254. Cuprous Complexes and Dioxygen. IX[1]). Formation of a Unique Trimeric Species $Cu_3L_2^{3+}$ and Ligand Oxidation (L = *cis, cis*-1,3,5-Cyclohexanetriamine)

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Summary

The complexation of Cu^+ by the potentially tripod-like ligand *cis,cis*-1,3,5-cyclohexanetriamine (chta) has been studied potentiometrically in aqueous acetonitrile (an). The expected tetracoordinated species $Cu(chta)\cdot(an)^+$ was formed only at rather high pH with $\log K(Cu(an)^+ + chta \rightleftharpoons Cu(chta)\cdot(an)^+) = 6.94$. Quite unexpectedly the most stable complex in neutral solution was the trimetric species $Cu_3(chta)_2^{3+}$ with $\log K(3\,Cu^+ + 2\,chta \rightleftharpoons Cu_3(chta)_2^{3+}) = 31.75$. In addition, the ternary complexes $Cu(LH_2)\cdot(an)^{3+}$ and $Cu(LH)\cdot(an)^{2+}$ (L = chta) are formed at low pH.

From model considerations, $Cu_3(chta)_2^{3+}$ must contain two ligand molecules with all amino groups in equatorial position, linked by three linearly coordinated Cu^+-ions. $Cu_3(chta)_2^{3+}$ shows no measurable reactivity towards dioxygen. At pH-values above 9, very rapid O_2-uptake due to $Cu(chta)\cdot(an)^+$ is observed. In this reaction, Cu^+-autoxidation is stoichiometrically coupled to ligand oxidation, followed by a much slower Cu-catalyzed secondary reaction of the primary oxidation product of chta. Hydrogen peroxide and likely also superoxide, are involved in the coupled Cu^+/ligand oxidation.

Introduction. – With simple ligands, especially monodentate amines, the autoxidation of cuprous complexes preferably proceeds *via* a tetracoordinated species $CuL_3O_2^+$, unless a dimeric transition state and two-electron transfer are enforced by steric reasons [1–3]. The structure of $CuL_3O_2^+$, albeit unknown, almost surely is pyramidal with C_{3v}-symmetry for three identical ligands L (*cf.* **I** in *Scheme*, below).

On the other hand, with typical monodentate amino donor ligands such as NH_3 or imidazole, no higher than two-coordinate linear complexes can be detected

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by equilibrium measurements, even at high ligand concentrations or in mixed solvent systems [2] [4] [5]. Distorted tetrahedral coordination of Cu^+ has been verified by X-ray analysis in plastocyanin [6] and is generally believed to be important in cuprous enzymes [7]. We therefore were interested to see, if the general pyramidal structure **I** could be enforced by some tripod-like triamines which show a strong preference for facial coordination in octahedral complexes. Virtually nothing seems to be known about the complexation of Cu^+ to ligands of this type. In view of the general preference of Cu^+ for tetrahedral coordination in the solid state, and in line with an X-ray study of (diethylenetriamine)copper(I) carbonyl [8], the formation of such complexes would seem to be a reasonable possibility, even if monodentate amines form only linear 1:2-complexes with Cu^+ in solution. If cuprous complexes with structure **I** are indeed enforced by tripod-like ligands, they might well be worth of further study, since the fourth position could easily accomodate a great variety of ligands, including CO and O_2 without much sterical change in the overall complex.

Here we report on some quite unexpected results with the tripod-like ligand *cis, cis*-1,3,5-cyclohexanetriamine (chta). Work on a series of other facially coordinating triamines is in progress.

Experimental. – The ligand chta was prepared from a mixture of the 1,3,5-*N,N′,N″*-Triacetyl-1,3,5-cyclohexanetriamine isomers [9] by acid hydrolysis and isolation of the *cis,cis*-product as $Ni(chta)_2(NO_3)_2$ [10]. The complex was converted into the perchlorate with a threefold excess of 30% $HClO_4$-solution. After precipitation with ethanol and recrystallization from aq. ethanol chta · 3 $HClO_4$ · 3 H_2O was characterized by its m.p., 377–378 K, and elemental analysis, $C_6H_{24}Cl_3N_3O_{15}$; found: C 15.0, H 5.0, N 8.7, Cl 21.8%; calc.: C 14.9, H 5.0, N 8.7, Cl 21.9%. Its ^{1}H-NMR. spectrum in D_2O (δ 1.65 (*qa*), δ 2.50 (*d*), δ 3.50 (*t*)) closely corresponds to that reported for chta · 3 HCl · H_2O [11].

