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Photo-induced Reduction of Cu(II)–Benzimidazolylthioether Chelates. The Formation of 1,6-Bis(N-methylbenzimidazol-2-yl)-2,5-dithiahexane Copper(I) Perchlorate from the Corresponding copper(II) Compound by Photo-induced Reduction in Dimethylformamide

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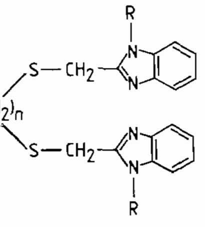
Bis(benzimidazolyl)bis(thioether)copper chelates have been shown to be interesting coordination compounds, having a five-coordinate geometry in the case of Cu(II) and a linear two-coordinate geometry in the case of Cu(I) [1–5], as schematically indicated in Fig. 1. It appeared that for certain derivatives of these chelating ligands, Cu(I) compounds were formed spontaneously during the preparation of the Cu(II) salts, apparently with simultaneous oxidation of the solvent [3].

Such a system, stabilising both Cu(I) and Cu(II), is of interest in view of current studies on type-I copper proteins ('blue copper proteins'), and model compounds mimicking their structure and redox properties.

We now wish to report on a photo-induced reduction of some Cu(II) compounds with chelating ligands containing benzimidazole and thioether groups:



Results and Discussion

Upon irradiation (λ = 254 nm) of 1,6-bis(N-methylbenzimidazol-2-yl)-2,5-dithiahexanecopper(II) perchlorate [Cu(BMBDH)(ClO$_4$)$_2$] in MeOH (10^{-3} *M*) in a quartz cuvet the green solution discolours within hours. Monitoring of the UV/VIS spectrum as a function of time shows a decrease of the intensity of the Cu(II) d–d transition (λ_{max} = 650 nm, *cf.* Fig. 2), while no new Cu(II) bands appear. The reduction proceeds even faster in DMF, and within half an hour the conversion is complete. Both in MeOH and DMF a dark reaction has also been observed, but at a much smaller rate than upon irradiation.

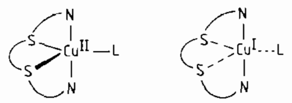


Fig. 1. Observed coordination geometries of Cu(II) and Cu(I) with N_2S_2 chelating ligands containing benzimidazole groups.

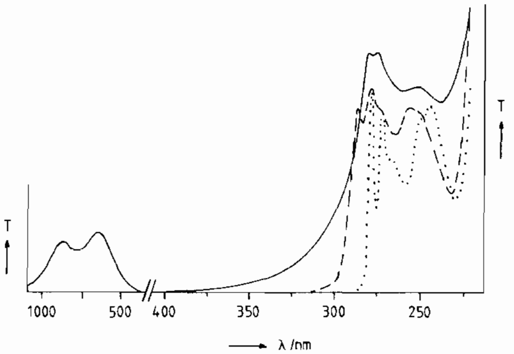


Fig. 2. Transmission spectra, recorded in DMF (1000–450 nm) and MeOH (450–200 nm), of Cu(BMBDH)(ClO$_4$)$_2$-[$\lambda_{max}(\epsilon)$: 880(180), 650(235), 280(15530), 275(15580), 253(12320): ———, BMBDH [287(11000), 279(12300), 247(10870)] : – – –, and benzimidazole [279(6105), 272(5260), 245(5440)] : ......; ε values are in l mol^{-1} cm^{-1}.

Irradiation of the Cu(II) complex in DMF on a preparative scale afforded a grey powder after precipitation with diethyl ether. The IR spectrum (KBr) of this powder points toward the presence of the corresponding Cu(I) compound as well as to some DMF, as compared with reference samples of Cu(BMBDH)ClO$_4$ and DMF (Table I). The ^{1}H NMR spectrum (DMSO) shows peaks of both BMBDH [7.56 (m, 4H), 7.29 (m, 4H), 4.30 (s, 4H), 3.77 (s, 6H) and 3.10 (s, 4H) ppm] and DMF [7.98 (s), 2.81 (s) and 2.65 (s) ppm]. Cu analysis of several samples showed a composition CuClO$_4$·BMBDH·xDMF (x = 0.5 ± 0.2). The formation of the Cu(I) compound has been confirmed unequivocally by recording the IR spectrum of the substrate in DMF solution immediately after irradiation. In the fingerprint region a characteristic pattern was found at

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TABLE I. Main Bands (cm^{-1}) in the IR Spectra of the Product Formed upon Irradiation of $Cu(BMBDH)(ClO_4)_2 \cdot H_2O$ in DMF (I), of $Cu(BMBDH)ClO_4$ (II) and the Starting Cu(II) Compound (III).

