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154. Cuprous Complexes and Dioxygen, VII[1]). Competition between One- and Two-Electron Reduction of O_2 in the Autoxidation of $Cu(1\text{-Methyl-2-hydroxymethyl-imidazole})_2^+$

by **Andreas D. Zuberbühler**

Institut für Anorganische Chemie, Spitalstrasse 51, CH-4056 Basel (Switzerland)

(22. X. 75)

Summary. The complexation of 1-methyl-2-hydroxymethyl-imidazole (L) with Cu(I) and Cu(II) has been studied in aqueous acetonitrile (AN). Cu(I) forms three complexes, $Cu(AN)L^+$, CuL_2^+, and $Cu(AN)H_{-1}L$, with stability constants $\log K(Cu(AN)^+ + L \rightleftharpoons Cu(AN)L^+) = 4.60 \pm 0.02$, $\log\beta_2 = 11.31 \pm 0.04$, and $\log K(Cu(AN)H_{-1}L + H^+ \rightleftharpoons Cu(AN)L^+) = 10.43 \pm 0.08$ in 0.15 M AN. The main species for Cu(II) are CuL^{2+}, $CuH_{-1}L^+$, $CuH_{-1}L_2^+$, and $CuH_{-2}L_2$.

The autoxidation of CuL_2^+ was followed with an oxygen sensor and spectrophotometrically. Competition between the formation of superoxide in a one-electron reduction of O_2 and a path leading to H_2O_2 *via* binuclear $(CuL_2)_2O_2^{2+}$ was inferred from the rate law

$$-d[O_2]/dt = [CuL_2^+]^2[O_2]\left(\frac{k_a}{1+k_b[CuL^+]} + \frac{k_c[L]+k_d+(k_f/[L]+k_g+k_h[L])/[H^+]}{[CuL_2^+]+k_e[Cu(II)]_{tot}}\right)$$

with $k_a = (2.31 \pm 0.12)\cdot 10^4\,M^{-2}s^{-1}$, $k_b = (1.0 \pm 0.2)\cdot 10^3\,M^{-1}$, $k_c = (2.85 \pm 0.07)\cdot 10^2\,M^{-2}s^{-1}$, $k_d = 3.89 \pm 0.14\,M^{-1}s^{-1}$, $k_e = 0.112 \pm 0.004$, $k_f = (2.06 \pm 0.24)\cdot 10^{-10}\,M\,s^{-1}$, $k_g = (1.35 \pm 0.07)\cdot 10^{-7}\,s^{-1}$, and $k_h = (6.8 \pm 1.4)\cdot 10^{-7}\,M^{-1}\,s^{-1}$.

The autoxidation of Cu(I) has been established to be an integral part of the reaction mechanism of several biological systems [2], including the copper-catalysed autoxidation of hemoglobin [3]. Low redox potential and easy formation of a 'cupric-like' tetracoordinate transitory dioxygen adduct have been inferred as prerequisites for rapid reaction [4] [5]. In several cases H_2O_2 was the metastable product of dioxygen reduction. Altough it has been uncertain whether this is achieved in aqueous solutions by one-electron steps with superoxide as an intermediate or *via* binuclear $Cu_2L_xO_2^{2+}$, in the organic solvents DMSO [1], CH_3COOH [6], and CH_3NO_2 [7] the latter mechanism has been found. *Pecht & Anbar* [8] postulated a dimeric transition

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[1]) Part VI, see [1].

state for the autoxidation of $Cu(dipy)_2^+$, whereas the kinetic data for several systems in H_2O are in favour of two consecutive one-electron steps [5] [9] [10].

The present study with 1-methyl-2-hydroxymethyl-imidazole (L) shows that both paths may be of comparable importance even for the same complex.

Experimental part

Materials. 1-Methyl-2-hydroxymethyl-imidazole [11] was purified by vacuum distillation (b.p. 103°/0.015 Torr) and crystallization from $CHCl_3$: m.p. 117° (lit.: 116° [11], 114° [12]). Prior conversion to the picrate [11] does not improve the quality of the product. Solutions of cuprous perchlorate [13] or *p*-toluenesulfonate [14] in CH_3CN were used as sources of Cu(I) and the copper content was determined spectrophotometrically using $\varepsilon_{600} = 53.5$ for the complex $Cu(NH_3)_4^{2+}$ (0.2 M NH_3/0.2 M NH_4Cl, 10% AN). CH_3CN was purified by fractionation from K_2CO_3 and P_2O_5. Twice distilled water was used throughout. Other reagents: Quality *p.a.*, used without further purification. Temperature: 20° ± 0.2°. Ionic strength: 0.2 (Na_2SO_4).

Measurements and equipment. Potentiometric titration curves were obtained under 99.99% N_2 with a Compensator E 388 (*Metrohm*) according to the criteria described in [15]. A small excess of H_2SO_4 was added to the samples, the solutions were then deaerated, the metal ion added in form of an air-free concentrated stock solution in CH_3CN by a micrometer syringe (Cu(I) only), and titrated with NaOH (Titrisol). Equilibrium constants were calculated from the individual titration curves by least squares fitting of the degree of neutralization α on a PDP 11 digital computer [15] [16]. Conditions: a) $[AN] = 0.149$, $[L]_{tot} = 3 \cdot 10^{-3}$, $[Cu(I)]_{tot} = 0$, $4.5 \cdot 10^{-4}$, or $8.8 \cdot 10^{-4}$; b) $[AN] = 0.149$, $[L]_{tot} = 6 \cdot 10^{-3}$, $[Cu(I)]_{tot} = 0$, $9.84 \cdot 10^{-4}$, $1.34 \cdot 10^{-3}$, $1.95 \cdot 10^{-3}$, or $2.51 \cdot 10^{-3}$; c) $[AN] = 0.375$, $[L]_{tot} = 4.9 \cdot 10^{-3}$, $[Cu(I)]_{tot} = 0$, $8.78 \cdot 10^{-4}$, or $1.76 \cdot 10^{-3}$; d) $[AN] = 0.736$, $[L]_{tot} = 9.62 \cdot 10^{-3}$, $[Cu(I)]_{tot} = 0$, $1.72 \cdot 10^{-3}$, or $3.45 \cdot 10^{-3}$; e) $[AN] = 0.095$, $[L]_{tot} = 3.04 \cdot 10^{-3}$, $[CuSO_4]_{tot} = 0$, $2.95 \cdot 10^{-4}$, or $5.90 \cdot 10^{-4}$; f) $[AN] = 0.187$, $[L]_{tot} = 1.48 \cdot 10^{-2}$, $[CuSO_4]_{tot} = 0$, $1.2 \cdot 10^{-3}$, or $2.4 \cdot 10^{-3}$.

