close to the values found in the present study. The question remains however as to at which site, c or d, does anation occur. For NCS^-, the available evidence favors anation at a d-H_2O ligand.[39] Monodentate anation of $HC_2O_4^-$ at a d-H_2O would also seem to correlate with the ultimate location of the chelating oxalate ligands at the d sites in the crystal structure of $[Mo_3O_4(C_2O_4)_3(OH_2)_3]^{2-}$.[3,4]

Rate constants for anation reactions on cationic aqua ions can generally be represented by $k_f = k_I K_{os}$,[40] where k_I represents the rate constant for the interchange step and K_{os} the outer-sphere ion-pair association constant. In order to decide whether the anation on the d site is dissociative or associative one can attempt to compare k_I and the water-exchange rate constant at that site. Such comparison requires the knowledge, or at least the magnitude of K_{os}. Its value, in the case of simple spherical ions, can be calculated by using the Fuoss model.[41] However, several groups[42] have highlighted the inadequacy of the model as applied to the case of nonspherical ion partners, which is highly relevant to the present study. For anation on $[Mo_3O_4(OH_2)_9]^{4+}$, the absence of detectable curvature in linear plots of k_{obs} against $[NCS^-]$ or $[HC_2O_4^-]$ in 10-fold excess up to 0.0035 M[10-12] suggests an upper limit of 10 M^{-1} for K_{os}. While calculations from the Fuoss model do not seem highly relevant, a lower limit of 0.5 M^{-1} for K_{os} can be estimated by assuming the incoming anion only interacting at one Mo(IV) center and thus only seeing formally a +0.33 charge at this deprotonated center (4.6 Å was taken as the distance of closest approach). This leads to a range between 0.4 and 8 s^{-1} for k_I by using an average value of 4 M^{-1} s^{-1} for k_f.[43] Such values, being somewhat smaller (~20 times) than the water-exchange rate constant, rules out an associative mechanism[44] at the d sites. The positive ΔS^{*} value (+35 J K^{-1} mol^{-1}) found here together with similar 1:1 anation rate constants found for NCS^- and $HC_2O_4^-$[12] are in support of a dissociative activation mode. A similar activation mode may also be relevant at the c sites.[45] The factor of 10^5 between the rate constants for water exchange at a d-H_2O as opposed to a c-H_2O, both cis conjugate base activated,[46] is probably a reflection of the much stronger trans effect of μ_2- vs μ_3-oxo groups, though it is surprising that this is not manifested through different Mo–OH_2 bond lengths. Such an indication of an I_d mechanism is initially surprising given the d^2 configuration of Mo(IV) but would not be inconsistent with the apparent coordination number of 8 per Mo if one includes the metal–metal-bonded framework.

The results presented have provided evidence for high acidity occurring for $[Mo_3O_4(OH_2)_9]^{4+}$ at the d-H_2O ligands (K_a^{298} = 0.24 M) trans to the μ_2-oxo groups. Such high acidity is surprising given that this Mo(IV) aqua ion is already in an extensively hydrolyzed state.

Water exchange at the c- and d-H_2O ligands proceeds only through the conjugate base ion, involving deprotonation of a d-H_2O, with rate constants for each that differ by 5 orders of magnitude; a behavior attributed to different trans effects of μ_2- and μ_3-oxo groups in the trinuclear ion. The μ_2- and μ_3-oxo groups of the "core" are extremely inert with a half-life >10 years for both suggested. The available evidence suggests that an I_d mechanism is relevant for water exchange at both sites and that initial complexation reactions occur exclusively through replacement of a d-H_2O.

Acknowledgment. We thank the Swiss National Science Foundation for supporting this research under Grant No 2.672-0.87 and Professor A. G. Sykes for helpful discussions and for supplying information prior to publication. D.T.R. wishes to thank the Nuffield Foundation and British Council for financial support. The Convention Intercantonale Romande pur l'Enseignement du Troisième Cycle en Chimie is also thanked for providing a visiting professorship in Lausanne to D.T.R.

Registry No. $[Mo_3O_4(OH_2)_9]^{4+}$, 74353-85-8; $[Mo_3O_4(OH_2)_9](CH_3C_6H_4SO_3)_4 \cdot 13H_2O$, 119390-73-7; H_2O, 7732-18-5.

