Binuclear Complexes

Diazene Complexes of Copper: Synthesis, Spectroscopic Analysis, and Electronic Structure**

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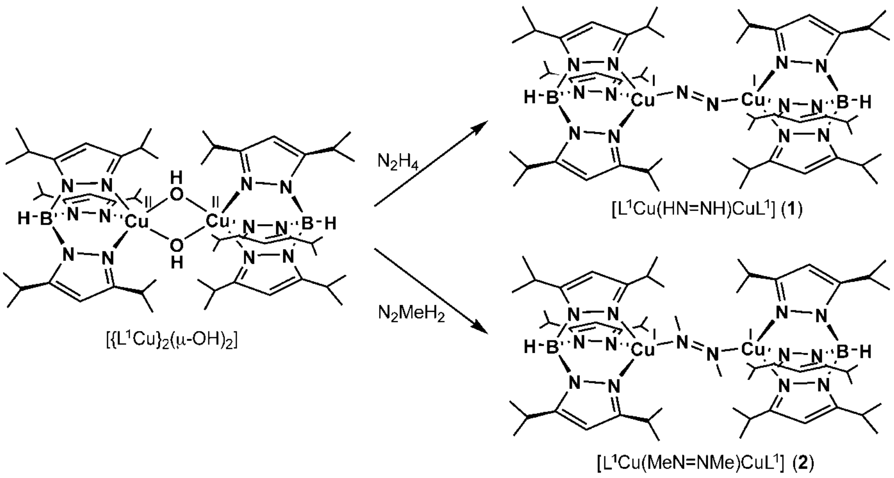
In memory of Dieter Sellmann

Diazene is a very interesting molecule as a result of its ability to stereoselectively reduce some unsaturated organic substrates (probably via the *cis* isomer)[1] as well as its relevance in biological nitrogen fixation. Evidence from X-ray analyses,[2] spectroscopic studies,[3] and density functional calculations[4] suggests that HN=NH (1,2-diazene) is a metal-bound intermediate in nitrogenase turnover. Diazene is extremely unstable in its free state and undergoes a bimolecular decomposition above −150 °C to give N_2 and N_2H_4.[5] Its stability is greatly enhanced, however, when its lone pairs are coordinated to transition metals. The general importance of nitrogen fixation has resulted in many research groups having tried to make model complexes with coordinated diazene, dinitrogen, or hydrazine ligands; the corresponding transition-metal–diazene complexes have been synthesized by Sellmann[6] amongst others.[7,8] However, in the case of Cu, only three crystal structures—a complex of a 1,2-disubstituted diazene ($[Cu_2Cl_2(MeN{=}NMe)]_n$)[9] and two hydrazine complexes ($[CuCN(N_2H_4)]_n$[10a] and $[CuCl(N_2H_4)(NaCl)]_n$[10b])—have been published, and to the best of our knowledge no structural and spectroscopic data for Cu^I–diazene complexes have been reported so far. Herein we report the crystal structures and UV/Vis absorption and resonance-Raman spectra of two related Cu^I complexes with bridging *trans*-1,2-diazene and *trans*-1,2-dimethyldiazene ligands. The coordination sphere of the Cu^I centers is completed by a hydrotris(pyrazolyl)borate-type tripod ligand. The electronic structure of these systems has been evaluated with the help of density functional (DFT) calculations.