The kinetics and the redox stoichiometry of the autoxidation were followed amperometrically with an oxygen sensor coupled to a high-impedance millivolt recorder [1]. The more rapid reactions at high pH were run on a *Varian* Techtron 635 equipped with manual stoppedflow equipment and a high-speed *Honeywell* E 196 recorder which allowed the measurement of reaction times down to 3s ($\lambda = 280$ nm). Usually no simple order reactions were observed and individual kinetic runs were evaluated by the method of initial rates. The kinetic parameters, as well as an estimate of their standard errors, were calculated with a program using the least squares fitting procedure suggested by *Marquardt* [17]. These calculations were done on a *Hewlett Packard* HP 9830 with expanded memory and a 9862 calculator plotter for graphical output. Since the method of initial rates yields a more or less constant relative error, the logarithms of the observed rate constants k_{obs} were given equal weights in the calculations. Those parameters which yielded a minimal value for the variance σ^2 (1) of log k were considered the 'best' estimates.

$$\sigma^2 = \sum_{i=1}^{I} \frac{(\log k_{obs} - \log k_{calc})^2}{I - n} \qquad (1)$$

(I: Number of data points, n: number of parameters)

Results. – *Equilibria.* Some of the titration curves are shown in Fig. 1 and 2. In aqueous acetonitrile, Cu(I) and 1-methyl-2-hydroxymethyl-imidazole (L) form a 1:1 complex, $Cu(AN)L^+$, and a 1:2 complex CuL_2^+. Above pH 10, a ligand-dependent deprotonation occurs and the formation of a precipitate is eventually observed. Deprotonation of the ligand is the predominant feature, when Cu^{2+} is the central ion. Two extra protons per metal ion are titrated near pH 7 (*cf.* Fig. 2). CuL^{2+}, $CuH_{-1}L^+$, $CuH_{-1}L_2^+$, and $CuH_{-2}L_2$ are the main complexes in solution, but the available data strongly indicate that the system may be rather complicated, with CuL_2^{2+}, CuL_3^{2+} and/or polymers as additional species. The equilibria needed to explain the experimental data and the values of the corresponding stability constants are compiled in Tab. 1 using $10^{3.28}$ [18], $10^{4.35}$ [13], and $10^{4.39}$ [10] for the overall stability constants of $Cu(AN)^+$, $Cu(AN)_2^+$, and $Cu(AN)_3^+$, respectively.

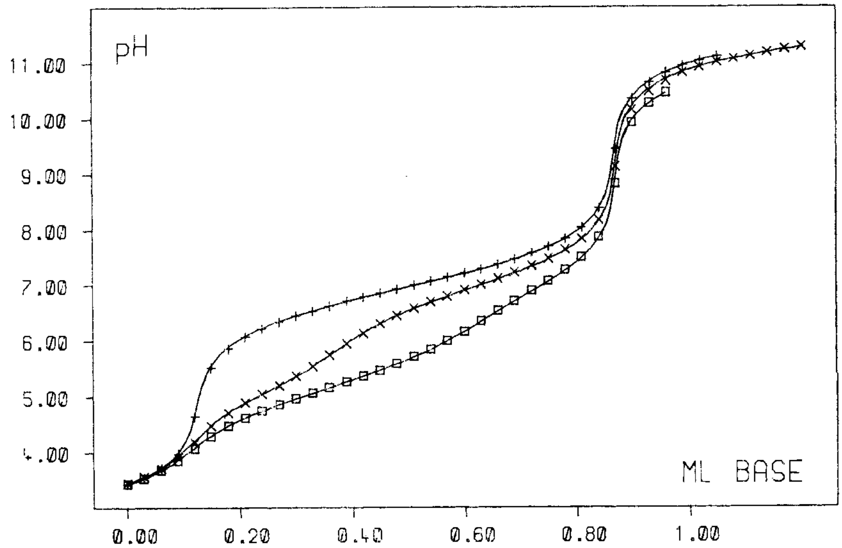

Fig. 1. *Potentiometric titration curves of 1-methyl-2-hydroxymethyl-imidazole and Cu(I).* [NaOH] = 0.4; [AN] = 0.149; $[L]_{tot} = 6 \cdot 10^{-3}$; $[H_2SO_4]_{tot} = 3.5 \cdot 10^{-3}$; + no Cu(I), × $[Cu(I)]_{tot} = 9.84 \cdot 10^{-4}$, □ $[Cu(I)]_{tot} = 1.95 \cdot 10^{-3}$; —— calculated

