Polynuclear Complex Formation and Peroxodisulphate Oxidation of Copper(II)–Dimethylglyoximate Complexes

By **Giorgio O. Morpurgo,*** Istituto Chimico, Università di Roma, 00185 Roma, Italy
Anthony A. G. Tomlinson, Laboratorio di Teoria e Struttura Elettronica e Comportamento Spettrochimico dei Composti di Coordinazione del CNR, Via Montorio Romano, 00131 Roma, Italy

The interaction of copper(II) with dimethylglyoxime (H_2dmg) has been studied potentiometrically in the range pH 2.5—11.0. For H_2dmg : Cu^{II} = 2 : 1, only [Cu(Hdmg)$_2$] is present in solution; no [Cu(Hdmg)]$^+$ has been detected. At H_2dmg : Cu^{II} = 1 : 1, the predominant species at pH 5 is still [Cu(Hdmg)$_2$], but at higher pH (5—6.5) there is evidence that the predominant species is a tetramer. This complex, and its glyoxime analogue, can be isolated and spectroscopic data and elemental analysis indicate an empirical formula [{Cu(Hdmg)(OH)}$_4$], for which a hydroxo-bridged structure retaining two [CuN$_4$] units is suggested. The same structure is retained in solution. The kinetics of oxidation of alkaline solutions of H_2dmg : Cu^{II} = 1 : 1 have been studied. The reactions proceed by interaction of the tetramer with peroxodisulphate to give two molecules of a dimer having mixed oxidation states for the metal. It is suggested that oxidation occurs preferentially at the hydroxo-bridges of the tetramer.

OXIDATION of a slightly alkaline solution of a copper(II) salt and dimethylglyoxime (H_2dmg) by powerful oxidizing agents such as sodium hypochlorite, bromine water, or ammonium peroxodisulphate is known to produce a strong absorption band at 520 nm.[1] Little is known of the species present in the original or the oxidized solutions which produce this band. In this paper we present evidence for species other than [Cu(Hdmg)$_2$] in aqueous solution and discuss their oxidation reactions with peroxodisulphate.

EXPERIMENTAL

Materials.—Copper(II) solutions were prepared from AnalaR or C. Erba copper sulphate and were standardized by titration against the disodium salt of ethylenediamine-tetra-acetic acid (H_4edta) in ammoniacal solution using murexide as indicator.[2] Commercially available H_2dmg was recrystallized from water. Weighed amounts of the dry product (m.p. 241 °C) were dissolved in water to give stock solutions of maximum concentration 4×10^{-3} mol dm^{-3}. Carbonate-free sodium hydroxide was prepared as described by Vogel[3] and standardized against AnalaR potassium hydrogenphthalate.

Potentiometric Titrations.—Titrations were carried out at 25 ± 0.1 °C in a double-walled Pyrex cell (total capacity 100 cm^3) fitted with a magnetic stirrer. The temperature was kept constant by thermostatting the outer jacket. Alkali was added from an Agla microsyringe (0.5 cm^3) fitted with a capillary glass nozzle. Further stirring was provided by a stream of carbon dioxide-free pure nitrogen, presaturated with water. The hydrogen-ion concentration was measured with a Radiometer 'pH 4' pH-meter fitted with glass and saturated calomel electrodes. The glass electrode was standardized before each titration with a Radiometer S 1001 (pH 6.5) buffer solution. Potentiometric titration curves were obtained for solutions containing (*i*) $HClO_4$, (*ii*) $HClO_4$ + H_2dmg, and (*iii*) $HClO_4$ + H_2dmg + Cu^{II}. Two sets of experiments were carried out, with H_2dmg : Cu^{II} = 2 : 1 and 1 : 1.

Kinetic Measurements.—These were carried out by following spectrophotometrically on a Beckmann DK-1A instrument the absorbance variations of solutions containing copper(II) sulphate and H_2dmg after the addition of peroxodisulphate. During the reaction the temperature was kept constant by circulating water through the cell holder. The ionic strength was maintained at 0.2 mol dm^{-3} (K[NO$_3$]). Peroxodisulphate solutions were freshly prepared, kept in the dark, and discarded when more than 5 h old. Potassium peroxodisulphate was a Merck pure product. Dimethylglyoxime, copper(II) solution, and buffer solution were mixed, in that order, just before each experiment. The complex solutions (2 cm^3), in a cuvette of 1-cm path length, were allowed to attain thermal equilibrium in the cell compartment and peroxodisulphate solutions were added by rapidly discharging the contents of Pederson pipettes (1—5 μl) using a nitrogen jet. Alternatively, two-compartment cells were used. Several sets of experiments were carried out at pH 10.90 and 7.90. For the former, the pH was adjusted with a mixture of Na[HCO$_3$] and Na$_2$[CO$_3$] as buffer and in the latter with H_3BO_3–Na[OH].

E.s.r. measurements were carried out on a Varian E 9 spectrometer equipped with a V 4557 liquid-nitrogen attachment. Diphenylpicrylhydrazyl (dpph) and Field-dial calibration were used.

RESULTS

Species present in Aqueous Cu^{II}–H_2dmg *Solutions.*—In order to interpret the kinetic data it is necessary to establish which species are present (predominantly) at different concentrations and pH. According to Vänngård and his

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[1] F. J. Welcher, 'Organic Analytical Reagents,' D. Van Nostrand, New York, 1955, vol. 3, p. 211.

[2] G. Schwarzenbach, 'Die Komplexometrische Titration,' Ferdinand Enke, Stuttgart, 1955, p. 68.

[3] A. I. Vogel, 'Quantitative Inorganic Analysis,' Longmans, London, 1951, p. 234.

co-workers,[4] up to pH *ca.* 11 the species present in $Cu^{II} : H_2dmg = 1 : 2$ solutions is $[Cu(Hdmg)_2]$, as deduced from the e.s.r. spectra of frozen solutions. Between pH 11.6 and 14.6, at the same mol ratio, the changes in e.s.r. spectra indicate that the planar structure of $[Cu(Hdmg)_2]$ is broken to give $[Cu(Hdmg)(OH)_y(OH_2)_x]^{y-}$ $(x + y \leqslant 4)$. Earlier solvent-extraction studies [5] led to the conclusion that species other than $[Cu(Hdmg)_2]$ are not present at pH <7.

