 and 250 nm, where the absorption change due to the aquation of the product $\text{Cr}(\text{py})^{3+}$ ion is also seen. At these wavelengths equation 2 for the consecutive first order reaction involving k_{2c} and k_1 paths was applied:

$$\frac{E}{d} = A_0 \left[\varepsilon_C + \frac{k_{2c}(\varepsilon_B - \varepsilon_A) + k_1(\varepsilon_A - \varepsilon_C)}{k_1 - k_{2c}} e^{-k_{2c}t} + \frac{k_{2c}(\varepsilon_C - \varepsilon_A)}{k_1 - k_{2c}} e^{-k_1t} \right] \quad (2)$$

where d is the path length, A_0 — initial concentration of $\text{cis-Cr}(\text{py})_2^{3+}$; molar absorptivity of $\text{cis-Cr}(\text{py})_2^{3+}$ is ε_A , that of the $\text{Cr}(\text{py})^{3+} + \text{Hpy}^+$ mixture is ε_B , and that of $\text{Cr}^{3+} + 2\text{Hpy}^+$ is ε_C . The absorption (E) measured as the function of time (t) was treated according to 2 by a non-linear least-squares computer program with all the parameters known and held fixed except k_{2c} or k_{2c} and ε_B . For a particular kinetic run a very good fitting with an average deviation of a few percent of the calculated from the experimental E values is obtained, in accord with the simple consecutive reaction scheme which does not involve the isomerization k_{2ct} path. The k_{2c} values thus obtained are presented in Table III. The nature of the k_{2c} dependence on acidity is shown in Figure 1. The rate constant increases with the inverse acid concentration and the curves show a trend of levelling off at higher $[\text{H}^+]^{-1}$ values. At a particular temperature the function is well represented by expression 3,

$$k_{2c} = (k_{\text{H}_2\text{O}} + k_{\text{OH}} K_a [\text{H}^+]^{-1}) / (1 + K_a [\text{H}^+]^{-1}) \quad (3)$$

which is consistent with reaction scheme 4.

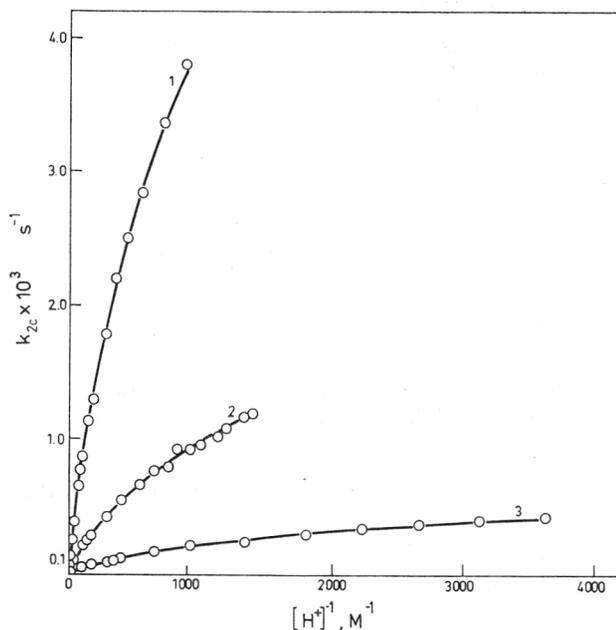
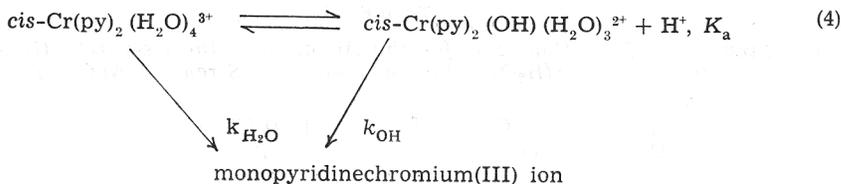


Figure 1. The first order rate constants observed for the aquation of *cis*-bispyridinechromium(III) to monopyridinechromium(III) complex in $\mu = 1.0$ M at (1) 75 °C, (2) 65 °C, and (3) 55 °C.

TABLE III

The First Order Rate Constants for the Aquation of the $\text{cis-Cr(py)}_2(\text{H}_2\text{O})_4^{3+}$ Ion to the $\text{Cr(py)}(\text{H}_2\text{O})_5^{3+}$ Ion in 1 M Ionic Strength (NaClO_4)

