

Oxidation of a Nitronyl Nitroxide by Copper(II) Ions: Synthesis and X-Ray Diffraction Characterization of 4,4,5,5-Tetramethyl-1-oxo-2-phenyl-4,5-dihydroimidazolium Perchlorate *N*(3)-Oxide

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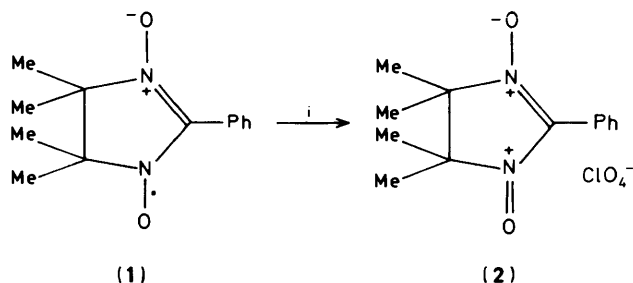
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In contrast to most transition-metal salts, copper perchlorate in acetonitrile oxidizes the nitronyl nitroxide radical (1) to the corresponding nitrosonium perchlorate (2) which is easily isolated in very good yield. Although more stable than the dialkyl analogues and thus easier to handle, this compound has all the oxidizing properties known for nitrosonium cations. Compound (2) has been characterized the X-ray diffraction. The structural data show equivalent N=O bond lengths of 1.225(4) Å and will be of great value in determining the oxidation state of the NO group in structurally characterized nitroxyl-metal complexes.

Nitroxyl free radicals are in an oxidation state intermediate between the hydroxylamino anion and the nitrosonium cation.^{1,2} The conversion of nitroxides into each of these species is well documented,^{1,2} and the synthesis of the corresponding nitrosonium cations especially has received much attention, as they are versatile reagents for the oxidation of organic substrates.¹⁻⁵ The properties of the hydroxylamine-nitroxyl-nitrosonium redox cycle have also been used to design electrochemical^{6,7} as well as chemical⁸ catalytic systems for the oxidation of the alcohols.

Recently Semmelhack⁸ has described such a catalytic system involving copper chloride and nitroxides, for the oxidation of alcohols to carbonyl compounds. The oxidizing species is assumed to be the nitrosonium ion obtained by electron transfer from the nitroxide to the copper(II) ion; copper(I) is then reoxidized to copper(II) by molecular oxygen. Although the oxidation of nitroxides into nitrosonium cations by some metal ions has been reported,⁹⁻¹¹ this was the first report of Cu^{II} providing this conversion.

We have long been involved in the synthesis and the study of copper-nitroxyl bound species and we recently reported the preparation of the adduct of copper chloride with 4,4,5,5-tetramethyl-2-phenyl-4,5-dihydroimidazol-1-oxyl 3-oxide (1).¹² This complex is a three-spin system in which the nitroxyl ligands have retained their free-radical character. The unusual magnetic properties exhibited by this compound prompted us to explore the possibility of modifying these properties by changing the chemical structure—especially the counter ions—around the copper atom. When copper(II) perchlorate was used in the place of copper chloride, 4,4,5,5-tetramethyl-1-oxo-2-phenyl-4,5-dihydroimidazolium perchlorate *N*(3)-oxide (2) was obtained (Scheme 1).



Scheme 1. Reagents: i, Cu(ClO₄)₂·6 H₂O in acetonitrile

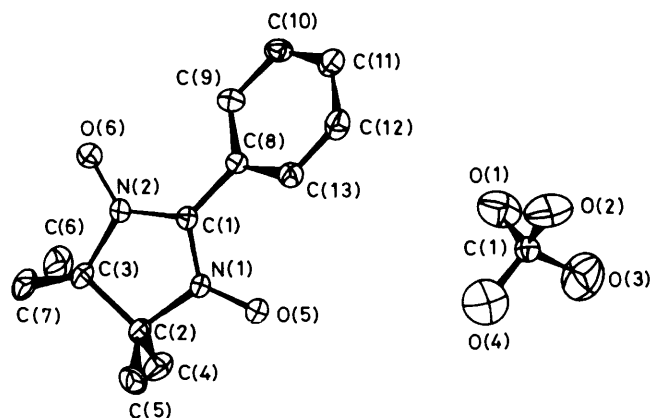


Figure 1. ORTEP representation of the three-dimensional X-ray structure of (2)

