Photochemistry of [Cu{HB(3,5-Me$_2$pz)$_3$}]$_2$X (X = O^{2-}, CO$_3{}^{2-}$) in non-aqueous solvents

Michele Aresta[a], Wojciech Macyk[b], Zofia Stasicka[b,*]

[a]*Department of Chemistry, University of Bari, Campus Univesitario, 70126, Bari, Italy*
[b]*Department of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060, Kraków, Poland*

Abstract

The photochemistry and thermal stability of [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$O (**1**) and [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$CO$_3$ (**2**) have been investigated in various solvents in view of their utilisation as catalysts in olefin functionalization reactions. Irradiation of the above complexes in chlorinated aliphatic solvents within the CT-band region generates the mononuclear complex [Cu(HB(3,5-Me$_2$pz)$_3$)Cl] (**4**), which exists as a tetracoordinated monomer in solution at room temperature, and as a dimer (pentacoordinated-Cu(II) species, **4″**) in a frozen solution or in the solid state. In coordinating solvents **4** is converted into the monomer pentacoordinated complex [Cu(HB(3,5-Me$_2$pz)$_3$)Cl(Solv)] (**4′**). The photo-generation of **4** implies the homolytic cleavage of the Cu–O bond in **1**, with formation of the reactive radical species [LCu(I)] and [LCu(II)O$^{\cdot}$] [L = (HB(3,5-Me$_2$pz)$_3$)]. **2** appears to be more stable than **1**, under the same conditions. The radical Cu(II)-species [LCu(II)O$^{\cdot}$], according to the solvent and conditions, can either be reduced to [LCu(I)], or undergo an intramolecular rearrangement. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The chemistry of transition metal complexes with poly(pyrazolyl)borate (scorpionate) ligands has been developed extensively since the late 60s, when for the first time such ligands were synthesized by Trofimenko [1,2]. Copper(I) and (II) scorpionates have attracted attention for their properties and reactivity [3–6]. Copper(II) hydrotris(pyrazolyl)-borates, for example, can be model of biosystems. Kitajima et al. have synthesized the μ-oxo complex [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$O (**1**), that is the precursor of [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$O$_2$, the model compound of oxo-haemocyanin and tyrosinase active sites [7–10]. Our interest for this class of complexes arose from their possible implication in carbon dioxide activation and fixation. Moreover, **1** has been already described to react with carbon dioxide yielding [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$CO$_3$ (**2**) [7–11].

While using **1** and **2** in photochemical reactions we discovered that they undergo several changes, depending on the solvent and experimental conditions. According to our knowledge, this is the first report on the photo-reactivity of copper hydrotris(pyrazolyl)borates[1]. Moreover, our studies were very helpful for explaining the features of the reaction of alkenes with CO$_2$/O$_2$ mixtures under UV/Vis irradiation in the presence of **1** [12].

2. Experimental section

All solvents (Aldrich Chemie) were purified using standard procedures [14] and stored under dinitrogen. The complexes: **1** and **2**, were synthesized according to the literature [11]. However, we have noticed that **1** can be synthesized from [Cu(HB(3,5-Me$_2$pz)$_3$)(PPh$_3$)] and iodosobenzene in 6 h, as reported in the literature [11], only in the presence of traces of dioxygen. Under strictly deoxygenated conditions this reaction practically does not proceed.

The IR spectra were taken with a Perkin-Elmer 883 IR spectrophotometer using KBr disks. A few drops of a concentrated solution of the product were placed on the disk in a short glass tube equipped with a stopcock under dinitrogen and evaporated to dryness by flowing dinitrogen.

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[1]Kitajima et al. reported light induced oxidation of cyclohexene with [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$O, however the fate of the complex was not studied [13].

*Corresponding author. E-mail: stasicka@trurl.ch.uj.edu.pl

The thin film which was formed was directly used for IR analysis.