Addition of an excess of hydrazine monohydrate (2.5 equiv) to a solution of the precursor $[(L^1Cu)_2(\mu\text{-}OH)_2]$ (L^1 = hydrotris(3,5-diisopropyl-1-pyrazolyl)borate anion)[11] in CH_2Cl_2/heptane (5:1) at −50 °C caused a gradual color change from blue to dark purple. Filtration, concentration, and cooling of this solution afforded $[L^1Cu(HN{=}NH)CuL^1]$ (**1**; yield: 60%) as a deep-purple, microcrystalline solid (Scheme 1).[12–14] The oxidation of hydrazine to diazene is mediated by the Cu^{II} centers, which are reduced to Cu^I-centers (similar hydrazine oxidations have been applied before to form diazene complexes[6,7]). The fact that a diazene unit had formed from hydrazine was evident from: a) the appearance of a strong absorption band at 573 nm (ε = 3500 $cm^{-1}\,mol^{-1}\,dm^3$), whereas monomeric and dimeric Cu^I–hydrazine complexes are colorless;[15] b) the appearance of a strong resonance-Raman band at 1358 cm^{-1}, which is the typical N–N stretching frequency of dimeric diazene complexes (see below); c) the observation of a small signal in the ^1H NMR spectrum at δ = 4.90 ppm which corresponds to the diazene hydrogens; and d) the X-ray crystal structure shown in Figure 1, where a planar *trans*-N_2H_2 ligand bridges the two Cu^I ions.[16] Together with the hydrotris(pyrazolyl)borate ligand, this leads to a distorted tetrahedral geometry at the Cu centers. Complex **1** has a crystallographic inversion center in the middle of the N=N bond. The N41–N41′ bond length (1.13(1) Å) is slightly shorter than those of the N–N bonds of previously reported diazene complexes (1.16–1.30 Å),[6–9] and is clearly not in the range found for hydrazine complexes



Scheme 1. Synthesis of complexes **1** and **2**.

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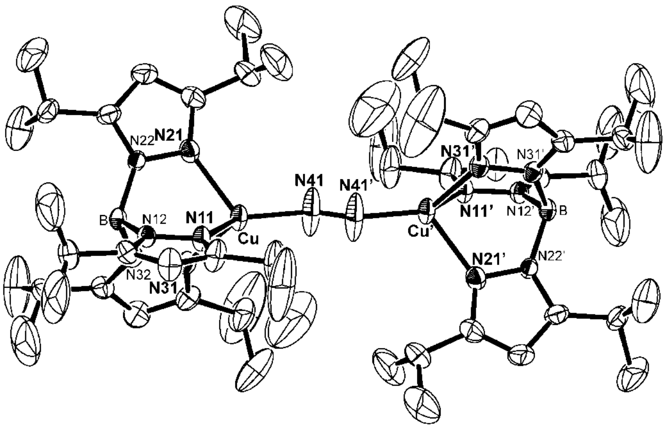

Figure 1. ORTEP view of $[L^1Cu(HN{=}NH)CuL^1]$ (**1**) showing 50% thermal ellipsoids and the atom-labeling scheme. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [°]: Cu–N41 1.841(8), Cu–N11 2.035(7), Cu–N21 2.082(7), Cu–N31 2.043(6), N41–N41′ 1.13(1), Cu···Cu′ 4.709(1); N41–Cu–N11 127.5(3), N41–Cu–N21 119.9(4), N41–Cu–N31 126.2(4), N11–Cu–N21 90.8(3), N11–Cu–N31 91.1(3), N21–Cu–N31 90.8(3), Cu–N41–N41′ 151.6(8).

($\Delta_{N\text{-}N}$ ~ 1.45 Å).[15] As can be seen in Figure 1, the nitrogen atoms N41 and N41′ both show thermal ellipsoids that are distorted in a direction orthogonal to the Cu-N-N-Cu plane. This result indicates a slight disorder in the crystal that might lead to the observed shortening of the N–N bond from the expected value for diazene complexes (ca. 1.25 Å). Correspondingly, the Cu–N41–N41′ angle (151.6(8)°) is more obtuse than the values reported for other diazene complexes (129–130°);[8] this is most probably a consequence of the small amount of disorder in the crystal and not an intrinsic structural property of **1**.