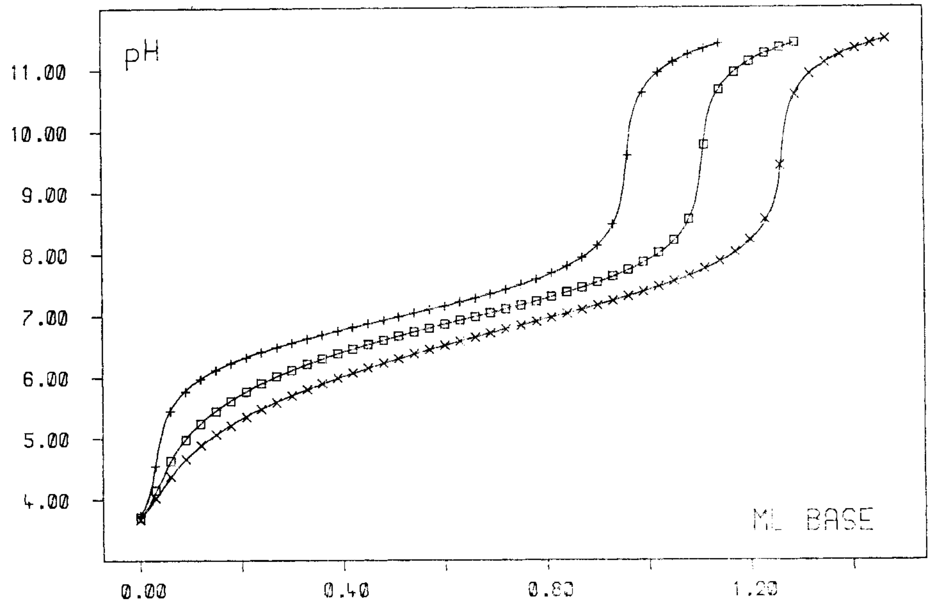

Fig. 2. *Potentiometric titration curves of 1-methyl-2-hydroxymethyl-imidazole and Cu(II).* [NaOH] = 0.4; [AN] = 0.148; $[L]_{tot} = 1.48 \cdot 10^{-2}$; $[H_2SO_4]_{tot} = 0.75 \cdot 10^{-2}$; + no Cu(II), □ $[Cu(II)]_{tot} = 1.2 \cdot 10^{-3}$, × $[Cu(II)]_{tot} = 2.4 \cdot 10^{-3}$; —— calculated

Table 1. *Equilibrium constants and their standard errors*

Reaction	[AN]	log K a)	number of runs n
$L + H^+ \rightleftharpoons LH^+$	b)	6.95 ± 0.02	9
$Cu(AN)^+ + L \rightleftharpoons Cu(AN)L^+$	0.149	4.60 ± 0.02 c)	6
	0.375	4.56 ± 0.01 c)	5
	0.736	4.53 ± 0.02 c)	3
$Cu^+ + 2L \rightleftharpoons CuL_2^+$	0.149	11.31 ± 0.04 c)	6
	0.375	11.09 ± 0.01 c)	5
	0.736	11.09 ± 0.01 c)	3
$Cu(AN)H_{-1}L + H^+ \rightleftharpoons Cu(AN)L^+$	0.149	10.43 ± 0.08 c)	5
	0.375	10.38 ± 0.02 c)	5
	0.736	10.31 ± 0.07 c)	3
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	d)	3.91 ± 0.04	5
$Cu^{2+} + L \rightleftharpoons CuH_{-1}L^+ + H^+$	d)	-2.35 ± 0.04	5
$Cu^{2+} + 2L \rightleftharpoons CuH_{-1}L_2^+ + H^+$	d)	0.90 ± 0.16	5
$Cu^{2+} + 2L \rightleftharpoons CuH_{-2}L_2 + 2H^+$	d)	-6.60 ± 0.08	5

a) Unweighted mean and standard error obtained from n individual titration curves.
b) Varied from 0.149–0.736 M. No influence of [AN] observed.
c) Using the values given in [18] for the stability of the binary complexes with AN.
d) 0.095 M or 0.148 M. No influence of [AN] observed.

Autoxidation. The ratio of total dioxygen consumed to Cu(I) initially present was 0.43 ± 0.03 (9 runs under different conditions), indicating that O_2 is largely reduced to H_2O_2. Thus about 2 mol of Cu(II) are formed per mol of O_2 consumed and we assume that at the beginning of the reaction the stoichiometry is exactly 2:1. All kinetic experiments were performed under conditions such that CuL_2^+ was the only cuprous complex present in appreciable concentrations. The influence on the rate of autoxidation was studied for the parameters $[CuL_2^+]$, $[O_2]$, [L], [Cu(II)], pH, and [AN]. Unless otherwise stated $[O_2]_{tot}$ was between $5 \cdot 10^{-5}$ and $7 \cdot 10^{-5}$, $[AN] = 0.04$, and pH $= 6.95 \pm 0.02$ (1:1 buffer of L and LH^+). Pseudo secondorder rate constants k_{obs} were obtained from initial rates of dioxygen consumption or formation of cupric complexes (2). The correlation of amperometric and spectrophotometric

$$k_{obs} = -d[O_2]_{t=0}/([O_2]\,[CuL_2^+] \cdot dt)_{t=0} = +d[Cu(II)]_{t=0}/(2[O_2]\,[CuL_2^+] \cdot dt)_{t=0} \qquad (2)$$

measurements is based on the redox stoichiometry mentioned above.

The rate law for the autoxidation of CuL_2^+ is more complicated than that described previously for other Cu(I)-imidazole complexes [4] [5]. In fact, nonlinear relationships were found between the rate of dioxygen consumption and $[CuL_2^+]$, [L], [Cu(II)], and pH. In addition, the effect caused by variation of one of the parameters greatly depended on the value of the others. Thus it was not possible to deduce the form of the rate law by simple inspection of the experimental results. Instead, numerical treatment of the whole set of data was necessary to distinguish between several plausible possibilities and to obtain the final set of parameters. A total of 173 data points, grouped into 15 series (A–P, see below) within which only one of the parameters was varied, was used for the final calculations. Log k_{obs} and calculated curves are shown in Fig. 3–6. The height of all data points corresponds to 2σ (1), which is 0.06 and 0.13 log units for the results of the amperometric and spectrophotometric experiments, respectively.

