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NMR Relaxation Studies in Solutions of Transition Metal Complexes. IX. Dynamics of Equilibria in Aqueous Solutions of some Copper(II)–Nitrilotriacetate–B Ligand Mixed Ligand Complexes

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The formation constants of the complexes formed in the copper(II)–nitrilotriacetate (NTA^{3-}) parent and in the copper(II)–NTA^{3-}–glycinate, copper(II)–NTA^{3-}–ammonia and copper(II)–NTA^{3-}–methylamine mixed ligand equilibrium systems in aqueous solution have been determined by pH-metry at 25 °C in 1 M *KCl. The dynamics of equilibria have been studied using the NMR relaxation technique.*

The glycinate ligand is thought to be more loosely bound to the central copper(II) ion in the mixed complex than in the parent one. In spite of this the ligand exchange rate is much slower, thus the thermodynamic stabilization is reflected in the increase of the kinetic stability of the mixed ligand complex also.

The surprisingly high molar relaxation coefficient of the CuNTANH$_3$ mixed complex is interpreted by the fast formation and dissociation of the mixed ligand complex,

$$CuNTA^- + NH_3 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} CuNTANH_3^-$$

with a forward rate constant of 2.1 × 10^8 M^{-1} *s^{-1}.*

Introduction

The results of the study of the dynamics of equilibria in aqueous solutions of a number of copper(II)–amine and –amino acid binary complexes and of the copper(II)–bipyridyl–glycine mixed ligand system have been reported earlier [1–3]. The most important conclusions of these studies were that the rate determining step of the ligand exchange process is the Jahn–Teller inversion of the tris complex, and that the kinetic background of the thermodynamic stabilization of the mixed copper(II)–bipyridyl–glycine complex is the lability of the *cis*-octahedral Cu(bipy)$_2^{2+}$ complex.

The copper(II)–nitrilotriacetate (NTA^{3-})–B ligand complexes show also significant stabilization if the B ligands are mono- or bidentate, *i.e.* the equilibrium constants for the

$$Cu(NTA)_2^{4-} + CuB_2^{m-} \rightleftharpoons 2CuNTAB^{(2+m/2)-}$$

processes are much higher than the statistical value of four. This stabilization, however, is an inherent consequence of the difference in the K_1/K_2 ratios, as was explained by Martin and Prados [4] as well as by Sóvágó and Gergely [5].

The aim of the present work was to see how the thermodynamic stabilization, the number of donor groups and the pK of B ligands are reflected in the kinetic parameters of the ligand exchange reactions taking place in the Cu(II)–NTA^{3-}–glycine, Cu(II)–NTA^{3-}–ammonia and Cu(II)–NTA^{3-}–methylamine systems. These mixed complexes are especially well suited to study these effects, because only the B ligands have labile –NH protons, thus the exchange of B ligands between the para and diamagnetic sites, and the effect of the water molecule(s) remaining in the first coordination sphere are influencing the T_2 relaxation time of the water protons only.

The formation constants of the complexes formed have also been determined using pH-potentiometry and spectrophotometry, to have the concentration distribution of the complexes at exactly the same condition which is used in the relaxation measurements.

Experimental

A Radiometer PHM-52 instrument with GK-2301B electrode, calibrated for –log [H$^+$] according to Irving *et al.* [6] was used for pH-titrations at 25 °C. The pK of ammonia and methylamine, as well as their CuNTA$^-$ + B ⇌ CuNTAB$^-$ equilibrium constants

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TABLE I. Composition of the Initial Solutions Used in the Relaxation Titrations.

B ligand	T_{CuNTA^-}	$T_{NTA^{3-}}$	T_B
	0.040	0.000	–
	0.040	0.018	–
–	0.040	0.030	–
	0.020	0.009	–
	0.020	0.018	–
NH_3	0.020	–	2.00
	0.030	–	2.00
CH_3NH_2	0.020	–	2.00
	0.030	–	2.00
glycine	0.020	–	0.10
	0.030	–	0.10
	0.040	–	0.20

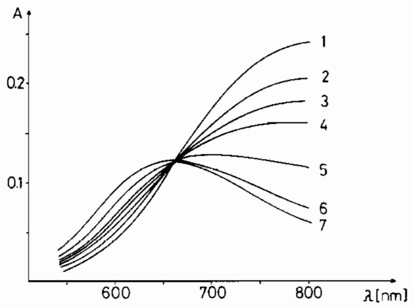

Fig. 1. The spectra recorded in the $CuNTA^-$–glycine system at different neutralization degrees. T_{CuNTA} = 0.004 *M* for all curves, $T_{glycine}$ = 0.006 *M* for curves 1–6, and $T_{glycine}$ = 0.030 for curve 7. The neutralization degrees are as follows: curve 1. $[KOH]/T_{CuNTA}$ = 0.000; curve 2. $[KOH]/T_{CuNTA}$ = 0.250; curve 3. $[KOH]/T_{CuNTA}$ = 0.375; curve 4. $[KOH]/T_{CuNTA}$ = 0.500; curve 5. $[KOH]/T_{CuNTA}$ = 0.750; curve 6. $[KOH]/T_{CuNTA}$ = 1.000; curve 7. $[KOH]/T_{CuNTA}$ = 7.000.