UV-Vis-NIR spectra were recorded in a 1 cm quartz cuvette using Shimadzu UV-3101 PC apparatus. Diffuse reflectance spectra of solid materials were taken using the same spectrophotometer equipped with a diffuse reflectance accessory. The solid samples were spread onto Al_2O_3 plates.

Approximately 2–2.5×10^{-4} mol dm^{-3} solutions saturated with the appropriate gas were used for experiments. The irradiation of solutions thermostated at 293 K was made using the Osram XBO 150 W xenon arc lamp installed in a light condensing lamp housing (PTI, A1010S). The appropriate monochromatic or cut-off filters (335, 530 nm; Schott) were used when necessary.

The EPR spectra were recorded using Varian E3 spectrometer operating at the X band. The samples were examined inside the TE-102 cavity of the EPR instrument (9.25 GHz, T = 77 K).

The JEOL MStation 700 (FD 2 kV) was used for MS/FD+ analysis.

3. Results and discussion

We have investigated the thermal and photochemical reactivity of **1** and **2** in several solvents in which they are soluble, as dichloromethane, chloroform, carbon tetrachloride, tetrahydrofuran, toluene, and benzene. **1** is practically insoluble in water, acetonitrile, methanol, isooctane and dimethylformamide. It may be worth to note that CH_2Cl_2 is used in the synthesis of **1**, while $CHCl_3$ is the usual solvent for the synthesis of the carbonate derivative **2**. Complex **1** and its carbonate derivative **2** in CH_2Cl_2 show absorption bands at $\lambda_{max} = 335$ ($\varepsilon \approx 2600$ M^{-1} cm^{-1}) and 345 nm ($\varepsilon \approx 10000$ M^{-1} cm^{-1}), respectively. In the case of **1**, the band is assigned to O $\rightarrow$ Cu LMCT [7,11,13]. Other less strong bands at $\lambda_{max} = 655$ nm ($\varepsilon \approx 100$ M^{-1} cm^{-1}) for **1** and 680 nm ($\varepsilon \approx 300$ M^{-1} cm^{-1}) for **2** are assigned to the d–d transitions in the copper(II) complexes [7,11,15].

Opposite to **2**, which is stable in all studied solvents if kept in the dark, **1** is thermally stable only in benzene or toluene under argon. In chloroform, however, a slow dark process was observed at room temperature. Increase of the 335 and 655 nm bands was accompanied by their bathochromic shifts, while the absorptions below 287 nm decreased (with the formation of an isosbestic point at 287 nm). In THF **1** undergoes similar thermal transformation. In carefully purified and deoxygenated THF, the increase of the CT-band, the decrease of the absorption below 285 nm and the bathochromic shift of the CT ($340 \rightarrow 345$ nm) and d–d ($665 \rightarrow 675$ nm) bands are observed within hours.

When, however, neat THF saturated with oxygen or air is irradiated within UV region then a photochemical reaction proceeds generating hydroperoxide groups [16]. Using irradiated THF as a solvent entails the colour change of **1** or **2** solution from pale green to intense purple. The spectrum of

the solution and its low thermal stability are identical with those already reported for the μ-peroxo complex $[Cu(HB(3,5\text{-Me}_2pz)_3)]_2O_2$, **3** [15]. The formation of **3** can be easily explained considering the reaction of **1** or **2** with peroxide groups photogenerated in THF. It is worthy to note that the synthetic methodology described in the literature for the synthesis of the μ-peroxo complex is based on the use of hydrogen peroxide.

The photochemical transformation of the complexes depends not only on the solvent used but also on the irradiation region. In fact, irradiation of **1** within its d–d band in chloroform ($\lambda_{irr} > 530$ nm) produces the same spectral changes as those observed during thermal reaction. The effect of radiation is to accelerate the dark process. Conversely, the irradiation within the CT-band if **1** or **2** generates new significant changes, that we have investigated in detail.

