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EPR-spectroscopic detection and characterization of a Cu^{II} complex with a peroxycarboximidic acid

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A copper(II) complex with peroxycarboximidic acid formed upon the interaction of alkaline hydrogen peroxide with acetonitrile was detected and characterised for the first time.

The following reaction of nitriles with alkaline hydrogen peroxide to afford amides (Radzishevski reaction) is well known:[1]

$$RCN + 2HOOH \rightarrow RC(O)NH_2 + O_2 + H_2O \quad (1)$$

Since this is a first-order reaction with respect to hydrogen peroxide, Wilberg suggested that the rate-determining step is the formation of peroxycarboximidic acid intermediate **X**.[2]

$$RCN + 2HOOH \rightarrow \underset{\mathbf{X}}{HN{=}C(OOH)R} + HOOH \rightarrow RC(O)NH_2 + O_2 + H_2O \quad (2)$$

Until now, this intermediate has not been isolated or observed spectroscopically. It is believed that **X** reacts rapidly with any available reducing agent.[3]

$$HN{=}C(OOH)R + S \rightarrow RC(O)NH_2 + SO \quad (3)$$

The oxidising systems based on hydrogen peroxide and nitriles were developed to epoxidise olefins and to oxidise amines (in 60–70% yields).[3]

Recently, we found that copper and iron hydroxides catalyse the oxidation of organic substrates (including light hydrocarbons) by H_2O_2 in weakly basic aqueous solutions.[4,5] It was assumed that peroxo complexes of Cu and Fe are key intermediates in these oxidations.[6,7] The studies on the peroxo complexes of copper in the weakly basic water/acetonitrile solvent systems led us to the discovery of new unstable copper(II) species. Here, we report on the EPR-spectroscopic detection and characterization of this new species identified as a complex of copper(II) with peroxycarboximidic acid intermediate **X**.

For preparation of the sample, $Cu(NO_3)_2$ (0.0015 mol) was stirred with a magnetic stirrer at 20 °C in 25 ml of water containing NaOH (0.1 mol) and MeCN (3 mol). Then, hydrogen peroxide (to a concentration of 0.05 mol dm^{-3}) was added. Immediately, the reaction mixture became pale yellow and $Cu(OH)_2$ precipitated. After 3–4 min of stirring, all initially formed $Cu(OH)_2$ dissolved and the solution turned to pale pink. Pink complex **1** was formed.† It exhibits a UV-VIS band at 540 nm and displays an EPR spectrum (15 °C) shown in Figure 1(*a*).

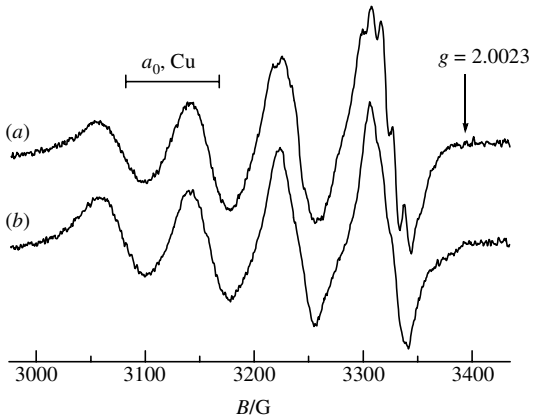

Figure 1 X-band (9.3 GHz) EPR spectra recorded 5 min after the addition of hydrogen peroxide to a solution of $Cu(NO_3)_2$ in (*a*) H_2O–MeCN–NaOH (15 °C) and (*b*) H_2O–CD_3CN–NaOH (25 °C). [$Cu(NO_3)_2$] = 0.0015 mol dm^{-3}, [H_2O_2] = 0.05 mol dm^{-3}, [NaOH] = 0.1 mol dm^{-3}, [CD_3CN] = [MeCN] = 3 mol dm^{-3}.

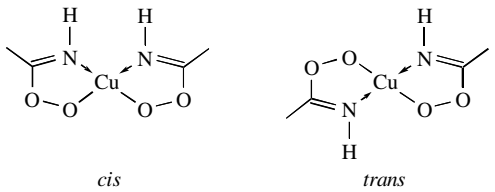

Figure 2 Structure of complex **1**.

The concentration of **1** monitored by UV-VIS or EPR spectroscopy decreased in parallel with the diminishing of the concentration of hydrogen peroxide in the sample determined by the reaction with Ti^{IV}. The half-life time of **1** was about 5 min at 20 °C for the sample of Figure 1. After completion of the reaction, the $Cu(OH)_2$ precipitate forms again. The addition of a fresh portion of hydrogen peroxide to the sample in which all initially added H_2O_2 was consumed restored the concentration of **1**. This procedure can be repeated many times. After completion of the reaction, acetamide was identified as the only product by gas chromatography.