In Fig. 3 log k_{obs} is plotted against log $[CuL_2^+]$ for various conditions. At pH 9.39 (curve A), and at pH 6.95 with [L] = 0.05 (curve B), k_{obs} is essentially independent of $[CuL_2^+]$, the rate of autoxidation being directly proportional to $[CuL_2^+]$. When a more dilute 1:1 buffer of the ligand is used ([L] = 0.005, curve C), the slope of the best straight line is 0.26 ± 0.01. In the presence of $4 \cdot 10^{-3}$ M Cu(II) (curve D) the rate of autoxidation is proportional to $[CuL_2^+]^2$ for $[CuL_2^+] < 10^{-4}$ M, and the relationship changes towards direct proportionality at higher concentrations.

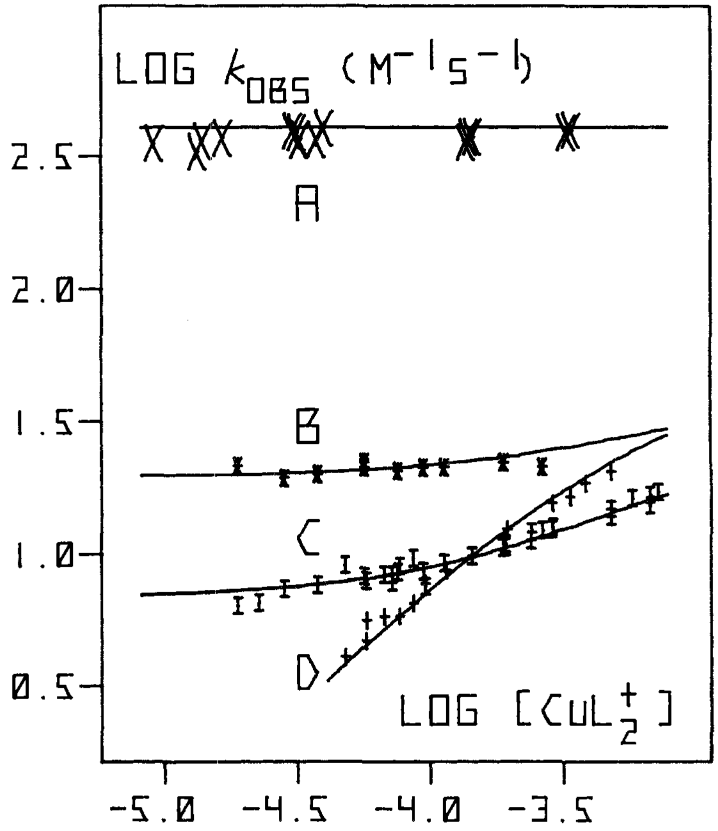

Fig. 3. *Dependence of autoxidation rate on* $[CuL_2^+]$. A: [L] = 0.02, pH = 9.39, $[O_2] = 1.25 \cdot 10^{-4}$; B,C,D: pH = 6.95, $[O_2] = (0.5–0.7) \cdot 10^{-4}$; B: [L] = 0.05; C: [L] = 0.005; D: [L] = 0.08, $[Cu(II)]_{tot} = 0.004$; —— calculated with (3)

In Fig. 4, the effect of varying [L], the concentration of uncomplexed deprotonated ligand, is shown. Under all conditions the rate of autoxidation is enhanced with increasing [L]; however this is less pronounced at high (curves E, F) than at low pH (curves G, H, I). On the other hand, above pH 8 the term which is inversely proportional to [L] becomes increasingly important (left parts in E and F), whereas this is hardly noticeable in neutral solution (G, H, I).