I Photoproduct	II Cu(I)	III Cu(II)	Assignment
		3440	νOH
2950	2950	2955	νCH
2920	2920	2920	νCH
1665			νC=O (DMF)
1489	1482	1498	
1453	1449	1459	
1399	1399	1390	
1258	1258	1255	
1240	1240	1239	
1083	1088	1095	ClO_4 (ν_3)
744	741	758	
624	619	621	ClO_4 (ν_4)

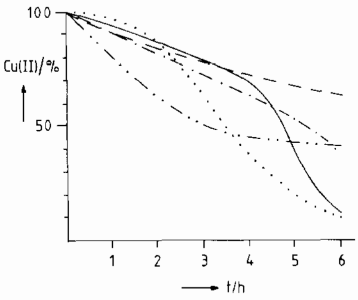

Fig. 3. Irradiation of $CuX_2 \cdot BBDH$ in MeOH (2×10^{-3} *M*); decrease of the Cu(II) amount as a function of time, determined from the absorbance at 650 nm: X = Cl (———), Br (– – –), BF_4^- (·······), ClO_4^- (–·–·–) and NO_3^- (–··–) respectively.

771 and 752 cm^{-1}, which is also present in a reference sample of $Cu(BMBDH)ClO_4$ measured in DMF, but which is totally absent in the solution of the Cu(II) starting compound (peaks at 788, 765 and 754 cm^{-1}).

Upon irradiation of the Cu(II) compound in CH_3CN only a slight decrease of the Cu(II) absorption was observed. Irradiation in a CH_3CN/iPrOH mixture (90:10/v:v; this ratio being chosen for reasons of solubility of substrate and product) afforded – upon handling under the same conditions as with DMF as a solvent – the Cu(I) product only in impure form as a brown powder (Cu: calcd. 11.66%; found 10.99%). Use of a CH_3CN/MeOH mixture (80:20/v:v) as medium gave a brown product of unclear composition (Cu: only 6.5%; IR: bands of the Cu(I) compound but also a strong band at 3430 cm^{-1} assigned to a ν_{OH}). Other solvents were not considered in view of limiting factors such as the solubility of the substrate.

The rate of reduction is markedly enhanced by addition of benzophenone or acetophenone as a sensitizer. No matter the solvent used, pure Cu(I) compounds could not be obtained. In all cases white products were isolated and IR spectroscopy indicated the presence of the Cu(I) product, but Cu analyses were always far too low (about 6–9%). The presence of products like benzpinacol which might result from reactions of the sensitizer could not be established by IR spectroscopy. Using fluorenone, pyrene or *m*-methoxyacetophenone as a sensitizer no photoreduction was observed at all. Upon excitation these sensitizers – contrary to benzophenone or acetophenone – do not abstract hydrogen from other molecules [6]. This infers that on using the latter two sensitizers the reduction of the Cu(II) compound is not induced by energy transfer from the sensitizer, but rather by radicals such as the benzophenone ketyl radical (chemical sensitization) [7]. This is substantiated by the fact that reduction of the amount of benzophenone by a factor of ten did not affect the course of the photoreaction. The essential steps in the reduction of the Cu(II) compound are then proposed to be as follows:

$$^1D \xrightarrow{h\nu(254\ nm)} {^1D}^* \longrightarrow {^3D}^*$$

$$^3D^* + RH_2 \rightarrow DH\cdot + RH\cdot$$

$$RH\cdot\ (\text{or } DH\cdot) + Cu(II) \rightarrow R\ (\text{or } D) + Cu(I) + H^+$$

(D stands for benzophenone or acetophenone, RH_2 stands for solvent).

Hydrogen abstraction from the solvent by the photo-excited sensitizer yields two radicals, either of which may reduce Cu(II) with simultaneous formation of the oxidized solvent and starting sensitizer respectively. Reduction of Cu(II) by carbon-centered radicals is well known [8]. When MeOH or iPrOH is used as a solvent, the primary formed hydroxyalkyl radicals are converted into formaldehyde and acetone respectively [9]. In the case of DMF as a solvent the initial hydrogen abstraction occurs from one of the methyl groups of DMF [10]. The resulting radical may either reduce Cu(II) with simultaneous formation of an iminium salt [11], or dimerize [12].