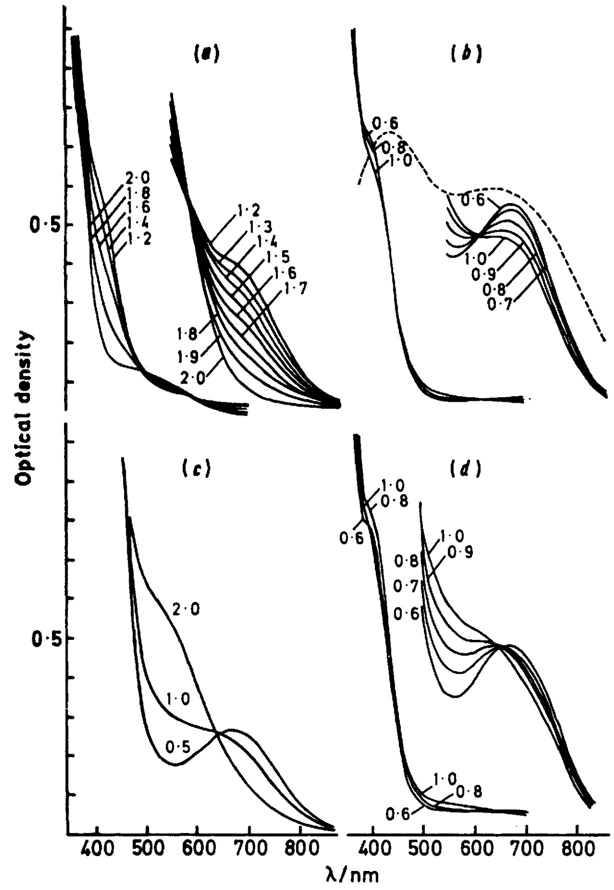

FIGURE 1 Visible spectra of solutions containing copper(II) sulphate (1.0×10^{-3} mol dm^{-3}) and different amounts of H_2dmg at pH 7.90 (upper curves) and 10.90. The numbers refer to moles of H_2dmg per mol of copper. Cell path length: 1 and 10 cm for (*a*), (*b*), and (*d*); 5 cm for (*c*). The broken line in (*b*) is the reflectance spectrum of $[\{Cu(Hdmg)(OH)\}_4]$

The e.s.r. measurements were repeated at both room and liquid-nitrogen temperature for the ratios $Cu^{II} : H_2dmg = 1 : 2$, $1 : 1$, and $1 : 0.5$ for pH $\leqslant 10.9$. In all cases, only a single signal was found, typical of a $[CuN_4]$ species, with the same slight shifts as found by Vänngård and his co-workers. However, there were considerable changes in intensity on varying the $Cu^{II} : H_2dmg$ ratio which arouses suspicion that further, ' e.s.r.-silent,' species may be present. The weakest spectra were obtained for $Cu^{II} : H_2dmg = 1 : 0.5$ at pH 7.9 and 10.9. (*g* and *A* values are not reported since they are virtually identical to those in ref. 4.)

The optical spectra confirm that other species are present. At $Cu^{II} : H_2dmg = 1 : 2$ and pH 7.90, a band at 458 nm with a shoulder at 505 nm was observed. This may be compared with a band at 520 nm in the reflectance and in the single-crystal spectrum of $[Cu(Hdmg)_2]$; [6] the difference is presumably due to weak co-ordination of water.[7] The crystal structure of $[Cu(Hdmg)_2]$ shows it to consist of dimers, the free oxime oxygens being co-ordinated to a second Cu^{II} at relatively short distances [Cu–O(axial) 2.30 Å] to give a five-co-ordinate structure.[8] Addition of Cu^{II} to this complex, still at pH 7.90, gives rise to a further species, characterized by bands at 680 and 410 nm, in equilibrium with $[Cu(Hdmg)_2]$, showing two clear isosbestic points at 585 and 490 nm corresponding to a 1 : 1 mol ratio. At $Cu^{II} : H_2dmg = 1 : 0.5$ (pH 7.90) the band at 680 nm increased in intensity, giving isosbestic points with that of the 1 : 1 species at 610 and *ca.* 445 nm. At pH 10.90 no isosbestic points were found when the $Cu^{II} : H_2dmg$ ratio increased from 0.5 to 1. At higher ratios the system behaved as at pH 7.90 [Figure 1(*d*)].

Confirmation of this conclusion comes from the variations in the ligand bands on addition of Cu^{II} (Figure 2). At $Cu^{II} : H_2dmg = 1 : 2$ and pH 7.90, the band at 225 nm, assigned to a $\pi^* \leftarrow \pi$ transition of *trans*-H_2dmg,[9] was almost halved in intensity (from ε 13 600 to 7 600 $dm^3 mol^{-1} cm^{-}$). At $Cu^{II} : H_2dmg = 1$ there was no change in this band and a new band appeared at 320 nm. At $Cu^{II} : H_2dmg = 1 : 0.5$, the band at 320 nm remained high in intensity and a further band appeared at 245 nm. The fact that the energy and intensity of the transition at 225 nm do not change indicates that (*i*) H_2dmg is always co-ordinated