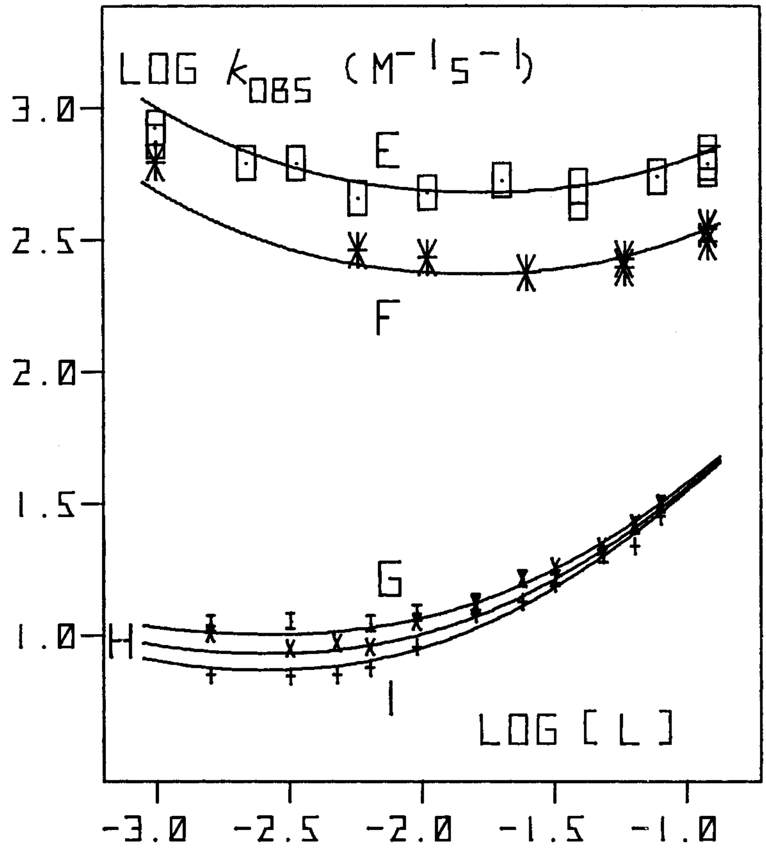

Fig. 4. *Dependence of autoxidation rate on* [L]. E: [CuL_2^+] = 1.2 · 10^{-4}, pH = 9.47, [O_2] = 1.25 · 10^{-4}; F: [CuL_2^+] = 1.41 · 10^{-4}, pH = 9.15, [O_2] = 1.25 · 10^{-4}; G, H, I: pH = 6.95, [O_2] = (0.5–0.7) · 10^{-4}; G: [CuL_2^+] = 1.94 · 10^{-4}; H: [CuL_2^+] = 9.94 · 10^{-5}; I: [CuL_2^+] = 3.54 · 10^{-5}; ——calculated with (3)

Fig. 5 shows the influence of added cupric complex. Inhibition is observed when Cu(II) is present in a tenfold excess over Cu(I). For [L] = 0.01 (curve M) the inhibition clearly reaches a limit, when $[Cu(II)]_{tot}$ exceeds 0.01 M. At higher [L] (curves K and L), the approach to maximum inhibition cannot be concluded directly from the experimental data.

Finally, in Fig. 6, log k_{obs} is plotted against pH for $[L]_{tot} = 0.082$ (curve N). The rate increases linearly with $1/[H^+]$ between pH 8.5 and 9.5, it reaches a lower limit in neutral solution. Instrumental limitations prevented studies at higher

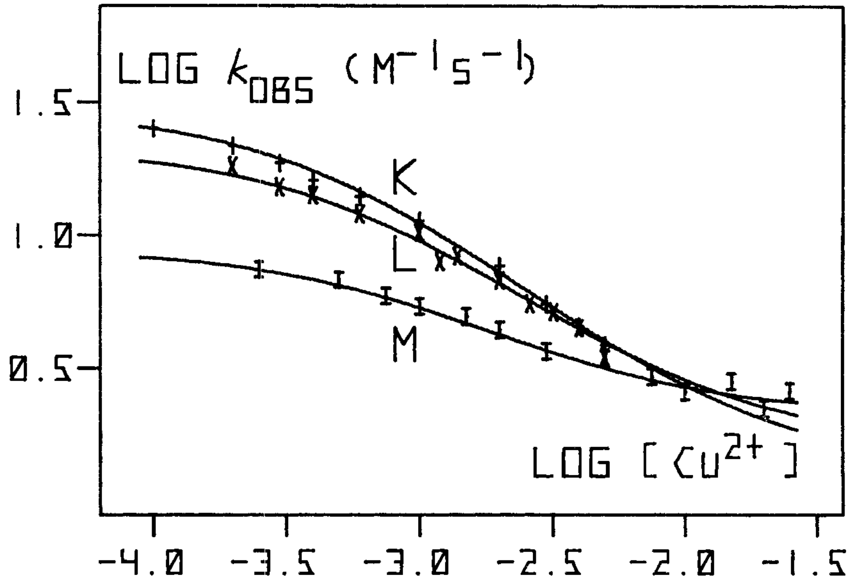

Fig. 5. *Dependence of autoxidation rate on [Cu(II)].* pH = 6.95; [O$_2$] = (0.5–0.7) · 10^{-4}; K: [CuL$_2^+$] = 5.96 · 10^{-5}, [L] = 0.08; L: [CuL$_2^+$] = 7.55 · 10^{-5}, [L] = 0.05; M: [CuL$_2^+$] = 1.01 · 10^{-4}, [L] = 0.01; —— calculated with (3)

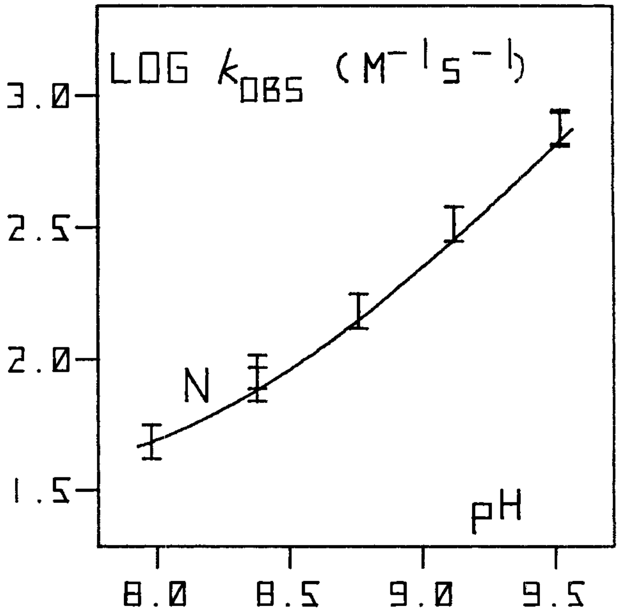

Fig. 6. *Dependence of autoxidation rate on pH.* N: [CuL$_2^+$] = 1.45 · 10^{-4}, [L]$_{tot}$ = 0.082, [O$_2$] = 1.25 · 10^{-4}; —— calculated with (3)

alkalinities. Two additional series (O: $[CuL_2^+] = 1.41 \cdot 10^{-4}$, $[L]_{tot} = 0.032$, $[O_2] = 1.25 \cdot 10^{-4}$, pH = 7.80–9.58; P: $[CuL_2^+] = 1.45 \cdot 10^{-4}$, $[L]_{tot} = 0.002$, $[O_2] = 1.25 \cdot 10^{-4}$, pH = 7.38–9.59) gave essentially the same picture as curve N in Fig. 6, with allowance for the different influence of [L] on the high and low pH terms, respectively.