Fig. 1(a) shows the spectral changes recorded during the irradiation ($\lambda_{irr} = 334$ nm) of **1** dissolved in $CHCl_3$ saturated with dinitrogen. The increase in absorbance and the bathochromic shift of the 335 nm band to $\sim$350 nm were observed upon first stage of irradiation. The bathochromic shift was also accompanied by the formation of new bands at 510 and *ca.* 1010 nm, and the decrease of the absorbance at 660 nm and <325 nm. The colour of the irradiated solution changed from pale blue-green to red-brown. Upon prolonged irradiation (Fig. 1(b)) the absorbance at <290 nm increased while in the range 290–410 nm decreased with a bathochromic shift of the band at 30 nm. The bands at 510 and 1010 nm reached their maximum, while the band at 660 nm disappeared. Such solution, saturated with CO_2, does not afford carbonate **2**. The same behaviour, with some minor differences, is observed in other chlorinated aliphatic solvents like: chloroform, carbon tetrachloride and dichloromethane, but not in benzene, toluene and THF. From the irradiated chloroform solution (red-brown) it is possible to isolate a green solid (infrared band at 2509 cm^{-1}, ν_{BH}). This solid turns brown when re-dissolved in chloroform or THF where presents similar electronic spectrum ($\sim$360, 510 nm) with some difference in the near-IR region: band at $\sim$1010 nm in CH_2Cl_2, and more blue-shifted in THF. In chlorinated solvents dioxygen or air do not produce effects different from dinitrogen, at least for a short term irradiation.

No formation of 510 neither 1010 nm bands can be observed even after 17 days of thermal changes of **1** in $CHCl_3$ at room temperature, however, CT-irradiation ($\lambda > 335$) of the formed thermal product leads to formation of the 510 and 1010 nm bands.

The irradiation of **2** in chloroform within the CT-band produces the changes shown in Fig. 2 and a product identical to that obtained from **1** under the same conditions.