Supplementary Material Available: Anisotropic displacement parameters (Table S1), calculated hydrogen positions (Table S2), complete bond lengths (Table S3) and bond angles (Table S4), O···O distances for the considered H-bond interactions (Table S5), and selected least-squares weighted planes and dihedral angles (Table S6) (8 pages); observed and calculated structure factors (Table S7) (36 pages). Ordering information is given on any current masthead page.

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(39) In anation studies with excess NCS^-, two kinetically distinct isomeric forms of $[Mo_3O_4(NCS)]^{3+}$ have been identified involving possible NCS^- coordination independently at the c and d positions.[11] Isomer 1 is obtained following 1:1 anation and has the faster aquation rate, consistent with occupancy of the d position, with respect to isomer 2 obtained following aquation of $[Mo_3O_4(NCS)_2]^{2+}$. Occupancy of the c position is thought to arise during formation of $[Mo_3O_4(NCS)_2]^{2+}$. Anation at a d position was also favored by Murmann[4] following an observation that the rates of complexation by both Cl^- and $HC_2O_4^-$ were too fast to be consistent with the measured rate of water exchange at a c-H_2O.

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(43) The values of $k_f \sim 4$ M^{-1} s^{-1} is an average value of the anation rate constants recently obtained from complexation of NCS^- (4.8 M^{-1} s^{-1}) and $HC_2O_4^-$ (3.3 M^{-1} s^{-1}) with $[Mo_3O_4(OH_2)_8(OH)]^{3+}$. The similarity of anation rate constants obtained here for both ligands was cited as evidence in favor of an I_d mechanism.[12]

(44) Associatively activated interchange steps have rate constants usually in excess of the water-exchange rate constants: Wilkins, R. G. *The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes*; Allyn & Bacon: Boston, MA, 1974.

(45) A positive ΔS^{*} value of ~30 J K^{-1} mol^{-1} was found for water exchange at the c-H_2O on $[Mo_3O_4(OH_2)_9]^{4+}$.[4]

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Notes

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Effect of Ring Size on the Dissociation Kinetics of Copper(II)-Tetraamine Complexes

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A considerable amount of experimental material relating to the thermodynamics of transition-metal complexes with linear aliphatic tetraamines has been reported.[1-4] In particular for copper(II) complexes, it has been found that the stability of these complexes is dependent to a very large extent on the sizes of the three linked chelate rings.[2,5] It was of interest to see the effect of ring size on the dissociation kinetics of these copper(II) complexes.

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Table I. Rate Constants for the Dissociation of Linear Copper(II)–Tetraamine Complexes at 25.0 °C and μ = 5.0 M (HNO_3 + $NaNO_3$)[a]

	k_{obsd},[b] s^{-1}			
[HNO_3], M	Cu(2,3,2-tet)$^{2+}$	Cu(3,2,3-tet)$^{2+}$[c]	Cu(2,2,2-tet)$^{2+}$	Cu(3,3,3-tet)$^{2+}$
0.10	0.157	6.10	165	49.2
0.20	0.164	6.16	176	50.8
0.25	0.169	6.19	190	51.1
0.30	0.174	6.20	202	51.6
0.40	0.181	6.25	215	52.7
0.50	0.189	6.32	234	53.5
0.75	0.210	6.44	251	54.5
1.00	0.216	6.58	284	56.4
1.25	0.234	6.67	312	57.8
1.50	0.261	6.78	347	59.2
1.75	0.284	6.92	378	61.1
2.00	0.291	7.04	413	62.0
2.25	0.323	7.17	436	64.2
2.50	0.350	7.30	465	65.8

[a] Conditions: [Cu(2,3,2-tet)$^{2+}$] = 2.02 × 10^{-3} M, wavelength 520 nm; [Cu(3,2,3-tet)$^{2+}$] = 2.01 × 10^{-3} M, wavelength 543 nm; [Cu(2,2,2-tet)$^{2+}$] = 2.03 × 10^{-3} M, wavelength 575 nm; [Cu(3,3,3-tet)$^{2+}$] = 2.02 × 10^{-2} M, wavelength 589 nm. [b] Mean value of at least four kinetics runs. [c] Reference 6.