were determined from the pH-titrations in 2 *M* solutions of the appropriate hydrochlorides. The Cu(II)–NTA^{3-} and the Cu(II)–NTA^{3-}–glycine systems were studied in 1 *M* KCl. The spectra of some of the systems were recorded with a Beckman Acta M4 spectrophotometer, to help the evaluation of the potentiometric studies.

The T_2 relaxation times of water protons were measured at 25 ± 1 °C by a Newport N20 instrument at 2.5 MHz, using the single echo technique [7]. The measurements were carried out by titrating the initial solutions with KOH. The composition of the initial solutions used for relaxation measurements are collected in Table I.

The equilibrium constants and the concentration distribution of the complexes were calculated by the use of the program PSEQUAD [8]. The relaxation measurements were evaluated by using the least squares principle to minimize the percentage deviation between the measured and calculated relaxation rates according to the models described in the following section.

Results and Discussion

Equilibria

The formation constant of the $CuNTA^-$ complex is too high to be measured pH-metrically, thus

TABLE II. Logarithm of the Stepwise Equilibrium Constants of the Species Formed in the Systems Studied.

Equilibrium	log K
$NTA^{3-} + H^+ \rightleftharpoons HNTA^{2-}$	9.32
$HNTA^{2-} + H^+ \rightleftharpoons H_2NTA^-$	2.27
$H_2NTA^- + H^+ \rightleftharpoons H_3NTA$	1.79
$G^- + H^+ \rightleftharpoons HG^{\mp}$	9.63
$HG^{\mp} + H^+ \rightleftharpoons H_2G^+$	2.50
$NH_3 + H^+ \rightleftharpoons NH_4^+$	9.53
$CH_3NH_2 + H^+ \rightleftharpoons CH_3NH_3^+$	10.96
$CuNTA^- + NTA^{3-} \rightleftharpoons Cu(NTA)_2^{4-}$	4.14 4.47[a]
$CuNTA^- + OH^- \rightleftharpoons CuNTAOH^{2-}$	4.52 4.39[b] 4.40[c]
$CuNTA^- + NH_3 \rightleftharpoons CuNTANH_3^-$	3.74 2.55[c]
$CuNTA^- + CH_3NH_2 \rightleftharpoons CuNTACH_3NH_2^-$	4.09
$CuNTA^- + G^- \rightleftharpoons CuNTAG^{2-}$	5.39 5.44[b]

[a] 20 °C, 0.1 *M* KNO_3 [16]. [b] 25 °C, 0.073 [12]. [c] 25 °C, 0.1 *M* KNO_3 [9].

only the equilibrium constants for the $CuNTA^- + NTA^{3-} \rightleftharpoons Cu(NTA)_2^{4-}$ and $CuNTA^- \rightleftharpoons CuNTAH_{-1}^{2-} + H^+$ processes were calculated from the $4 < pH < 11.3$ parts of the titration curves. The further hydrolysis of $CuNTAH_{-1}^{2-}$ was also detected by Still [9], with a pK of about 11.0. Our titration curves, however, could be fitted well, without trend, up to pH 11.3 so that the further hydrolysis of $CuNTA^-$ is not supported.

Figure 1 illustrates the results of the spectrophotometric measurements. The isosbestic point proves that only two species, $CuNTA^-$ and $CuNTAG^{2-}$ are present in the system, *i.e.* the NTA^{3-} ligand is not replaced by a second glycine, and the $CuNTAG_2^{3-}$ complex is not formed in the system, even in ligand excess. No isosbestic points were found in the $CuNTA^-$–ammonia and –methylamine systems, but the mol ratio curves indicated unambiguously that $CuNTA(NH_3)_2^-$ or $CuNTA(CH_3NH_2)_2^-$ complexes were not formed in significant concentration up to 0.05 *M* B ligand concentrations. The equilibrium constants calculated are collected in Table II.

Table II contains some of the previously determined values from the literature. The agreement in general is satisfactory, if the difference in the ionic strength is taken into account.