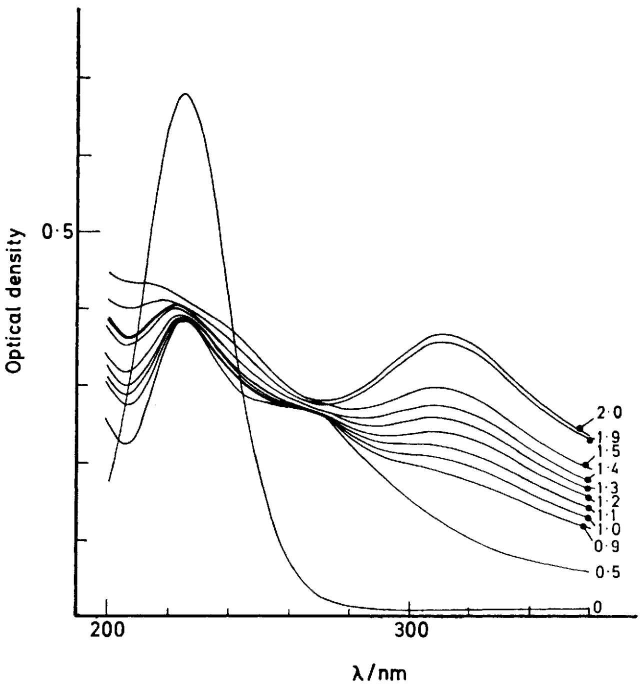

FIGURE 2 Spectrophotometric variation on the addition of copper(II) sulphate to H_2dmg (10^{-3} mol dm^{-3} at pH 7.90). The numbers refer to moles of Cu^{II} per mol of H_2dmg. Cell path length 0.1 cm

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[4] R. E. Falk, E. Ivanova, B. Roos, and T. Vänngård, *Inorg. Chem.*, 1970, **9**, 556.

[5] D. Dyrssen and M. Hennichs, *Acta Chem. Scand.*, 1961, **15**, 47.

[6] S. Yamada and R. Tsushida, *J. Amer. Chem. Soc.*, 1953, **75**, 6351.

[7] B. J. Hathaway, *Structure and Bonding*, 1973, **14**, 49.

[8] A. Vaciago and L. Zambonelli, *J. Chem. Soc.* (*A*), 1970, 218.

[9] M. Bossa and G. Morpurgo, *Ricerca Sci.*, 1967, **37**, 1131.

as a bidentate ligand and (*ii*), apart from the species $[Cu(Hdmg)_2]$ and $[Cu_2(Hdmg)]^{3+}$, at a 1 : 1 ratio there also exists $[Cu(Hdmg)]^+$.

Isolation of Solid Species.—Addition of an electrolyte such as $Na_2[SO_4]$, $Na[O_2CMe]$, NaI, or $Na[ClO_4]$ to slightly alkaline solutions (pH 8—10) with $[Cu^{II}] = [H_2dmg] = 4 \times 10^{-4}$ *mol dm*$^{-3}$ gave a green-brown flocculent precipitate on standing. This compound was separated by centrifugation, washed with water, and dried ***in vacuo***. It is almost insoluble in water. Its reflectance spectrum is very similar to that of $Cu^{II} : H_2dmg = 1 : 1$ solutions at pH *ca.* 8 (Figure 1). The i.r. spectrum in Nujol mull showed a strong double peak at 490, 505 cm^{-1} and a band at 455 cm^{-1}, in addition to most of the bands of $[Cu(Hdmg)_2]$.[10] Elemental analysis gave in the best case: C, 23.2; H, 3.85; N, 13.15% {Calc. for [Cu(Hdmg)(OH)]: C, 24.6; H, 4.1; N, 14.3%}; other analyses gave a lower $[Hdmg]^-$ content.

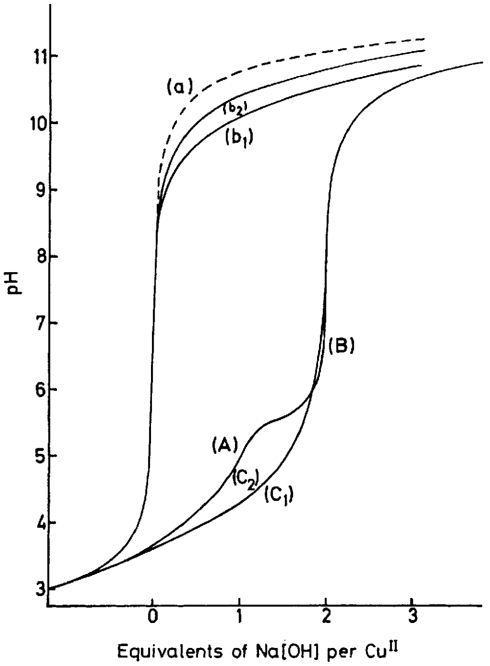

FIGURE 3 Potentiometric titrations of solutions containing: $HClO_4$ (*a*); $HClO_4$, Cu^{2+} and H_2dmg in 1 : 2 ratio (C_1); $HClO_4$, Cu^{2+} and H_2dmg in 1 : 1 ratio (C_2). Curve (b_1) is the reference for (C_1) and (b_2) that for (C_2)

Using glyoxime (H_2L) in place of H_2dmg, neutralization was sufficient to obtain a similar precipitate {Found: C, 14.55; H, 2.80; Cu, 38.0; N, 13.1. Calc. for [Cu(HL)(OH)]: C, 15.0; H, 2.5; Cu, 38.5; N, 12.5%}. This product has a strong i.r. band at 460 cm^{-1}. Infrared bands at *ca.* 500 cm^{-1} are believed to arise from the Cu–O modes of hydroxide groups bridging two copper atoms.[11] **CAUTION:** The complex [Cu(HL)(OH)] continuously loses weight up to 140—150 °C and then explodes.

Potentiometric Titrations.—Figure 3 shows the potentiometric-titration curves corresponding to cases (*i*)—(*iii*) (see Experimental section). Curve (C_1), for $[H_2dmg] : [Cu^{II}] = 2 : 1$, shows an inflection when 2 mol of base per mol of Cu^{II} are added. The overall equilibrium in the buffer zone can then be written as below. Following a treatment

$$Cu^{2+} + 2H_2dmg \rightleftharpoons [Cu(Hdmg)_2] + 2H^+$$

developed by Irving and Rossotti,[12] $\bar{n}_A$, the average number of protons bound to the ligand (in the present case, $[Hdmg]^-$) may be used to calculate $\bar{n}$, the average number of ligands per copper(II) ion. It was found that $\bar{n}$ was a function of $[Hdmg^-]$ but not of $[Cu^{II}]$, *i.e.* only mononuclear complexes are present in these solutions. The stability constant of the complex was determined by a graphical method.[13] The results showed that no appreciable amount of $[Cu(Hdmg)]^+$ is present and that $[Cu^{II}(Hdmg)_2]$ is predominant in solution. A value of $\log \beta_2 = 18.65$ was obtained, in reasonable agreement with that (19.24) obtained by solvent-extraction methods [5] considering that the two values relate to solutions of different ionic strengths.

