

254. Cuprous Complexes and Dioxygen. VIII¹).
Steric Factors Controlling One- or Two-Electron Reduction of O₂ by
Cuprous Complexes with Substituted Imidazoles

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Summary

In aqueous acetonitrile (AN), Cu(I) forms the complexes Cu(AN)L⁺ and CuL₂⁺ with a series of substituted imidazoles (L). Stability constants log *K* of Cu(AN)⁺ + L ⇌ Cu(AN)L⁺ and log β₂ were near 5 and 12, resp., log units for all ligands. The rate of autoxidation is described by $-d[O_2]/dt = [CuL_2^+][O_2](k_a / (1 + k_b[CuL_2^+]) + (k_c[L] + k_d) / ([CuL_2^+] + k_e[Cu_{tot}^{II}]))$, implying competition between one- or two-electron reduction of O₂. The value of *k_c* decreases from 5500 M⁻²s⁻¹ for unsubstituted imidazole to about 40 M⁻²s⁻¹ for 2-methylimidazole or 1,2-dimethylimidazole and essentially zero for the corresponding 2-ethyl-derivatives. On the other hand, *k_a* and *k_b* are much less influenced by the nature of the ligands, all values being near 5 · 10⁴ M⁻²s⁻¹ and 10³ M⁻¹, respectively, for the complexes with the last four bases. Thus rather subtle steric changes may strongly influence the relative importance of different pathways in the reduction of dioxygen by cuprous complexes.

In a previous paper [1] we have presented kinetic evidence for simultaneous one- and two-electron reduction paths in the autoxidation of Cu(1-methyl-2-hydroxymethylimidazole)₂⁺ (MEOHIM). In order to obtain information on the factors governing the relative importance of either mode of O₂ reduction, we have studied the autoxidation of the Cu(I) complexes with 2-methylimidazole (MEIM), 1,2-dimethylimidazole (DIMEIM), 2-ethylimidazole (ETIM), 1-methyl-2-ethylimidazole (MEETIM), 1,2,4-trimethylimidazole (TRIMEIM), and 1,2,4,5-tetramethylimidazole (TEMEIM). With the choice of this series of ligands (L) we could concentrate mainly on sterical factors while keeping electronic influences relatively small. Included in this comparative study are some earlier results with unsubstituted imidazole (IM) [2] and 1-methylimidazole (N-MEIM) [3].

Experimental part

Materials. - 1-Methyl-2-ethylimidazole (MEETIM) was prepared according to [4] and purified by fractional distillation, b.p.₁₁ 94-95°. TRIMEIM [5] was synthesized from 2,4-dimethyloxazole-5-carboxylic acid [6] and methylamine, distilled i.v. and crystallized from light petroleum; m.p. 87-88°.

¹) Part VII, see [1].

DIMEIM (*Fluka*) was distilled i.V. prior to use: b.p.₁₃ 88° (lit.: b.p. 205–206° [7]). The other ligands were purified by recrystallization: MEIM (*Fluka*, m.p. 142–144°, lit.: 139° [8], from benzene); ETIM (*Fluka*, m.p. 82–85°, lit.: 79–80° [9], from light petroleum); and TEMEIM (*BASF*, Ludwigshafen²), m.p. 51–54°, lit.: 58° [10], from light petroleum). Solutions of cuprous perchlorate [11] or *p*-toluenesulfonate [12] in CH₃CN were standardized spectrophotometrically [1] by titration with EDTA after oxidation to Cu²⁺. CH₃CN (*Fluka*) was fractionated from K₂CO₃ and P₂O₅. Twice distilled water was used throughout. Other reagents were of quality *p.a.* or better, and used without further purification.

Measurements and equipment. - Temperature 20 ± 0.2°, ionic strength 0.2 (Na₂SO₄). Ligand protonation constants and complex stability constants were obtained by potentiometric titration of 50 ml samples containing 0.15M AN, unless stated otherwise. 0.4 or 0.2M NaOH (Titrisol) was used for solutions with [L] 6 or 3 mM, respectively. The conditions are summarized in *Table 1*, together with the

 Table 1. *Equilibrium measurements*

Ligand	[L _{tot}] (mM)	[Cu ⁺] _{tot} (mM)	logK ^{H^a})	logK ₁ ^a)	logβ ₂ ^a)
MEIM	3	0, 0.5, 1	8.094	4.98 ^b), 4.90	11.94 ^b), 11.90
MEIM	6	0, 0.96, 1.88, 3.5	8.109	4.99, 4.98, 4.93	11.97, 11.88, 11.94
DIMEIM	3	0, 0.49, 0.93	8.211	5.01 ^b), 4.91	11.88, 11.90
DIMEIM	6	0, 1.58, 3.2	8.223 ^c)	4.835, 4.825	11.78, 11.74
ETIM	3	0, 0.44, 0.86	7.995	4.77 ^d), 4.79 ^d)	11.81 ^d), 11.83 ^d)
ETIM	6	0, 1.3, 2.6	8.021	4.77, 4.80	11.79, 11.81
MEETIM	3.4	0, 0.48, 0.89	8.120	4.66, 4.67	11.51, 11.46
MEETIM	6	0, 1.3, 2.6	8.140 ^c)	4.70 ^c), 4.71 ^c)	11.54 ^c), 11.50 ^c)
TRIMEIM	3	0, 0.47, 0.9	8.638 ^c)	4.71 ^c), 4.81 ^c)	11.90 ^c), 11.86 ^c)
TEMEIM	3	0, 0.48, 0.96	9.209	4.89, 4.85	12.20, 12.21
TEMEIM	6	0, 1.1, 2.3	9.201 ^c)	4.95, 4.84 ^c)	12.23, 12.26 ^c)