Relaxation Studies

The relaxation rate of water protons in the binary $Cu(II)–NTA^{3-}$ system could be fitted without trend with a linear combination of the concentration of the complexes formed up to pH ~ 10.5.

$$T_2^{-1} = T_{20}^{-1} + r_{CuNTA}[CuNTA^-] +$$

$$+ r_{Cu(NTA)_2}[Cu(NTA)_2^{4-}] + r_{CuNTAH_{-1}}[CuNTAH_{-1}^{2-}]$$

where:

T_2 = the measured relaxation time,
T_{20} = the relaxation time of water protons in the absence of paramagnetic species
r_i = the molar relaxation coefficient of the i-th complex

If the points above pH ~ 10.5 are also included in the calculation then a definite trend is observed, indicating the disturbing effect of a new proton-exchange process at higher pH values. This disturbing effect, however, has no influence on the evaluation of the data given in the mixed ligand systems, thus the identification of this process was not attempted.

The molar relaxation coefficients calculated are collected in Table III, together with the same data for the bis ethylenediamine and bis glycinato complexes. If we assume that the molar relaxation coefficients are proportional to the number of water molecules remaining in the first coordination sphere, then the value given for $r_{Cu(NTA)_2}$ is surprisingly high, indicating that two water molecules are bound to the copper(II) ion. The difference between the r_i values of bis ethylenediamine and bis glycinato complexes are also rather high to be explained by the difference in the number of water molecules bound to copper(II).

TABLE III. Molar Relaxation Coefficient of Some Copper(II) Complexes.

Species	r_i (M^{-1} s^{-1})
$CuNTA^-$	714
$Cu(NTA)_2^{4-}$	427
$CuNTAOH^{2-}$	1512
$Cu(glycine)_2$	440[a]
$Cu(ethylenediamine)_2^{2+}$	360[b]

[a]Ref. [11]. [b]Ref. [1].

Oakes and Smith [10] have recently studied the $Mn^{2+}–EDTA^{4-}$ complex by NMR relaxation. They stated that the second sphere relaxation originating from the protons of water molecules hydrogen-bonded to the coordinated carboxylate oxygen may be comparable to, or even higher than, the effect of water molecule(s) remaining in the first coordination sphere. The results collected in Table III can also be explained by taking into account this phenomenon.

The molar relaxation coefficient for the $CuNTAH_{-1}^{2-} = CuNTAOH^{2-}$ complex is much higher than could be expected from the effect of the remaining water molecule(s). Its explanation is that a fast, but relaxation-controlled

$$CuNTAO\overset{*}{H} + HOH \rightleftharpoons CuNTAOH + \overset{*}{H}OH$$

proton exchange takes place in the solution. The paramagnetic relaxation time calculated for the coordinated OH proton is about 7×10^{-6} sec, much higher than the relaxation time of the OH protons in the $Cu(OH)_4^{2-}$ hydroxo complex (1.4×10^{-6} s), determined in a separate experiment. This indicates a much weaker Cu–OH interaction in the $CuNTAOH^{2-}$ than in $Cu(OH)_4^{2-}$.

The experimental results and the calculated curves in the mixed ligand equilibrium systems are illustrated on the $CuNTAG^{2-}$ system as an example (Fig. 2).

Because the $Cu(NTA)_2^{4-}$ complex is not formed under the given concentration ratios, the curves were fitted by taking into account the molar relaxation coefficient of the mixed complex, the

$$CuNTA\overset{*}{B} + B \overset{k_2}{\rightleftharpoons} CuNTAB + \overset{*}{B}$$

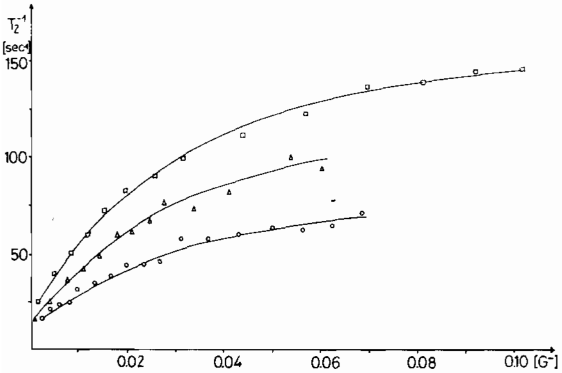

Fig. 2. The reciprocal relaxation time as a function of free glycinate concentration in the CuNTA$^-$–glycine system. Notations: ○–○–○ T_{CuNTA} = 0.020 *M*, $T_{glycine}$ = 0.10 *M*; △–△–△ T_{CuNTA} = 0.030 *M*, $T_{glycine}$ = 0.10 *M*; □–□–□ T_{CuNTA} = 0.040 *M*, $T_{glycine}$ = 0.20 *M*.

exchange rate constant, as well as the paramagnetic relaxation times of the –NH protons of the B ligands, beside the known molar relaxation coefficients of $CuNTA^-$ and $CuNTAOH^{2-}$.

$$T_2^{-1} = T_{20}^{-1} + 714[CuNTA^-] + 1512\,[CuNTAOH] + \\ + r_{CuNTAB}[CuNTAB] + \\ + \frac{Y}{2[H_2O]}\,\frac{k_2[B]}{1 + k_2T_{2B}[B]}\,[CuNTAB]$$

where Y is the number of labile protons in the B ligands. The parameters calculated for r_{CuNTAB}, k_2 and T_{2B} are collected in Table IV, together with the results given for the Cu(glycinate)$_2$ complex earlier [11].