According to quantitative EPR measurements, the concentration of **1** can reach 50% of the copper species present in solution. In the absence of acetonitrile, no EPR active species were observed in the reaction of $Cu(NO_3)_2$ with alkaline hydrogen peroxide. When benzonitrile was used instead of acetonitrile, a pink EPR active copper(II) complex resembling intermediate **1** was also observed. In the case of benzonitrile, the intermediate formed can be isolated due to its poor solubility as a metastable solid admixture to $Cu(OH)_2$. Its concentration reached 20% of copper in the sample. The IR spectrum of this intermediate (CsI pellet) exhibits a band at 3208 cm^{-1} assigned to stretching vibrations of the N–H bond, and bands at 896, 871 and 842 cm^{-1} assigned to O–O vibrations. The latter bands disappeared simultaneously with the decomposition of a pink intermediate. Previously, three bands in the same region were observed by resonance Raman spectroscopy for alkylperoxo complexes LCuOOR, where L is a trispyrazolylborate ligand, and R is *tert*-butyl or cumyl. These three bands were assigned to mixed O–O/C–O/C–C vibrations in which the O–O percentage determines the isotope shifts and rR intensities.[8]

Thus, the presented data show that **1** is a mononuclear complex of copper(II) with an unstable product of the reaction of H_2O_2 with RCN. This unstable product, most probably, contains an O–O bond.

The shape of the EPR spectrum of **1** [Figure 1(*a*)] centered at g_0 = 2.12 is typical of mononuclear Cu^{II} species. It exhibits four lines due to the hyperfine interaction of an unpaired electron

† *General experimental details*. Reagent grade $Cu(NO_3)_2$, MeCN and 30% H_2O_2 were used without further purification. Commercial CD_3CN from Aldrich was used. The EPR spectra (20 °C) were recorded in a flat quartz cell furnished with a Bruker ER-200D X-band spectrometer. The EPR spectra (–196 °C) were recorded in glass tubes (5 mm in diameter) in a quartz finger dewar vessel. The concentrations of paramagnetic centres were measured by comparing the second integrals of EPR spectra of the test sample and the reference crystal of $CuCl_2 \cdot 2H_2O$ at –196 °C. The EPR spectra were simulated using the EPR1 program.[16] The UV-VIS spectra were recorded on a Uvikon 923 spectrometer, and the IR spectra were measured on a FTIR BOMEM MB-102 instrument.

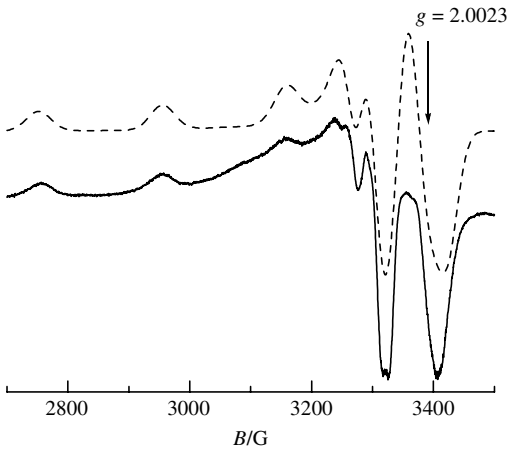

Figure 3 X-band (9.3 GHz) EPR spectrum (–196 °C) recorded 5 min after the addition of hydrogen peroxide to a solution of $Cu(NO_3)_2$ in H_2O–MeCN–NaOH. $[Cu(NO_3)_2] = 0.0015$ mol dm^{-3}, $[H_2O_2] = 0.05$ mol dm^{-3}, [NaOH] = = 0.1 mol dm^{-3}, $[CD_3CN] = [MeCN] = 3$ mol dm^{-3}. Dotted line shows a theoretical spectrum with the parameters specified in the text.

with a copper nucleus ($I = 3/2$, $a_0 = 86$ G). Besides, the upfield component of the spectrum displays an additional hyperfine structure (ahfs). The observed splitting ($a = 11$ G) is typical of ahfs from nitrogen nuclei. However, the splitting pattern observed (approximately 1:3:6:6:3:1) is far from that expected for ahfs from two nitrogen nuclei (1:2:3:2:1). The splitting pattern 1:3:5:5:3:1 resembling the experimental one can be obtained on the assumption of the existence of equal amounts of two types of complexes with 1:2:3:2:1 splitting patterns ($a = 11$ G) and slightly different g_0 values (the shift between two spectra of about 10 G).

To exclude the impact of ahfs from hydrogen nuclei to the observed spectrum, CD_3CN, D_2O and NaOD were used for preparation sample instead of ordinary reagents (hfs from deuterium is lower than that from proton by a factor of 6). EPR spectra coincided for deuterated and ordinary reagents at the same temperature. Thus, the observed ahfs is due to only nitrogen nuclei.

Note that the shape of the EPR spectrum of **1** is very temperature sensitive. Figure 1(*b*) shows the EPR spectrum of **1** obtained in the $CD_3CN/H_2O/H_2O_2$ system at 25 °C. It can be seen that the ahfs structure almost disappeared in this spectrum. The EPR spectrum of this sample recorded at 12 °C coincided with the spectrum shown in Figure 1(*a*).