a) $K^H = [LH^+]/[L][H^+]$, $K_1 = [Cu(AN)L^+]/[Cu(AN)^+][L]$, $\beta_2 = [CuL_2^+]/[Cu^+][L]^2$, mixed constants, with $[H^+]$ taken as $\exp(-pH)$ are given.

b) $[AN] = 0.169M$.

c) Mean values from two different titration curves.

d) Mean from 3 curves.

logK values obtained from the individual curves. The least squares fitting of the degree of neutralization α (1) was done on a PDP 11 digital computer [13] [14] or on a *Hewlett Packard* HP 9821 with expanded

$$\sigma_a^2 = \sum_{i=1}^I \frac{(ml_{exp} - ml_{calc})^2}{EQ^2 \cdot (I - n)} \quad (1)$$

(I, n: number of data points, parameters; ml_{exp}, ml_{calc}: experimental and calculated ml of base added; EQ: equivalence point)

memory using the *Newton-Gauss* technique modified according to *Marquardt* [15].

The kinetics and stoichiometry of the autoxidation were followed amperometrically with a *Beckman* 39065 polarographic oxygen sensor. Individual kinetic runs were evaluated by the method of initial rates. The combined data for each ligand were subjected to numerical analysis using the *Marquardt* procedure [15] on the HP 9821 and minimizing the variance $\sigma_{\log k}^2$ (2). All uncertainties in the parameters are

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

indicated by twice their standard errors. Graphical output was obtained on a 9862 calculator plotter. The other experimental details were as described [1] [13].

²) We thank the *Badische Anilin- und Sodafabrik* for a generous gift of this compound.

Results. - Stability constants. All ligands (L) described in this paper form the complexes $\text{Cu}(\text{AN})\text{L}^+$ (K_1) and CuL_2^+ (β_2) with Cu^+ in aqueous acetonitrile, as expected from results with unsubstituted imidazole [16] or 1-methyl-2-hydroxy-methylimidazole [1]. With MEIM and ETIM, additional protons, most likely from the pyrrole nitrogen, were released at high pH, and eventually a precipitate formed. Such parts of the titration curves were disregarded for the calculation. In Table 2, the ligand protonation constants and the complex formation constants of the six systems are summarized. The basicity of the ligands increases with the number of alkyl substituents, the ethyl group being slightly less effective than the methyl group. Thus the lowest $\log K^{\text{H}}$ is obtained with ETIM (8.01) and the highest for the tetra-methylated compound TEMEIM (9.20), while unsubstituted imidazole has 7.11 [19]. No such straightforward trends are observed for the complex stability constants. Both $\log K_1$ and $\log \beta_2$ are fairly constant within this series of ligands, varying irregularly from 4.69 (MEETIM) to 4.94 (MEIM) and 11.51 (MEETIM) to 12.23 (TEMEIM), respectively.

Table 2. Ligand protonation constants and complex stability constants

Ligand	$\log K^{\text{H}^{\text{a}}}$	$\log K_1^{\text{a)b}}$	$\log \beta_2^{\text{a)b}}$
MEIM	8.10 ± 0.02 (2) ^c	4.94 ± 0.04 (5)	11.93 ± 0.03 (5)
DIMEIM	8.22 ± 0.02 (3) ^c	4.90 ± 0.08 (4)	11.83 ± 0.08 (4)
ETIM	8.01 ± 0.03 (2)	4.78 ± 0.02 (8) ^c	11.82 ± 0.02 (8) ^c
MEETIM	8.13 ± 0.03 (3)	4.69 ± 0.02 (6)	11.51 ± 0.03 (6)
TRIMEIM	8.64 ± 0.02 (2) ^c	4.76 ± 0.11 (4)	11.88 ± 0.07 (4)
TEMEIM	9.20 ± 0.02 (2) ^c	4.87 ± 0.09 (5)	12.23 ± 0.03 (5)

^a) Unweighted mean with twice the standard error and number of individual titration curves.

^b) Using $10^{3.28}$, $10^{4.35}$, and $10^{4.39}$ for the overall stability constants of $\text{Cu}(\text{AN})^+$ [17], $\text{Cu}(\text{AN})_2^+$ [11], and $\text{Cu}(\text{AN})_3^+$ [18], respectively.

^c) Calculated uncertainties of less than 0.02 log units were not accepted because of possible systematic errors.