Direct irradiation of the Cu(II) compound may induce several electronic transitions. The UV/VIS sepctrum of $Cu(BMBDH)(ClO_4)_2$ is characterized by two bands (Fig. 2): an asymmetric band of low intensity with maxima at λ = 880 and 650 nm, as usually found for Cu(II) d–d transitions in distorted five-coordinate Cu(II) complexes [13] and a band below λ = *ca.* 420 nm. The latter band is dominated by absorptions at λ = 280, 275 and 253 nm caused by electronic transitions of the ligand and more specifically the benzimidazole moiety. The difference in absorption between the Cu(II) compound and BMBDH (*e.g.* ϵ = 3000 l/mol cm at λ = 280 nm) suggests the presence of additional ligand → Cu(II) charge-transfer (LMCT) bands in the $\lambda < 300$ nm region [14]. The absorption between 420 and 300 nm is assigned to π(N) → Cu(II) and σ(S) → Cu(II) charge-tranfer bands [15–18].

Recution of Cu(BMBDH)$(ClO_4)_2$ occurs upon irradiation in quartz glass, but not in pyrex. This implies that the photoreactive state is reached only upon absorption of $\lambda < 300$ nm radiation, which might indicate that reduction of the Cu(II) proceeds *via* excitation of BMBDH, followed by an intramolecular LMCT step, or eventually directly *via* a photoinduced LMCT reaction. Exploratory irradiations of other compounds of formula $CuX_2 \cdot L$ with X = Cl, Br, NO_3, BF_4, ClO_4 and L = BBDH of BBDHp, using MeOH as solvent, showed that all these compounds undergo photoreduction. However, there seem to be significant differences in rate and mechanism for the various compounds, as is illustrated by the different decreases in intensity of the UV absorption band at $\lambda \approx 650$ nm, as depicted for some compounds in Fig. 3.

Experimental

Physical Measurements

^{1}H NMR spectra were measured at 100 MHz on a JEOL-PS 100 spectrometer, chemical shifts (δ) are given in ppm relative to TMS. IR spectra were recorded on a Perkin Elmer 580B spectrometer. UV and VIS spectra were measured on Beckman-DB and Beckman DK-2A spectrophotometers. Metal analyses were carried out using standard EDTA titration techniques. Other elemental analyses were performed Dr. Pascher, Bonn, F.R.G.

Materials

EMBDH

This has been prepared by methylation of BBDH [1] in an acetone/KOH mixture with methyl iodide [19]. Yield 82%; m.p. 210–211 °C. *Anal.* Calcd. for $C_{20}H_{22}N_4S_2$: C, 62.79; H, 5.80; N, 14.65. Found: C, 62.5; H, 5.9; N, 14.2. ^{1}H NMR (CF_3COOD, δ): 7.78 (s, 8H), 4.34 (s, 4H), 3.01 (s, 4H). IR (KBr, cm^{-1}): 3055 (w), 2920 (w), 1500 (m), 1470 (s), 1437 (s), 1389 (s), 1332 (s), 1284 (m), 1254 (s), 1239 (m), 1210 (s), 1003 (m), 859 (m), 746 (s), 432 (m).

Cu(BMBDH)$(ClO_4)_2 \cdot 2H_2O$

This was prepared by adding 370 mg (1.5 mmol) $Cu(ClO_4)_2 \cdot 6H_2O$ dissolved in 10 ml of absolute EtOH to a boiling solution of 570 mg (1.5 mmol) BMBDH in 325 ml of EtOH. The green product was isolated at room temperature by filtration, washed with dry ether and dried *in vacuo*. *Anal.* Calcd. for $CuC_{20}H_{26}N_4S_2O_{10}$: Cu, 9.34; C, 35.2; H, 3.82; N, 8.23. Found: Cu, 9.1: C, 35.1: H, 3.5: N, 7.4. It seems likely that upon standing some initially coordinated EtOH is replaced by H_2O, as is also the case for the corresponding BBDH complex [2].