To confirm the structural analysis and the obtained NMR spectrum of **1**, the dimethyldiazene derivative **2** was prepared from the reaction between $[(L^1Cu)_2(\mu\text{-}OH)_2]$ and *N,N′*-dimethylhydrazine dihydrochloride (neutralized by aqueous NaOH or triethylamine) at −50 °C.[17] Cooling of the reaction mixture led to the precipitation of red crystals of $[L^1Cu(MeN{=}NMe)CuL^1]$ (**2**; yield: 64%; Scheme 1).[13,14] Unfortunately, the structure determination of **2** is incomplete because of the poor quality of the crystals obtained (see Supporting Information).[16] The N41–N41′ bond length (1.27(2) Å) is in the normal range for *trans*-diazene complexes (1.16–1.30 Å).[6–9] Moreover, the Cu–N41–N41′ angle (132(1)°) is only slightly more obtuse than in previously reported diazene complexes because of steric interactions of the methyl groups bound to the bridging nitrogen atoms. The presence of an MeN=NMe bridge in **2** is also shown by resonance-Raman (see below) and ^{1}H NMR spectroscopy (see Supporting Information). The repulsion of the methyl substituents of the MeN=NMe group in **2** results in the copper coordination sphere being distorted and, correspondingly, the Cu···Cu′ distance in **2** (4.786(5) Å) is longer than that in **1** (4.709(1) Å). However, the Cu···Cu′ distances in both **1** and **2** are significantly longer than those of a previously reported μ-η^2:η^2 peroxo complex (3.560(3) Å)[11] and a μ-η^2:η^2 disulfido complex (4.028 (3) Å).[18]

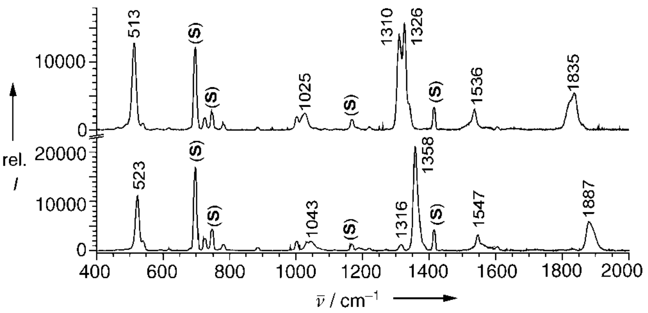

Figure 2. Resonance-Raman spectra (excitation: 568 nm, CH_2Cl_2) of $[L^1Cu(HN{=}NH)CuL^1]$ (**1**; bottom) and the corresponding ^{15}N-labeled complex (top). S denotes solvent peaks.

Figure 2 shows the resonance-Raman spectra of **1** and of the corresponding ^{15}N-labeled compound. These spectra can be understood based on the previously reported peak assignments[19] for the diazene-bridged Fe^{II} complexes $[(Fe\text{'}N_HS_4\text{'})_2(N_2H_2)]$ ('N_HS_4'-H_2 = 2,2'-bis(2-mercaptophenylthio)diethylamine) and $[\{Fe\text{'}S_4\text{'}(PPr_3)\}_2(N_2H_2)]$ ('S_4'-H_2 = 1,2-bis(2-mercaptophenylthio)ethane),[6] and a DFT calculation on a model of **1** (see Supporting Information). Table 1 summarizes the assignments. The most intense band at 1358 cm^{-1} is assigned to the N–N stretch $\tilde{\nu}$(N-N); it shifts to about 1320 cm^{-1} on isotope labeling, close to the weak band at 1316 cm^{-1} in the unlabeled complex. Both vibrations subsequently mix strongly and, hence, the 1316 cm^{-1} absorption steals intensity from the N–N stretch and also shows a slight shift to lower wavenumbers (1310 cm^{-1} in the labeled complex). In the case of the above-mentioned Fe^{II}–diazene complexes, $\tilde{\nu}$(N–N) appears at 1382 and 1365 cm^{-1}, respectively, which confirms this assignment.[6] The symmetric N–N–H bend for **1** is found at 1547 cm^{-1} and the symmetric Cu–N stretch is observed at 523 cm^{-1}. In addition to these fundamental absorptions, several overtones and combination modes are also observed (Table 1). For comparison, the Raman spectrum of **2** is shown in Figure 3. This spectrum is assigned on the basis of the results for **1** and a DFT calculation on a model of **2** (Table 2). In this case, mode-mixing of the N–N stretch with the modes of the methyl substituents (namely, H–C–H bends, the symmetric C–N stretch, and