Table II. Measured and Corresponding Mechanistic Rate Constants for the Dissociation of Copper(II)–Tetraamine Complexes at 25.0 °C and μ = 5.0 M (HNO_3 + $NaNO_3$)

measd rate const	mechanistic rate const	Cu(2,3,2-tet)$^{2+}$	Cu(3,2,3-tet)$^{2+}$[a]	Cu(2,2,2-tet)$^{2+}$	Cu(3,3,3-tet)$^{2+}$	Cu(Cyclam)$^{2+}$[a]
k_{2H}, M^{-1} s^{-1}	$(k_{12}/k_{21})k_{23}$	0.0763	0.493[b]	123.6	6.48	3.15 × 10^{-4}[b]
k_{1d}, s^{-1}	$(k_{12}/k_{21})k_{24}$	0.148	6.06	160.3	49.60	very small
k_{2H}/k_{1d}		0.516	0.081	0.771	0.131	very large

[a] Reference 6. [b] k_{1H} in ref 6.

Table III. Selected Structural Data for Copper(II)–Tetraamine Complexes and the Thermodynamic Functions for the Complexation Reactions of Copper(II) with Linear Tetraamines at 25.0 °C

	Cu(2,2,2-tet)$^{2+}$	Cu(2,3,2-tet)$^{2+}$	Cu(3,2,3-tet)$^{2+}$	Cu(3,3,3-tet)$^{2+}$
Cu–N dist, Å	2.008 (7)–2.030 (5)	2.016 (6)–2.032 (6)	2.012 (8)–2.031 (8)	2.02 (2)–2.04 (2)
trans N–Cu–N angle, deg	154.0 161.0	176.4 (3) 178.5 (4)	173.3 (4) 176.2 (3)	159.4 (7) 169.4 (7)
conformation of chelate rings	gauche gauche gauche	gauche chair gauche	chair gauche chair	chair chair chair
coordn geometry about Cu^{II}	distorted square pyramidal	tetragonally distorted octahedral	distorted square pyramidal	tetragonally distorted octahedral
log k	20.2	23.9	21.8	17.3
ΔH_f, kcal mol^{-1}	−21.6	−27.7	−25.5	−19.5
ΔS, eu	19.5	16.5	13.1	12.8
ref	1, 9, 12, 13	1, 8, 12, 13	7, 12, 13	1, 8, 12, 13

Previously we have reported the dissociation kinetics of the copper(II) complex of 1,5,8,12-tetraazadodecane, 3,2,3-tet, in strongly acidic, aqueous media.[6] In the present work the kinetics of the dissociation reactions of copper(II) complexes of 1,4,7,10-tetraazadecane, 2,2,2-tet, 1,4,8,11-tetraazaundecane, 2,3,2-tet, and 1,5,9,13-tetraazatridecane, 3,3,3-tet, were investigated at 25.0 °C in 0.1–5.0 M HNO_3 (eq 1).

$$CuL^{2+} + 4H^+ \rightarrow Cu^{2+} + H_4L^{4+} \qquad (1)$$

Crystal structure determinations of these four copper(II)–tetraamine complexes have been reported,[7-9] thus providing the opportunity to elaborate the ways in which the different structures of the coordinated tetraaza ligands convey properties on the acid-assisted dissociation kinetics of their metal complexes.

Experimental Section

Reagents. The complex Cu(3,2,3-tet)$(ClO_4)_2$ was the same as that reported earlier.[7] Copper perchlorate was prepared from copper carbonate and perchloric acid and was recrystallized from water. The complexes Cu(2,3,2-tet)$(ClO_4)_2$, Cu(2,2,2-tet)$(ClO_4)_2$, and Cu(3,3,3-tet)$(ClO_4)_2$ were prepared from copper(II) perchlorate and from 2,3,2-tet, 2,2,2-tet, and 3,3,3-tet (Aldrich Chemical Co.), respectively.[8-10] These complexes were recrystallized twice from water. All other chemicals used in this work were of GR grade from Merck or Aldrich.

