Oxidation of Bis(phenanthroline)copper(I) Complexes by Molecular Oxygen in Nitromethane Solution

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The oxidation product of the reaction of $[Cu(Rphen)_2]ClO_4$ with oxygen in nitromethane solution (where Rphen = 1,10-phenanthroline, 5-methyl-1,10-phenanthroline, 5,6-dimethyl-1,10-phenanthroline, 5-chloro-1,10-phenanthroline) has been isolated and identified. These copper(II) complexes have a nitromethanide anion incorporated in the first co-ordination sphere. The electronic spectrum of $[Cu(Rphen)_2(CH_2NO_2)]ClO_4$ is consistent with a *cis*-distorted octahedral configuration.

FRESHLY prepared solutions of $[Cu(Rphen)_2]ClO_4$ in nitromethane are dark brown, with an absorption maximum in the visible region near 445 nm. The final visible spectrum of these solutions after oxygenation does not exhibit the 445 nm band, but the solutions absorb at 380, 685, and 1030 nm and are green in colour. Since the absorption maximum in the region 700—1000 nm corresponds typically to *d–d* transitions of copper(II) ion,[1] it is concluded that these complexes, like other copper(I) compounds, are sensitive to oxidation by molecular oxygen dissolved in the solvent.[2–6] No changes are observed if the solvent used to prepare the solution of copper(I) complex is previously saturated with nitrogen.

EXPERIMENTAL

Nitromethane used as solvent was from Matheson, Coleman, and Bell (Practical). It was purified by successive distillations under reduced pressure. Nitromethane saturated with air was used to dissolve the copper(I) complexes. After the reaction was completed, the solute was precipitated with benzene. The green precipitate was recrystallized from nitromethane. The complexes $[Cu(Rphen)_2]ClO_4$ and $[Cu(phen)_2](ClO_4)_2$ were prepared by the standard literature method.[7] 1,10-Phenanthroline used to prepare the complexes was from Aldrich and the substituted phenanthrolines were from G. Frederick Smith. Sodium–nitromethane was prepared by Nef's method from sodium ethoxide and nitromethane.[8]

TABLE 1

Analytical data for the complexes

Compound	Found (%) C	Found (%) H	Found (%) N	Found (%) Cu	Calculated (%) C	Calculated (%) H	Calculated (%) N	Calculated (%) Cu
$[Cu(phen)_2]ClO_4$	55·3	3·15	10·7	12·2	55·1	3·1	10·7	12·1
$[Cu(phen)_2(CH_2NO_2)]ClO_4$	51·2	3·05	11·9	10·3	51·4	3·1	12·0	10·9
$[Cu(5\text{-}Mephen)_2]ClO_4$	56·8	3·6	10·3	11·0	56·6	3·65	10·2	11·5
$[Cu(5\text{-}Mephen)_2(CH_2NO_2)]ClO_4$	53·6	3·75	11·4	10·1	53·2	3·55	11·3	10·2
$[Cu(5,6\text{-}Me_2phen)_2]ClO_4$	57·9	4·2	9·5	12·0	58·0	4·15	9·7	11·0
$[Cu(5,6\text{-}Me_2phen)_2(CH_2NO_2)]ClO_4$	55·5	4·05	10·3	11·0	54·4	4·1	10·9	9·9

Hydrogen, carbon, and nitrogen were determined with a Perkin-Elmer microanalyser. Copper was determined with a Perkin-Elmer 303 atomic absorption spectrophotometer (Table 1). Magnetic measurements were determined by the Gouy method at room temperature. The magnetic field was calibrated by use of $[Ni(en)_3]S_2O_3$ as standard. Diamagnetic corrections were calculated from Pascal's constants and magnetic moments from the expression $\mu_{\text{eff}} = (\chi_m T)^{1/2}$. Molar conductivities of freshly prepared solutions (10^{-3}M), in purified nitromethane, were determined with a Wayne–Kerr bridge.

Since $Cu[(Rphen)_2]ClO_4$ are stable to oxidation by molecular oxygen in the solid state, no special precautions were taken to record the i.r. spectra (KBr pellets). A Perkin-Elmer 421 spectrometer was used to obtain these spectra. The u.v. and visible spectra were recorded on a Unicam SP 8000, and on a Carl Zeiss spectrophotometer.

RESULTS AND DISCUSSION

The oxidation reaction is confirmed by the fact that the products are no longer diamagnetic (Table 2). The values obtained for the magnetic moments of the reaction products are similar to those reported previously in the literature for normal copper(II) complexes in general.[9,10] Here as in other cases the cupric ion exhibits a moment

TABLE 2

Molecular conductivities and magnetic moments of 1,10-phenanthroline complexes of copper

Compound	Conductivity Ω^{-1} cm^2 mol^{-1}	Magnetic moment B.M.
$[Cu(Rphen)_2](ClO_4)$ [a]	82—87	Diamagnetic
$[Cu(Rphen)_2(CH_2NO_2)](ClO_4)$	83—87	1·80—1·86
$[Cu(phen)_2](ClO_4)_2$	176 [b]	1·89—1·94 [b,c]

[a] Rphen = 1,10-phenanthroline,5-methyl-1,10-phenanthroline, 5,6-dimethyl-1,10-phenanthroline, 5-chloro-1,10-phenanthroline. [b] Ref. 9. [c] Ref. 10.