The spectral features of the CT-irradiation product **1** or **2** in chlorinated solvents closely resemble the electronic spectra of known mononuclear copper(II) chloroscorpionate complexes, e.g. $[Cu(HB(3,5\text{-}i\text{-Pr}_2pz)_3)Cl]$ [17] and $[Cu(HB(3\text{-}t\text{-Bupz})_3)Cl]$ [18]. These data suggest that $[Cu(HB(3,5\text{-Me}_2pz)_3)Cl]$ (**4**), is formed in the photoreaction
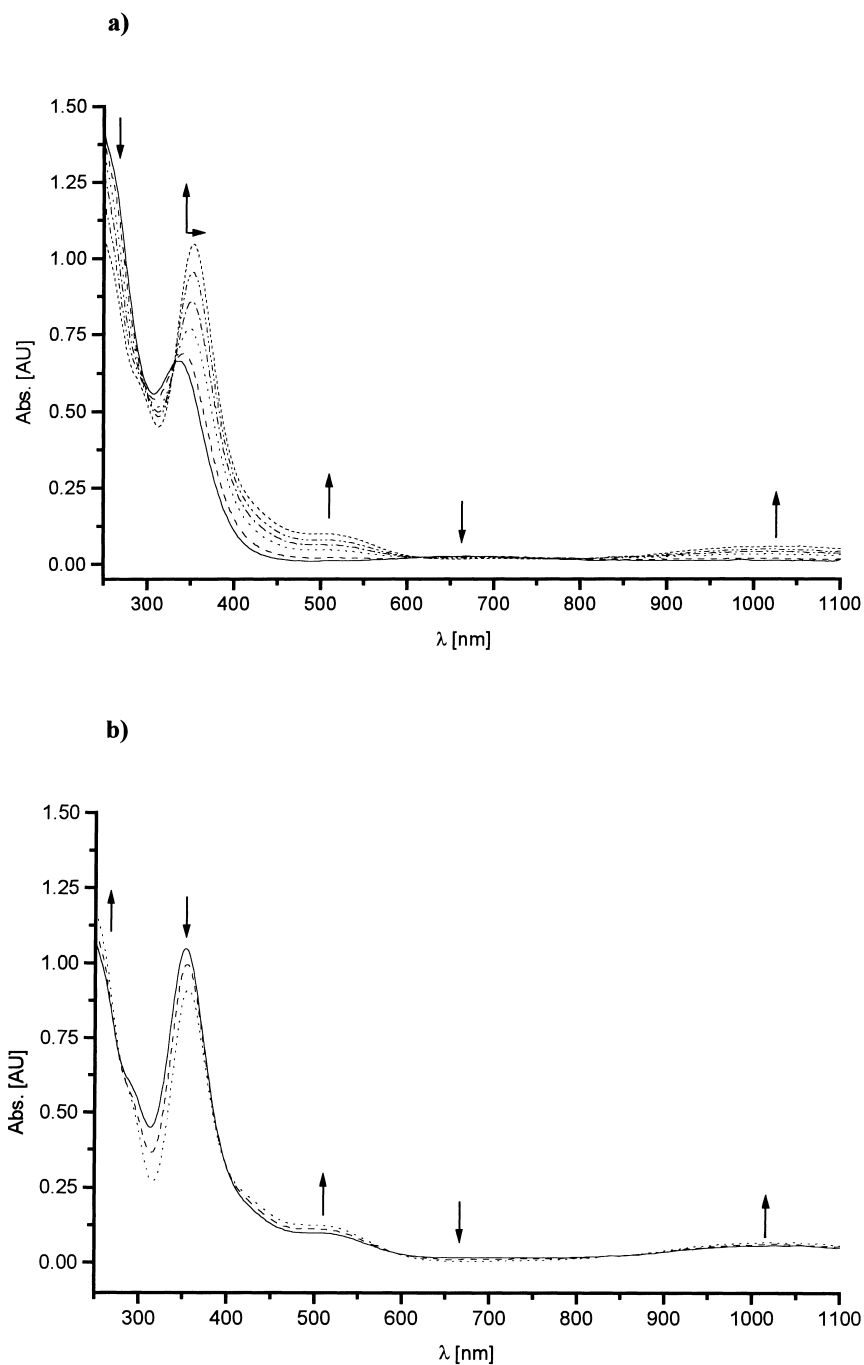
a)

b)

Fig. 1. Spectral changes recorded upon irradiation of a solution of **1** in chloroform saturated with dinitrogen: (a) first 120 min, and (b) consecutive 35 min $(2.5 \times 10^{-4} \text{ mol dm}^{-3}; \lambda_{\text{irr}} > 335 \text{ nm})$. Arrows show spectral changes during irradiation.

of **1** and **2**. Other tetracoordinated mononuclear copper(II) scorpionates have electronic spectra similar to that of **4** [17–20]. Support of the [Cu(HB(3,5-Me₂pz)₃)Cl] formulation for **4** comes from the MS/FD+ analysis: among others the peak for 395 molecular mass was detected.

The position of the d–d band of photoproduct **4** is solvent dependent. In non-coordinating solvents (e.g. CHCl₃) it is located at *ca.* 1010 nm. If a coordinating solvent (acetonitrile or DMF) is added, it shifts to *ca.* 740 and 760 nm,

respectively. Such hypsochromic shift can be interpreted on the basis of the formation of monomeric pentacoordinated species [Cu(HB(3,5-Me₂pz)₃)Cl(Solv)] (**4′**) (Solv = DMF or acetonitrile) (Scheme 1). The analogous coordination has already been observed for [Cu(HB(3,5-*i*-Pr₂pz)₃)Cl] [17].