Discussion

Nitrosonium ions are generally prepared by use of strong oxidizing species such as *m*-chloroperbenzoic acid,^{4,5} or halogens.¹⁷ As shown by electrochemical studies, the conversion of the nitroxyl into the corresponding nitrosonium species requires a potential of only *ca.* +0.4 V (*vs.* Ag/AgNO₃).^{6,18} This value is much below the one reported for the Cu^I/Cu^{II} couple for solutions of Cu(ClO₄)₂ in acetonitrile.¹⁹ Therefore the nitrosonium salt is the expected product of the reaction of nitroxide free radicals with copper perchlorate. The easy isolation of the compound as reported here for (2) is probably due to its insolubility, which prevents further reaction with water or hydroxylated species. Compound (2) has all the oxidizing properties already described for solutions of the homologous chloride.¹³

The reaction of transition-metal perchlorates with the nitroxide free-radical TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) has been previously described.²⁰ It affords a metal-nitroxyl adduct except with copper(II) perchlorate. In that case the product of the reaction is the piperidinium salt corresponding to a three-electron reduction of the nitroxide.²¹ However a transient nitrosonium ion corresponding to a one-electron oxidation process of the nitroxide has been proposed in the mechanism of this reaction.

In the solid state the compound exists as discrete nitrosonium cations and perchlorate anions (Figure 1). The overall features

Table 1. Positional parameters ($\times 10^4$)

| | x | y | z |
|-------|-----------|----------|----------|
| Cl | 3 208(2) | 7 983(1) | 6 393(1) |
| O(1) | 3 042(8) | 7 394(4) | 7 123(3) |
| O(2) | 3 578(8) | 7 374(4) | 5 703(3) |
| O(3) | 1 597(8) | 8 390(6) | 6 072(5) |
| O(4) | 4 385(9) | 8 756(5) | 6 535(4) |
| O(5) | 8 904(4) | 8 909(3) | 3 969(3) |
| O(6) | 13 098(4) | 6 606(3) | 3 668(3) |
| N(1) | 10 284(5) | 8 532(3) | 3 806(3) |
| N(2) | 12 288(5) | 7 423(3) | 3 647(2) |
| C(1) | 10 676(5) | 7 527(3) | 3 883(3) |
| C(2) | 11 679(6) | 9 204(3) | 3 491(3) |
| C(3) | 13 080(6) | 8 397(4) | 3 334(3) |
| C(4) | 10 785(8) | 9 756(4) | 2 673(4) |
| C(5) | 12 240(7) | 9 964(4) | 4 231(4) |
| C(6) | 14 886(6) | 8 523(5) | 3 872(4) |
| C(7) | 13 234(8) | 8 196(5) | 2 369(4) |
| C(8) | 9 545(5) | 6 713(3) | 4 146(3) |
| C(9) | 9 470(6) | 5 783(3) | 3 711(3) |
| C(10) | 8 363(6) | 5 022(4) | 3 933(4) |
| C(11) | 7 332(7) | 5 196(4) | 4 570(4) |
| C(12) | 7 405(6) | 6 122(4) | 5 000(3) |
| C(13) | 8 513(6) | 6 892(4) | 4 798(3) |

Table 2. Bond angles ($^\circ$) and bond lengths (\AA)