Kinetics Measurements. The kinetics of the acid-catalyzed dissociation reactions of the copper complexes were studied with a Union Giken RA-401 stopped-flow spectrophotometer equipped with a Union RA-415 rapid-scan attachment, and the temperature was maintained at 25.0 ± 0.1 °C for all the solutions studied. Absorbance vs time data were collected at 520, 589, and 575 nm for the dissociation reactions of Cu(2,3,2-tet)$^{2+}$, Cu(3,3,3-tet)$^{2+}$ and Cu(2,2,2-tet)$^{2+}$, respectively. Pseudo-first-order conditions were maintained by using at least a 40-fold excess of acid in each run. Good first-order kinetics were observed in all cases. The rate constants were obtained by a linear least-squares fit for the data by using an IBM PC computer. Recrystallized $NaNO_3$ was used to maintain constant ionic strength at μ = 5.0 M in all solutions. The concentration of the copper(II) complex employed for the kinetic work is 2.00 × 10^{-3} M. The concentrations of acid are in the range 0.10–5.00 M.

Results

The kinetics of the dissociation reactions of these copper(II)–tetraamine complexes were studied at 25.0 °C, with μ = 5.0 M (HNO_3 + $NaNO_3$), and in 0.1–5.0 M HNO_3. Under these conditions, the dissociation reactions of these complexes were found

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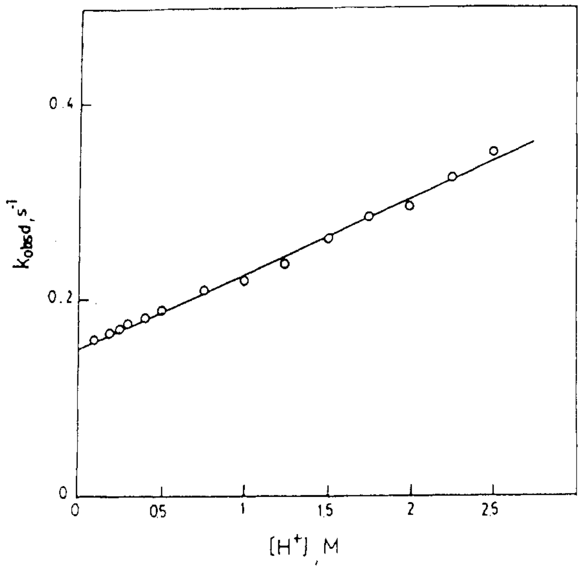

Figure 1. Plot of k_{obsd} vs [H$^+$] for the dissociation of Cu(2,3,2-tet)$^{2+}$ at 25.0 ± 0.1 °C and μ = 5.0 M (HNO_3 + $NaNO_3$).

to proceed to completion, and the observed pseudo-first-order rate constants are given in Table I. Plots of k_{obsd} vs [H$^+$] give straight lines according to eq 2. The symbols of the rate constants k_{2H}

$$k_{obsd} = k_{2H}[H^+] + k_{1d} \qquad (2)$$

and k_{1d} are the same as those used by Read and Margerum.[11] The plot for the dissociation reaction of Cu(2,3,2-tet)$^{2+}$ is shown in Figure 1; the other complexes show a similar behavior. The values of k_{2H} and k_{1d} obtained in these plots are listed in Table II together with the rate constants for the dissociation of Cu(3,2,3-tet)$^{2+}$ reported previously.[6]

Discussion

The X-ray crystal structures[7-9] and the thermodynamic data[1,12,13] of the copper(II) complexes of these four ligands have been reported. A comparison of the selected structural and thermodynamic data for these complexes is given in Table III. For these complexes, the four donor N atoms of the tetraamine form a distorted plane; the equatorial Cu–N distances span a rather narrow range, 2.01–2.04 Å. Each of these complexes contains three stable fused chelate rings, the chair form of the six-membered rings and/or the gauche form of the five-membered rings. The complexes in which five- and six-membered rings alternate, e.g., Cu(2,3,2-tet)$^{2+}$ and Cu(3,2,3-tet)$^{2+}$, are more stable than the complexes in which the chelate rings are either all five-membered (Cu(2,2,2-tet)$^{2+}$) or all six-membered (Cu(3,3,3-tet)$^{2+}$) rings.