Crystalline catalase was a *Merck* product. The source of Cu(I) was $Cu(CH_3CN)_4ClO_4$ [12] in aq. acetonitrile (an). CH_3CN was distilled over K_2CO_3 and over P_2O_5 prior to use. Other analytical-grade reagents were used without further purification.

The complexation of Cu(I) by chta was studied by potentiometric titration with 0.4 M NaOH (*Titrisol, Merck*) under N_2. The majority of the titration curves was obtained in the presence of 2% (*v/v*) CH_3CN-solution: 50 ml samples: $[\text{chta}]_{\text{tot}} = 0.002$ M, $[\text{Cu(I)}]_{\text{tot}} = 0$ M, 0.008 M, 0.0016 M, 0.0019 M, or 0.0022 M; 25 ml samples: $[\text{chta}]_{\text{tot}} = 0.004$ M, $[\text{Cu(I)}]_{\text{tot}} = 0.0016$ M or 0.0032 M.

To check the formation of ternary complexes with CH_3CN as additional ligand some curves were obtained with 1% CH_3CN-solution: 50 ml samples, $[\text{chta}]_{\text{tot}} = 0.002$ M, $[\text{Cu(I)}]_{\text{tot}} = 0$ M, 0.0008 M, or 0.0016 M. Each experiment was done in duplicate. For numerical treatment, the titration curves were combined into two batches for both concentrations of CH_3CN. Details of the automatic titration apparatus and the data acquisition system as well as the program used for numerical treatment are described elsewhere [13].

The kinetics and the stoichiometry of O_2-uptake were studied with an oxygen electrode as described [14]. ^{1}H-NMR. spectra were obtained on a *Varian 360* spectrometer. All equilibrium and kinetics experiments were done at 293 K in twice distilled water with $I = 0.2$ (Na_2SO_4).

Equilibria. – Description of the potentiometric titration curves by a series of 1:1 complexes $CuLH_2^{3+}$, $CuLH^{2+}$, and CuL^+ (L = chta) was completely unsatisfactory. Standard deviations (σ_{ml}) in ml of base consumed were about 0.01 to 0.02 in the numerical treatment of single curves while with our apparatus they should be around 0.001 to 0.003 [13], that is one order of magnitude less, for single curves. Even in the combined treatment of several independent experiments σ_{ml} should be less than 0.005 ml.

Introduction of 1:2-complexes like $Cu(LH_2)_2^{5+}$, $Cu(LH)_2^{3+}$, or CuL_2^+ did not improve the situation and no evidence was obtained for dinuclear species like Cu_2LH^{3+} or Cu_2L^{2+}. Looking for more complicated complexes we found that the data could only be explained after inclusion of $Cu_3L_2^{3+}$ into the model. As a matter of fact, this complex proved to be the most important species at moderate pH-values of about 6–9. The presence of $Cu_3L_2^{3+}$ was further substantiated by the fact that even 125 mol-% Cu(I) per ligand can be kept in solution up to pH 9.1 in the presence of chta whereas any uncomplexed Cu(I) would precipitate around pH 6–7. At high pH, the expected 1:1-complex CuL^+ is formed, while around pH 6 there is evidence for the protonated species $CuLH_2^{3+}$ and $CuLH^{2+}$ as minor components. After inclusion of $Cu_3L_2^{3+}$ into the equilibrium model, completely satisfactory values were obtained for σ_{ml}: 0.0015 and 0.0020 ml for the two batches with addition of 1% CH_3CN and two independent titration curves per batch; 0.0045 and 0.0036 ml for the batches with addition of 2% CH_3CN and six titration curves per batch. The complexation of Cu^+ by chta thus could be explained by the equilibria compiled in *Table 1*.

The effect of including or neglecting $Cu_3L_2^{3+}$ is demonstrated in *Figure 1* where the experimental data of one titration curve are plotted together with calculated curves obtained either with the equilibrium constants from *Table 1* (solid line) or with the 'best' equilibrium constants for 1:1-complexes alone (dotted line).