Of the several rate laws obtained from different plausible reaction schemes two yielded practically identical variances σ^2, as defined by (1). The one which was used to calculate the solid lines in Fig. 3–6 is given by (3), with $k_a = (2.31 \pm 0.12) \cdot 10^{-4}\ \text{M}^{-2}\text{s}^{-1}$, $k_b = (1.0 \pm 0.2) \cdot 10^3\ \text{M}^{-1}$, $k_c = (2.85 \pm 0.07) \cdot 10^2\ \text{M}^{-2}\text{s}^{-1}$, $k_d = 3.89 \pm 0.14\ \text{M}^{-1}\text{s}^{-1}$, $k_e = 0.112 \pm 0.004$, $k_f = (2.06 \pm 0.24) \cdot 10^{-10}\ \text{M s}^{-1}$, $k_g = (1.35 \pm 0.07) \cdot 10^{-7}\ \text{s}^{-1}$, and $k_h = (6.8 \pm 1.4) \cdot 10^{-7}\ \text{M}^{-1}\text{s}^{-1}$.

$$-d[O_2]/dt = 1/2\, d[Cu(II)]/dt = \qquad (3)^{2)}$$

$$[CuL_2^+]^2[O_2] \left(\frac{k_a}{1 + k_b[CuL_2^+]} + \frac{k_c[L] + k_d + 1/[H^+]\,(k_f/[L] + k_g + k_h[L])}{[CuL_2^+] + k_e[Cu(II)]_{tot}} \right)$$

The overall standard error of log k_{obs} was 0.030 log units or 7% in k_{obs} for the 9 series run at pH 6.95 with the oxygen sensor and 0.065 log units or 16% in k_{obs} for the spectrophotometric measurements. Since the overlap between the two kinds of experiments was small, the two sets were treated separately.

The uncertainties of the parameters are indicated by their standard errors as obtained from the *Newton-Gauss* treatment of the data during the final iteration of the fitting process [17]. Of the parameters k_a–k_h in (3), k_h, describing the enhancement of the autoxidation rate by uncomplexed ligand at high pH, is the least well defined. Although its value differs from zero by almost 5 times its standard error, application of the F-test to the overall variance in log k (1) with and without this constant showed significance at the 90% level only. All other parameters are highly significant based on the F-test.

k_{obs} proved to be independent of $[O_2]$, [AN], and $[H_3BO_3]$ (used as buffer for the measurements at high pH) under the conditions studied. The corresponding series Q–U are not shown in the figures and were not used for calculation of the constants, since this would have put undue weight on these special experimental conditions. Instead, arithmetic means and standard errors for log k were obtained and compared with the values calculated from (3). The results are compiled in Tab. 2.

The most simple sequence of elementary steps sufficient to explain the pH-independent part of the rate law (3) is given by (4)–(9). Cu(II) is used to indicate the

Table 2. *Observed and calculated values for pseudo second-order rate constants obtained by variation of $[O_2]$, $[AN]$, or $[H_3BO_3]$*

Curve	Parameter varied	$[CuL_2^+]$	[L]	pH	log k_{obs}	log k_{calc}
Q	$[O_2]$: $(0.25–2.5) \cdot 10^{-4}$	$1.63 \cdot 10^{-4}$	0.05	6.94	1.39 ± 0.03	1.36
R	$[O_2]$: $(0.09–2.5) \cdot 10^{-4}$	$1.14 \cdot 10^{-4}$	0.05	6.94	1.36 ± 0.04	1.34
S	[AN]: 0.038–0.57	$1.47 \cdot 10^{-4}$	0.02	6.94	1.12 ± 0.02	1.14
T	[AN]: 0.015–0.21	$7.04 \cdot 10^{-5}$	0.002	9.51	2.83 ± 0.03	2.89
U	$[H_3BO_3]$: 0.02–0.2	$1.41 \cdot 10^{-4}$	0.032	8.96	2.27 ± 0.05	2.22

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2) In the alternative rate law, k_d is replaced by $k_d/(1 + k_b[CuL_2^+])$ and the values of the final parameters $k_a - k_e$ are shifted to $k_a = (2.23 \pm 0.11) \cdot 10^4\,\text{M}^{-2}\,\text{s}^{-1}$, $k_b = (6.1 \pm 1.3) \cdot 10^2\,\text{M}^{-1}$, $k_c = (2.85 \pm 0.07) \cdot 10^2\,\text{M}^{-2}\,\text{s}^{-1}$, $k_d = 4.06 \pm 0.14\,\text{M}^{-1}\,\text{s}^{-1}$, and $k_e = 0.111 \pm 0.004$ (3a).

sum of all cupric species. Although it is not likely that all these complexes have identical reactivities towards $O_2^{\cdot}$, all attempts to assign individual rate constants to some of the compounds identified potentiometrically, failed. This at least excludes the possibility that one of the minor species, the relative concentration of which

$$CuL_2^+ + O_2 \xrightleftharpoons[k_{-4}]{k_{+4}} CuL_2O_2^+ \qquad (\pm 4)$$

$$CuL_2O_2^+ + CuL_2^+ \xrightarrow{k_{+5}} 2Cu(II) + H_2O_2 \qquad (+5)$$

$$CuL_2^+ + O_2 \xrightleftharpoons[k_{-6}]{k_{+6}} Cu(II) + O_2^{\cdot} \qquad (\pm 6)$$

$$CuL_2^+ + L \xrightleftharpoons[k_{-7}]{k_{+7}} CuL_3^+ \qquad (\pm 7)$$

$$CuL_3^+ + O_2 \xrightarrow{k_{+8}} Cu(II) + O_2^{\cdot} \qquad (+8)$$

$$CuL_2^+ + O_2^{\cdot} \xrightarrow{k_{+9}} Cu(II) + H_2O_2 \qquad (+9)$$

varies strongly with the experimental conditions, was solely responsible for (–6). The alternative rate law (3a) is obtained by replacing (+6) by the formation of $O_2^{\cdot}$ *via* monomolecular decomposition of $CuL_2O_2^+$ (+6a).