The kinetic results can be explained by the general mechanism proposed by Margerum and co-workers (Figure 2).[11] In strongly acidic, aqueous media, both the direct protonation pathway (I → II → III → V → VI) and the solvation or the proton-assisted pathway (I → II → IV → V → VI) make contributions to the rates of these reactions. As shown in Figure 2, the cleavage of the first Cu–N bond involves the formation of an intermediate (V) with the donor group displaced from the normal chelation position. The metal ion becomes solvated, and there is protonation and rotation of the leaving donor group. In these reactions, acid and solvent assist the dissociation by protonation and solvation of the intermediate to a large extent, with the result that the breakage of the second copper–nitrogen bond is faster than the recombination of the first copper–nitrogen bond. Therefore, the rate-determining step for the dissociation reactions of these complexes is the breakage of the first copper–nitrogen bond.

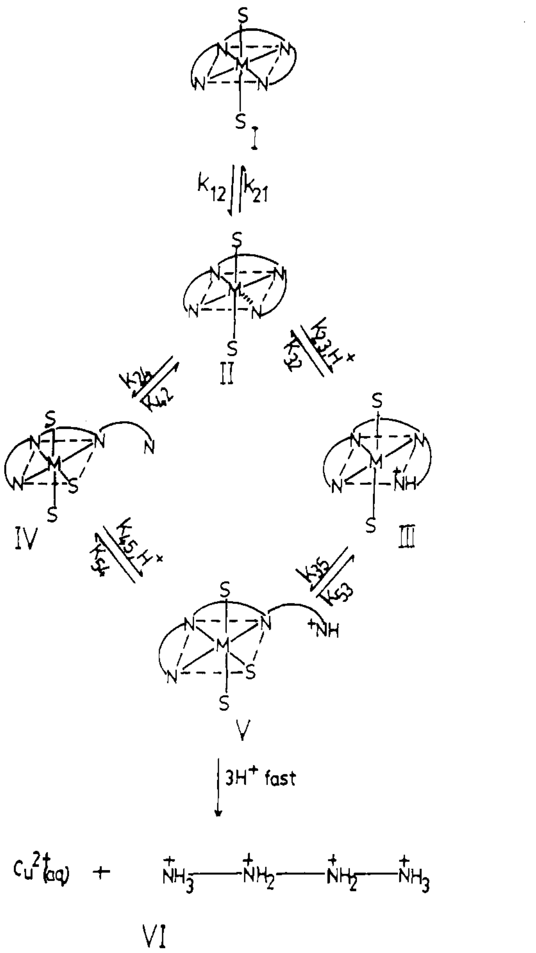

Figure 2. Proposed stepwise mechanism for the dissociation of linear copper(II)–tetraamine complexes in strongly acidic media.

The rate constants k_{2H} and k_{1d} (Table II) depend heavily on the nature of the tetraamine, the leaving group, and vary over 3 orders of magnitude. These results suggest that the degree of bond breaking in the rate-determining step is large or appreciable, and these reactions are probably of dissociative activation. As shown in the first step of the mechanism (I → II in Figure 2), one nitrogen donor is dissociated from copper(II) without its replacement by a solvent molecule. In this species (II) the amine N is still in the first coordination sphere of copper(II). Thus this amino group with a lone pair available on the nitrogen is basic and susceptible to protonation to form species III, which undergoes rapid metal ion solvation to form species V. If this amino group in species II is unrestricted and able to move easily out of the first coordinate sphere, species II is more susceptible to solvent attack. Thus the solvation (I → II → IV → V → VI) pathway are the main pathway; the presence of acid has little effect.[11] On the other hand, if the movement of the donor away from copper(II) is hindered in some way, acid can enhance the rate of dissociation to a large extent. The ratio k_{2H}/k_{1d} represents the relative rate of dissociation by the protonation and the solvation pathways.[11,14] On the basis of these considerations, we may expect that the values of k_{2H}/k_{1d} for macrocyclic tetraamine complexes are much larger than those for linear tetraamine complexes,[15] and the values of k_{2H}/k_{1d} for the linear tetraamine complexes containing terminal five-membered rings are larger than those for the complexes containing terminal six-membered rings. This sequence of k_{2H}/k_{1d}, Cu(Cyclam)$^{2+}$ ≫ Cu(2,2,2-tet)$^{2+}$, Cu(2,3,2-tet)$^{2+}$ > Cu(3,3,3-tet)$^{2+}$, Cu(3,2,3-tet)$^{2+}$, is found experimentally (Table II).