Since all our titration mixtures contained significant amounts of CH_3CN (1 or 2%, corresponding to 0.19 and 0.38 mol/l, respectively), Cu(I) which was not complexed to chta was mainly present in the form of $Cu(an)^+$ ($\log\beta_1 = 3.28$ [15]), $Cu(an)_2^+$ ($\log\beta_2 = 4.35$ [12]), and $Cu(an)_3^+$ ($\log\beta_3 = 4.39$ [16]). These values were also used in the interpretation of the kinetics experiments (see below). For the calculation of the equilibrium constants, the concentration of the free metal ion, $[Cu^+]$, was taken as the sum of all these species concentrations *(Eqn. 1)*.

$$[Cu^+] = [Cu_{aq}^+] + [Cu(an)^+] + [Cu(an)_2^+] + [Cu(an)_3^+] \qquad (1)$$

Table 1. *Proton association constants of chta and formation constants of Cu(I)/chta-complexes at 293 K and I = 0.2 (Na_2SO_4)*

Equilibrium	$\log K^*$ [a)] 1% an	2% an	$\Delta\log K^*$ (per Cu^+)	No. of an[b)]	$\log K$[c)]
$LH_2^{2+} + H^+ \rightleftharpoons LH_3^{3+}$	7.76[d)]	7.76[d)]	–	–	–
$LH^+ + H^+ \rightleftharpoons LH_2^{2+}$	9.07[d)]	9.04[d)]	–	–	–
$L + H^+ \rightleftharpoons LH^+$	10.50[d)]	10.43[d)]	–	–	–
$LH_2^{2+} + Cu^+ \rightleftharpoons CuLH_2^{3+}$	2.98[e)]	2.79[e)]	0.19	1[f)]	3.60
$LH^+ + Cu^+ \rightleftharpoons CuLH^{2+}$	4.26[e)]	3.89[e)]	0.37	1	4.76
$L + Cu^+ \rightleftharpoons CuL^+$	6.38[e)]	6.07[e)]	0.31	1	6.94
$2\,L + 3\,Cu^+ \rightleftharpoons Cu_3L_2^{3+}$	22.56[e)]	20.39[e)]	0.72	0	31.75

[a)] Equilibrium constants depending on [an] neglecting the formation of $Cu(an)^+$, $Cu(an)_2^+$, and $Cu(an)_3^+$. [b)] Number of an-molecules bound to Cu(I)/chta-complexes (per mol of Cu^+). [c)] an-Independent formation constants, as defined by *Equilibria 2–5*. [d)] Mean from three independent titration curves. [e)] Mean from two independent batches of 2 (1% an-solution) or 6 (2% an-solution) titration curves, *cf. Experimental*. [f)] Uncertain value, species might be mixture of $Cu(LH_2)\cdot(an)^{3+}$ with $Cu(LH_2)\cdot(an)_2^{3+}$.

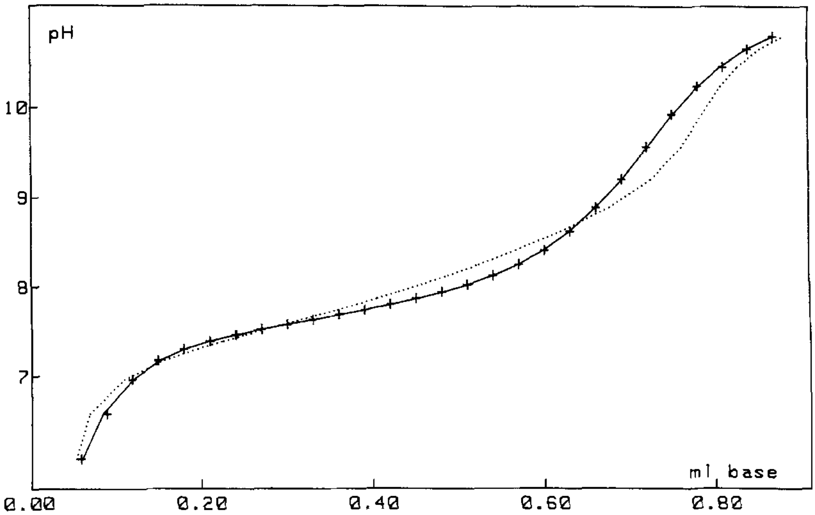


Fig. 1. *Potentiometric titration curve of 0.002* M *chta and 0.0019* M *Cu^+ in 2% aqueous acetonitrile* (+ Experimental points; ——— curve calculated with complete model *(Eqn. 2-5)* and equilibrium constants compiled in *Table 1;* $\sigma_{ml} = 0.0015$; ······· calculated with 'best' set of constants of monomeric species for this individual titration curve: $\sigma_{ml} = 0.022$; CuL^+: $\log K^* = 6.34$; $CuLH^{2+}$: $\log K^* = 4.44$; $CuLH_2^{3+}$: insignificant).

