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“Jumping Crystals”: Oxygen-Evolving Metal-Nitroxide Complexes

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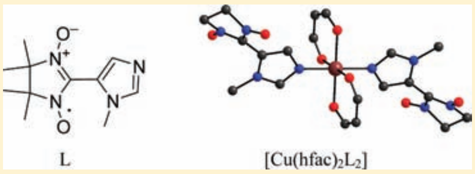
Supporting Information



ABSTRACT: The crystals of heterospin complexes [$M(hfac)_2L_2$] (where M = Cu, Ni, Co, or Mn; hfac = hexafluoroacetylacetonate; and L = nitronyl nitroxide, 4,4,5,5-tetramethyl-2-(1-methyl-1H-imidazol-5-yl)-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl) were found to make unusual jumping motions. Under ambient conditions, the jumping and various displacements of crystals lasted for several weeks. The mechanical motion was accompanied by the cracking and disintegration of crystals, and a solid [$M(hfac)_2(L^1)_2$] complex with the corresponding imino nitroxide 4,4,5,5-tetramethyl-2-(1-methyl-1H-imidazol-5-yl)-4,5-dihydro-1H-imidazole-1-oxyl (L^1) was detected. The jumping was accompanied by the spontaneous elimination of oxygen, the source of which was the nitronyl nitroxyl fragment of coordinated L. An X-ray study of [$M(hfac)_2L_2$] (where M = Cu, Ni, Co, or Mn) showed that the molecular structure of all [$M(hfac)_2L_2$] and their packing in the solid state were identical. The packing of [$M(hfac)_2L_2$] was concluded to be critical to the mechanical effect. In complexes with different stoichiometries or different sets of diamagnetic ligands ([$Cu(hfac)_2L]_2$, [$Cu(hfac)(acac)L]\cdot EtOH$, [$CuPiv_2L_2]\cdot 2CH_2Cl_2$, and [$Cu(hfac)_2L_2Cu_2Piv_4]\cdot 3C_7H_8$ (where acac is acetylacetonate and Piv is trimethylacetate), or free L), the effect vanished when the packing changed.

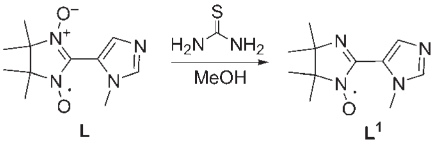
INTRODUCTION

Systems capable of liberating oxygen *under normal conditions* are generally the objects of biochemical studies of oxygen storage and oxygen transport proteins.[1] Of primary interest is photosynthesis. It is driven by photosystems I and II, which are two large protein−cofactor complexes located in the thylakoid membrane and acting in series.[2] A special Making Oxygen forum discussed the synthesis of O_2 from water, using rather complex artificial and natural systems containing highly active catalytic centers.[3] However, compounds that evolve oxygen *under normal conditions* are rare.[4] We found this ability in [$M(hfac)_2L_2$] heterospin complexes, where hfac = hexafluoroacetylacetonate; M = Cu, Ni, Co, or Mn; and L = nitronyl nitroxide (4,4,5,5-tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl). In large-scale processes, the elimination of O_2 by solid [$M(hfac)_2L_2$] is accompanied by the specific jumping behavior of crystals. The jumping results from an abrupt cracking of crystals, followed by fast separation of their fragments. This paper describes the synthesis and structure of these unusual complexes and some other heterospin compounds related to [$M(hfac)_2L_2$] and examines whether they can also make these chemomechanical motions.

EXPERIMENTAL SECTION

General Considerations. *N*,*N*′-(2,3-Dimethylbutane-2,3-diyl)bis(hydroxylamine) and 4,4,5,5-tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (L) were prepared using known procedures.[5,6] All the solvents used were reagent quality. All commercial reagents were used without additional purification. The reactions were monitored via thin-layer chromatography (TLC), using Silica gel 60 F_{254} aluminum sheets (Merck). The yields are given for pure substances obtained after recrystallization. The melting points were determined using a “Boetius” melting point apparatus. Microanalyses were performed with a Carlo Erba 1106 analyzer.

4,4,5,5-Tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-1-oxyl (L^1). A solution of L (250 mg, 1.05 mmol) and thiourea (30 mg, 0.39 mmol) in MeOH (10 mL) was stirred for 10 h at room temperature. PbO_2 (1.25 g, 5.23 mmol) was added. The mixture was stirred for another 2 h and then filtered and evaporated. The residue was recrystallized from a mixture of ethylacetate and hexane. The red orange needle precipitate was separated by filtration. Yield: 160 mg (69%), mp 161−162 °C. $\mu_{eff}/\beta = 1.73$ (295 K). Calculated for $C_{11}H_{17}N_4O$ (%): C, 59.7; H, 7.7; N, 25.3. Found (%): C, 59.8; H, 7.8; N, 25.1.