temp. °C	$[\text{HClO}_4]$ mM	$[\text{cis-Cr(py)}_2(\text{H}_2\text{O})_4^{3+}]$ mM $\times 10^2$	$k_{2c} \times 10^4$ s ⁻¹
55.0	0.276	1.66	4.20
55.0	0.321	1.93	4.03
55.0	0.376	2.26	3.73
55.0	0.451	2.71	3.37
55.0	0.556	3.34	2.93
55.0	0.752	4.52	2.52
55.0	1.08	5.27	2.00
55.0	1.54	5.27	1.55
55.0	2.48	5.27	1.07
55.0	3.00	9.79	0.917
55.0	3.52	5.27	0.828
55.0	5.76	1.84	0.572
55.0	10.1	3.22	0.397
55.0	1002	4.60	0.110
65.0	0.715	4.30	11.9
65.0	0.752	4.52	11.6
65.0	0.836	5.03	10.8
65.0	0.877	5.27	10.2
65.0	0.999	5.27	9.5
65.0	1.08	5.27	9.2
65.0	1.22	5.27	9.3
65.0	1.33	5.27	9.0
65.0	1.55	5.27	8.07
65.0	1.89	5.27	6.67
65.0	2.53	5.27	5.53
65.0	3.52	5.27	4.17
65.0	5.76	1.84	2.97
65.0	7.16	9.79	2.53
65.0	10.1	3.22	1.93
65.0	29.9	4.60—5.27	0.92
65.0	1000	4.60	0.377
75.0	1.13	5.27	38.0
75.0	1.39	5.27	33.7
75.0	1.82	5.27	28.3
75.0	2.28	5.27	25.0
75.0	2.88	5.27	22.0
75.0	3.68	5.27	17.8
75.0	5.76	1.84	13.1
75.0	7.20	2.30	11.5
75.0	10.1	3.22	8.7
75.0	11.8	9.79	7.6
75.0	14.4	4.60	6.72
75.0	29.6	4.60	3.88
75.0	58.8	4.60	2.52
75.0	1031	4.60	1.12
80.0	1000	6.08	1.96
85.0	1000	6.08	3.40
90.0	1000	6.08	6.08



The k_{2c} rate constants from Table III were treated simultaneously for all the acidities and temperatures according to modified equation 3 by a non-linear least-squares computer program. The equation was modified by substituting rate constants $k_{\text{H}_2\text{O}}$ and k_{OH} with the corresponding Eyring rate equation ($\alpha = 1$) and the equilibrium constant K_a by the van't Hoff isotherm. The enthalpies (kcal mol⁻¹) and entropies (cal mol⁻¹ K⁻¹) of activation thus obtained are 25.2 ± 0.2 and -4.59 ± 0.71 for the aquation of $\text{cis-Cr(py)}_2(\text{H}_2\text{O})_4^{3+}$, and 25.4 ± 0.6 and 4.28 ± 1.66 for the aquation of $\text{cis-Cr(py)}_2(\text{OH})(\text{H}_2\text{O})_3^{2+}$. The standard enthalpy and entropy of acid dissociation reaction (4) are 12.7 ± 0.8 kcal mol⁻¹ and 23.2 ± 2.3 cal mol⁻¹ K⁻¹.

The corresponding constants extrapolated to 25 °C have the values $k_{\text{H}_2\text{O}} = 2.0 \times 10^{-7}$ s⁻¹, $k_{\text{OH}} = 1.2 \times 10^{-5}$ s⁻¹, and $K_a = 6.0 \times 10^{-5}$ M. The uncertainties quoted are standard deviations.

In fitting the rate data according to the modified equation 3 each k_{2c} rate constant was weighted according to the reciprocal of its square. The calculated values of the rate constants agree with the experimentally observed values with an average deviation of 2.0% and a maximal individual deviation of 7.1%.

The simpler form of the rate law 3 given by $k_{\text{obsd}} = k_0 + k_{-1} [\text{H}^+]^{-1}$ for the aquation of monosubstituted complexes of aquachromium(III) ions has been often observed⁶ and interpreted in terms of a higher reactivity of hydroxo-over aqua-species of the complex. The separation of the composite k_{-1} values to the individual k_{OH} and K_a values is usually not achieved⁶. The high acidity range used in this work and the magnitudes of the individual constants required application of the full form of the rate law 3 to describe the acidity dependence of the rate constants observed and enabled separation of the k_{OH} from the K_a value.

The ratio $k_{\text{OH}}/k_{\text{H}_2\text{O}} = 60$ has been found, showing that the $\text{cis-Cr(py)}_2(\text{OH})(\text{H}_2\text{O})_3^{+2}$ species is only moderately more reactive than the $\text{cis-Cr(py)}_2(\text{H}_2\text{O})_4^{3+}$ species. Low ratios of reactivity of hydroxo over aqua species for substitutions of the chromium(III) center, as compared to high ratios for the cobalt(III) center, have long been known⁷. Swaddle has argued that the ratios for chromium(III) are low due to the unusually high reactivities of aqua species brought about by an associative (I_a) mechanism of their substitution reactions. The ratio found here for the aquation of the cis-Cr(py)_2^{3+} complex, even lower than expected, is consistent with such a contention.

