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Communication

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# Redox-Induced Change in the Ligand Coordination Mode

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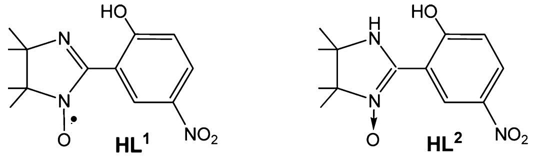
Supporting Information

**ABSTRACT:** The reaction of cobalt(II) pivalate with a spin-labeled Schiff base ($HL^1$) in organic solvents formed trinuclear complex $[Co_3(Piv)_2L^1_2L^2_2]\cdot$Solv (Solv is $Me_2CO$ and/or $C_7H_{16}$ and $CH_3CN$) containing both nitroxide $L^1$ and the product of its single-electron reduction, nitrone $L^2$. The formation of $[Co_3(Piv)_2L^1_2L^2_2]$ was a consequence of an unusual phenomenon, which we called "redox-induced change in the ligand coordination mode". A reduction of $L^1$ to $L^2$ led to a change in the set of donor atoms and even in the size of the metallocycle. This phenomenon was also found for mononuclear $[CrL^1_2L^2]$ and $[FeL^1_2L^2]\cdot Me_2CO$.

Stable organic radicals are valuable tools for solving some fundamental problems.[1] Among these, nitroxides are the most persistent organic paramagnets.[2] The sensitivity of their magnetic properties to the local environment and intramolecular effects, as well as long half-lives, make them attractive tools in various fields, especially in biochemistry, biophysics, and materials science.[3] They are used to perform nitroxide-mediated polymerizations and nitroxide-catalyzed oxidations of alcohols in organic synthesis. They are promising as contrast agents for magnetic resonance imaging. Rechargeable organic batteries were created on their basis.[4] They have always attracted the attention of researchers as paramagnetic organic building blocks, which can be used for the synthesis of heterospin molecular magnets. Copper(II) complexes with nitroxides were used to create "breathing crystals".[5]

When investigating the products of the reaction of binuclear cobalt pivalate with the stable nitroxide 2-(2-hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl ($HL^1$; Scheme 1), we detected a new phenomenon, which we called "redox-induced change in the ligand coordination mode". This effect is difficult to reveal without using a stable nitroxide in the reaction. It can be useful in determining the functions of biological objects; publications on metalloproteins often indicate that their functions are ill-defined, and their studies are often complicated by changes in their functioning.[6]

**Scheme 1. Nitroxide ($HL^1$) and Nitrone ($HL^2$) Molecules**



It was found that the reaction of $[Co_2(H_2O)(Piv)_4(HPiv)_4]$ with $HL^1$ in an acetone/heptane mixture at a ratio of $HL^1/[Co_2(H_2O)(Piv)_4(HPiv)_4] \sim 1/1$ formed heterospin complex $[Co_3(Piv)_4L^1_2]$ (**1**; Figure 1a). The situation was quite different when the starting reagent ratio $HL^1/[Co_2(H_2O)(Piv)_4(HPiv)_4]$ in the acetone/heptane mixture was varied from ~1.6 to ~2. Under these conditions, there were many solid products, with the main product among them being $[Co_3(Piv)_2L^1_2L^2_2]\cdot Me_2CO\cdot C_7H_{16}$ ($\mathbf{2}\cdot Me_2CO\cdot C_7H_{16}$). Its yield was 20% at best (see the Supporting Information, SI). However, $\mathbf{2}\cdot Me_2CO\cdot C_7H_{16}$ was of greatest interest because, along with $L^1$, it contained $L^2$, the product of single-electron reduction of the radical,[7] i.e., the corresponding hydroxylamine coordinated in the form of its prototropic isomer, nitrone (Figure 1b). The structure of the trinuclear fragment **2** is close to that of **1** except that two bridging

