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Communications

The First Metal Complex Involving an α-H-Containing Nitroxide

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On the basis of the 25-year studies on the synthesis of metal complexes with nitroxides, it was believed that nitroxides were kinetically stable during complex formation only if all substituents in the α-position to the nitroxyl group were hydrocarbons.[2] This concept was extended to the recent extensive investigations in the design of molecular ferromagnets based on metal complexes with stable nitroxides. Since in molecular ferromagnets the hydrocarbon substituents should be as small as possible, as is the case with methyl groups, the number of stable nitroxides employed at present in the design of molecular ferromagnets is extremely limited. In fact, it includes only the 2,2,5,5- and 4,4,5,5-tetramethyl derivatives of 3- and 2-imidazoline, respectively.[2,3] According to current concepts, nitroxides with one of the carbon atoms being α to the nitroxyl group and carrying an H atom are kinetically unstable and disproportionate to diamagnetic compounds.[4]

Recently, *tert*-butyl diphenylmethyl nitroxide, L, has been reported as a representative of a new family of such α-H-containing nitroxides which are stable in the solid state as well as in solution.[5] In these spin carriers the extensive functionalization of the carbon framework is possible and since the $N^\bullet-O$ group is less sterically hindered than that in fully α-substituted analogs, the use of such spin carriers as building blocks in the design of exchange-coupled species is anticipated.[3,6] This stimulated our search for a route to the synthesis of metal complexes with the new type of nitroxides. In this study we report a preliminary account of the coordination properties of this nitroxide ligand, which shows the obtained metal complex to be unexpectedly highly stable.

The reaction of bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II) hydrate, $Cu(hfac)_2H_2O$, with L in hexane yields a mixed-ligand complex of the composition $Cu(hfac)_2L$ as needles[7] suitable for an X-ray diffraction study.[8] The coordination sphere (Figure 1) of the Cu(II) ion is best described as a distorted square pyramid whose basal plane contains O(1), O(2), and O(3) belonging to the hfac anions and O(5), the nitroxyl oxygen atom of the coordinated $N^\bullet-O$ group of L. The axial position is occupied by the remaining O(4) atom of an hfac anion. For the following discussion of importance is the fact that the O(5) atom of the coordinated $N^\bullet-O$ group of L is in the equatorial plane of the coordination polyhedron. It is noteworthy that the structural features of the coordination polyhedron in $Cu(hfac)_2L$ are very similar to those observed in the analogous copper complex containing the "classical" stable

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(7) Satisfactory analyses were obtained. The synthetic procedure and analytical data for (*tert*-butyl diphenylmethyl nitroxide)bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II), $Cu(hfac)_2L$, and electrochemical data for L are deposited as supplementary material.

(8) X-ray data for $Cu(hfac)_2L$ ($C_{27}H_{22}CuF_{12}NO_5$): dark green prism, 0.3 × 0.4 × 0.6 mm, MW 732.00, triclinic, space group $P\bar{1}$ (No. 2) at 293 K; $a = 9.322(1)$ Å, $b = 10.699(1)$ Å, $c = 17.278(1)$ Å, $\alpha = 91.947(8)^\circ$, $\beta = 75.458(8)^\circ$, $\gamma = 111.457(10)^\circ$, $V = 1544.9(2)$ Å^3, $Z = 2$, $d(\text{calc}) = 1.574$ g/cm^3. Data were collected on an Enraf-Nonius CAD-4 automatic diffractometer with the $\theta/2\theta$ scan technique in the range $1.2 \le \theta \le 24.99^\circ$ (Mo Kα, $\lambda = 0.710\,69$ Å; $0 \le h \le 10$, $-12 \le k \le 11$, $-17 \le l \le 20$). A total of 3032 reflections gave 2818 reflections with $I_{hkl} > 2\sigma(I)$ which were used in the refinement of the structure. The structure was solved by a Patterson synthesis (SHELXS-86), and the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located. Refinement was performed on F^2 by full-matrix least-squares methods (SHELXL-93). For 2818 $I_{hkl} > 2\sigma(I)$ and 470 variable parameters $R_1 = 0.038$ and $wR_2 = 0.0546$; GOF = 0.663.

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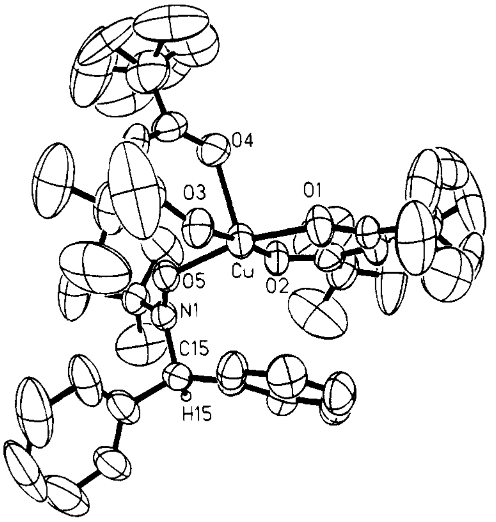