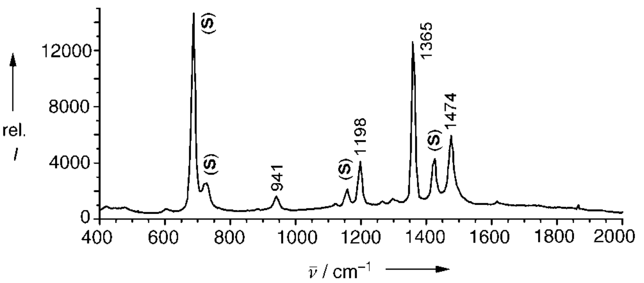

Figure 3. Resonance-Raman spectrum (excitation: 514 nm, CH_2Cl_2) of $[L^1Cu(MeN{=}NMe)CuL^1]$ (**2**). S denotes solvent peaks.

Table 1: Raman assignments of complex **1**.

Mode	Symbol	Cu-N_2H_2-Cu (**1**) exp. (Figure 2)[a]	calcd	[(Fe'N_HS_4')$_2$(N_2H_2)] exp. (ref. [19])
ν_S(Cu−N)	A	523 (513)	512	not observed
γ_S		not observed	603	667/659
	2 × A	1043 (1025)	–	–
ν(N−N)	B	1358 (1326/1310)	1421	1382
δ_S(N−N−H)		1547 (1536)	1573	1480
	A + B	1887 (1835)	–	–

[a] Band positions in the ^{15}N-labeled material are given in brackets.

Table 2: Raman assignments of complex **2**.

Mode[a]	Cu-N_2Me_2-Cu (**2**) exp. (Figure 3)	calcd
ν_S(**Cu−N**)	not observed	251/341
δ_S(**N−C−H**) + ν_S(C−N) + ν_S(Cu−N)	941	959
ν_S(**C−N**) + δ_S(N−C−H) + ν_S(Cu−N)	1198	1214
ν(**N−N**) + δ_S(H−C−H) + ν_S(C−N)	1365	1416
δ(**H−C−H**) + ν(N−N)	1474	1491/1529

[a] The dominant contribution to a mode is given first in bold type.

N−C−H bends) complicates the interpretation. However, since the N−N stretch should show the strongest resonance enhancement in the Raman spectrum, its assignment to the peak at 1365 cm^{-1} is straightforward, and is also in agreement with the calculations.

Previous work has shown that diazene is a σ-donor and π-acceptor ligand.[19] However, the d^{10} electron configuration of the Cu^I ion means that no σ donation from the diazene into the d orbitals of copper is possible in **1** and **2**. Correspondingly, the interaction between the Cu^I center and the diazene corresponds to a pure back-bond. This bonding description is in agreement with the results of the DFT calculations for **1** and **2**. Figure 4 shows a schematic molecular orbital (MO) diagram for **1**. The LUMO corresponds to the antibonding combination of π_v^*—the π* orbital of the diazene perpendicular to the Cu-N_2H_2-Cu plane—and the in-phase combination of the d_{xz} orbitals on the copper atoms. The corresponding out-of-phase combination of the d_{xz} orbitals is the HOMO, which is essentially nonbonding to the ligands. The bonding MO between d_{xz} and π_v^* is found at lower energy. This electronic structure is different from that obtained for the Fe^{II}–diazene complexes, where both a σ and a π bond between the metal and the diazene ligand are found.[19]

Figure 5 shows the absorption spectrum of **1** together with resonance-Raman profiles of the peaks at 523, 1358, 1547, and 1887 cm^{-1}, which all show resonance enhancement with respect to the intense absorption of **1** at 573 nm. This band is therefore assigned as a $d_{xz} \rightarrow \pi_v^*$ (HOMO→LUMO) charge-transfer (CT) transition, as shown in Figure 4. This is similar to the Fe^{II}–diazene systems, where the corresponding CT transition is found at 580 and 620 nm for [(Fe'N_HS_4')$_2$(N_2H_2)] and [{Fe'S_4'(PPr_3)}$_2$(N_2H_2)], respectively.[6] In the case of **2**, the corresponding CT transition is at 484 nm (see Supporting Information).