| | | | |
|-------------------|----------|-------------|----------|
| O(1)–Cl–O(2) | 111.0(1) | Cl–O(1) | 1.379(3) |
| O(1)–Cl–O(3) | 108.7(3) | Cl–O(2) | 1.384(3) |
| O(1)–Cl–O(4) | 112.3(3) | Cl–O(3) | 1.363(3) |
| O(2)–Cl–O(3) | 102.7(3) | Cl–O(4) | 1.348(3) |
| O(2)–Cl–O(4) | 113.0(3) | O(5)–N(1) | 1.223(3) |
| O(3)–Cl–O(4) | 108.7(3) | O(6)–N(2) | 1.228(3) |
| O(5)–N(1)–C(1) | 124.0(3) | N(1)–C(1) | 1.342(3) |
| O(5)–N(1)–C(2) | 120.3(3) | N(1)–C(2) | 1.513(3) |
| C(1)–N(1)–C(2) | 115.7(3) | N(2)–C(1) | 1.343(3) |
| O(6)–N(2)–C(1) | 124.1(3) | N(2)–C(3) | 1.515(3) |
| O(6)–N(2)–C(3) | 120.4(3) | C(1)–C(8) | 1.455(3) |
| C(1)–N(2)–C(3) | 115.5(3) | C(2)–C(3) | 1.549(4) |
| N(1)–C(1)–N(2) | 106.0(3) | C(2)–C(4) | 1.511(4) |
| N(1)–C(1)–C(3) | 126.4(3) | C(2)–C(5) | 1.519(4) |
| N(2)–C(1)–C(8) | 127.6(3) | C(3)–C(7) | 1.527(4) |
| N(1)–C(2)–C(3) | 101.3(3) | C(3)–C(6) | 1.504(4) |
| N(1)–C(2)–C(4) | 106.9(3) | C(8)–C(9) | 1.387(3) |
| N(1)–C(2)–C(5) | 105.5(3) | C(8)–C(13) | 1.380(4) |
| C(3)–C(2)–C(4) | 115.5(3) | C(9)–C(10) | 1.378(4) |
| C(3)–C(2)–C(5) | 115.7(3) | C(10)–C(11) | 1.365(4) |
| C(4)–C(2)–C(5) | 110.7(3) | C(11)–C(12) | 1.370(4) |
| N(2)–C(3)–C(2) | 101.4(3) | C(12)–C(13) | 1.383(4) |
| N(2)–C(3)–C(6) | 107.2(3) | | |
| N(2)–C(3)–C(7) | 105.0(3) | | |
| C(2)–C(3)–C(6) | 116.0(3) | | |
| C(2)–C(3)–C(7) | 115.0(3) | | |
| C(6)–C(3)–C(7) | 111.0(3) | | |
| C(1)–C(8)–C(9) | 118.7(3) | | |
| C(1)–C(8)–C(13) | 120.6(3) | | |
| C(9)–C(8)–C(13) | 120.7(3) | | |
| C(8)–C(9)–C(10) | 119.4(3) | | |
| C(9)–C(10)–C(11) | 120.1(3) | | |
| C(10)–C(11)–C(12) | 120.6(3) | | |
| C(11)–C(12)–C(13) | 120.5(3) | | |
| C(8)–C(13)–C(12) | 118.7(3) | | |

of the cation are almost identical with those previously observed for the corresponding free radical.²² The five-atom fragment O(5)–N(1)–C(1)–N(2)–O(6) is nearly planar; the least-squares plane defined by these atoms shows a maximum deviation of 0.01 Å. The bonds around the nitrogen atoms are also planar as shown by the sum of the bond angles [359.7° for N(1), 359.9° for N(2)]. On the other hand the five-membered heterocyclic

ring is not planar; the tetramethylethylene moiety is twisted out of the O(5)–N(1)–C(1)–N(2)–O(6) plane. The methyl groups are thus staggered relative to one another, probably in order to relieve steric repulsion. The phenyl plane makes an angle of 39° with the O(5)–N(1)–C(1)–N(2)–O(6) plane, suggesting some weak resonance interaction between the ring π -system and the *N*-oxide *N*-oxonium π -system. This value of 39° brings the *ortho* hydrogen atoms on the phenyl ring to within 2.62 Å of O(5) and 2.68 Å of O(6) values.

Most of the bond lengths and angles are normal and need no further comment. However, as expected, the NO bond length [1.225(4) Å] is smaller than the one found in the corresponding free radical [1.27(2) Å].²² This smaller distance is consistent with a higher bond order in the more oxidized compound and with the presence of the unpaired electron in an antibonding orbital in the free radical, since the conversion of the radical into the cation involves the loss of this unpaired electron. In the nitronyl free radical (1) the two NO groups are identical and the unpaired electron is equally delocalized as shown by the e.p.r. spectrum, which exhibits the characteristic pattern of two equivalently coupled nitrogen nuclei. Surprisingly, this conjugation is not reflected in the NO bond lengths since the 1.27 Å NO bond length in (1) is equivalent to those found in other non-conjugated dialkyl nitroxides: 1.296 Å in TEMPO.²³

Concerning the corresponding cations, one should notice also the similarity of the NO bond lengths [1.225(4) Å] in (2) and (1.19 Å) in TEMPO⁺ ClO₄[−].²⁴ Although the molecular structure of the latter compound has probably been determined at a low level of accuracy, the two values of the N=O bond fall well within the range expected for a nitrogen–oxygen double bond.