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somewhat above the spin-only value for the one unpaired electron configuration of d^9, 1·73 B.M. However, the isolated oxidation products possess molar conductivities in the range 83—87 Ω^{-1} cm^2 at 23 °C in 10^{-3}M nitromethane solution. These values are comparable with those of other univalent electrolytes in this solvent,[9] and are practically half those of the diperchlorate: $[Cu(phen)_2](ClO_4)_2$, (Table 2).

This apparent contradiction can only be explained by the fact that an anionic species has entered the first co-ordination sphere. The reaction product would then have the general formula $[Cu(Rphen)_2X]ClO_4$. The nature of X was determined by i.r. spectra. The spectra of the products have new maxima at 1550 and 1270 cm^{-1}, which are absent in the spectra of $[Cu(Rphen)_2]ClO_4$ and $[Cu(phen)_2](ClO_4)_2$. These bands can be assigned to vibrations of the NO_2 group, in the $CH_2NO_2^-$ ion.[11] The $CH_2NO_2^-$ is generated by the acid–base equilibrium: $CH_3NO_2 \rightleftharpoons CH_2NO_2^- + H^+$. This equilibrium would be displaced to the right, as the protons are consumed to form the products corresponding to the reduced molecular oxygen.

Therefore, the oxidation is followed by a reaction of the type.

$$[Cu(Rphen)_2]^{2+} + X^- \longrightarrow [Cu(Rphen)_2X]^+$$

where X is $CH_2NO_2^-$. To verify this step, the diperchlorate $[Cu(phen)_2](ClO_4)_2$ was made to react with sodium–nitromethane. The blue-green solution immediately turned green, and the visible spectrum was identical with that of the isolated product. The absorption maxima shifted from 735 to 685 nm, and from 890 to 1030 nm, thus indicating that the same species is formed.

TABLE 3

Electronic spectra

Absorbing species	Solvent	Band maxima/nm ($\bar{\nu}$/kK)		
$[Cu(phen)(OH_2)_{4-x}(solvent)_x]^{2+}$	Acetone [a]	700 (14·3)		
$[Cu(phen)_2(solvent)]^{2+}$	Acetone [a]	720 (13·9)	910 (11·0)	
	Acetonitrile	735 (13·6)	890 (11·2)	
	Nitromethane	735 (13·6)	890 (11·2)	380 (2·6)
$[Cu(phen)_2(CH_2NO_2)]^+$	Acetonitrile	685 (14·6)	1030 (9·7)	380 (2·6)
$[Cu(bipy)_2(ONO)]NO_3$	Solid [b]	685 (14·6)	1055 (9·5)	

[a] Ref. 22. [b] Ref. 20.

This type of reaction has been used before to obtain five-co-ordinate species of copper(II), X being Cl^-, Br^-, I^-, SCN^-, NO_2^-, $HCOO^-$, $MeCOO^-$ and $PhCOO^-$.[9] Therefore, the products of the oxidation reaction of the copper(I) complexes of phenanthroline in nitromethane solution could be five-co-ordinate species. This would be possible if the nitromethane ion acted as a monodentate ligand co-ordinating by one of its oxygens. The appearance of the 380 nm absorption band in the visible spectrum of the products indicates that the nitromethanate ion is co-ordinating through oxygen.[12] If the copper(II) complexes were really five-co-ordinate, they would be in the trigonal bipyramid configuration since a square pyramidal geometry is sterically hindered. Both trigonal bipyramid and square pyramidal configurations are known for five-co-ordinate compounds of copper(II),[13-19] though the latter is most common. In solution these compounds could easily be transformed to distorted octahedral species by attack of the solvent, since this type of equilibrium is energetically favourable.

However, nitromethane is known to co-ordinate both by one and by two of its oxygens.[12] If the nitromethane ion was acting as a chelate group, the configuration of the copper(II) complexes would be that of a *cis*-distorted octahedron. Unfortunately, a criterion based on the electronic spectrum, which was used in earlier work [20] to distinguish between these two stereochemistries, has been shown to be unreliable.[21]

It has been reported that the pseudo-octahedral monocomplex has its band maximum at 700 nm.[22] Therefore it is reasonable to assume that a distorted octahedral biscomplex would exhibit a maximum at higher energy because of the greater field produced by the second phenanthroline molecule. The visible spectrum of $[Cu(phen)_2(solvent)]^{2+}$ shows instead, that the higher energy transition of the bis-complex lies 400—700 cm^{-1} lower than in the spectrum of the mono-complex (Table 3), and this strongly suggests that the band is not due to an octahedral complex. This complex is assigned a trigonal bipyramid structure.[22] The high energy transition of $[Cu(phen)_2(solvent)]^{2+}$ lies somewhat below than that of $[Cu(phen)_2(CH_2NO_2)]^+$ which can be used as evidence to assign a distorted octahedral configuration to $[Cu(phen)_2(CH_2NO_2)]^+$.

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Finally, the visible spectrum of $[Cu(phen)_2(CH_2NO_2)]^+$ is very similar to that of $[Cu(bipy)_2(ONO)]NO_3$ (Table 3). The latter is known from crystallographic data to have a distorted octahedral stereochemistry.[23] Therefore, the close similarity of the solution spectra and the reflectance spectra suggests that the stereochemistry of the copper(II) ion is the same in both cases.

The reaction studied is an example of a redox reaction with a change in geometry of the complex, since the copper(I) compound is tetrahedral.[24] Kinetic studies of this reaction are in progress.

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