The equilibrium constants thus calculated are dependent on [an], and from the variation of the values with [an] the number of an-molecules bound to the individual chta-complexes can be calculated. It follows from the equilibrium constants of the an-complexes that by going from 1 to 2% an the apparent stability constants of the chta-complexes should decrease by 0.60, 0.30, or 0.00 log units per Cu^+ if 0, 1, or 2 molecules of an per Cu^+ were bound. The results given in *Table 1* clearly indicate that no an is bound to $Cu_3L_2^{3+}$. For all monomeric species the best description is the ternary 1:1:1 complex, *viz.* $Cu(L) \cdot (an)^{3+}$, $Cu(LH) \cdot (an)^{2+}$, and $Cu(LH_2) \cdot (an)^{3+}$. The precision of the results for the last species is not sufficient to allow a decision if $Cu(LH_2) \cdot (an)^+$ is the only relevant species with the twice protonated chta, LH_2, or if in addition a $Cu(LH_2) \cdot (an)_2^{3+}$-complex with two coordinated molecules of an is formed. However, such a complex is *a priori* rather unlikely, since in no Cu(I)/amine/an-system ternary three-coordinate species have been found so far. The complete picture for the Cu(I)/chta-complexes in aq. CH_3CN thus is given by *Equations 2-5.*

$$Cu(an)^+ + LH_2 \rightleftharpoons Cu(LH_2) \cdot (an)^{3+} : \log K_2 = 3.60 \quad (2)$$

$$Cu(an)^+ + LH \rightleftharpoons Cu(LH) \cdot (an)^{2+} : \log K_3 = 4.76 \quad (3)$$

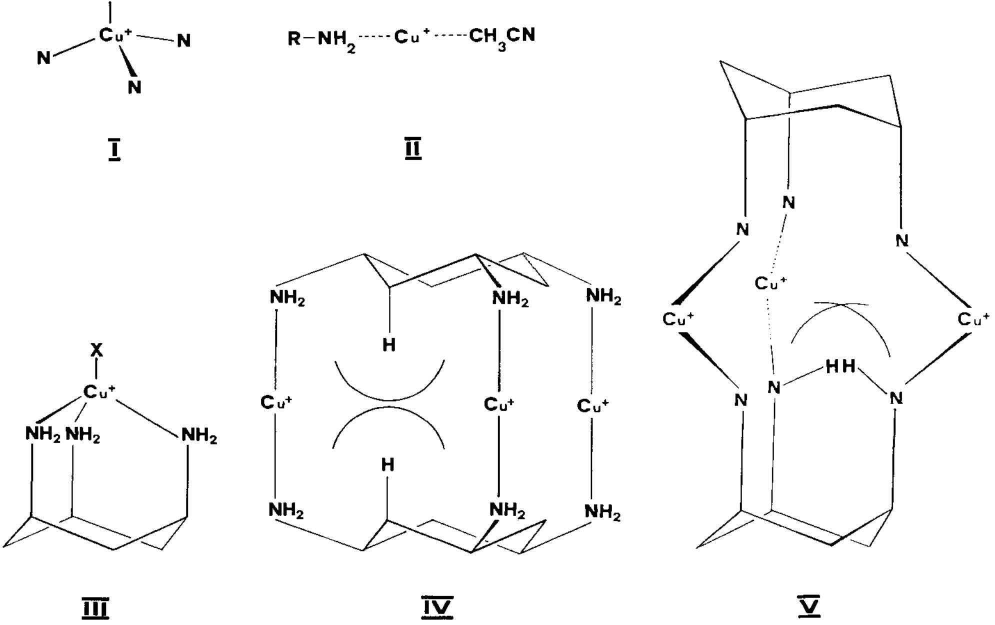
$$Cu(an)^+ + L \rightleftharpoons Cu(L) \cdot (an)^+ : \log K_4 = 6.94 \quad (4)$$