It is seen from Table IV, the T_{2B} of the $-NH_2$ protons of glycine is much higher in the mixed complex than in the parent one, indicating that the glycine is more loosely bound to the central ion in $CuNTAG^{2-}$ than in CuG_2. This result is in agreement with the finding of Hopgood and Angelici [12], namely that the usual geometry around the central copper(II) ion is distorted in this mixed complex. In spite of this, the exchange rate is much slower from the mixed complex, *i.e.* the thermodynamic stabilization mentioned in the introduction is accompanied by increased kinetic stability. This is probably the consequence of the repulsive forces between the $CuNTAG^{2-}$ and the attacking glycinate ion, which are absent in the case of the ligand exchange from the parent complex.

It should be mentioned moreover that the Jahn–Teller inversion of the intermediate $CuNTAG_2^{3-}$ is probably the rate determining step in this case, as for a number of parent complexes [2]. To prove this, however, the equilibrium constant of the $CuNTAG^{2-} + G^- \rightleftharpoons CuNTAG_2^{3-}$ process should be determined. Its determination, however, would demand the use of such a high glycinate concentration that the glycinate might replace the NTA^{3-}, so that the evaluation would be extremely complicated.

TABLE IV. Kinetic Parameters Describing the Relaxation Behaviour of the Copper(II)–NTA^{3-}–B Ligand Mixed Ligand Systems. The appropriate parameters of the CuG_2 system are also given for comparison.

B ligand	r_{CuNTAB} M^{-1} s^{-1}	k_2 M^{-1} s^{-1}	T_{2B} s
Glycine	448	6.8×10^6	3.2×10^{-6}
Ammonia	1450	3.8×10^7	2.3×10^{-6}
Methylamine	530	1.1×10^7	0.8×10^{-6}
Cu(glycine)$_2$	440	7.7×10^7	0.92×10^{-6}

The difference in the k_2 and T_{2B} values for the ammonia and methylamine ligands is in accordance with the increased electron density of the ligands, reflected in the pK values and in the equilibrium constants for the $CuNTA^- + B \rightleftharpoons CuNTAB^-$ processes also.

The increase of the r_{CuNTAB} values in the glycine–methylamine– ammonia order, and especially the high value for the ammonia system is surprising. If the water molecules remaining in the first coordination sphere and/or the second sphere broadening were responsible for this, then $r_{CuNTANH_3^-} \sim 450$ would be expected.

The possible explanation of the deviation is that the effect of the

$$CuNTA^- + NH_3 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} CuNTANH_3^-$$

formation and dissociation process is reflected in the molar relaxation coefficient. Accepting this interpretation, $k_b = (2[H_2O]/3)(r_{CuNTANH_3} - 450) = 3.7 \times 10^4$ s^{-1} dissociation rate constant, *i.e.*, 2.1×10^8 M^{-1} s^{-1} forward rate constant can be calculated for the above process. This result seems to be reasonable, although no directly comparable data are available in the literature. The only possible comparison is the formation rate constant of the $CuNH_3^{2+}$ complex, determined by Diebler and Rosen [2.0×10^8 M^{-1} s^{-1}) [13], as well as by Sokol, Fint and Rorabacher (2.3×10^8 M^{-1} s^{-1}) [14].

A 5.5×10^7 M^{-1} s^{-1} forward rate constant for the $CuNTA^- + CH_3NH_2 \rightleftharpoons CuNTACH_3NH_2$ process can be calculated from the $r_{CuNTACH_3NH_2}$ given in

Table IV, although it is uncertain because the correction is comparable to the measured molar relaxation coefficient.

The big difference in the relaxation behaviour of the $CuNTANH_3^-$ and $CuNTAG^{2-}$ complexes is evidently the consequence of the difference in their formation constant, *i.e.* the much smaller dissociation rate of the $CuNTAG^{2-}$ complex.

The stepwise formation constants for the well known copper(II)–ammonia system, however, are near to or less than the equilibrium constant for the $CuNTANH_3^-$ complex, so that seems to be a reasonable assumption that the proton relaxation studies might give information on the stepwise dissociation and formation rate constants of the different copper(II)–ammonia complexes. The results of these relaxation studies are reported in a following paper [15].

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