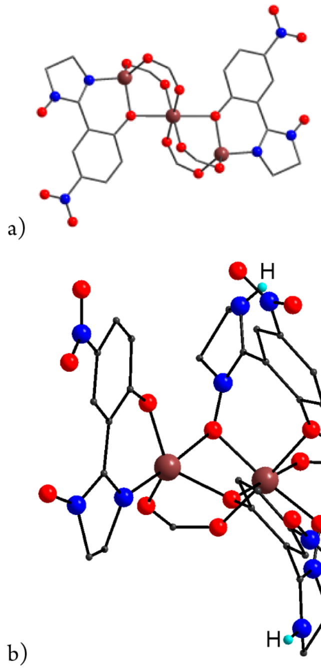


**Figure 1.** Crystal structures of molecules **1** (a) and **2** (b). Key: Co, brown; N, blue; O, red; H, cyan.

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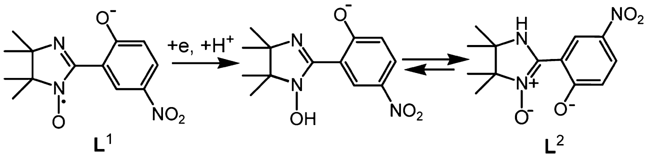
bidentate Piv molecules in the latter were replaced by two bridging tridentate $L^2$ molecules. The N−O distances in the nitroxyl fragment $L^1$ and the nitrone fragment $L^2$ are quite different, 1.272(9) and 1.277(7); 1.352(6) and 1.368(6), respectively. We also managed to localize the H atom in the amidine oxide fragment $HL^2$.

During the formation of $2{\cdot}Me_2CO{\cdot}C_7H_{16}$, we actually observed the multifunctional behavior of $L^1$, which was never observed for transition-metal complexes with nitroxides. In molecule **2**, some part of $L^1$ performs the function of a substituting ligand, while the rest of the molecules in this radical undergo a redox transformation into $L^2$ (Scheme 2).

**Scheme 2. Transformation into $L^2$**



The redox process provokes not only a change in the electronic state of the ligand but also a change in its coordination mode. While the terminal $L^1$ molecules form the six-membered metallocycles typical for Schiff bases in both **1** and **2**, the reduction to hydroxylamine followed by prototropic rearrangement to the nitrone $L^2$ drives the N atom at the third position of the imidazoline ring out of coordination and leads to its rotation through 53.5° (compared with $L^1$) relative to the nitrophenol fragment, which ultimately leads to coordination of the O atom of the nitrone group and the formation of a seven-membered metallocycle.

It might be assumed that the function of the ligand changed on passing from **1** to **2** because $L^2$ performs the bridging function but not the function of the terminal ligand, as $L^1$ does. However, our experiments showed that mononuclear complexes containing both $L^1$ and $L^2$ can be formed. Figure 2 shows the structure of the isolated $[CrL^1_2L^2]$ (**3**) and $[FeL^1_2L^2]{\cdot}Me_2CO$ (**4**), in which the metal is surrounded by two $L^1$ molecules and one $L^2$, which forms a seven-membered ring with the metal.

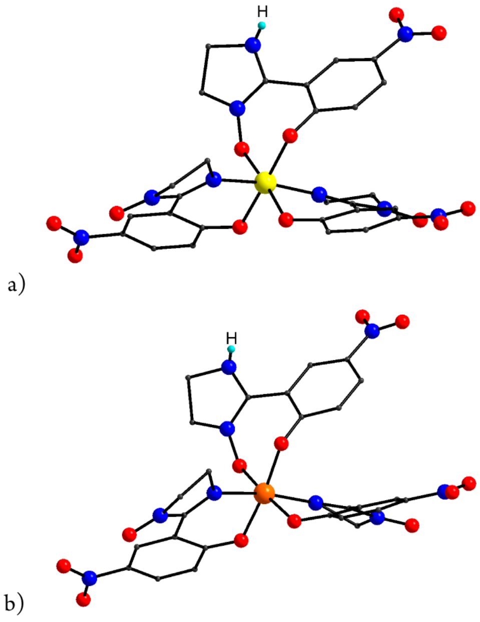


**Figure 2.** Crystal structures of molecules **3** (a) and **4** (b). Key: Cr, yellow; Fe, orange; N, blue; O, red; H, cyan.

It is believed that the factors that allowed us to detect the formation of **2**−**4** are the ability of the metal to be at different oxidation levels and the kinetic stability of both the paramagnetic ligand and the product of its single-electron reduction. For example, if $L^1$ reacts with binuclear nickel(II) pivalate instead of its cobalt(II) analogue, the product is $[Ni_3(Piv)_4(HPiv)_4L^1_2]$ (**5**) containing unchanged $L^1$ (see the SI). When using nickel(II), we have never recorded the formation of complexes containing $L^2$. This conclusion is fully consistent with the data obtained elsewhere,[8,9] where the metals capable of easily changing their oxidation level were also used.