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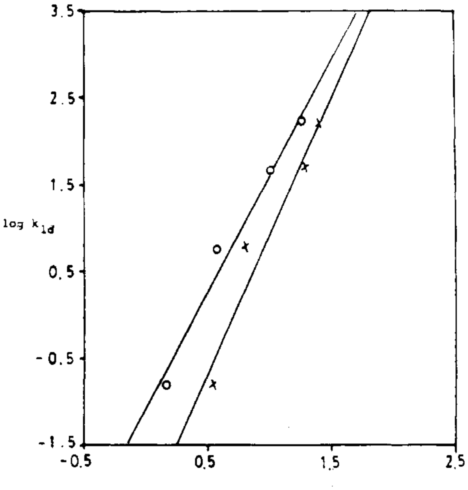

Figure 3. log k_{1d} as a function of log (180° – the N–Cu–N bond angle): (O) large trans N–Cu–N bond angle; (X) small trans N–Cu–N bond angle.

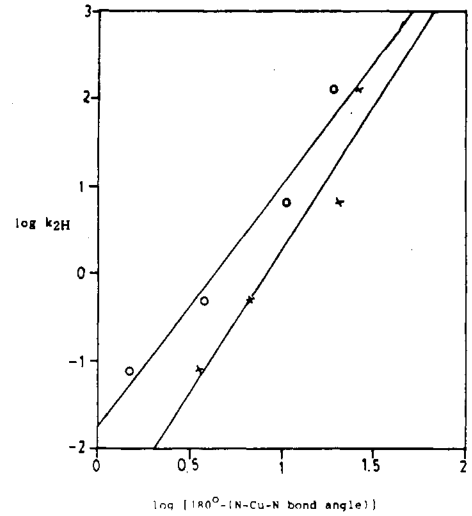

Figure 4. log k_{2H} as a function of log (180° – the N–Cu–N bond angle): (O) large trans N–Cu–N bond angle; (X) small trans N–Cu–N bond angle.

Both k_{2H} and k_{1d} increase in the order Cu(2,3,2-tet)$^{2+}$ < Cu(3,2,3-tet)$^{2+}$ < Cu(3,3,3-tet)$^{2+}$ < Cu(2,2,2-tet)$^{2+}$ (Table II). This is not the same order of the instability constants of these complexes (Table III). Although Cu(2,2,2-tet)$^{2+}$ is much more stable than Cu(3,3,3-tet)$^{2+}$, it dissociates faster than Cu(3,3,3-tet)$^{2+}$ (Table II and III). As shown in Table III, the observed Cu–N bond lengths of these complexes do not differ significantly; the conformations of the chelate rings are the most stable six-membered chair and five-membered gauche forms.

As shown in Figure 2, the initial phase of the chelate ring-opening step involves some angular distortion of the bond angles in the chelate rings. This led us to think that there must be a relation between the bond angles and the kinetic properties of these complexes. Within the Cu(2,3,2-tet)$^{2+}$ unit, the N–Cu–N bond angles (178.5 and 176.4) are very close to 180°.[8] Consequently, the N_4 donor set in this complex nearly matches the symmetry properties of the Cu(II) orbital; on this basis, a relatively inert complex is expected (and found). Deviations of the homologous, crystallographically characterized Cu(3,2,3-tet)$^{2+}$, Cu(3,3,3-tet)$^{2+}$, and Cu(2,2,2-tet)$^{2+}$ complexes from this idealized bonding arrangement are reflected by the kinetic data.[7,8] As shown in Table III the N–Cu–N bond angles vary in the order Cu(2,3,2-tet)$^{2+}$ > Cu(3,2,3-tet)$^{2+}$ > Cu(3,3,3-tet)$^{2+}$ > Cu(2,2,2-tet)$^{2+}$; thus, the rate constants k_{2H} and k_{1d} are expected to vary in the order Cu(2,3,2-tet)$^{2+}$ < Cu(3,2,3-tet)$^{2+}$ < Cu(3,3,3-tet)$^{2+}$ < Cu(2,2,2-tet)$^{2+}$. This sequence is found experimentally (Table II).