Kinetics. - All measurements were done under conditions where the 1:2 complexes CuL_2^+ are the only cuprous species present in appreciable concentration. For each ligand $[\text{CuL}_2^+]$, $[\text{L}]$, $[\text{Cu}(\text{II})_{\text{tot}}]$, pH, $[\text{O}_2]$, and $[\text{AN}]$ were varied in order to obtain the experimental rate law. Unless stated otherwise, pH was maintained at the value of $\log K^{\text{H}}$ by using equivalent amounts of free L and ligand hydrosulfate, while $[\text{O}_2]$ was 0.04–0.06 mM. As for 1-methyl-2-hydroxymethylimidazole (MEOHIM) [1], relationships of variable exponential order were normally found between the rate of autoxidation and $[\text{CuL}_2^+]$, $[\text{L}]$, or $[\text{Cu}(\text{II})_{\text{tot}}]$. Pseudo second order rate constants k_{obs} (3) were calculated from initial rates and their logarithmic values

$$k_{\text{obs}} = -d[\text{O}_2]_{t=0} / ([\text{O}_2][\text{Cu}(\text{II})_{\text{tot}}]dt)_{t=0} \quad (3)$$

subjected to the least squares fitting process (2), since the individual data points could be assumed to have roughly constant relative errors. As $\text{Cu}(\text{TRIMEIM})_2^+$ and $\text{Cu}(\text{TEMEIM})_2^+$ were found to be essentially inert towards O_2 (see below), the kinetics were studied for the other four ligands only. For each of them at least

100 data points grouped into 9-14 series were measured. k_{obs} (3) was found to be dependent on $[\text{CuL}_2^+]$, $[\text{L}]$, and $[\text{Cu(II)}_{\text{tot}}]$, but independent of pH , $[\text{O}_2]$, and $[\text{AN}]$. Thus the series with the former three entities as variables were used to obtain the 'best' set of rate constants by minimizing $\sigma_{\log k}$ (2), while the others provided a possibility to check the results. The experimental conditions are summarized in Table 3, along with the comparison between observed and calculated $\log k$ values when pH , $[\text{O}_2]$, or $[\text{AN}]$ were varied. Selected series are shown in Figures 1-4. The solid lines in all figures were calculated using the final set of parameters and the general rate law as discussed below.

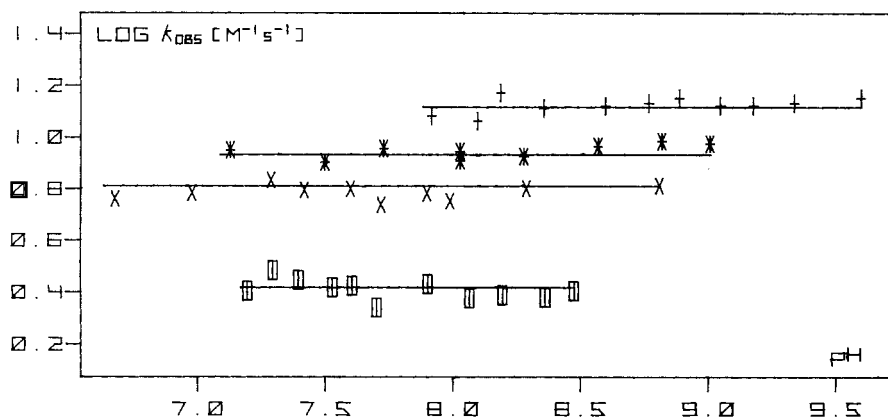


Fig. 1. pH -Dependence of k_{obs} . +: L=MEIM, $[\text{CuL}_2^+]$ 0.137 mM, $[\text{L}]$ 0.04M (A11); *; L=DIMEIM, $[\text{CuL}_2^+]$ 0.101 mM, $[\text{L}]$ 4 mM (B10); x: L=ETIM, $[\text{CuL}_2^+]$ 0.15 mM, $[\text{L}]$ 0.04M (C9); □: L=MEETIM, $[\text{CuL}_2^+]$ 0.116 mM, $[\text{L}]$ 0.01M (D6); - curves calculated with (4) and values of Table 4.