[$Cu(hfac)_2L_2$]. A mixture of $Cu(hfac)_2$ (0.1007 g, 0.21 mmol) and L (0.1000 g, 0.42 mmol) was dissolved in CH_2Cl_2 (2 mL). Ethanol (3 mL) was carefully added to the resulting solution in such a way that the ethanol layer covered CH_2Cl_2. Dark blue crystals formed within a few hours. They were filtered off, washed with cold ethanol, and dried in air. Yield: 90%. Calculated for $C_{32}H_{36}N_8O_8F_{12}Cu$ (%): C, 40.4; H, 3.8; N, 11.8; F, 23.9. Found (%): C, 40.7; H, 3.9; N, 11.6; F, 24.6. The complex

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is readily soluble in Me_2CO, CH_2Cl_2, and $CHCl_3$, but is sparingly soluble in CH_3OH and C_2H_5OH. When stored under normal conditions for a few days, the solutions of the complex gradually changed color from blue to orange and $[Cu(hfac)_2(L^1)_2]$ crystallized from them.

$[M(hfac)_2L_2]$. $[M(hfac)_2L_2]$ (where M = Mn, Co, or Ni) was synthesized using a procedure similar to that used to obtain $[Cu(hfac)_2L_2]$. For $[Co(hfac)_2L_2]$: Yield: 75%−80%. Calculated for $C_{32}H_{36}N_8O_8F_{12}Co$ (%): C, 40.6; H, 3.8; N, 11.8; F, 24.1. Found (%): C, 40.6; H, 3.9; N, 11.8; F, 23.5. For $[Mn(hfac)_2L_2]$: Yield: 70%. Calculated for $C_{32}H_{36}N_8O_8F_{12}Mn$ (%): C, 40.7; H, 3.9; N, 11.9; F, 24.2. Found (%): C, 40.5; H, 3.9; N, 11.7; F, 24.9. For $[Ni(hfac)_2L_2]$: Yield: 95%. Calculated for $C_{32}H_{36}N_8O_8F_{12}Ni$ (%): C, 40.6; H, 3.8; N, 11.8; F, 24.1. Found (%): C, 40.7; H, 4.1; N, 11.8; F, 24.4.

$[Cu(hfac)_2L]_2 \cdot CH_2Cl_2$. A mixture of $Cu(hfac)_2$ (0.1007 g, 0.21 mmol) and L (0.0500 g, 0.21 mmol) was dissolved in CH_2Cl_2 (2 mL). Hexane (3 mL) was carefully added to the solution. The resulting solution was allowed to remain in an open flask. After 5 h, the resulting dark blue crystals were filtered off, washed with cold hexane, and dried in air. Yield: 56%. The complex is soluble in the majority of organic solvents. Calculated for $C_{43}H_{40}N_8O_{12}Cl_2F_{24}Cu_2$ (%): C, 34.1; H, 2.7; N, 7.4; F, 30.1. Found (%): C, 34.2; H, 2.7; N, 7.2; F, 29.9.

$[Cu(hfac)(acac)L] \cdot EtOH$. A mixture of $Cu(hfac)_2$ (0.1007 g, 0.21 mmol), $Cu(acac)_2$ (0.0552 g, 0.21 mmol), and L (0.1000 g, 0.42 mmol) was dissolved in CH_2Cl_2 (2 mL). Ethanol (5 mL) was carefully added to the resulting solution. After 36 h, blue violet crystals formed. They were filtered off, washed with cold ethanol, and dried in air. Yield: 60%. Calculated for $C_{23}H_{31}N_4O_7F_6Cu$ (%): C, 42.3; H, 4.8; N, 8.6; F, 17.5. Found (%): C, 41.9; H, 4.6; N, 8.5; F, 17.4.

$[Cu_2Piv_4Cu(hfac)_2L_2] \bullet 3C_7H_8$. A solution of $[Cu(hfac)_2L_2]$ (0.1 g, 0.1 mmol) in CH_2Cl_2 (5 mL) was added to the solution of $[Cu_2Piv_4(MeOH)_2]$ (0.063 g, 0.1 mmol) in CH_2Cl_2 (1 mL). The solvent was then removed with an air flow, and the residue was dissolved in toluene (3−4 mL). The resulting dark blue solution was filtered. After 5−7 days, dark blue prisms were filtered off. Yield: 82%. Found (%): C, 49.4; H, 5.6; N, 6.5; F, 12.6. Calculated for $C_{73}H_{96}N_8O_{16}F_{12}Cu_3$ (%): C, 49.8; H, 5.5; N, 6.4; F, 12.9.