When solutions containing Cu^{II} and H_2dmg in a 1 : 1 ratio were titrated a point of inflection (A) was found in the titration curve in the pH 5.5—6.0 region, depending on the copper concentration. Point (A) corresponds to one $[OH]^-$ per copper ion and the colour of the solution was brown. On adding more alkali up to two $[OH]^-$ per copper ion, a second point of inflection, (B), was found and the solution became green-brown. For copper concentrations greater than 0.8×10^{-3} mol dm^{-3} a faint opalescence formed, which disappeared on addition of more alkali (pH >8).

Up to point (A) the reaction taking place is assumed to be the same as that occurring with a 1 : 2 ratio of $[Cu^{II}] : [H_2dmg]$ and the data were treated accordingly. The values so obtained for $\log \beta_2$ at several copper concentrations are collected in Table 1. At the lower concentrations the values closely approximate those obtained previously, but an increasing difference is found with increasing concentration of copper. This suggests that a hydrogen-dissociation-dependent polymerization also occurs. Since one more mol of base per mol of Cu^{II} is needed to reach point (B) in the titration curve, reaction (1) may be considered.[13-16] Applying the law of mass action to (1)

TABLE 1

Dependence of $\log \beta_2$ on copper concentration (mol dm^{-3})

$10^3[Cu^{2+}] = 10^3[H_2dmg]$	$\log \beta_2$
1.0	19.48
0.8	19.43
0.5	19.40
0.2	19.36
0.1	19.25

$$n[Cu(Hdmg)_2] + nCu^{2+} + nH_2O \rightleftharpoons [\{Cu(Hdmg)(OH)\}_{2n}] + 2nH^+ \quad (1)$$

gives (2) assuming that $[Cu^{2+}] = [Cu(Hdmg)_2]$. The total

$$K_{2n} = [\{Cu(Hdmg)(OH)\}_{2n}][H^+]^{2n}/[Cu^{2+}]^{2n} \quad (2)$$

concentration of copper is given by (3). Combining (2)

$$c_{Cu} = 2n[\{Cu(Hdmg)(OH)\}_{2n}] + [Cu^{2+}] \quad (3)$$

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[10] J. E. Caton, jun., and C. V. Banks, *Inorg. Chem.*, 1967, **9**, 1670.

[11] V. Baran, *Co-ordination Chem. Rev.*, 1971, **6**, 65 and refs. therein.

[12] H. M. Irving and H. S. Rossotti, *J. Chem. Soc.*, 1954, 2904.

[13] L. G. Sillèn, *Acta Chem. Scand.*, 1954, **8**, 299, 318.

[14] S. Hietanen and L. G. Sillèn, *Acta Chem. Scand.*, 1954, **8**, 1607.

[15] R. L. Gustafson, L. F. Richards, and A. E. Martell, *J. Amer. Chem. Soc.*, 1960, **83**, 1526.

[16] K. S. Rajan and A. E. Martell, *J. Inorg. Nuclear Chem.*, 1964, **26**, 1927.

and (3) we obtain (4). Assuming that a single polymer

$$K_{2n} = (c_{Cu} - [Cu^{2+}])[H^+]^{2n}/2n[Cu^{2+}]^{2n} \qquad (4)$$

exists in solution, it may be shown that, at constant $\bar{z}$ (the average number of hydroxide ions which react per metal ion in the formation of a metal complex) $c_{Cu}/[Cu^{2+}] = X$ is a constant. Multiplying both sides of (4) by c_{Cu}^{2n-1}

$$K_{2n}c_{Cu}^{2n-1} = [(X - 1)/2n]X^{2n-1}[H^+]^{2n} \qquad (5)$$

gives (5) and thence (6).

$$\left(\frac{\log c_{Cu}}{\log [H^+]}\right)_{\bar{z}} = \frac{2\bar{n}}{2\bar{n} - 1} \qquad (6)$$

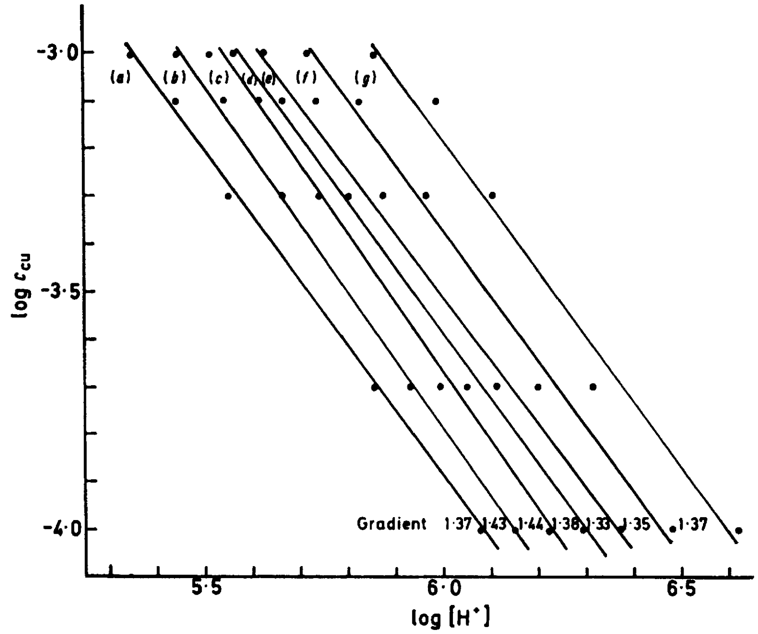

FIGURE 4 log c_{Cu} as a function of log[H⁺]; $\bar{z}$ = 0.2 (*a*), 0.3 (*b*), 0.4 (*c*), 0.5 (*d*), 0.6 (*e*), 0.7 (*f*), and 0.8 (*g*)