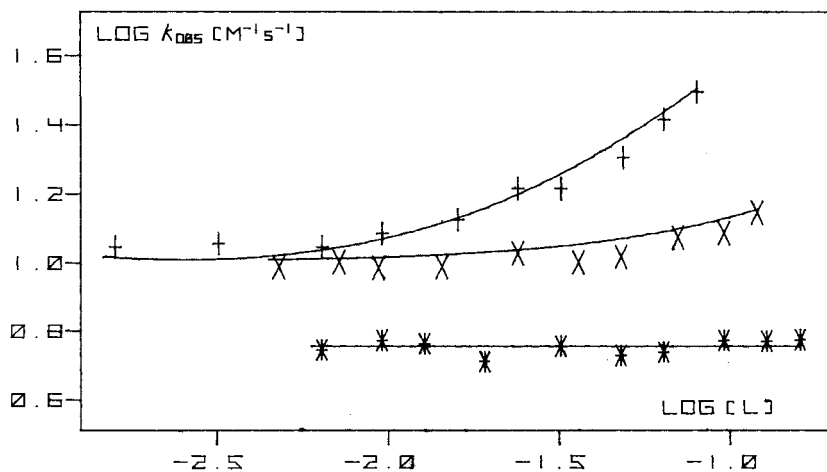


Fig. 2. Ligand-dependence of k_{obs} . +: L=1-methyl-2-hydroxymethylimidazole, $[\text{CuL}_2^+]$ 0.192 mM, pH 6.95 [1]; x: L=MEIM, $[\text{CuL}_2^+]$ 0.111 mM (A6); *; L=ETIM, $[\text{CuL}_2^+]$ 0.129 mM (C4); - curves calculated with (4) and values of Table 4.

Table 3. Experimental conditions for kinetic runs and pseudo second-order rate constants obtained by variation of pH, [O₂], or [AN]

Ligand	Curve	Parameter varied	[CuL ₂ ⁺] (mM)	[L] ^{a)} (M)	log k _{obs} ^{b)}	log k _{calc} ^{c)}	Number of points
MEIM ^{d)}	A1	[CuL ₂ ⁺]: 0.043-0.603 mM	var	0.005	-	-	9
MEIM ^{d)}	A2	[CuL ₂ ⁺]: 0.071-0.45 mM	var	0.05	-	-	8
MEIM ^{d)}	A3 ^{e)}	[CuL ₂ ⁺]: 0.062-0.55 mM	var	0.1	-	-	11
MEIM ^{d)}	A4	[CuL ₂ ⁺]: 0.031-0.155 mM	var	0.005	-	-	16
MEIM ^{d)}	A5	[L]: 0.0024-0.12M	0.171	var	-	-	13
MEIM ^{d)}	A6	[L]: 0.0024-0.12M	0.111	var	-	-	10
MEIM ^{d)}	A7 ^{f)}	[Cu(II) _{tot}]: 0.05-5 mM	0.080	0.18	-	-	11
MEIM ^{d)}	A8	[Cu(II) _{tot}]: 0.05-5 mM	0.079	0.12	-	-	15
MEIM ^{d)}	A9	[Cu(II) _{tot}]: 0.1-5 mM	0.108	0.1	-	-	13
MEIM ^{d)}	A10	[Cu(II) _{tot}]: 0.1-5 mM	0.122	0.05	-	-	8
MEIM ^{d)}	A11	pH: 7.92-9.66	0.137	0.04	1.13 ± 0.02	1.12	11
MEIM ^{d)}	A12	[O ₂]: 0.01-0.25 mM	0.161	0.05	1.16 ± 0.03	1.17	13
MEIM ^{d)}	A13	[O ₂]: 0.02-0.135 mM	0.270	0.05	1.33 ± 0.02	1.31	8
MEIM ^{d)}	A14	[AN]: 0.038-0.95M	0.139	0.05	1.07 ± 0.02	1.12	10
DIMEIM	B1	[CuL ₂ ⁺]: 0.033-0.289 mM	var	0.1	-	-	11
DIMEIM	B2	[CuL ₂ ⁺]: 0.033-0.289 mM	var	0.005	-	-	11
DIMEIM	B3 ^{e)}	[CuL ₂ ⁺]: 0.033-0.289 mM	var	0.1	-	-	13
DIMEIM	B4	[L]: 0.005-0.1M	0.210	var	-	-	11
DIMEIM	B5	[L]: 0.013-0.1M	0.041	var	-	-	8
DIMEIM	B6	[Cu(II) _{tot}]: 0.02-2.0 mM	0.054	0.1	-	-	8
DIMEIM	B7	[Cu(II) _{tot}]: 0.1-10 mM	0.042	0.1	-	-	12
DIMEIM	B8	pH: 7.33-8.80	0.085	0.01	0.84 ± 0.02	0.89	10
DIMEIM	B9	pH: 7.89-9.61	0.194	0.04	1.18 ± 0.02	1.13	11
DIMEIM	B10	pH: 7.13-9.01	0.101	0.004	0.95 ± 0.02	0.93	9
DIMEIM	B11	[O ₂]: 7.2-237 μM	0.165	0.1	1.07 ± 0.03	1.12	14
DIMEIM	B12 ^{e)}	[O ₂]: 8.4-240 μM	0.179	0.064	1.00 ± 0.03	1.02	13
DIMEIM	B13	[AN]: 0.025-0.40M	0.110	0.02	0.9 ± 0.02	0.96	10
DIMEIM	B14	[AN]: 0.038-0.61M	0.152	0.01	1.03 ± 0.02	1.05	11
ETIM	C1	[CuL ₂ ⁺]: 0.054-0.44 mM	var	0.005	-	-	9
ETIM	C2	[CuL ₂ ⁺]: 0.054-0.44 mM	var	0.05	-	-	7
ETIM	C3	[CuL ₂ ⁺]: 0.12-0.76 mM	var	0.05	-	-	8
ETIM	C4	[L]: 0.006-0.16M	0.129	var	-	-	10
ETIM	C5	[L]: 0.0035-0.1M	0.207	var	-	-	12
ETIM	C6	[L]: 1.8-16 mM	0.207	var	-	-	7
ETIM	C7	[Cu(II) _{tot}]: 0.004-1 mM	0.309	0.05	-	-	14
ETIM	C8	[Cu(II) _{tot}]: 0.004-1 mM	0.080	0.05	-	-	15
ETIM	C9	pH: 6.7-8.8	0.150	0.04	0.79 ± 0.02	0.81	9
ETIM	C10	[O ₂]: 0.019-0.11 mM	0.195	0.05	0.87 ± 0.02	0.90	10
ETIM	C11	[AN]: 0.02-0.75M	0.150	0.02	0.77 ± 0.02	0.81	10
MEETIM	D1	[CuL ₂ ⁺]: 0.033-0.693 mM	var	0.1	-	-	14
MEETIM	D2	[CuL ₂ ⁺]: 0.033-0.693 mM	var	0.01	-	-	14
MEETIM	D3 ^{e)}	[CuL ₂ ⁺]: 0.033-0.693 mM	var	0.05	-	-	12
MEETIM	D4	[L]: 0.005-0.1M	0.231	var	-	-	11
MEETIM	D5	[Cu(II) _{tot}]: 0.005-0.5 mM	0.065	0.05	-	-	13
MEETIM	D6	pH: 7.20-8.50	0.116	0.01	0.41 ± 0.02	0.42	11
MEETIM	D7	[O ₂]: 0.025-0.25 mM	0.231	0.01	0.71 ± 0.03	0.66	7
MEETIM	D8	[O ₂]: 0.02-0.25 mM	0.116	0.01	0.37 ± 0.04	0.42	14
MEETIM	D9	[AN]: 0.05-0.43M	0.231	0.02	0.67 ± 0.01	0.66	10