$$3\,Cu^+ + 2\,L \rightleftharpoons Cu_3L_2^{3+} : \log K_5 = 31.75 \quad (5)$$

Since Cu(I)-complexes neither have useful electronic absorption spectra nor an ESR. signal, no direct information is available on the structure of the four chta-complexes. However, inference is possible from the general coordination chemistry of Cu(I) and also from the values of the respective stability constants. $Cu(LH_2) \cdot (an)^{3+}$ is not problematic. A linear two-coordinate species (structure **II**) has to be assumed, corresponding to those obtained with other amines or in ternary Cu(I)/amine/an-systems [1] [2] [4] [17]. The relatively low stability is in line with the overall (3+)-charge of the complex. $Cu(LH) \cdot (an)^{2+}$ in principle could be a chelate complex with axial amino groups. However, steric hindrance between Cu^+ and the uncoordinated amino group would be rather severe, if not prohibitive. Also, the equilibrium constant, $\log K_3 = 4.78$, is completely in line with chta acting as a monodentate ligand and thus a structure **II** corresponding to that of $Cu(LH_2) \cdot (an)^{3+}$ is preferred. $Cu(L) \cdot (an)^+$, $\log K_4 = 6.93$, on the other hand is too stable for a monodentate amino complex. Since chelation is only possible with axial conformation of the amino groups and coordination of only two N-atoms is essentially excluded in this situation, this complex must be described by the structure **III**, that is by the general structure **I**. The conclusions about the structures of the different complexes are further substantiated by the results of the kinetics experiments (see below).

For the trinuclear complex $Cu_3L_2^{3+}$ two structures **IV** and **V** with axial or equatorial amino groups are suggested by inspection of molecular models. Structure **IV** is preferred to **V** for several reasons. First, chta is substantially less stable in the configuration with axial substituents than with equatorial ones. In addition, there would be rather strong interaction of the amino H-atoms in the

Scheme



conformation enforced in **V**. Further, with **V**, one would expect easy coordination of an, but this is definitely not the case. Finally, the most stable geometry of Cu(I) coordinated to two N-donors is the linear one and this is only possible in **IV**. X-ray structures of linear two-coordinate Cu(I)-complexes with N-donors have been described recently for 1,7-bis(2-benzimidazolyl)-2,6-dithiaheptane [18] and *N,N,N',N'*-tetrakis(2-benzimidazolylmethyl)-1,2-ethanediamine [19], the latter complex containing two parallel (N-Cu(I)-N)-moieties. In fact, a tetrameric structure which in many respects closely resembles the one proposed here for $Cu_3(chta)_2^{3+}$ has been found some time ago for (1,3-dimethyltriazeno)copper(I), $[Cu(CH_3NNNCH_3)]_4$ [20].

Thus all the evidence is in favor of the structure **IV** where both the metal ions and the ligands are in their most stable surroundings and no steric hindrance of any significance is suggested by molecular models.

Autoxidation. – In weakly acidic solution, pH 4–6.5, the autoxidation is completely described by the reactivity of the aquo-ion, Cu_{aq}^+. The following parameters were varied: $[chta]=(0.19–1.0)\cdot 10^{-3}$ M, $[Cu(I)]_{tot}=(0.5–5.0)\cdot 10^{-4}$ M, $[O_2]=(0.23–2.75)\cdot 10^{-4}$ M, pH = 3.9–6.5, and [an] = 0.19–0.76 M. The pH was controlled by dilute acetate or phosphate buffers which had no effect in concentrations below 0.01 and 0.003 M, respectively. All experiments could be combined into the single, simple rate law *(Eqn. 6)* with $k_6=(5.7\pm 0.6)\cdot 10^4\,M^{-1}\,s^{-1}$, independent of [chta] and of the pH. This value for k_6 is significantly higher than that obtained

$$-d[O_2]/dt = k_6[Cu_{aq}^+][O_2] \qquad (6)$$

previously in 0.2 M nitrate solution, *viz.* $4.1\cdot 10^4\,M^{-1}\,s^{-1}$ [15] or $(3.5\pm 0.5)\cdot 10^4\,M^{-1}\,s^{-1}$ [16]. This difference, however, only reflects the change in background electrolyte and has nothing to do with the presence of chta. Thus, in the absence of chta, experiments in 0.01 M 1:1 acetic acid/acetate buffer consistently gave $k(Na_2SO_4)/k(KNO_3)=1.4–1.6$.

It follows from the above experiments that the protonated chta-complexes $Cu(LH_2)\cdot(an)^{3+}$ and $Cu(LH)\cdot(an)^{2+}$ do not contribute significantly to the O_2-consumption. This is in line with their suggested structural analogy to the ternary cuprous 1:1:1-complexes with CH_3CN and NH_3 or imidazole, both of which also have no measurable reactivity toward O_2 [2].

In neutral solution, pH 6.5–7.5, the autoxidation becomes dependent on [chta] and on pH. The pH-dependence for [chta] = 0.003 M, $[Cu(I)]_{tot}=5\cdot 10^{-5}$ M, and [an] = 0.38 M is given in *Figure 2*.