Figure 1. ORTEP view of the molecular structure of Cu(hfac)$_2$L showing the numbering of the atoms. Thermal ellipsoids are drawn at the 35% probability level. Selected bond distances (Å) and angles (deg): Cu–O1 1.964(4), Cu–O2 1.909(4), Cu–O3 1.943(4), Cu–O4 2.205(4), Cu–O5 1.962(3), N1–O5 1.288(4), N1–C15 1.478(6), C15–H15 0.98(1); O1–Cu–O2 92.4(2), O1–Cu–O3 89.9(2), O1–Cu–O4 102.0(2), O1–Cu–O5 163.5(1), O2–Cu–O3 175.4(2), O2–Cu–O4 95.8(2), O2–Cu–O5 92.0(1), O3–Cu–O4 87.6(2), O3–Cu–O5 84.7(1), O4–Cu–O5 93.3(1).

nitroxide 2,2,6,6-tetramethylpiperidine-1-oxyl (Tempo).[9] Within the ligand, the hydrogen atom (H(15)) is clearly located 0.98(1) Å from the α-carbon atom C(15). The two phenyl rings are planar and make an angle of 72°. Dihedral angles involving these phenyl rings and the nitroxyl fragment O(5)N(1)C(15) are 66 and 113°, respectively. The $N^\bullet$–O bond length, 1.288(4) Å, is characteristic of the $^3/_2$-order bond, which shows unambiguously the free radical nature of the ligand.[10]

Further similarities with previously reported copper(II)–nitroxide complexes are seen in their magnetic data. Cu(hfac)$_2$L is diamagnetic at room temperature due to the strong antiferromagnetic coupling between the spin carriers (magnetic susceptibility of the complex was measured by the Faraday method). The full coupling of Cu(II) and the coordinated $N^\bullet$–O group spins is also responsible for the absence of ESR signals for the solid complex. This magnetic behavior is fully consistent with the equatorial ligation of the nitroxyl oxygen to the copper center.[3,6] Therefore, as far as copper(II) is concerned, this new type of nitroxide ligand shows the same coordination and magnetic properties as those already reported for numerous stable nitroxides.

However, in contrast to the reactivity of the nitroxides containing $N^\bullet$–O as the only donor group, the formation of Cu(hfac)$_2$L occurs by the direct reaction of the water-containing Cu(hfac)$_2$H$_2$O with L. This ease of formation is surprising because the coordination chemistry of nitroxides is highly dependent on the poor Lewis basicity of the nitroxyl group. It is indeed known that complex formation requires not only that the metal center carry electron-withdrawing groups such as hexafluoroacetylacetonates but also that water not compete as a ligand with the free radical.[2] Preliminary measurements show that L is slightly more basic than Tempo, but easy complex formation can also be a consequence of the better accessibility of the nitroxyl group due to the presence of the less sterically hindered α-carbon atom. No changes in Cu(hfac)$_2$L composition and properties were detected after storing the complex under usual conditions for 3 months. It should be noted that in solid Cu(hfac)$_2$L the $N^\bullet$–O oxygen and α-hydrogen atom are trans to each other (Figure 2). Maybe such a structure of the O–N–C–H fragment is unfavorable for the elimination of the hydrogen atom and L transition to the corresponding nitrone.[11]

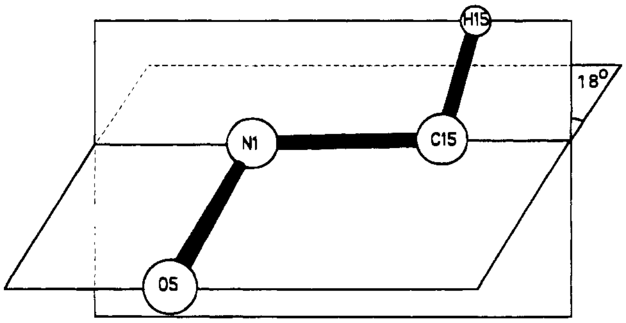

Figure 2. Structure of the O–N–C–H fragment.

Finally, the stability of the complex in solution also deserves special mention. It should be noted that attempts to grow a single crystal of free L have not been successful. Hexane solutions of L decompose in 1 day. Cu(hfac)$_2$L is stable in a hexane solution at least a few days. On cooling of the solution, pure Cu(hfac)$_2$L is isolated as well-formed crystals. This is particularly surprising since Cu(II) compounds very often catalyze oxidation processes.[12] In special circumstances, even fully substituted nitroxides oxidize to the nitroxonium species in the presence of Cu(II) compounds.[13] In contrast, solutions of Cu(hfac)$_2$L are unexpectedly stable. Electrochemical data for free L are in complete agreement with these findings since the oxidation of L occurs at a potential (0.61 V) 0.36 V higher than that of Tempo (0.25 V).[7]

In summary, L, as a representative of a new family of α-H-containing nitroxides, exhibits coordination properties similar to those previously reported for classical fully α-substituted analogs. However, the better accessibility of the coordination center and the high stability toward electron transfer are very promising for the future design of molecular exchange-coupled species.

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Supplementary Material Available: Text giving the synthetic procedure and analytical data for Cu(hfac)$_2$L and electrochemical data for the individual L and listings of crystal data and structure refinement parameters as well as positional and isotropic thermal parameters, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters for Cu(hfac)$_2$L (Tables S1–S5) (14 pages). Ordering information is given on any current masthead page.

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