a) Free, deprotonated ligand. pH-dependencies: variable [LH⁺], otherwise [LH⁺] = [L].

b) k_{obs}: M⁻¹s⁻¹, log k_{obs} with twice the standard error.

c) Using data of Table 4.

d) [AN] = 0.038M for MEIM, other ligands: 0.095M.

e) [Cu(II)_{tot}]: 5 mM (A3), 10 mM (B3), 4 mM (D3), other curves: zero, unless varied.

f) pH: 8.5.

As indicated in *Figure 1* the rate of autoxidation was independent of pH for all systems, as long as the concentration of the free unprotonated ligand, [L], was kept constant. Variation of pH was achieved by mixing variable amounts of the ligand hydrosulfates $(\text{LH})_2\text{SO}_4$ with the desired amount of free L, maintaining the ionic strength at 0.2 with Na_2SO_4 .

In *Figure 2* ligand dependences are given for ETIM, MEIM, and MEOHIM. No influence of [ETIM] on $\log k_{\text{obs}}$ can be seen in the range of 0.006–0.12M. The effect of increasing [MEIM] (x) is rather weak if compared to the results with MEOHIM (+) [1]. Together with the series A1-A4 (*cf. Table 3*) where $[\text{CuL}_2^+]$ was varied at different but constant [MEIM], an increasing rate of autoxidation with increasing [MEIM] could be unequivocally established, however. Results for MEETIM or DIMEIM were very similar to those with ETIM and MEIM, respectively, and are not depicted in *Figure 2*.