A plot of $-\log[H^+]$ against $-\log c_{Cu}$ at constant z gave a straight line of gradient $2\bar{n}/(2\bar{n} - 1)$ (Figure 4).* The average gradient was 1.38 ± 0.07. The value of 1.333, which would be obtained by substituting $\bar{n} = 2$ into equation (6), is the closest to that obtained experimentally. This suggests that the main species is a tetramer of formula $[\{Cu(Hdmg)(OH)\}_4]$, in the region (A)—(B). In order to test this conclusion, we assumed that only the tetramer is present. Equation (1) can then be rewritten as (7), and

$$2[Cu(Hdmg)_2] + 2Cu^{2+} + 4H_2O \overset{K_7}{\rightleftharpoons} [\{Cu(Hdmg)(OH)\}_4] + 4H^+ \qquad (7)$$

the equilibrium constant K_7 is obtained from equations (8)—(10). Values of K_7, calculated using equation (10) at

$$K_7 = [\{Cu(Hdmg)(OH)\}_4][H^+]^4/[Cu^{2+}]^4 \qquad (8)$$

$$\bar{z} = \frac{4[\{Cu(Hdmg)(OH)\}_4]}{2[Cu(Hdmg)_2] + [\{Cu(Hdmg)(OH)\}_4]} \qquad (9)$$

$$K_7 = \frac{16\bar{z}[H^+]^4}{\{2[Cu(Hdmg)_2] - [H^+]^3\}(4 - \bar{z})} \qquad (10)$$

various $\bar{z}$ and copper concentrations, are given in Table 2. The variations of the constant are in a definite direction, *i.e.* higher at higher $\bar{z}$, which indicates that the system is more complicated than that described by the simple equation (7). The low solubility of the compounds prevented a wider variation in concentration and a more detailed analysis is exceedingly difficult.

TABLE 2

Values of K_7 calculated at different $\bar{z}$ and copper concentrations

$10^3[Cu^{2+}]$/mol dm^{-3}	$\bar{z}$ 0.4	0.5	0.6	0.7	0.8
1.0	12.79	12.84	13.03	13.42	13.81
0.8	12.89	13.14	13.17	13.56	13.09
0.5	12.81	12.94	13.13	13.51	13.89
0.2	12.41	12.64	12.79	13.13	13.43
0.1	12.63	12.84	13.05	13.48	13.89

Oxidation Reactions of Cu^{II}–H_2dmg *Complexes*.—The oxidation by peroxodisulphate of solutions containing a constant concentration of copper was dependent on the hydrogen-ion and H_2dmg concentrations. At pH 7.90 a very intense band appeared at 520 nm, while at pH 10.90 the spectrum was characterized by a strong band at 950 nm. In the range pH 7.90—10.90 both bands were present. A Cu^{II} : H_2dmg molar ratio of 1 : 1 gave the maximum intensity of the colours at a given time and pH. The variations in band intensity with time was dependent on the initial concentration of the oxidizing agent. Figure 5 shows the intensity variations of the band at 950 nm (pH 10.90) with time, at fixed concentrations of copper and ligand, for different additions of $[S_2O_8]^{2-}$. The band at 520 nm behaved similarly. In both cases the absorbance increased with time at the beginning (formation curve),

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* $\bar{z} = \bar{n} - 1$ is obtained by considering that the total number of Na[OH] equivalents per copper ion is two at pH ≃ 6 (*i.e.* $\bar{n} = 2$): one equivalent is required for the formation of $[Cu(Hdmg)_2]$ while consuming all the H_2dmg and only half of the total copper, the other being used to form the olate complex.

reached a maximum, and then decreased (decay or decomposition curve).

Stoicheiometry. The dependence of the decomposition rates on peroxodisulphate concentration, measured from the gradient of the decomposition curve at fixed absorbance, was linear for the kinetics at both pH 7.90 and 10.90. By extrapolation, it was found that the zero decomposition rate was reached when 1 mol of peroxodisulphate had been added per 4 mol of copper, *i.e.* one out of two copper ions is oxidized if the oxidizing agent acts as a two-electron acceptor. One equivalent of $[OH]^-$ per two copper ions is also required to keep the pH of an unbuffered solution constant at the value of 10.90 during the oxidation reaction. Thus (assuming that the species oxidized is the tetramer), and omitting the ligands for clarity, the stoicheiometry is as in (11).

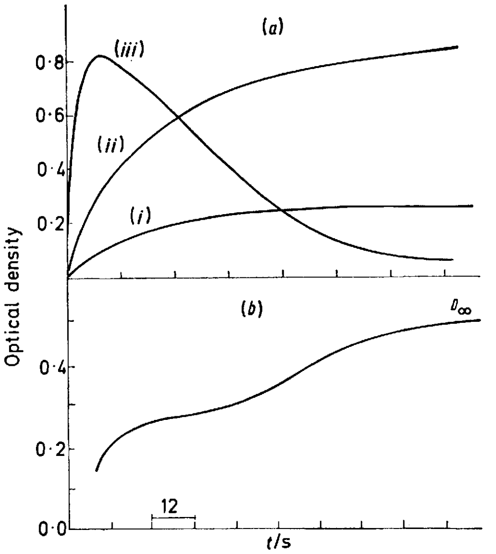

FIGURE 5 (*a*) Optical-density changes on oxidation of $[Cu^{2+}] = [H_2dmg] = 3.0 \times 10^{-4}$ mol dm^{-3} solutions at pH 10.90. Peroxodisulphate concentration = 0.11×10^{-4} (*i*), 0.75×10^{-4} (*ii*), and 6.0×10^{-4} mol dm^{-3} (*iii*). (*b*) Optical-density changes at 950 nm during oxidation at 7 °C. $[Cu^{2+}] = [H_2dmg] = 3.0 \times 10^{-4}$ mol dm^{-3}, $[S_2O_8^{2-}] = 6.0 \times 10^{-3}$ mol dm^{-3}, pH 10.90

$$(Cu^{II})_4 + [S_2O_8]^{2-} \longrightarrow (Cu^{II}{}_2{\cdot}Cu^{III}{}_2) + 2[SO_4]^{2-} + 2H^+ \quad (11)$$