The results are rationalized on the basis of the equilibrium constants of the Cu(I)/chta-complexes. Included into *Figure 2* is the 'best' curve obtained on the assumption that $Cu(L)\cdot(an)^+$ is the only reactive species in addition to the uncomplexed metal ion. The bimolecular rate constant for the autoxidation of $Cu(L)\cdot(an)^+$ *(Eqn. 7)* was calculated to $k_7=(1.07\pm 0.12)\cdot 10^4\,M^{-1}\,s^{-1}$. Neither the protonated species $Cu(LH)\cdot(an)^{2+}$ or $Cu(LH_2)\cdot(an)^{3+}$ nor the trimeric $Cu_3L_2^{3+}$ seem to contribute at all to the O_2-consumption.

$$-d[O_2]/dt = k_7[Cu(L)\cdot(an)^+][O_2] \qquad (7)$$

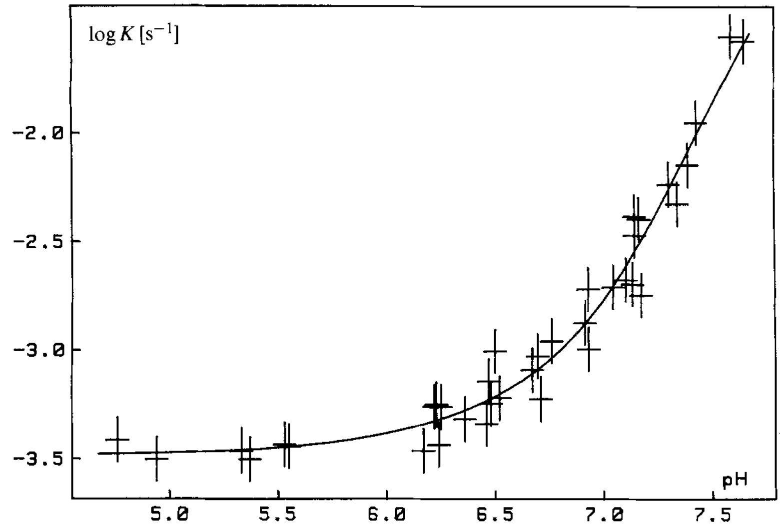


Fig. 2. *pH-Dependence of chta-autoxidation* ($k = -d[O_2]/([O_2] \cdot dt)$; $[chta]_{tot} = 3 \cdot 10^{-3}$ M; [an] = 0.38 M; ------ $[Cu(I)]_{tot} = 5 \cdot 10^{-5}$ M; + experimental points; ——— calculated assuming $Cu(L) \cdot (an)^+$ and Cu^+_{aq} to be the only reactive species)

The numerical treatment of the data given in *Figure 2* still leaves open the number of an-molecules bound to the redox-active complex, since the active species is not necessarily identical with the one observed potentiometrically in the equilibrium measurements. This question is solved by studying the dependence on [an], the results of which are shown in *Figure 3*. Obviously, the results are best explained with $Cu(L) \cdot (an)^+$ as the reactive complex (solid line), the same species as found in the equilibrium measurements.

The weak phosphate buffer used in the measurements for the an-dependence had no effect on the rate of autoxidation. In higher concentrations, phosphate buffer leads to an increase in the rate of autoxidation. For pH = 6.5, [chta] $= 2.5 \cdot 10^{-4}$ M, [an] = 0.38 M, and $[Cu(I)]_{tot} = 10^{-4}$ M, the kinetics could be described by *Equation 8* with $k_8 = 65 \pm 6$ M^{-1} when the total phosphate concentration was

$$-d[O_2]/dt = k_{obs}[Cu(chta) \cdot (an)^+](1 + k_8[phosphate]_{tot}) \qquad (8)$$

varied from $1.5 \cdot 10^{-3}$ M to $3 \cdot 10^{-2}$ M. Under the same conditions, but in the absence of chta, phosphate buffer has no effect on the rate of autoxidation. This acceleration by buffer bases is by no means general, however. On the contrary, *e.g.* diethylbarbiturate strongly inhibits the autoxidation and the effect of buffers was not studied further in detail.