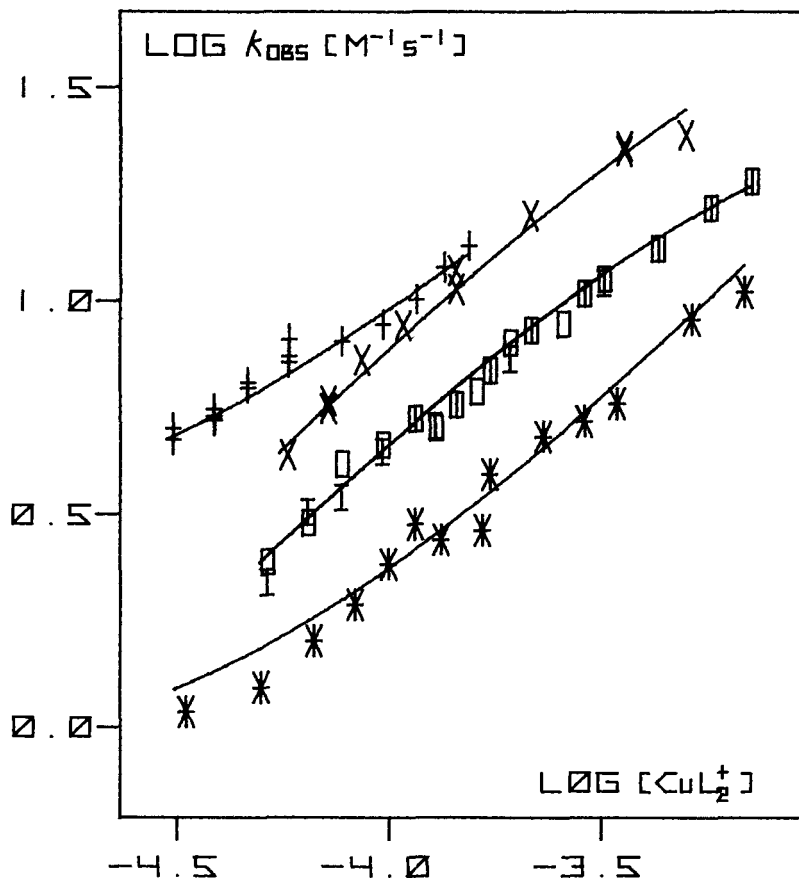


Fig. 3. Dependence of k_{obs} on $[\text{CuL}_2^+]$. +: [MEIM]=0.005M (A4); x: [MEIM]=0.1M, $[\text{Cu(II)}_{\text{tot}}]=0.005\text{M}$ (A3); □: [ETIM]=0.005M (C1); I: [ETIM]=0.05M (C2); ▣: [ETIM]=0.05M (C3); *: [MEETIM]=0.1M (D1); - curves calculated with (4) and values of *Table 4*.

Figure 3 shows some of the series with $[\text{CuL}_2^+]$ as the variable. k_{obs} increases with $[\text{CuL}_2^+]$ for all systems studied. With MEIM, an upward curvature for $\log k$ vs. $\log [\text{CuL}_2^+]$ is obtained in the absence of Cu^{2+} and at relatively low concentrations of $[\text{CuL}_2^+]$ (+, series A4), reflecting one term which is independent of $[\text{CuL}_2^+]$ and one proportional to that parameter. On the other hand, in the presence of 5 mM Cu^{2+} (x, A3) a downward curvature is observed, indicating a higher limiting value of k_{obs} . Points of three series with ETIM are given in Figure 3 (C1-C3). No influence of $[\text{ETIM}]$ is present, in line with the results shown in Figure 2, and no deviation from proportionality between k_{obs} and $[\text{Cu}(\text{ETIM})_2^+]$ is seen at low concentrations. For MEETIM as ligand (*) the opposite is true, k_{obs} approaching a minimum value at low $[\text{Cu}(\text{MEETIM})_2^+]$. Curves for L=DIMEIM closely correspond to those of MEIM and are not given in the Figure.

The rate law (4) which is identical with the pH-independent terms of the expression obtained for MEOHIM [1], gave satisfactory agreement between calculated and experimental pseudo second order rate constants.

$$-d[\text{O}_2]/dt = [\text{CuL}_2^+]^2 [\text{O}_2] \left(\frac{k_a}{1 + k_b [\text{CuL}_2^+]} + \frac{k_c [\text{L}] + k_d}{[\text{CuL}_2^+] + k_e [\text{Cu}(\text{II})_{\text{tot}}]} \right) \quad (4)$$

The final set of parameters, together with their estimated uncertainties ($\pm 2\sigma_k$), the overall standard deviation in $\log k$, $\sigma_{\log k}$ (2), and the number of degrees of freedom are compiled in Table 4. For all ligands $\sigma_{\log k}$ was within the narrow range of 0.03 to 0.04 log units (7–10% in k_{obs}) reflecting the uncertainties connected with data obtained by the method of initial rates. All critical parameters were tested for significance by applying the F-test to the overall variances in

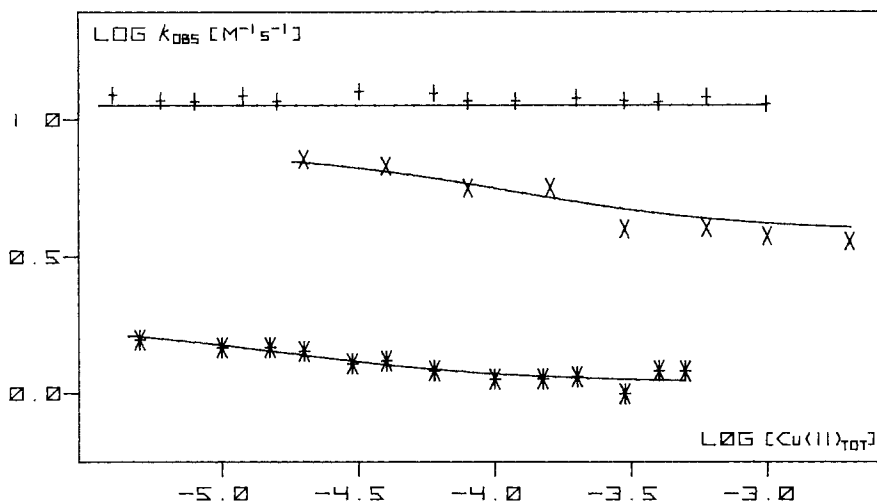


Fig. 4. Dependence of k_{obs} on $[\text{Cu}(\text{II})_{\text{tot}}]$. +: L=ETIM, $[\text{CuL}_2^+]=0.309$ mM, $[\text{L}]=0.05$ M (C7); x: L=DIMEIM, $[\text{CuL}_2^+]=0.054$ mM, $[\text{L}]=0.1$ M (B6); *: L=MEETIM, $[\text{CuL}_2^+]=0.065$ mM, $[\text{L}]=0.05$ M (D5); - curves calculated with (4) and values of Table 4.