4 is green in the solid state (the reflectance spectrum shows a maximum at 765 nm), whereas red-brown in non-coordinating solvents (max at 510, 1010 nm). The red-brown colour is associated to the tetracoordinated monomer,
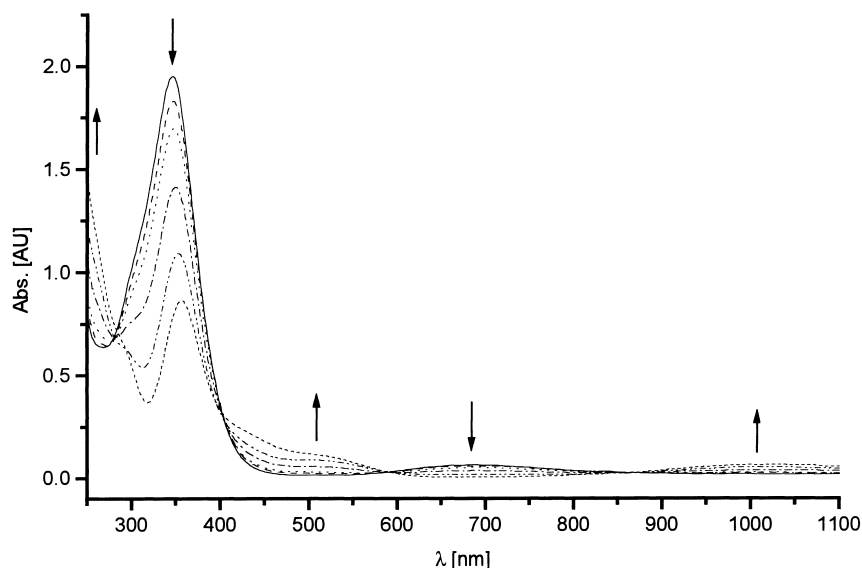
Fig. 2. Spectral changes recorded upon irradiation of a solution of **2** in chloroform saturated with CO_2 (or dinitrogen) for 110 min (2.5×10^{-4} mol dm^{-3}; $\lambda_{irr} > 335$ nm). Arrows show spectral changes during irradiation.

4, while the green can be assigned to a dimer [Cu(HB(3,5-Me$_2$pz)$_3$)Cl]$_2$ (**4″**). Analogous dimers have already described [21,22]: Roundhill et al. [22] isolated and described the green solid [Cu(HB(pz)$_3$)Cl]$_2$, that maintained the doubly Cl-bridged structure also in dichloromethane. The reflectance spectrum of the solid obtained by solvent evaporation from an irradiated chloroform solution of **1**, repeats the spectral features of [Cu(HB(pz)$_3$)Cl]$_2$ in dichloromethane [22]. It is worthy to note that the steric hindrance of substituents in the scorpionate ligand can stabilise the monomer structure. In fact, [Cu(HB(3,5-*i*-Pr$_2$pz)$_3$)Cl] is brown and monomer in both the solid state and solution [17].

Support to the formation and properties of [Cu(HB(3,5-Me$_2$pz)$_3$)Cl] came from EPR experiments. **1** and **2** are EPR silent because the two Cu(II) centres are antiferromagnetically coupled through the oxo bridge. However, the spectrum of an irradiated dichloromethane solution of **1** at 77 K (Fig. 3) presents signals that are typical of a square pyramidal Cu(II): $g_\perp = 2.065$, $g_\| = 2.317$, $A_\| = 162$ G, $A_\perp = 18$ G. These features recall the values found for monomer pentacoordinated Cu(II) scorpionate complexes:

[Cu(HB(3,5-*i*-Pr$_2$pz)$_3$)Cl(DMF)] [17], [Cu(HB(3-*t*-Bupz)$_3$)NO$_2$] [23], [Cu(HB(3,5-*i*-Pr$_2$pz)$_3$)(mCPBA)] (mCPBA = *m*-chloroperbenzoic acid) [24], and others [20,25,26]. Also for the dimer [Cu(HB(pz)$_3$)Cl]$_2$ ($T = 77$ K) Roundhill et al. [22] reported two signals: $g = 2.10$, $g = 2.29$, but the hyperfine structure of the spectrum could not be observed and $g_\perp$ and $g_\|$ parameters were not assigned. By comparison, the EPR spectra of tetrahedral Cu(II) species are characterised by three signals at: $g_x \sim 2.3$–2.45, $g_y \sim 2.1$–2.2, $g_z \sim 2.0$ [17,18]. Hence, formation of the doubly Cl-bridged dimer **4″** (both copper centres are pentacoordinated) seems to be substantiated. The different behaviour of **4** (that bears the HB (3,5-Me$_2$pz)$_3$$^-$ ligand and can be either monomer or dimer) and [Cu(HB(pz)$_3$)Cl]$_2$ (that is always dimer in solution and in the solid state) can be ascribed to the different steric hindrance of the ligands. With more hindered scorpionate ligands (e.g. HB (3,5-*i*-Pr$_2$pz)$_3$$^-$), the dimer has not been observed at all. The structural considerations together with experimental data seem to suggest that **4** could exist as a pentacoordinated dimer **4″** at low temperatures or in solid
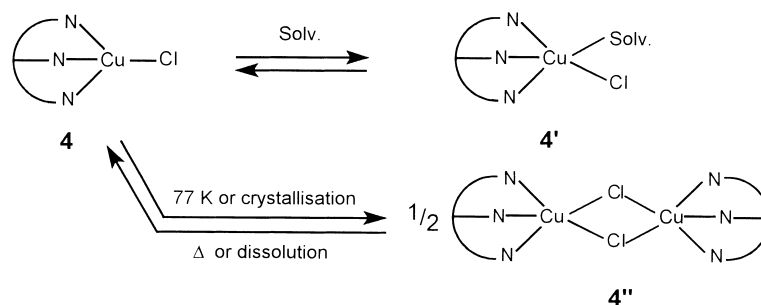

Scheme 1. Different forms of the [LCu(II)Cl] complex appearance: monomeric tetracoordinated (**4**), monomeric pentacoordinated (**4′**) and dimeric one (**4″**) [hydrotris(3,5-dimethylpyrazol-l-yl)borate ligand is presented schematically].

$g_\parallel = 2.32$

$A_\parallel = 162$ G

$g_\perp = 2.065$

$A_\perp = 18$ G
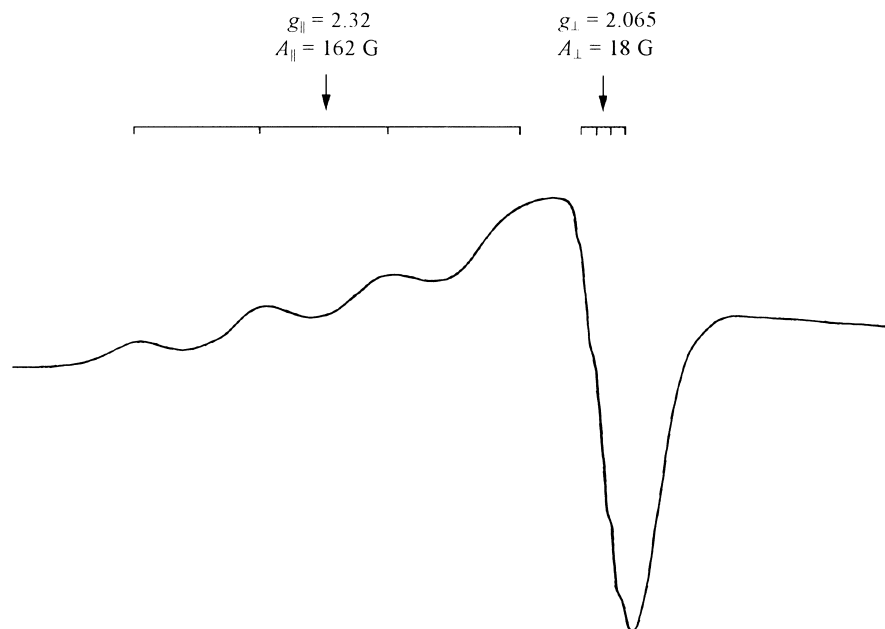
Fig. 3. EPR spectrum of an irradiated dichloromethane solution of **1**.

state, at room temperature in non-coordinating solvents it is mostly the tetracoordinated monomeric form **4**, while in the presence of coordinating solvents pentacoordinated monomeric form **4′** is prevailing (Scheme 1).