Oxidation reactions in the presence of excess of copper at pH 10.90. *Formation.* The optical density (*D*) of solutions containing $[S_2O_8^{2-}] = 0.15 \times 10^{-4}$ mol dm^{-3} and equimolar concentrations of copper and H_2dmg in the range 4×10^{-4}—12.5×10^{-4} mol dm^{-3} appeared to increase with time up to a constant value (D_∞). No appreciable decomposition was found under these experimental conditions. Plots of $\ln(D_\infty - D_t)$ against time were linear to at least 80% completion of the formation reaction. The reaction appears to be pseudo-first order in $[S_2O_8^{2-}]$. The quantity $1/k_{obs.}$ ($k_{obs.}$ = pseudo-first-order constant, see Table 3) varied linearly with $1/[Cu^{2+}]^2$, as shown from plots of the data in Table 4, thus indicating a complex reaction mechanism. A mechanism which fits the experimental data is [17] as in equations (12)—(14). Here (D) is the oxidized product which absorbs at 950 nm. For conditions such that the

TABLE 3

Pseudo-first-order constants ($k_{obs.}$) * for the oxidation reaction (formation) at different temperatures and copper concentrations ($[Cu^{2+}] : [H_2dmg] = 1 : 1$, $[S_2O_8^{2-}] = 0.15 \times 10^{-4}$ mol dm^{-3}, pH 10.90)

$\frac{10^4[Cu^{2+}]}{mol\ dm^{-3}}$	$10^3k_{obs.}/s^{-1}$				
	15	21	31	41	51 °C
3.00		1.79			
3.50		1.83			
4.00		2.04	3.49	5.27	8.27
5.00		2.75	4.42	7.73	9.73
6.00	3.08	3.98	6.70	9.00	13.80
6.75			7.65	11.30	14.70
6.95	3.32	4.80			
7.50		5.55			
8.00	4.53	5.87	10.00	14.90	19.60
8.34		7.00			
9.00		7.82			
10.00	6.65	8.70	14.00	18.20	26.60
11.00		10.70			
12.00	8.65	12.00	17.80	26.20	31.50
12.50		12.80			

* Maximum error ±6% for the slower runs (*i.e.* those at 15 and 21 °C) and 3—4% for the others.

TABLE 4

Variation of the electron-exchange rate constant with temperature

$\frac{\theta_c}{°C}$	10^3k_1	10^3k_2
	s^{-1}	
15.0	28.0	
21.0	37.0	3.5
31.0	30.0	7.8
41.0	37.0	23.9
51.0	40.0	44.1

$$\underset{(A)}{2[\{Cu(Hdmg)(OH)\}_2]} \overset{K_1}{\rightleftharpoons} \underset{(B)}{[\{Cu(Hdmg)(OH)\}_4]} \quad (12)$$

$$[\{Cu(Hdmg)(OH)\}_4] + [S_2O_8]^{2-} \overset{K_2}{\rightleftharpoons} \underset{(C)}{([\{Cu(Hdmg)(OH)\}_4]{\cdot}S_2O_8)} \quad (13)$$

$$([\{Cu(Hdmg)(OH)\}_4]{\cdot}S_2O_8) \xrightarrow{k_1} \underset{(D)}{2[Cu^{II}Cu^{III}(Hdmg)_2(OH)_2]} + 2[SO_4]^{2-} + 2H^+ \quad (14)$$

concentration of (B) is small with respect to that of (A) (*i.e.* pH 10.90), equation (15) is applicable and k_1 and K_1K_2 may

$$1/k_{obs.} = (1/k_1K_1K_2[(D)]^2) + (1/k_1) \qquad (15)$$

be calculated from the intercept and gradients of the plots obtained from the data in Table 4.

Oxidation reactions in the presence of excess of peroxodisulphate. (*a*) *Formation.* When peroxodisulphate was in large excess ($[Cu^{2+}] = [H_2dmg] = 3 \times 10^{-4}$, $[S_2O_8^{2-}] = 25 \times 10^{-4}$—$90 \times 10^{-4}$ mol dm^{-3}) the kinetic curves appeared as in Figure 5. The species (D) forms in two sequential and well separated steps. The height of each step is one sixth of that calculated assuming complete formation of this species in the absence of decomposition. On decreasing the excess of peroxodisulphate to $< 25 \times 10^{-4}$ mol dm^{-3}, the kinetic behaviour described in equation (2) was gradually approached. These observations can be explained by assuming that each molecule of (B) reacts with

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[17] E. C. Ashby, R. B. Duke, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1967, **89**, 1964.

$[S_2O_8]^{2-}$ according to the following reaction scheme, where $Cu^{2+}(X)$ is an unidentified species containing two Cu^{2+} and two $Hdmg^-$:

$$(B) + [S_2O_8]^{2-} \longrightarrow (D) + Cu^{2+}(X) \qquad (16)$$

$$Cu^{2+}(X) + [S_2O_8]^{2-} \longrightarrow (D) \qquad (17)$$

$$(D) + [S_2O_8]^{2-} \longrightarrow \text{decomposition products} \qquad (18)$$

(*b*) *Decomposition*. The concentration of peroxodisulphate was varied in the range 6×10^{-4}—50×10^{-4} mol dm^{-3} for $[Cu^{2+}] = [H_2dmg] = 3 \times 10^{-4}$ mol dm^{-3}. A linear relation between $\ln D_{(D)}$ and time was found for values far from the maximum of the kinetic plot. The reciprocal of the pseudo-first-order rate constant, $1/k_{obs.}'$, varied linearly with $1/([S_2O_8{}^{2-}] - 1.5 \times 10^{-4})$,* which suggests a decomposition mechanism of the type in equations

$$(D) + [S_2O_8]^{2-} \overset{K_3}{\rightleftharpoons} [(D)\cdot S_2O_8] \qquad (19)$$

$$[(D)\cdot S_2O_8] \xrightarrow{k_2} \text{decomposition products} \qquad (20)$$

(19) and (20) for which $1/k_{obs.}' = (1/k_2K_3[S_2O_8{}^{2-}]) + (1/k_2)$, in agreement with the data in Table 5.