There are two trans N–Cu–N bond angles for each of these copper(II)-tetraamine complexes (Table III). Plots of log k_{1d} vs log (180° – the large N-Cu-N bond angle) and log k_{1d} vs log (180° – the small N-Cu-N bond angle) are shown in Figure 3. Analogous plots for log k_{2H} are shown in Figure 4. On the basis of these results, we are able to conclude that it is not the instability constant but the trans N–Cu–N bond angle that affects the dissociation rate constant of the copper(II)–tetraamine complex, and the linear correlation between log k_{1d} (or log k_{2H}) and log (180° – the N–Cu–N bond angle) could serve as a basis for predictions.

Acknowledgment. The support of the Chemistry Research Center, National Science Council of the Republic of China, under Grants NSC 75-0208-M007-04 and NSC 76-0208-M007-66 is gratefully acknowledged.

Registry No. Cu(2,2,2-tet)$^{2+}$, 45840-81-1; Cu(2,3,2-tet)$^{2+}$, 45980-55-0; Cu(3,3,3-tet)$^{2+}$, 46242-92-6.

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Spectroscopic and Solution Properties of the Cobalt(III) Hexaimidazole Ion

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The imidazole side chain of histidine is a very common ligand of metal ions in metalloproteins. Some well-known examples are the enzymes such as carboxypeptidase A, carbonic anhydrase, thermolysin, superoxide dismutase, and alkaline phosphatase, metal-carrying proteins such as transferrin and conalbumin, and redox proteins such as hemerythrin.[1] It was shown[2] that the optical spectra of cobalt(III)-substituted metalloproteins can be employed in identifying the ligands of the metals in the native enzymes. The study described herein led to the spectroscopic characterization of the parent cobalt(III) hexaimidazole compound $Co(ImH)_6^{3+}$.

Experimental Section

The synthesis of $Co(ImH)_6(ClO_4)_3$ was done by H_2O_2 oxidation of $Co(ImH)_6(ClO_4)_2$. The conditions of the oxidation reactions were optimized by following in situ the sharp ^{59}Co NMR spectra of the $Co(ImH)_6(ClO_4)_3$ ion with the chemical shift of 8940 ppm relative to $K_3Co(CN)_6$.

For the oxidation of a reaction mixture containing $Co(ClO_4)_2 \cdot 6H_2O$ (3.8×10^{-3} mol), imidazole (0.27 mol), and $HClO_4$ (0.09 mol) in 30 mL of water 0.02 mol of H_2O_2 was added within a period of 1 h at room temperature. $Co(ImH)_6(ClO_4)_3$ was purified by using chromatography on an SE-Sephadex G50 column, eluted with a linear gradient of $Ba(ClO_4)_2$ (0.05–0.1 M). The Ba^{2+} ions were removed by careful addition of H_2SO_4, and the $BaSO_4$ precipitate was removed by filtering. $Co(ImH)_6(ClO_4)_3$ was crystallized by slow evaporation of its aqueous solution. The crystals were filtered and washed with cold dilute $HClO_4$.

Anal. Found (calcd) for $Co(ImH)_6(ClO_4)_3$: C, 27.7 (28.2); H, 3.09 (3.16); N, 21.0 (21.95); Cl, 14.5 (13.9); Co, 8.8 (7.7). The yield of the oxidation reaction (in situ) was 40%, and the final yield of the synthesis was 25%. Solutions of $Co(ImH)_6Cl_3$ were prepared by dissolving $Co(ImH)_6(ClO_4)_3$ in KCl, cooling the solution, and filtering the precipitated $KClO_4$.

Caution! Although we have experienced no difficulties with the perchlorate salts described here, these should be regarded as potentially explosive and handled accordingly.

NMR measurements were done by using a Bruker AM-360 WB NMR spectrometer. All spectra were taken at ambient temperature, which was about 20 °C. Proton NMR spectra were obtained from D_2O solutions of $Co(ImH)_6$ with 3-(trimethylsilyl)propionic-*2,2,3,3-d₄* acid

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