$$CuL_2O_2^+ \xrightarrow{k_{+6a}} Cu(II) + O_2^{\cdot} \qquad (+6a)$$

Assuming (±7) to be in rapid equilibrium lying over to the left and applying the steady state approximation to $[CuL_2O_2^+]$ and $[O_2^{\cdot}]$, we obtain the theoretical rate law (10), which is equal to the pH-independent part of (3) with $k_{+4}k_{+5}/k_{-4} = k_a$,

$$-d[O_2]/dt = [CuL_2^+]^2[O_2]\left(\frac{k_{+4}k_{+5}/k_{-4}}{1 + (k_{+5}/k_{-4})[CuL_2^+]} + \frac{(k_{+7}k_{+8}/k_{-7})[L] + k_{+6}}{[CuL_2^+] + k_{-6}/k_{+9})[Cu(II)]}\right) \qquad (10)$$

$k_{+5}/k_{-4} = k_b$, $k_{+7}k_{+8}/k_{-7} = k_c$, $k_{+6} = k_d$, and $k_{-6}/k_{+9} = k_e$. A similar expression corresponding to (3a) is obtained if (+6) is replaced by (+6a).

The complete rate law (3) indicates that both $CuH_{-1}L$ (k_f) and $CuH_{-1}L_2$ (k_g) contribute to the consumption of O_2 at high pH. Neither of these species has been identified potentiometrically and thus the actual reactivities are not known. On the other hand, we can conclude from the results of series Z (variation of [AN] at high pH) that $Cu(AN)H_{-1}L$, which is formed near pH 10, does not autoxidize significantly. This is probably due to the electron-with-drawing effect of AN and in line with the inertness of the mixed complexes $Cu(AN)Im^+$ [5] and $Cu(AN)HHi^{2+}$ [19] with imidazole and monoprotonated histamine, respectively. Chelation must be involved in the autoxidation of $CuH_{-1}L$ and $CuH_{-1}L_2$, but whether this is only true for the transition state of the autoxidation or also for $CuH_{-1}L$ and $CuH_{-1}L_2$ themselves is unknown.

Discussion. – For the cuprous complexes studied so far the rate of autoxidation in aqueous solution was always proportional to the concentrations of Cu(I) and O_2. *Crumbliss & Poulos* [20] discussed this in detail, it was not possible under these conditions to decide whether the reduction of O_2 to H_2O_2 occurs as two one-electron steps with $O_2^{\overline{\cdot}}$ as intermediate or in a single two-electron step *via* a binuclear transition state $(CuL_x)_2O_2^{2+}$ and the question of inner- or outer-sphere oxidation of the Cu(I)-complex also remained open.

For the autoxidation of the cuprous 2,2′,2″-terpyridine complex *Crumbliss et al.* [20], preferred, on the basis of thermodynamic considerations, the two-electron step which avoids the formation of the energetically unfavourable species $O_2^{\overline{\cdot}}$ or $HO_2^{\cdot}$. *Pecht & Anbar* [8] came to the same conclusion for the 2,2′-bipyridine complex. However, both groups used old values for the reduction potential for the $O_2/HO_2^{\cdot}$ couple [21], which are too negative. Recent results indicate that these values were wrong by more than 0.2 V and the generally accepted E° $(O_2/O_2^{\overline{\cdot}})$ now seems to be -0.33 ± 0.01 V [22]; thus the one-electron mechanism is now compatible with the thermodynamics for these systems.

The rate law (3) found in this study consists of two independent terms reflecting two different paths of dioxygen reduction. The only logical explanation for the first, which contains the parameters k_a and k_b seems to be the formation of 2 mol of Cu(II) and 1 mol of H_2O_2 *via* a binuclear transition state $(CuL_2)_2O_2^{2+}$ (steps (± 4) and $(+5)$). This reaction path is well established for other systems such as Cu(I) in nonaqueous solvents [1] [6] [7], Fe^{2+} in strong acid [23], and a very large number of Co(II)-complexes [24]. With Co(II), dimeric species like $Co_2L_x\mu O_2$ or $Co_2L_x\mu(O_2, OH)$ are well characterized products or intermediates of autoxidation.

The most prominent feature in the second term of (3) is the inhibition of the autoxidation by cupric copper ($k_e = k_{-6}/k_{+9}$). To our knowledge, no such inhibition of Cu(I) autoxidation is described in the literature. Since in our system O_2 is reduced to H_2O_2, and the oxidation of Cu(I) is essentially complete, the obvious conclusion is that superoxide is formed as an intermediate (± 6), $(+8)$.

The inhibition of autoxidation by the oxidized form of the metal ion has been observed for the ferrous complex with iminodiacetate [25]. This was used as evidence for the *Haber-Weiss* mechanism [26] of stepwise dioxygen reduction. However, in contrast with our results, no limiting value for inhibition by Fe^{3+} was observed by *Kaden & Fallab* [25], indicating that one-electron reduction of O_2 is the only significant path in that system.