The acid dissociation equilibrium constant $K_a = 6.0 \times 10^{-5}$ M found for the cis-Cr(py)_2^{3+} complex at 25 °C and $\mu = 1.0$ M is close to the $K_a = 3.6 \times 10^{-5}$ M value reported for the hexaaquachromium(III) ion⁹.

cis-Bisamminechromium(III) ion aquates by losing the first ammine ligand 3 times faster than the second ammine¹⁰. Similarly, the first amine-chromium(III) bond rupture occurs by a factor of 2 to 16 faster than the second one in the aquation of the ligand-tetraaquachromium(III) complexes, where

the ligand stands for a series of aliphatic polyamines bound to Cr(III) in a *cis*-bidentate mode¹¹. The same qualitative trend is observed now for the aquation of *cis*-Cr(py)₂(H₂O)₄³⁺, which proceeds about 10 times faster than the aquation of Cr(py)(H₂O)₅³⁺.³ A more specific comparison of the reactivities of bisaminechromium(III) ions is obscured by the difference in the extent of steric crowding of different amine ligands and by the possibility of pyridine-chromium(III) π bonding¹². However, the lack of the *cis*- to *trans*- isomerization was also observed in the aquation of the *cis*-Cr(NH₃)₂(H₂O)₄³⁺ ion¹⁰.

REFERENCES

1. P. Pfeiffer, *Z. Anorg. Allg. Chem.* **31** (1902) 401.
2. H. L. Schläfer and R. Kollrack, *Z. phys. Chem.* **18** (1958) 348.
3. A. Bakač and M. Orhanović, *Inorg. Chem.* **10** (1971) 2443.
4. A. Bakač and M. Orhanović, *Z. Naturforsch.* **29b** (1974) 134.
5. A. Bakač, R. Marčec, and M. Orhanović, *Inorg. Chem.* **13** (1974) 57.
6. C. S. Garner and D. A. House, *Transition Metal Chem.*, **6** (1970) 149; M. Orhanović and M. Avdagić, *Inorg. Chem.* **12** (1973) 492.
7. F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd ed., J. Wiley and Sons, Inc., New York, 1967. p. 180.
8. G. Guastalla and T. W. Swaddle, *Can. J. Chem.* **51** (1973) 821.
9. E. A. Deutsch, *Ph. D. Thesis*, Stanford University, 1967, p. 85.
10. L. Mønsted and O. Mønsted, *Acta Chem. Scand.* **27** (1973) 2121.
11. a) R. F. Childers, Jr., K. G. Vander Zyl, Jr., D. A. House, R. G. Hughes, and C. S. Garneer, *Inorg. Chem.* **7** (1968) 749. b) D. K. Lin and C. S. Garner, *J. Amer. Chem. Soc.* **91** (1969) 6637. c) D. A. Kamp, R. L. Wilder, S. C. Tang, and C. S. Garner, *Inorg. Chem.* **10** (1971) 1396.
12. a) J. Glerup, O. Mønsted, and C. E. Schäffer, *Proc. Int. Conf. Coord. Chem.* **16** (1974) 2.14a. b) C. D. Flint and A. P. Matthews, *Inorg. Chem.* **14** (1975) 1008. c) A. Bakač, V. Butković, and M. Orhanović, *Croat. Chem. Acta* **48** (1976) 35.

SAŽETAK

Kinetika akvacije *cis*-bispiridintetraakvakrom(III) iona

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cis- i *trans*-Bispiridintetraakvakrom(III)-ioni bili su priredeni i karakterizirani u otopini. Kinetika akvacije *cis*-izomera ispitivana je kao funkcija kiselosti i temperature. Proces teče akvacijom u Cr(H₂O)₅py³⁺ ion bez reakcijskog puta izomerizacije, a zakon brzine ima oblik $-d \ln [\text{Cr}(\text{H}_2\text{O})_4(\text{py})_2^{3+}] / dt = (k_{\text{H}_2\text{O}} + k_{\text{OH}} K_a [\text{H}^+]^{-1}) / (1 + K_a [\text{H}^+]^{-1})$. Entalpija/kcal mol⁻¹ i entropija/cal mol⁻¹ K⁻¹ su 25.2 i -4.6 za akvaciju *cis*-Cr(H₂O)₄(py)₂³⁺ iona (*k*_{H₂O} put), a 25.4 i 4.3 za akvaciju *cis*-Cr(H₂O)₃(OH)(py)₂²⁺ iona (*k*_{OH} put). Standardna entalpija i entropija za reakciju disocijacije kiseline *cis*-Cr(H₂O)₄(py)₂³⁺ su 12.7 kcal mol⁻¹ i 23.2 cal mol⁻¹ K⁻¹. Odgovarajuće konstante ekstrapolirane na 25 °C imaju vrijednosti *k*_{H₂O} = 2.0 × 10⁻⁷ s⁻¹, *k*_{OH} = 1.2 × 10⁻⁵ s⁻¹ i *K*_a = 6.0 × 10⁻⁵ M.

cis-hidroksi specija reagira samo 60 puta brže od *cis*-akva specije, što je u skladu s doprinosom asocijativnog mehanizma u procesu akvacije *cis*-akvo specije.

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