In basic solution, pH 9–11, some unexpected effects were observed. The ratio of O_2 consumed per Cu(I) initially present, $\Delta[O_2]/[Cu(I)]_{tot}$, increases significantly above the values 1:4 or 1:2 which are found when O_2 is reduced by Cu(I) either to H_2O or to H_2O_2. In addition, the reaction clearly becomes biphasic. The first part is completed within 1–2 min and the kinetics are too rapid to be followed by

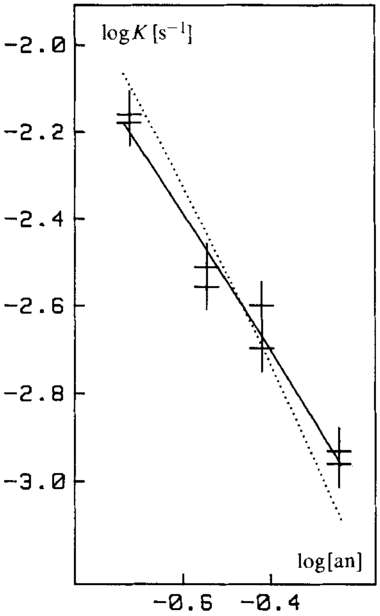


Fig. 3. *an-Dependence of chta-autoxidation* ($k = -d[O_2]/([O_2] \cdot dt)$; pH = 6.68; $[chta]_{tot} = 2 \cdot 10^{-3}$ M; $[Cu(I)]_{tot} = 10^{-4}$ M; + experimental points; ——— calculated assuming $Cu(L) \cdot (an)^+$ to be the reactive species, · · · · · assuming CuL^+ to be reactive)

the O_2-electrode. The subsequent secondary process needs several hours for completion. Although the amount of O_2 consumed clearly exceeds the amount attributable to Cu(I)-oxidation, it is by no means equivalent to the amount of chta present. The redox stoichiometry depends on several parameters, such as the metal-to-ligand ratio, pH, the presence of additional Cu^{2+}, and others. In the corresponding experiments we have concentrated on the stoichiometry of the fast, first reaction, which was calculated from the amount of O_2 consumed after 2 min. Occasionally, the reaction was allowed to go to completion and the stoichiometry of the total consumption of O_2 was obtained also. A choice of typical results with $[chta] = 10^{-3}$ M are summarized in *Table 2*.

As given in *Table 2*, the ratio $\Delta[O_2]/[Cu(I)]_{tot}$ decreases with increasing Cu-concentration (A–F). The upper limit of the fast reaction closely corresponds to a 1:1 molar stoichiometry which is successively reduced to 1:2 at high $[Cu(I)]_{tot}$. The amount of O_2 consumed in the slow secondary reaction parallels this trend. Also, $\Delta[O_2]/[Cu(I)]_{tot}$ is pH-dependent (G–I), decreasing with increasing pH. Finally, the ratio is lowered by the addition of Cu^{2+} (J–L). Cu^{2+} added at the end of the primary reaction increases the rate of the secondary process.

The only explanation for the above observations is the oxidation of chta coupled to the autoxidation of Cu(I). Since this reaction is limited to dilute solutions and high (ligand : copper)-ratios, isolation of the small amounts of oxidation product will be difficult and first attempts have not been successful.

Table 2. *Stoichiometry of O_2 consumed per Cu(I) initially present at high pH and for [chta] = 10^{-3} M*

Exp.	$[Cu(I)]_{tot}$ (mM)	$[O_2]_{tot}$ (mM)	pH	$\Delta[O_2]/[Cu(I)]_{tot}$		Additional reagent
				fast[a])	total	
A	0.024	0.25	10.47	1.03 ± 0.07[b])	2.92	–
B	0.048	0.25	10.47	0.93	n.s.[c])	–
C	0.072	0.25	10.47	0.79	n.s.	–
D	0.096	0.25	10.47	0.75 ± 0.03[b])	1.52	–
E	0.144	0.25	10.47	0.65 ± 0.04[b])	0.92	–
F	0.240	0.25	10.47	0.60	n.s.	–
G	0.200	1.25	9.13	1.05	n.s.	–
H	0.200	1.25	10.23	0.88	n.s.	–
I	0.200	1.25	11.34	0.72	n.s.	–
J	0.200	1.25	9.15	1.03	n.s.	–
K	0.200	1.25	9.15	0.81	n.s.	Cu^{2+} 0.20 mM[d])
L	0.200	1.25	9.15	0.59	n.s.	Cu^{2+} 0.40 mM[d])
M	0.048	0.25	10.50	0.80	0.80	edta 0.096 mM[e])
N	0.100	1.25	10.47	0.60	0.90	$S_2O_4^{2-}$ 0.05 mM[f])
O	0.024	0.06	10.47	0.62	0.62	catalase 4 μg/ml[d])
P	0.024	0.06	10.47	0.60	0.60	catalase 6 μg/ml[d])
Q	0.144	0.25	10.47	0.68	0.70	catalase 4 μg/ml[d])
R	0.024	0.06	10.47	1.08	1.08	catalase 4 μg/ml[e])

[a]) Amount of O_2 consumed after 2 min. [b]) Mean and standard deviation from four experiments. [c]) n.s.: Secondary reaction present, but not studied to end. [d]) Added before addition of Cu(I). [e]) Added at the end of the initial fast reaction. [f]) Added after 25 min. Reaction stops completely after very rapid decrease in $[O_2]$.