$[CuPiv_2L_2] \bullet 2CH_2Cl_2$. A solution of L (0.112 g, 0.48 mmol) in CH_2Cl_2 (3 mL) was poured in the solution of $[Cu_2Piv_4(MeOH)_2]$ (0.07 g, 0.12 mmol) in CH_2Cl_2 (2 mL). The resulting dark blue solution was filtered, and hexane (3 mL) was added to it very slowly. After 1−2 days, oblong dark violet crystals precipitated. They were filtered off and washed with hexane (2 mL). Yield: 98% (0.18 g). Found (%): C, 48.0; H, 6.7; N, 13.5. Calculated for the partially desolvated $C_{33}H_{54}N_8O_8Cl_2Cu$ product (%): C, 48.0; H, 6.6; N, 13.6.

$[Cu(hfac)_2(L^1)_2]$. A mixture of $Cu(hfac)_2$ (0.0540 g, 0.11 mmol) and L^1 (0.0500 g, 0.23 mmol) was dissolved in CH_2Cl_2 (2 mL). Ethanol (4 mL) was carefully added to the resulting solution in such a way that an ethanol layer covered CH_2Cl_2. After 5 h, long orange crystals formed. They were filtered off, washed with cold ethanol, and dried in air. Yield: 88%. The complex is readily soluble in acetone, CH_2Cl_2, and $CHCl_3$, but is sparingly soluble in methanol and ethanol. Calculated for $C_{32}H_{36}N_8O_6F_{12}Cu$ (%): C, 41.8; H, 3.9; N, 12.2; F, 24.8. Found (%): C, 41.7; H, 4.0; N, 11.8; F, 24.7.

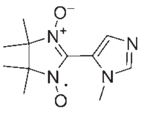
All of the compounds prepared by these procedures were isolated as perfectly shaped single crystals suitable for an X-ray study.

X-ray Crystallographic Studies. X-ray diffraction (XRD) experiments were performed on a SMART APEX CCD (Bruker AXS) diffractometer (Mo Kα, λ = 0.71073 Å). The 2θ range was <47°, because of the weak reflections of all crystals. The structures were solved by direct methods and refined by full-matrix least-squares analysis in an anisotropic approximation for non-hydrogen atoms. The positions of the majority of H atoms were calculated. The methyl H atoms were refined isotropically in a rigid group approximation. All calculations were performed with the Bruker SHELXTL Version 6.14 program package. Crystal data, experimental details, and selected bond lengths and angles for all compounds are given in the Supporting Information.

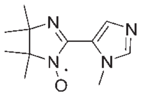
The magnetic susceptibilities (dc) were measured on a Quantum Design MPMS*XL* Superconducting Quantum Interference Device at 2−300 K in a homogeneous external magnetic field of up to 49.5 kOe. The molar magnetic susceptibility (χ) was calculated using Pascal's Additive Scheme, including diamagnetic corrections.

■ RESULTS AND DISCUSSION

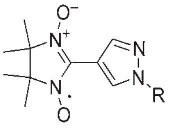
Synthetic Aspects and Chemomechanical Motion. Previously, so-called "breathing crystals" were found among the stereochemically nonrigid heterospin complexes of $Cu(hfac)_2$ and nitronyl nitroxides with heterocyclic substituents in the lateral chain. The single crystals of these compounds have a remarkable ability of experiencing considerable reversible deformations in repeated cooling−heating cycles[7] without any loss of quality or structure.[7b,c] The deformations provoke the magnetic anomalies that are similar to spin transitions in the character of the $\mu_{eff}(T)$ dependence.[8] To find new compounds of this type, we performed a reaction of $Cu(hfac)_2$ with the nitronyl nitroxide 4,4,5,5-tetramethyl-2-(1-methyl-1*H*-imidazol-5-yl)-4,5-dihydro-1*H*-imidazole-3-oxide-1-oxyl (L). The choice of L as a paramagnetic ligand was dictated by the fact that the mutual arrangement of the nitronyl nitroxyl fragment and the imine N atom in its molecule was topologically similar to the arrangement in nitronyl nitroxides with pyrazolyl-(NIT-PzR) or *meta*-pyridine-substituted (NIT-*m*-Py) nitronyl nitroxide studied previously, whose $Cu(hfac)_2$ complexes are typical "breathing crystals."[7a]



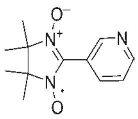
L



L¹



NIT-PzR



NIT-*m*-Py

For $[Cu(hfac)_2L_2]$, no magnetic anomalies were recorded at 2−350 K (see Figure 1). Solid $[Cu(hfac)_2L_2]$, however, had a nontrivial distinction. For crystals placed in a Petri dish at room temperature, visualization revealed a chaotic motion. Observation under a standard microscope showed the jumping motion. Real-time film recording of this movement showed that the jumping lasted for <0.07 s. The jumping became more active after the crystals were heated to ∼28−32 °C, almost stopped when they were placed in a refrigerator, and restarted when they were again heated to room temperature. The cooling and heating of $[Cu(hfac)_2L_2]$ crystals were repeated many times, but the result was the same.