An additional hyperfine structure observed in Figure 1(*a*) can be described as a superposition of spectra from two copper complexes each of them containing two nitrogen atoms in a coordination sphere. Thus, most probably, **1** incorporates two peroxycarboximidic acid ligands and exists in solution in the form of two isomers, *e.g.*, *cis*–*trans* isomers (Figure 2). Such isomers are known for related bis(*N*-R)salicylaldiminatocopper(II) complexes.[9] The EPR spectrum (20 °C) of bis(*N*-methyl)salicylaldiminatocopper(II) is a superposition of the spectra of two isomers.[10]

The EPR spectrum of a frozen solution of **1** (–196 °C, Figure 3) is well described by a theoretical spectrum (dotted line) with the following parameters: $g_1 = 2.221$, $A_1 = 226$ G, $g_2 = 2.061$, $A_2 = 22.1$ G, $g_3 = 2.0584$, $A_3 = 19.4$ G. These parameters are typical of plane mononuclear copper(II) species with O and N donor ligands. An additional hyperfine structure from the NH=C(Me) fragment is unresolved in the EPR spectrum shown in Figure 3.

During the last decade, much effort has been devoted to the design and synthesis of inorganic models of the catalytic sites of noncoupled binuclear copper enzymes, where a peroxide intermediate may be activated by coordination to only one copper ion.[8,11–15] Some mononuclear alkylperoxo and hydroperoxo copper(II) complexes were structurally and spectroscopically characterised.[11–15] Complex **1** can be considered as an intermediate of the interaction of a hydroperoxo complex of copper(II) with an organic substrate (acetonitrile in our case). Evidently, a study of this species is important for the elucidation of the mechanisms of catalytic oxidation. The advantage of the test system is its simplicity. The reaction proceeds in water as a solvent, and the catalyst used incorporates only water molecules and OH groups in its composition.

In conclusion, we observed for the first time a complex of copper(II) with peroxycarboximidic acid formed in the reaction of alkaline hydrogen peroxide with acetonitrile by EPR spectroscopy.

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References

1 E. N. Zilberman, *Reaktsii nitrilov* (*Reactions of Nitriles*), Khimiya, Moscow, 1972 (in Russian).
2 K. B. Wiberg, *J. Am. Chem. Soc*., 1953, **75**, 3961.
3 G. B. Payne, P. H. Deming and P. H. Williams, *J. Org. Chem*., 1961, **26**, 659.
4 A. O. Kuzmin, G. L. Elizarova, L. G. Matvienko, E. N. Savinova and V. N. Parmon, *Mendeleev Commun*., 1998, 210.
5 G. L. Ellizarova, L. G. Matvienko, A. O. Kuzmin, E. R. Savinova and V. N. Parmon, *Mendeleev Commun*., 2001, 15.
6 G. L. Elizarova, L. G. Matvienko, O. L. Ogorodnikova and V. N. Parmon, *Kinet. Katal*., 2000, **41**, 366 [*Kinet. Catal.* (*Engl. Transl.*), 2000, **41**, 332].
7 G. L. Elizarova, L. G. Matvienko and V. N. Parmon, *Kinet. Katal*., 2000, **41**, 839 [*Kinet. Catal.* (*Engl. Transl.*), 2000, **41**, 760].
8 P. Chen, K. Fujisawa and E. Solomon, *J. Am. Chem. Soc*., 2000, **122**, 10177.
9 S. Yamada and A. Takeuchi, *Coord. Chem. Rev.*, 1982, **43**, 187.
10 V. F. Anufrienko, E. G. Rukhadze, G. V. Panova and A. G. Onuchina, *Dokl. Akad. Nauk SSSR*, 1966, **171**, 601 [*Dokl. Chem.* (*Engl. Transl.*), 1966, **171**, 1088].
11 F. Champloy, N. Benali-Cherif, P. Bruno, I. Blain, M. Pierrot, M. Reglier and A. Michalowicz, *Inorg. Chem*., 1998, **37**, 3910.
12 A. Wada, M. Harata, K. Hasegawa, K. Jitsukawa, H. Masuda, M. Mukai, T. Kitagawa and H. Einaga, *Angew. Chem., Int. Ed. Engl*., 1998, **37**, 798.
13 I. Sanyal, P. Ghosh and K. D. Karlin, *Inorg. Chem*., 1995, **34**, 3050.
14 N. Kitajima, T. Katayama, K. Fujisawa, Y. Iwata and Y. Moro-oka, *J. Am. Chem. Soc*., 1993, **115**, 7872.
15 N. Kitajima, K. Fujisawa and Y. Moro-oka, *Inorg. Chem*., 1990, **29**, 357.
16 A. A. Shubin and G. M. Zhidomirov, *Zh. Strukt. Khim*., 1989, **30**, 67 [*J. Struct. Chem.* (*Engl. Transl.*), 1989, **30**, 414].

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