The redox behaviour of transition metal-nitroxyl systems is currently being investigated in our laboratory.

Experimental

Preparation of 4,4,5,5-Tetramethyl-1-oxo-2-phenyl-4,5-dihydroimidazolium Perchlorate N(3)-Oxide (2).—To a solution of (1)¹³ (233 mg, mmol) in acetonitrile (8 ml) was added copper perchlorate hexahydrate (372 mg, 1 mmol). The deep blue solution turned red as it was stirred for 5 min. The solution was allowed to stand at room temperature when crystallization occurred and filtration afforded red crystals (256 mg) suitable for X-ray analysis; m.p. 205–210 °C (explosion) (Found: C, 46.9; H, 4.85; Cl, 10.75; N, 8.35; O, 28.6; C₁₃H₁₇N₂O₆Cl requires C, 46.91; H, 5.15; Cl, 10.65; N, 8.45; O, 28.84%). Cooling of the remaining solution at 0 °C afforded a second crop composed mainly of cuprous perchlorate tetra-acetonitrile complex.¹⁴

Crystal Data.—C₁₃H₁₇ClN₂O₆, *M* = 332.7. Monoclinic, *a* = 7.641(3), *b* = 13.002(7), *c* = 15.366(7) Å, β = 98.72(3)°, *V* = 1 508.9 Å³, space group *P*₂₁/*n*, *Z* = 4, *D*_c = 1.34, *D*_o = 1.30 g cm^{−3}, *t* = 20 °C.

Weissenberg and precession photographs taken on a regularly shaped crystal (0.22 × 0.19 × 0.23 mm) showed a monoclinic cell. The systematic absences (*h*0*l*, *h* + 1 = 1 = 2*n* + 1; 0*k*0, *k* = 2*n* + 1;) were only compatible with the space group *P*₂₁/*n*.

Data Collection and Processing.—The same crystal was mounted on an Enraf-Nonius CAD-4 four-circle diffractometer, ω mode, scan angle = $0.80 + 0.35 \tan \theta$, scan speed 0.42–3° mm^{−1}, graphite-monochromatized Mo-*K*_α (0.7107 Å) radiation; cryst. detector dist. = 368 mm; detector window = height, 4 mm; width, 2.25 + 3.50 tgθ (mm); take off angle = 6°; test reflections = (240), (204) accurate cell constants were derived from least-squares refinement of the setting angles of 25 reflections. The intensities of 5 305 independent reflections

($2^\circ < \theta < 25^\circ$) were collected. Three standard reflections were periodically checked and showed no significant variation during the course of data collection. The data were collected for Lorentz and polarization factors but not for absorption. Among the independent reflections, 1 581 had $F_o > 3 F_c$ and were used to refine the structural parameters.

Structure Solution and Refinement.—The structure was solved by conventional Patterson and Fourier methods using the SHELX-76 package.¹⁵ Final full-matrix least-squares refinement employed anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions (C–H = 1.09 Å) for the phenyl ring and determined by Fourier maps for the methyl groups; all hydrogen atoms were given fixed isotropic thermal parameters one unit greater than the final isotropic B value of the corresponding carbon atom. This refinement converged to conventional R factors, $R_1 = 0.055$ and $R_2 = 0.052$;* in the final cycle no parameter shifted by more than one-tenth of its estimated standard deviation. Neutral atomic scattering factors, including anomalous terms for Cl were taken from ref. 16.

Final atomic positional parameters are listed in Table 1. Bond distances and angles are tabulated in Table 2. Thermal parameters are available on request from the Cambridge Crystallographic Data Centre.†

$$* R_1 = w(F_o - F_c)/F_o; R_2 = (F_o - F_c)^2 / (wF_o)^2$$

† See Instructions for Authors (1987), para. 3.6.3, in *J. Chem. Soc., Perkin Trans. 1*, 1987, Issue 1.

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Received 30th May 1986; Paper 6/1062