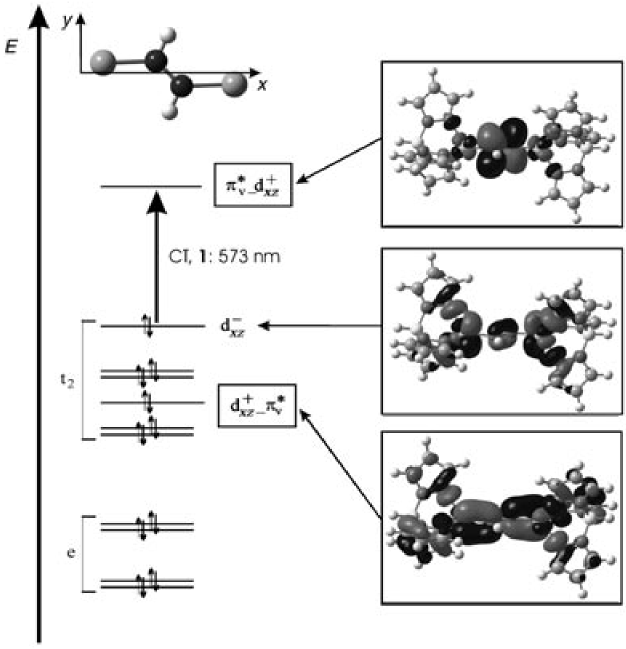

Figure 4. Schematic MO diagram of **1**. The insert in the top left corner shows the chosen coordinate system for the labeling of the orbitals. The orbital π_v^* (v = vertical) corresponds to the π* function of diazene orthogonal to the Cu-N(H)=N(H)-Cu plane. The inserts on the right show important MO contours.

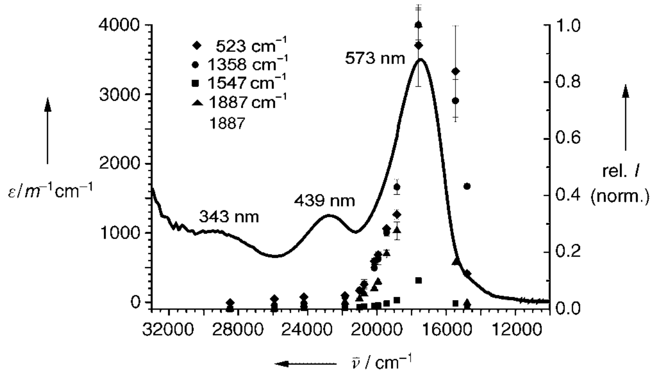

Figure 5. Resonance-Raman profiles of important vibrations of **1** plotted against the absorption spectrum.

We have described the preparation and characterization of novel Cu^I–diazene complexes. Spectroscopic results and crystal structures have been presented and related to known Fe^{II}–diazene complexes, thus proving the identity of the former compounds. In addition, the electronic structure of the Cu^I–diazene bond has been investigated with the help of density functional calculations.

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[1] a) E. J. Corey, D. J. Pasto, W. L. Mock, *J. Am. Chem. Soc.* **1961**, *83*, 2895; b) E. E. van Tamelen, R. S. Dewey, R. J. Timmons, *J. Am. Chem. Soc.* **1961**, *83*, 3725; c) E. E. van Tamelen, R. S. Dewey, R. J. Timmons, *J. Am. Chem. Soc.* **1961**, *83*, 3729; d) E. E. van Tamelen, R. J. Timmons, *J. Am. Chem. Soc.* **1962**, *84*, 1067.

[2] a) J. Kim, D. C. Rees, *Science* **1992**, *257*, 1677; b) B. Schmid, M. W. Ribbe, O. Einsle, M. Yoshida, L. M. Thomas, D. R. Dean, D. C. Rees, B. K. Burgess, *Science* **2002**, *296*, 352; c) O. Einsle, F. A. Tezcan, S. L. A. Andrade, B. Schmid, M. Yoshida, J. B. Howard, D. C. Rees, *Science* **2002**, *297*, 1696.

[3] a) B. E. Smith, *Adv. Inorg. Chem.* **1999**, *47*, 159; b) J. B. Howard, D. C. Rees, *Chem. Rev.* **1996**, *96*, 2965; c) B. K. Burgess, D. J. Lowe, *Chem. Rev.* **1996**, *96*, 2983; d) R. R. Eady, *Chem. Rev.* **1996**, *96*, 3013.