Stable organic radicals are ligands capable of generating various redox processes. Because we are not going to discuss the metal complexes with phenoxyls, semiquinolates, verdazyls, and other radicals here,[10] we dwell only on the redox processes that occur during the formation of transition-metal complexes with nitroxides. As is known, in a reaction of a nitroxide with a transition metal, the radical can be reduced to the corresponding hydroxylamine and then form the product of cocrystallization of the starting radical and the nitrone complex.[11a] The products of metal reduction by hydroxylamine, which was oxidized to the corresponding nitroxide, were isolated.[12] Evidently, the product of reduction of the radical is more saturated with electron density and hence has stronger donor properties. For this reason, the metal is more liable to coordinate nitrone or its deprotonated hydroxylamine form but not the radical.[5,11] In studies of the products of the reactions of metals with biradicals (dinitroxides), unusual compounds were isolated, in which one of the nitroxyl groups was reduced to the hydroxylamine anion during the reaction.[8]

A very interesting effect of the reductively induced oxidation of the metal center was described. If in the complex dication $[M^{II}(L^{\bullet})_2]^{2+}$, where M = $Co^{II}$ and $Fe^{II}$ and $L^{\bullet}$ is the nitroxide radical, one of $L^{\bullet}$ molecules is reduced to $L^-$, then the other $L^{\bullet}$ oxidizes $M^{II}$ to $M^{III}$. As a result, solid salts $[M^{III}(L^-)_2]^+$ are isolated. The formation of intermediate $[M^{II}(L^{\bullet})(L^-)]^+$ species was recorded only in solution.[9]

Recently, Okazawa, Hashizume, and Ishida described a new class of spin-transition-like copper(II) nitroxide complexes, whose nontrivial structural peculiarity was the presence of coordinated O atoms of both nitroxyl and the corresponding hydroxylamine anion.[13]

As mentioned above, the redox process in our case provoked a change not only in the electronic state of the ligand but also in its coordination mode. Because redox reactions occur during the formation of $2{\cdot}Me_2CO{\cdot}C_7H_{16}$, it is not surprising that various impurity products are formed in the course of synthesis (see the SI) and the yield of $2{\cdot}Me_2CO{\cdot}C_7H_{16}$ is considerably lower than that of **1**. The $2{\cdot}Me_2CO{\cdot}C_7H_{16}$ crystals are thin elongated brown plates, which can be readily distinguished from other products because they mark themselves. After 2 or 3 min, the filtered off $2{\cdot}Me_2CO{\cdot}C_7H_{16}$ crystals start to lose the solvate molecules, crack, and jump (see the movies in the SI).

Note that $2{\cdot}Me_2CO{\cdot}C_7H_{16}$ often crystallizes in a mixture with the solvate $2{\cdot}1.5Me_2CO$, which is stable in air and exists as two modifications (see the SI). The desire to increase the yield of **2** led to the use of various solvents and their mixtures in the synthesis and recrystallization of the compound. It was found that, along with the above-described solvates, we can reproducibly obtain $2{\cdot}3Me_2CO{\cdot}C_7H_{16}$ and $2{\cdot}MeCN$. Because the majority of solvates are unstable under normal conditions, the crystals of the compounds were collected from under the layer of the mother solution and placed in a closed capillary before X-ray diffraction analysis. The character of the chemomechanical activity of **2**·Solv crystals depended on the set of included solvate molecules (see the SI).

It is worth noting that the highest yield of **2** was achieved when an equimolar mixture of $HL^1$ and $HL^2$ was used in the synthesis (see the SI). If the synthesis is performed using only $HL^2$, **2** also formed. Because the solutions of $HL^2$ are stable in air for a long time, cobalt is obviously necessary for initiating the oxidation of $HL^2$ with air oxygen. Oxygen is also required; in the absence of dioxygen in the inert atmosphere, the reaction did not occur.

In the future we intend to study the redox-induced change in the ligand coordination mode phenomenon in more detail. Knowledge about the controlled use of this effect is important in biology[6] and can be of interest in solving medical chemistry problems.[14]

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental details, X-ray data in CIF format, additional figures, and two movies. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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