TABLE 5

Pseudo-first-order constants ($k_{obs.}'$) * for the oxidation reaction (decomposition) at different temperatures and peroxodisulphate concentrations ($[Cu^{2+}] = [H_2dmg] = 3.0 \times 10^{-4}$ mol dm^{-3}, pH 10.90)

$\frac{10^4[S_2O_8{}^{2-}]}{\text{mol dm}^{-3}}$	$10^4k_{obs.}/s^{-1}$			
	21	31	41	51 °C
6.5	13.5			
7.0		39.0	108	274
7.4	15.2			
8.0		46.0	110	296
9.0	15.5	54.2	118	236
10.0	17.6	54.2	128	300
15.0	21.2	61.5	148	372
18.0	22.9	58.0	146	340
20.0		56.0	176	500
21.0	23.7			
24.0	25.5			
25.0		64.5	179	480
30.0	28.8	57.0	205	356
39.0	29.7			
40.0		68.0	212	430
50.0	32.2	129	210	300

* Maximum error ±6% for the slower runs (those at 21 and 31 °C) and ⩽4% for the others.

(*c*) *Effect of acrylonitrile*. To determine the presence of $[SO_4]^-$ or $[S_2O_8]^-$ during the oxidation reaction, kinetic runs were conducted in the presence of acrylonitrile which is an effective scavenger of free radicals.[18] Neither in excess of copper ions ($[Cu^{2+}] = [H_2dmg] = 10^{-3}$, $[S_2O_8{}^{2-}] = 0.3 \times 10^{-4}$, acrylonitrile = 0.5 mol dm^{-3}, 21 °C) nor in excess of peroxodisulphate ($[Cu^{2+}] = [H_2dmg] = 3.0 \times 10^{-4}$, $[S_2O_8{}^{2-}] = 7 \times 10^{-4}$—$50 \times 10^{-4}$, [acrylonitrile] = 0.6 mol dm^{-3}, 7 °C) were appreciable changes detected. The 'two-step' kinetic runs obtained with large excesses of peroxodisulphate were not altered by the presence of acrylonitrile. The maximum quantity of oxidized product, as measured by $D_{(D)}$ at the top of the second step in Figure 5(*b*) was the same as in the absence of acrylonitrile. E.s.r. spectra of frozen and then thawed samples also gave no evidence of radical formation.

Activation parameters. The activation parameters were calculated from Arrhenius plots obtained from the data in Tables 4 and 5. For reaction (14), $E^{\ddagger} = 3.5 \pm 1.7$ kcal mol^{-1} † and $\Delta S^{\ddagger} = -58 \pm 3$ cal K^{-1} mol^{-1}; for reaction (20), $E^{\ddagger} = 16.2 \pm 1.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -17 \pm 5$ cal K^{-1} mol^{-1}.

Oxidation reactions in the presence of excess of peroxodisulphate at pH 7.90 (70 °C). (*a*) *Formation*. At a given excess of peroxodisulphate a plot of the reaction rate, v_0, as measured by the gradient of the tangent (ΔD s^{-1}) to the *D vs. t* plots of species absorbing at 520 nm (E) at $t = 0$, against the peroxodisulphate concentration was hyperbolic (Table 6). However, if the assumption was made that the formation is a pseudo-first-order reaction, and the reactions are as in (21) and (22) [(E) is a species similar to (D) but

$$(B) + [S_2O_8]^{2-} \overset{K_4}{\rightleftharpoons} [(B)\cdot S_2O_8] \qquad (21)$$

$$[(B)\cdot S_2O_8] \xrightarrow{k_3} (E) \qquad (22)$$

further protonated, see below], then we obtain (23) where

$$v_0 = k_3K_4[S_2O_8{}^{2-}]D_\infty/(1 + K_4[S_2O_8{}^{2-}]) \qquad (23)$$

D_∞ = optical density of (E) at $t = \infty$ in the absence of decomposition [$D_\infty = 1$ (extrapolated value) for the 0.8750-cm cells used in this work]. Rewriting equation (23) as (24) and plotting D_∞/v_0 against $1/[S_2O_8{}^{2-}]$, a straight

$$\frac{D_\infty}{v_0} = \frac{1}{k_3K_4[S_2O_8{}^{2-}]} + \frac{1}{k_3} \qquad (24)$$

line with an intercept was obtained. The value of k_3 was obtained. The value of k_3 was 4.98×10^{-2} s^{-1} and $K_4 = 243$ dm^3 mol^{-1}.

(*b*) *Decomposition*. The reactions are first order in [(E)] since $\ln D_{(E)}$ was linearly related to time for points of the kinetic plots not in the proximity of the maximum. A plot of the reciprocal of the pseudo-first-order rate

TABLE 6

Oxidation reaction at pH 7.90. Dependence of the function D_∞/v_0 (formation) and of $k_{obs.}'$ (decomposition) on the initial peroxodisulphate concentration ($[Cu^{2+}] = [H_2dmg] = 3.0 \times 10^{-4}$ mol dm^{-3}, 11 °C)

$\frac{10^4[S_2O_8{}^{2-}]}{\text{mol dm}^{-3}}$	D_∞/v_0	$10^3k_{obs.}'/s^{-1}$
7.5	97.8	
9.0	82.8	3.30
10.0	77.8	3.70
11.0	65.7	4.17
15.0	54.0	4.80
20.0	43.9	5.62
22.0	43.2	
24.0		5.80
25.0	38.6	5.97
27.0	37.0	6.45
30.0	33.6	6.60
40.0	31.7	7.35
50.0	29.3	7.65

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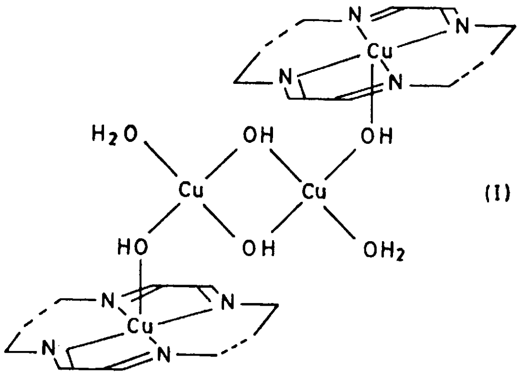
* The amount consumed in oxidizing the 1 : 1 Cu : H_2dmg complex in the formation reaction was subtracted from the initial peroxodisulphate concentration.