Table 4. Rate constants and estimated uncertainties ($\pm 2\sigma$)

Ligand	$k_a(\text{M}^{-2}\text{s}^{-1})$	$k_b(\text{M}^{-1})$	$k_c(\text{M}^{-2}\text{s}^{-1})$	$k_d(\text{M}^{-1}\text{s}^{-1})$	k_e	$\sigma_{\log k^a}$	Degrees of freedom
MEIM	$(7.8 \pm 0.6) \cdot 10^4$	1030 ± 360^b	35 ± 6	2.3 ± 0.3	0.18 ± 0.06	0.034	109
DIMEIM	$(8.3 \pm 0.5) \cdot 10^4$	2600 ± 500	20 ± 5	1.8 ± 0.3	0.6 ± 0.3	0.032	69
ETIM	$(5.25 \pm 0.19) \cdot 10^4$	1430 ± 230	≤ 1	≤ 0.1	- ^{e)}	0.029	80
MEETIM	$(1.65 \pm 0.06) \cdot 10^4$	- ^{c)}	≤ 1	0.71 ± 0.1	5.1 ± 3.4	0.039	61
MEOHIM	$(2.3 \pm 0.2) \cdot 10^4$	1000 ± 400	285 ± 13	3.9 ± 0.3	0.112 ± 0.008	0.031	168
IM	- ^{f)}	- ^{f)}	5500^g	14 ± 3^h	- ^{f)}		
N-MEIM	- ^{f)}	- ^{f)}	18000^h	105 ± 20^h	- ^{f)}		

a) Cf. eq. (2).

b) Significant at the 95% level only.

c) Best value: $280 \pm 190 \text{M}^{-1}$, not significant at the 90% level.

d) Values from [1].

e) No inhibition by Cu^{2+} .

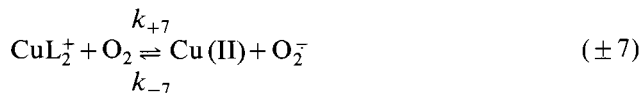
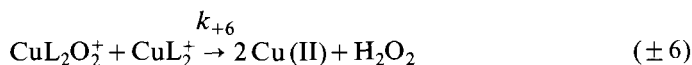
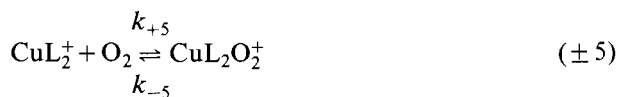
f) Not studied.

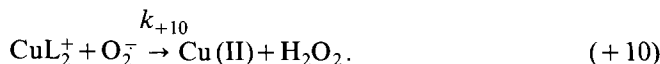
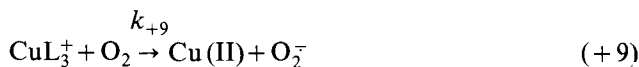
g) Cf. [2].

h) Cf. [3].

$\log k_{\text{obs}}$ calculated with and without that term in the rate law. Parameters which differed from zero by less than $\pm 2\sigma_k$ or which had less than 90% probability were dropped from the individual rate laws. Unless stated otherwise, all rate constants in Table 4 were significant at least at the 99% level.

The experimental rate law (4) suggests the existence of two different paths of O_2 reduction by cuprous complexes, one containing the terms k_a and k_b which is not influenced by Cu(II) , the other with k_c , k_d , and k_e . The minimum number of elementary steps needed to explain the data are given by (5)-(10).





Not included are further reactions of H_2O_2 . Such steps may not be important at the onset of O_2 reduction and would not influence the values of the parameters compiled in *Table 4*. However, from the variable redox stoichiometries of CuL_2^+ oxidized per mol of O_2 reduced in our systems it can be concluded that oxidation of CuL_2^+ by H_2O_2 and/or disproportionation of H_2O_2 by copper ions must be significant in these systems. CuL_3^+ was never identified potentiometrically. It was assumed to be present in negligible concentrations and in rapid equilibrium with CuL_2^+ . Elimination of CuL_2O_2^+ and O_2^- by the steady state approximation leads to a theoretical rate law, which is identical to (4) if we set $k_{+5}k_{+6}/k_{-5} = k_a$, $k_{+6}/k_{-5} = k_b$, $k_{+8}k_{+9}/k_{-8} = k_c$, $k_{+7} = k_d$, and $k_{-7}/k_{+10} = k_e$.