Cu(BMBDH)ClO_4

A solution of 1 mmol of $Cu(CH_3CN)_4ClO_4$ in 15 ml CH_3CN prepared *in situ* [2] was added to a boiling solution of 382 mg (1 mmol) BMBDH in 220 ml of abs. EtOH under nitrogen. The white crystals produced were filtered off at room temperature, washed with ether and dried *in vacuo*. The crystals are stable in air: upon storage for months no oxidation has been observed. *Anal.* Calcd. for $CuC_{20}H_{22}N_4S_2ClO_4$: Cu, 11.65; C, 44.03; H, 4.06; N, 10.27; S, 11.75. Found: Cu, 11.4; C, 43.8; H, 4.2; N, 10.3; S, 11.6. The several Cu(II)–BMBDH salts have been prepared analogous to the Cu(II) perchlorate compound. The synthesis of the Cu(II) compounds with BBDH and BBDHp as a ligand has been reported before [1–3]. The sensitizers were used as commercially available (Aldrich). All solvents (except EtOH) were *P.A.* quality (Merck, Baker) and were dried on molecular sieves 3A.

Photochemical Experiments

Small-scale irradiations were performed in a 1 cm quartz cuvet placed in a water-cooled cell holder. A Hanau TQ81 lamp was used as the radiation source. The substrate concentration was in general 2×10^{-3} *M*. Preparative scale irradiations were carried out in a home-made Rayonet-like reactor equipped with eight Philips TUV 15W low-pressure Hg lamps. In general a 10 or 40 ml quartz tube was used containing a 10^{-2} *M* solution of the substrate with a small amount of triethyl orthoformate for dehydration. After bubbling nitrogen gas through the solution for *ca.* 15 min the sample was irradiated till complete disappearance of the green colour. Diethyl ether was added dropwise (under nitrogen): the resulting precipitate was filtered off and dried *in vacuo*. For the sensitizing experiments the ratio of sensitizer:substrate was such that >99% of the incident radiation was absorbed by the sensitizer.

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References

1 P. J. M. W. L. Birker, J. Helder and J. Reedijk, *Recl. Trav. Chim. Pays-Bas, 99,* 367 (1980).
2 P. J. M. W. L. Birker, J. Helder, G. Henkel, B. Krebs and J. Reedijk, *Inorg. Chem., 21,* 351 (1982).
3 M. J. Schilstra, P. J. M. W. L. Birker, G. C. Verschoor and J. Reedijk, *Inorg. Chem.,* in press.
4 F. J. Rietmeijer, S. Gorter, P. J. M. W. L. Birker and J. Reedijk, *J. Chem. Soc., Dalton Trans.,* 1191 (1982).
5 P. J. M. W. L. Birker, E. F. Godefroi, J. Helder and J. Reedijk, *J. Am. Chem. Soc.,* in press.
6 S. L. Murov, 'Handbook of Photochemistry', Marcel Dekker, New York, 1973, p. 3
7 N. J. Turro, 'Modern Molecular Photochemistry', Benjamin/Cummings, Menlo Park, California, 1978, p. 261.
8 G. Ferraudi and S. Muralidharan, *Coord. Chem. Rev., 45,* 55 (1981).
9 J. K. Kochi, *J. Am. Chem. Soc., 84,* 2121 (1962).
10 M. Nakashima and E. Hayon, *J. Phys. Chem., 75,* 1910 (1971).
11 G. Roewer and G. Kempe, *Z. Chem., 21,* 75 (1981).
12 G. Roewer and G. Kempe, *Wiss. Z. TH Leuna-Merseburg, 18,* 87 (1976).
13 B. J. Hathaway and D. E. Diling, *Coord. Chem. Rev., 5,* 143 (1970).
14 E. Bernarducci, W. F. Schwindinger, J. L. Hughey, IV, K. Krogh-Jespersen and H. J. Schugar, *J. Am. Chem. Soc., 103,* 1686 (1981).
15 A. R. Amundsen, J. Whelan and B. Bosnich, *J. Am. Chem. Soc., 99,* 6730 (1977).
16 H. J. Prochaska, W. F. Schwindinger, M. Schwartz, M. J. Burk, E. Bernarducci, R. A. Lalancette, J. A. Potenza and H. J. Schugar, *J. Am. Chem. Soc., 103,* 3446 (1981).
17 J. V. Dagdigian, V. McKee and C. A. Reed, *Inorg. Chem., 21,* 1332 (1982).
18 E. W. Ainscough, A. M. Brodie and N. G. Larsen, *Inorg. Chim. Acta, 60,* 25 (1982).
19 Y. Kikugawa, *Synthesis,* 124 (1981).