MS/FD+ spectrum of the described irradiated solution of **1** in chloroform shows another very intensive signal for the molecular mass 720. It is characteristic for the [LCu(I)]$_2$ dimer. The characteristics of this compound was reported
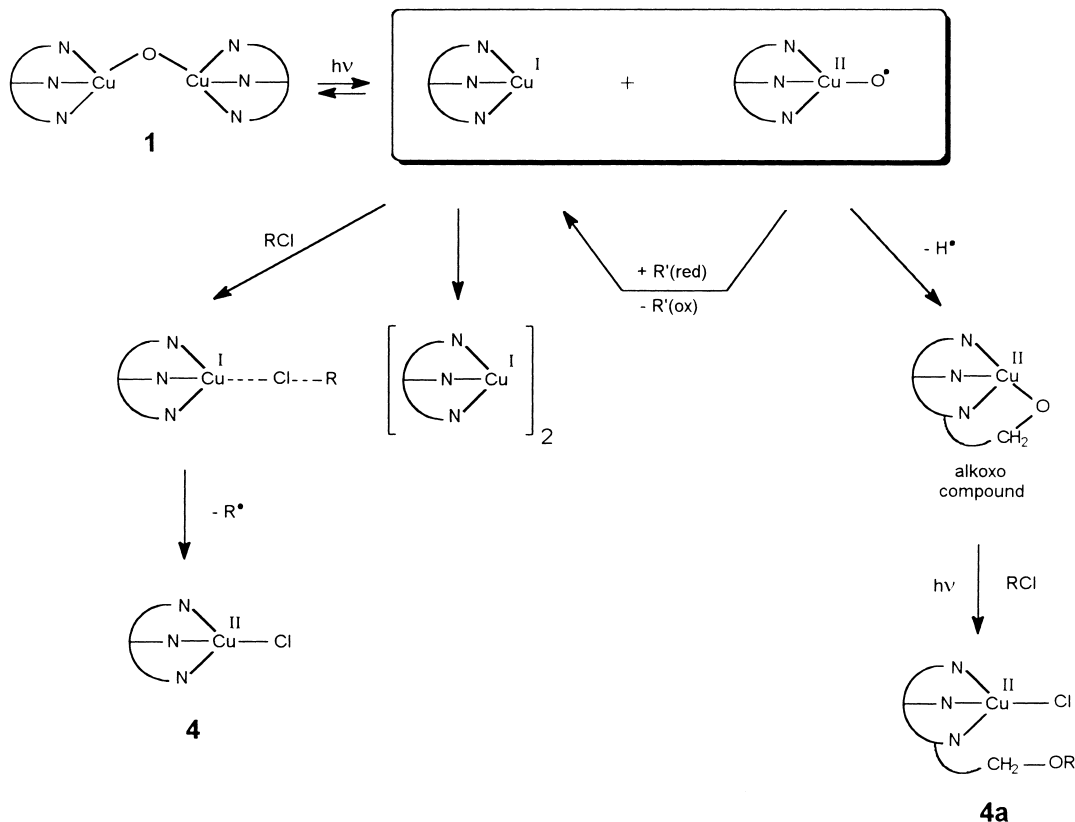
Scheme 2. Proposed mechanism of the photochemical and secondary thermal reactions induced by CT-irradiation of [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$O in chlorinated solvents.

[27,28]. Increase of the absorption in the UV-region <290 nm (Fig. 1(b), Fig. 2) is most probably associated with formation of this species.