TRIMEIM and TEMEIM, although forming the same complexes of very similar stabilities with Cu(I) show completely different behaviour towards dioxygen. In both cases the rate of O_2 uptake is much slower under comparable conditions and it steadily decreases with increasing ligand concentration up to 0.2M. Further, consumption of O_2 was preceded by an induction period or even by the setting free of some O_2 . Although O_2 eventually disappears from such solutions, no reactivity of CuL_2^+ towards O_2 in the sense discussed so far can be attributed to these systems. A possible explanation for this slow uptake of dioxygen lies in the reactivity of the 1:1 complexes and/or in Cu(II)-catalysed oxidation of the organic substrates. These reactions have not been studied in detail.

Discussion. - The evidence suggesting the elementary steps (± 5) - ($+10$) as well as the possibility of alternative mechanisms has been discussed in detail for the autoxidation of $\text{Cu}(\text{MEOHIM})_2^+$ [1]. The main result was that O_2 is reduced in that system *via* two independent paths (I and II). Part I of the rate law (4) with k_a and k_b as parameters has to be explained by the formation of H_2O_2 without interference of O_2^- as an intermediate (± 5), ($+6$). One-electron reduction of O_2 to O_2^- seems to be the obvious conclusion to be drawn from the other part of the rate law (II). Both possibilities have been discussed in the literature for related systems, normally with a strong preference for one of the paths [18] [20] [21]. The present work indicates that competition between one- and two-electron reduction of O_2 may not be an exceptional phenomenon in the autoxidation of cuprous complexes.

Crumbliss & Gestaut [22] have compared the autoxidation of cuprous complexes with several substituted phenanthrolines. From a linear correlation between $\log k_{\text{obs}}$ and the ligand protonation constants $\log K^{\text{H}}$ they concluded that electronic effects were a decisive factor in the rate of these reactions. In our study steric factors influencing the formation of species with enhanced coordination numbers were the main points of interest. The change in electron density at the coordinating nitrogen was kept small by using alkyl substituents throughout. Inspection of the data in

Table 4 indicates that path I, described by k_a and k_b , is not very susceptible to sterical changes. k_a values vary only within a factor of 5. No systematic trend is discernible. If MEETIM is disregarded, values of k_b are closer still, all being between 1000 and 2500 M⁻¹. The situation is quite different for path II. k_c varies over more than four orders of magnitude, from 18000 M⁻²s⁻¹ for N-MEIM, to less than 1 M⁻²s⁻¹ for the ethyl derivatives. Similar, if somewhat smaller, differences are found for k_d . Thus path II in which O₂ is reduced with the formation of O₂^{•-} as an intermediate is much more susceptible to steric influences than path I circumventing that species. No positive correlation was found between ligand basicity and the rate of autoxidation. In fact, the complexes with the most basic ligands TRIMEIM and TEMEIM (see *Table 2*) are essentially inert towards dioxygen, while the most reactive species, at least as far as path II is concerned, are obtained with the relatively weak bases IM and N-MEIM. Directly relating proton basicity in H₂O to σ -electron density may be dangerous. Nevertheless, alkyl substituents at the imidazole nucleus should *not reduce*, but rather increases the σ -donor properties of the heteroatom and we can safely conclude that in our system electronic factors do not play the role suggested in the autoxidation of substituted phenanthrolines [22].

An alternative explanation, common to both series of experiments, can be put forward tentatively. *Crumbliss & Gestaut* [22] have mentioned that correlation of $\log k_{\text{obs}}$ was possible not only with $\log K^{\text{H}}$ but also with the formal standard potentials for the Cu(II)L₂/Cu(I)L₂ couples (L = substituted phenanthroline). Also, a rough correlation has been noted in a survey of earlier studies of the interaction of cuprous complexes with dioxygen [23]. In the present case the stabilities of CuL₂⁺ are essentially the same for different ligands while those of the corresponding cupric complexes decrease strongly in the series IM ~ N-MEIM < MEIM, DIMEIM < ETIM, MEETIM ≪ TRIMEIM, TEMEIM, increasing the formal standard potentials of the Cu(II)/Cu(I) couples in the same order³). This order is identical to the one of decreasing k_c and k_d , as shown in *Table 4*. In the case of TRIMEIM and TEMEIM the redox potentials may well be high enough as to exclude reduction of O₂ to H₂O₂ or even to H₂O in alkaline solution for thermodynamic reasons. Since, because of sterical crowding, the formation of transient dioxygen adducts with increased coordination number [1-3] and the standard potentials of the cupric/cuprous couples both are adversely affected by alkyl substituents in ortho position to the coordinating nitrogen group, the relative importance of these two effects cannot be judged from the present study. No evidence for any direct influence of the σ -donor strength of the coordinating nitrogen was observed.

Steric factors play an important role in the autoxidation of cuprous complexes by path II with O₂^{•-} as an intermediate and apparently much less so if the formation of superoxide is avoided by a binuclear transition state (CuL₂)₂O₂²⁺ (path I), implying steric control of one- or two-electron reduction of dioxygen.

3) While IM and N-MEIM form stable 1:4 complexes with Cu²⁺ [24], no complexation is observed with TRIMEIM and TEMEIM. Only very limited amounts of Cu²⁺ are kept in solution by ETIM and MEETIM.

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