A path (± 7) $(+8)$ (k_c) with a transition state $CuL_3O_2^{+}$ which is probably tetracoordinated is far more efficient than $(+6)$ (k_d) in the formation of $O_2^{\overline{\cdot}}$; this resembles similar results for NH_3, imidazole, and N-methylimidazole [4] [5]. However, k_c = 285 $M^{-2}s^{-1}$, describing the autoxidation of CuL_2^{+} in the presence of a high excess of free L is significantly smaller than the corresponding terms for imidazole (5500 $M^{-2}s^{-1}$ [4]), where it is difficult even to observe the ligand-independent term, or N-methylimidazole (16000 $M^{-2}s^{-1}$ [5]). Steric reasons, making the formation of a tetracoordinated transition state more difficult, may be invoked. This postulate must be tested with other imidazoles.

Direct chemical or physical proof for the formation of $O_2^{\overline{\cdot}}$ will be difficult to obtain. Cu_{aq}^{2+} and $O_2^{\overline{\cdot}}$ react with a second order rate constant of more than 10^8 $M^{-1}s^{-1}$

[27] and our present results show that Cu(I) (+9) may be even more reactive towards O_2^{-} than is Cu(II) (−6), $k_{-6}/k_{+9} = k_e = 0.11$. This agrees with the observation of *Kozlov et al.* [28] that Cu_{aq}^{+} and $HO_2^{\cdot}$ react in a nearly diffusion controlled step ($k = 2.3 \cdot 10^9$ $M^{-1}s^{-1}$). Thus very simple copper complexes behave like efficient superoxide dismutases ($k = 2 \cdot 10^9$ $M^{-1}s^{-1}$) [29], and the concentration of O_2^{-} will always be below the limits of detection, for instance by ESR.

It may seem strange that CuL_2^+ should react with O_2 in two different ways, by forming either an unstable dioxygen adduct (±4), or O_2^{-} and Cu(II) in a bimolecular step (+6) according to (3). To avoid this difficulty one may be inclined to prefer the alternative law (3a) where (+6) is replaced by (+6a), describing a monomolecular decay of $CuL_2O_2^+$. However, ample evidence [4] [5] [10], (+8) is available that the transition state of the one-electron reduction of O_2 by cuprous complexes involves preferentially a central ion which is at least tetracoordinated; thus $Cu(H_2O)L_2^+$, rather than CuL_2^+ itself, is the probable reactant in step (+6). On the other hand, no evidence for the enhancement of the coordination number has been found for the two-electron reduction paths (±4), (+5) [1]. Thus both mechanisms must be considered equally plausible at present with (3) slightly preferred to (3a) as the variance σ^2 (1) obtained with the former rate law is somewhat lower.

In this study it has been possible for the first time to distinguish between one- and two-electron reduction paths for O_2 in the autoxidation of a cuprous complex in H_2O. Both ways are about equally effective for the particular system studied, a situation which has not been described so far for any metal ion.

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155. The Electronic Structure of Azuleno[1,2,3-*cd*]phenalene and Azuleno[5,6,7-*cd*]phenalene, a Comparison

by **Rolf Gleiter**¹), **Jens Spanget-Larsen**¹), **Erik W. Thulstrup**¹,²), **Ichiro Murata**³), **Kazuhiro Nakasuji**³) and **Christian Jutz**⁴)

Institut für Organische Chemie der Technischen Hochschule D-61 Darmstadt (West-Germany); Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560 (Japan); Organisch Chemisches Institut der Technischen Universität D-8 München (West-Germany).

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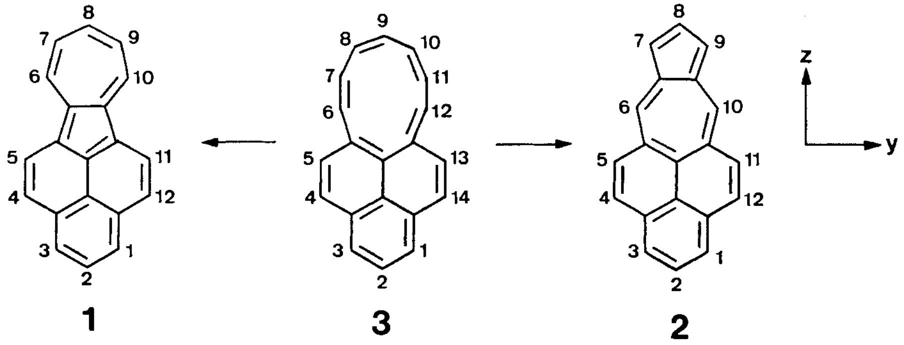
Summary. The photoelectron (PE.) spectra of azuleno[1,2,3-*cd*]phenalene (**1**) and azuleno-[5,6,7-*cd*]phenalene (**2**) have been recorded. The first five bands of both compounds could be assigned to transitions corresponding to removal of electrons from $4a_2$, $6b_1$, $5b_1$, $3a_2$ and $4b_1$ orbitals. This assignment is based mainly on a comparison between the observed ionization potentials and orbital energies calculated in a HMO and a PPP model.

The UV./VIS. polarized absorption spectrum of **1** in the region 10000–45000 cm^{-1} has been measured by means of the stretched film technique. The measurements were performed in polyethylene sheets at 77°K. Several bands could be assigned to $\pi^* \leftarrow \pi$ transitions calculated by a PPP-CI method.

A comparison between the electronic structures of **1** and **2** is made by means of a simple HMO diagram.

Azuleno[1,2,3-*cd*]phenalene (**1**) and azuleno[5,6,7-*cd*]phenalene (**2**) offer interesting opportunities for the application of perturbation theoretical arguments [1] in deriving their electronic structures from fragments. Two possibilities for **1** and **2**



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¹) Darmstadt.

²) Permanent address: Department of Chemistry, Aarhus University, DK-8 Aarhus, Denmark.

³) Osaka.

⁴) München.