The mechanism of the CT-photochemistry leading to formation of **4** is represented in Scheme 2. The homolytic cleavage of the Cu–O bond induced by the irradiation in the CT-band region, generates the [LCu(I)] and [LCu(II)O⁻] species (Scheme 2). The formation of [LCu(II)O⁻] by thermal decomposition of [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$O$_2$ has been proposed by Kitajima [9,15]. The photochemical generation of an active copper-oxygen radical has also been suggested to contribute to photochemical oxidation of cyclohexene and DMSO catalysed by **1** [12,13].

The coordinatively unsaturated [LCu(I)] complex should be highly unstable: it can either dimerize yielding [LCu(I)]$_2$ (the mass 720) or interact with the solvent and produce a Cl-extraction. Considering the possibility of a nucleophilic substitution, irradiation of **1** in the presence of Et$_4$NCl was performed. However, generation of **4** was not recorded. Thus, a radical mechanism is postulated (Scheme 2) in which the copper(I) species induces a homolytic splitting of the C–Cl bond extracting the chlorine radical what, in consequence, leads to copper oxidation and formation of **4**.

The [LCu(II)O⁻] complex (or its isomeric form [LCu(III)O]) is also very unstable [29]. We suggest, that the reactive [LCu(II)O⁻] radicals can be reduced also to [LCu(I)] (Scheme 2). Alternatively, an intramolecular reaction of [LCu(II)O⁻] can be envisaged: oxygen atom can interact with the methyl group in position 3 of one of the pyrazol ring generating more stable 'alkoxo' species. This kind of interaction was reported recently for [Co(II)(HB(3,5-*i*-Pr$_2$pz)$_3$)O⁻] radicals [30,31] and also for copper(II) complexes [32]. It is possible, that observed behaviour of the 335 nm band (its growth and bathochromic shift) is due to formation of the alkoxo species. Its stability can be relatively high – when irradiation of **1** was interrupted no further spectral changes were observed. Therefore, the next step can be considered also as the photochemical one. Again the plausible mechanism is the cleavage of the Cu–O bond and reaction with the solvent molecule. Finally, the [(ROL)CuCl], **4a**, is produced. Electronic and EPR spectra of **4a** should resemble those of the **4**. Hence, the final photoproduct can be a mixture of **4**, **4a**, [LCu(I)]$_2$ and other complexes.

The mechanism of CT photochemistry of **2** can differ in details from that shown in Scheme 2, due to the presence of and additional bridging ligand.

The heterolytic cleavage of the Cu–O bond could be observed, however, only as a consequence of the CT excitation: neither thermal reaction nor chemical deactivation of the d–d excited state lead to the redox mode. In these cases spectral changes resemble rather a reaction of **1** with CO$_2$ with formation of **2**. Therefore we conclude, that Cu–O–Cu structure is persisted and only an interaction of solvent with **1** takes place. This hypothesis is supported by higher thermal stability of **2** than **1** and by similarity in photochemical behaviour between **2** and the product of thermal solvatation of **1**.

4. Conclusion

We have compared in this paper the thermal and photochemical (d–d and CT-band) behaviour of scorpionate Cu-complexes **1** and **2** and shown the influence of the solvent. Upon irradiation of [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$O or [Cu(HB(3,5-Me$_2$pz)$_3$)]$_2$CO$_3$ in chlorinated aliphatic solvents in the CT-band region, the new mononuclear copper(II) complex [Cu(HB(3,5-Me$_2$pz)$_3$)Cl] is generated. This species may exist both in tetra- and penta-coordinated monomeric forms, as well as can dimerize.

Most likely, irradiation on the CT-band causes the cleavage of the Cu–O bond and the formation of reactive Cu(I) and Cu(II)-O radical species. The former can be responsible of the chlorine atom extraction from the solvent to afford **4**. [LCu(II)O⁻] can either be reduced to [LCu(I)] or undergo an intramolecular rearrangement to form an 'alkoxo' complex. Such CT-band photochemistry of the Cu-scorpionates could be involved in the photochemical C–H activation. The photogenerated forms could also originate new poly(pyrazolylborate) ligands.

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