† Throughout this paper: 1 cal = 4.184 J. 1 B.M. ≈ 9.27×10^{-24} A m^2.

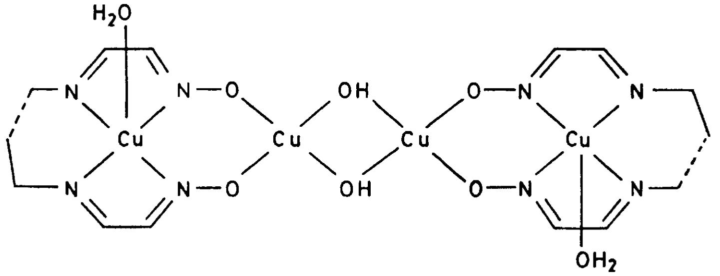
[18] M. Kolthoff, A. I. Medalia, and H. P. Raaen, *J. Amer. Chem. Soc.*, 1951, **73**, 1733.

constant $1/k_{obs.}$ against $1/([S_2O_8^{2-}] - 1.5 \times 10^{-4})$ (see footnote on p. 749) gave a straight line, suggesting a decomposition reaction similar to that found for (D); k_4 and K_5 were found to be 2.27×10^{-2} s^{-1} and 704 dm^3 mol^{-1}, respectively.

DISCUSSION



(I)



(II)

Many copper(II) chelate complexes with bidentate ligands form binuclear hydroxo-complexes, olates, often characterized by antiferromagnetic properties due to superexchange interaction.[19] The evidence for the existence of such a structure is strong and would also go some way to explaining the present oxidation mechanism. Two possible structures consistent with the spectroscopic results may be written for [{Cu(Hdmg)(OH)}$_4$]. Either structure would explain the appearance of an extra band at *ca.* 650 nm in the solution electronic spectrum, apart from the bands of [Cu(Hdmg)$_2$] itself. This band may be assigned as arising from a [CuO$_4$] chromophore (presumably with axially co-ordinated water molecules [20]). In order to explain the appearance of only one signal, that expected for [CuN$_4$], in the e.s.r. spectra under all experimental conditions, it must be assumed that the hydroxo-bridged part of the tetramer is e.s.r. ' silent.' {There was no evidence for $\Delta M_S = \pm 2$ transitions, in contrast to the situation present in solutions of [Cu(Hdmg)$_2$] in ethanol.[21]} Few bridged copper(II) complexes show this behaviour, although we note that it has recently been reported that [Cu$_2$(Hhpt)$_2$] (H$_3$hpt = heptane-2,4,6-trione), presumably having oxygen bridges, gives no detectable e.s.r. signal.[22] Unfortunately, the magnetic moment, measured for the analogous glyoxime complex (Table 7), is not that expected simply for 50% diamagnetic + 50% paramagnetic species, nor is the e.s.r. spectrum the same as that in solution. Further association may be present in the solid state. The solid is insoluble in water and even in co-ordinating organic solvents. Further speculation as to the structure is not warranted until crystals of the intermediate suitable for *X*-ray analysis can be obtained. However, the absence of any splitting in the i.r. (NO) stretching bands at 1 200 and 1 175 cm^{-1} favours structure (I).[20]

TABLE 7

Magnetic-susceptibility data for the separated copper–glyoxime solid

$\frac{T}{\text{K}}$	$\frac{10^3\chi_m}{\text{e.m. units}}$	$\frac{\mu}{\text{B.M.}}$
293.3	3.50	0.91
288.7	3.47	0.90
283.6	3.56	0.90
278.0	3.56	0.89
261.7	3.63	0.87
247.6	3.66	0.85
232.3	3.66	0.82
216.5	3.63	0.79
201.5	3.63	0.76
184.0	3.59	0.73
167.7	3.53	0.69
149.5	3.40	0.64
131.3	3.25	0.58
109.5	3.78	0.57
101.2	3.91	0.56
90.3	3.69	0.52

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[19] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.

[20] C. B. Singh and B. Sahoo, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1259.

[21] A. D. Toy, T. D. Smith, and J. R. Pilbrow, *Austral. J. Chem.*, 1973, **26**, 2349.

[22] A. B. Blake and L. R. Fraser, *J.C.S. Dalton*, 1974, 2554.

Turning to the oxidation by $[S_2O_8]^{2-}$, the mechanism at lower pH is similar to that at pH 10.90, but at pH 7.90 equilibrium (12) appears to be absent. Polynuclear hydroxo-complexes are known to undergo pH-dependent depolymerization reactions to form hydroxo-oxo- or only oxo-complexes of lower molecular weight.[11] Reaction (14) is suggested to be a two-electron exchange by peroxodisulphate. The extremely low activation energy of this oxidation may indicate that the apparent stabilization of the activated complex is due to partial electron transfer to two ' nascent ' sulphate ions instead of one, as occurs in the majority of cases.

According to Anbar,[23] oxidation reactions of copper complexes proceed *via* copper(III) species. This would be in agreement with the observation that a tetramer, (I) or (II), is present, *i.e.* it is improbable that Cu^{3+} would be stable in the presence of a reducing ligand such as $[Hdmg]^-$, were this present alone.

The low-energy bands in the electronic spectra of the oxidized species are presumably due to charge transfer (or intervalence transfer) involving the hydroxo- or oxo-groups. Charge-transfer bands are predicted to be more intense and of lower energy when the bridging groups are oxo-ligands, which is probably the case at the higher pH. In agreement with this, the absorption coefficients of the oxidized species at pH 7.90 and 10.90 are 8 400 (520) and 11 000 $dm^3\ mol^{-1}\ cm^{-1}$ (950 nm), respectively, per dimer.

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[6/626 *Received, 1st April,* 1976]

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[23] M. Anbar, in ' Mechanism of Inorganic Reactions,' ed. R. Gould, Amer. Chem. Soc., Washington, 1965.