[4] B. Hinnemann, J. K. Nørskov, *J. Am. Chem. Soc.* **2004**, *126*, 3920.

[5] N. Wiberg, H. Bachhuber, G. Fischer, *Angew. Chem.* **1972**, *84*, 889; *Angew. Chem. Int. Ed. Engl.* **1972**, *11*, 829.

[6] D. Sellmann, A. Hille, A. Rösler, E. W. Heinemann, M. Moll, G. Brehm, S. Schneider, M. Reiher, B. A. Hess, W. Bauer, *Chem. Eur. J.* **2004**, *10*, 819, and references therein.

[7] a) T.-Y. Cheng, A. Ponce, A. L. Rheingold, G. L. Hillhouse, *Angew. Chem.* **1994**, *106*, 703; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 657; b) J. P. Collman, J. E. Hutchison, M. S. Ennis, M. A. Lopez, R. Guilard, *J. Am. Chem. Soc.* **1992**, *114*, 8074; c) G. Huttner, W. Gartzke, K. Allinger, *J. Organomet. Chem.* **1975**, *91*, 47.

[8] Recent reviews: a) B. A. Mackay, M. D. Fryzuk, *Chem. Rev.* **2004**, *104*, 385; b) M. Hidai, *Coord. Chem. Rev.* **1999**, *185–186*, 99; c) D. Sellmann, J. Sutter, *Acc. Chem. Res.* **1997**, *30*, 460.

[9] I. D. Brown, J. D. Dunitz, *Acta. Crystallogr.* **1960**, *13*, 28.

[10] a) D. T. Cromer, A. C. Larson, R. B. Roof, Jr., *Acta. Crystallogr.* **1966**, *20*, 279; b) D. Cheng, C. Feng, S. Xia, *Transition Met. Chem.* **2000**, *25*, 635.

[11] N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, S. Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi, A. Nakamura, *J. Am. Chem. Soc.* **1992**, *114*, 1277.

[12] The diazene complex **1** is unstable in the solid state at room temperature, even under an argon atmosphere, which is in accord with the observations made for the diazene complexes mentioned above. If a small amount of dioxygen is present in the solution at −50 °C, **1** reacts immediately to form the bridging Cu^{II} μ-η^2:η^2 peroxo complex, $[(L^1Cu)_2(\mu\text{-}O_2)]$.[11]

[13] The new diazene complexes **1** and **2** exhibit satisfactory spectroscopic and analytical data (see Supporting Information).

[14] When a solution of **1** or **2** was warmed to above −40 °C under an argon atmosphere the color of the solution slowly changed to green. The nature of the decomposition products was unclear. For this reason, the characterization of these complexes in solution (NMR and electronic absorption spectroscopy) was performed on the reaction mixtures.

[15] K. Fujisawa, N. Lehnert, unpublished results.

[16] CCDC-235558 (**1**) and -235559 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). Note that the Cu-N-N-Cu subunit in **1** and **2** is planar, which is a clear indication of bound diazene; in the case of bridging hydrazine the Cu-N-N-Cu core is strongly bent.[15] The presence of Cu^I centers in **1** and **2** is evident from the fact that no counterions are found in either of the crystal structures.

[17] Either aqueous NaOH solution or triethylamine was used to neutralize *N,N′*-dimethylhydrazine dihydrochloride. The ^1H NMR spectroscopic data and X-ray crystallographic analysis indicated that triethylamine reacted only as a neutralizing agent.

[18] K. Fujisawa, Y. Moro-oka, N. Kitajima, *J. Chem. Soc. Chem. Commun.* **1994**, 623.

[19] a) N. Lehnert, B. E. Wiesler, F. Tuczek, A. Hennige, D. Sellmann, *J. Am. Chem. Soc.* **1997**, *119*, 8869; b) N. Lehnert, B. E. Wiesler, F. Tuczek, A. Hennige, D. Sellmann, *J. Am. Chem. Soc.* **1997**, *119*, 8879.