A few additional reagents were used for further characterization of the reaction. edta added after the fast reaction completely blocks any further uptake of O_2 (M). Stoichiometric amounts of dithionite were added some time after completion of the primary reaction in the hope of regenerating Cu^+ from Cu^{2+}. However, after very rapid consumption of some O_2, $S_2O_4^{2-}$ also completely blocks the secondary reaction, apparently without regeneration of Cu^+ (N). Catalase (0.004 or 0.006 mg/ml) was added from the beginning (O–Q) or at the end of the fast reaction (R). Several effects were observed: the slow secondary reaction is efficiently blocked by catalase in both cases (O, P, R). At low $[Cu(I)]_{tot}$, $\Delta[O_2]/[Cu(I)]_{tot}$ is reduced from a 1:1-stoichiometry to roughly 1:2 by adding catalase from the beginning (compare O and P with A)). At high $[Cu(I)]_{tot}$ the effect of catalase becomes marginal as far as the fast reaction is concerned (compare Q with E). In no case, a 1:4-stoichiometry for $\Delta[O_2]/[Cu(I)]_{tot}$ was found and never any increase in $[O_2]$ could be observed, when catalase was added at any stage of the reaction.

The effect of the additional reagents $S_2O_4^{2-}$, edta, Cu^{2+}, and catalase, while still leaving some basic questions open, must be interpreted as follows: in the fast, primary reaction, the autoxidation of Cu(I) is coupled to oxidation of chta. The 1:1 $\Delta[O_2]/[Cu(I)]_{tot}$ stoichiometry observed at low $[Cu(I)]_{tot}$ is most easily explained by assuming that O_2^- (free or complexed to Cu) is the reactive species attacking the organic ligand. This is supported by the fact that a 1:4-stoichiometry is not observed, even if catalase was present from the beginning. Thus attack of chta should occur before O_2 is reduced to H_2O_2. No free H_2O_2 is present at the end of the fast reaction, but it seems to be a reactive intermediate in this step. The slow secondary step is a Cu^{2+}-catalyzed reaction of the primary oxidation product of chta with O_2. H_2O_2 also plays a significant role in this reaction which is inhibited by catalase, edta, and $S_2O_4^{2-}$. The latter reagent most likely reduces the organic intermediate to an unreactive species, perhaps even back to chta. The chemical nature of the intermediate as well as the end product is unknown at present.

Originally, chta was selected as one of several tripod-like ligands for the study of equilibria and redox activity of Cu(I) with facially coordinating triamines. Unexpected results have been obtained for both equilibria and autoxidation with the Cu(I)/chta system, suggesting separate discussion.

The formation of the trimeric $Cu_3L_2^{3+}$ may appear somewhat less surprising because in this species (*cf.* **IV** in the *Scheme*) both the ligand (conformation with equatorial substituents) and the Cu^+-ion (linear coordination of two amino donors) are in their favorite state. Also, it has repeatedly been observed that these linear complexes show only little reactivity toward O_2.

Equally in line with previous studies is the observation that 1:1:1 ternary Cu(I)/chta/an-complexes are unreactive toward O_2 as long as the ligand is binding monodentately [2], suggesting structure **II** *(cf. Scheme)* not only for $Cu(LH_2) \cdot (an)^{3+}$ but also for $Cu(LH) \cdot (an)^{2+}$. On the other hand, the autoxidation of tetracoordinate Cu(I)-complexes, although not studied in many cases so far, can be quite rapid [21] [22] supporting the result obtained for $Cu(L) \cdot (an)^{+}$.

With the exception of easily dehydrogenated species such as aromatic amines or catechols, the autoxidation of organic, especially saturated aliphatic, substrates coupled to the autoxidation of Cu(I) has been less common so far in aq. solution. Quite obviously, highly reactive intermediates, attacking the organic substrate are formed during Cu(I)-autoxidation in the Cu(I)/chta-system. This phenomenon is, however very well-known in organic solvents as well as in enzymatic systems [23–25]. Because of the open questions in the Cu(I)/chta-system, direct analogies should not be taken too far. It also remains to be investigated if this system is unique in such an autoxidation of aliphatic amines or if similar reactions can also be found with related ligands at high pH.

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