When $[Cu(hfac)_2L_2]$ crystals were kept in a refrigerator for a year or more, they did not lose their jumping ability. If, however, the obtained batch of $[Cu(hfac)_2L_2]$ crystals was maintained under normal conditions, the jumping lasted for a month and then stopped and the crystals decayed into small particles. When the complex was grown as a large single crystal one or more millimeters in size in each of the three dimensions, it did not make the jumping motion at elevated temperatures, but it expelled small pieces to distances much longer than their size. The large crystal also ultimately experienced fragmentation after some time.

Few examples of "jumping crystals" are known[9] (the other terms used for describing this mechanical effect are "hopping crystals",[9h,i] "hopping effect",[9f,g] and "thermosalient solid"[9d,j]).

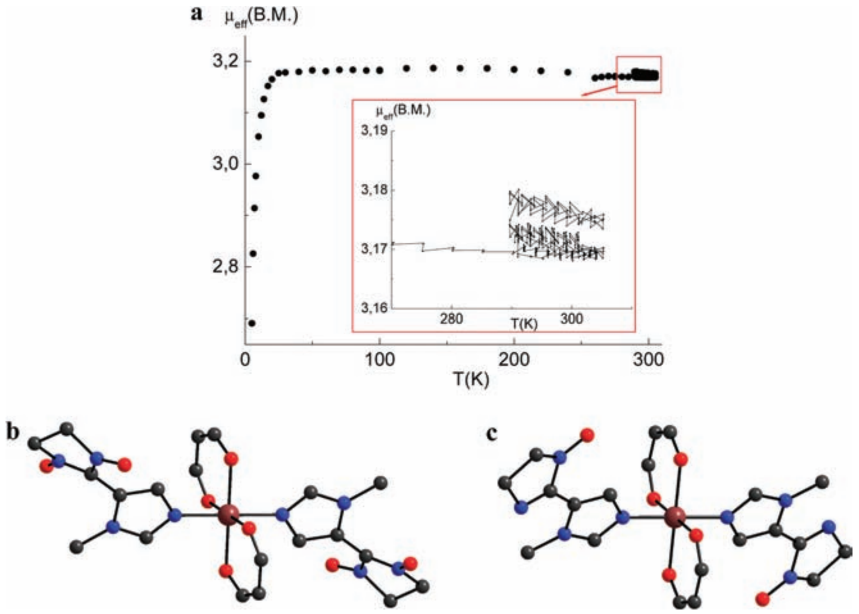


Figure 1. (a) Temperature dependence of the effective magnetic moment of $[Cu(hfac)_2L_2]$. (b) Molecular structure of $[Cu(hfac)_2L_2]$. (c) Molecular structure of $[Cu(hfac)_2(L^1)_2]$. (Legend: Cu, brown ball; O, red ball; C, black ball; and N, blue ball.) The H atoms and the CH_3 and CF_3 groups are omitted for clarity.

First, the examples were scarce. Second, the reason for the jumping in these instances was the polymorphic transformation of the substance. In the course of this transformation, the crystals behaved like abruptly bent bimetallic plates, with this behavior being the reason for the jumping. The jumping could be observed upon heating and cooling alike. It was noted that the initial and final structures were known in all such studies; some of the processes were reversible,[9f] but a clear relationship between the microstructural changes (detected in structural studies) and the macrostructural consequences of these changes has not been revealed.[9a]

For $[Cu(hfac)_2L_2]$ crystals, the situation was different. First, the jumping became more active only upon heating (not upon cooling). Second, the reason for the jumping was the solid-state reaction

$$[Cu(hfac)_2L_2](s) \rightarrow [Cu(hfac)_2(L^1)_2](s) + O_2(g)$$

which liberated gaseous O_2, but not the polymorphic transformation of the complex. The liberation of oxygen was recorded by mass spectrometry when $Cu(hfac)_2L_2$ was heated under vacuum. This was a rather slow process. The inset in Figure 1a shows the experimental $\mu_{eff}(T)$ dependences measured every hour for the same batch of crystals at 290−305 K and plotted on a large scale of magnetic moments. The $\mu_{eff}(T)$ curve shows a very weak rise of μ_{eff} for χ_M, calculated using an invariable molar mass for the sample. The tendency toward the gradual increase in μ_{eff} is caused by the loss of oxygen, ultimately leading to an increase in the specific concentration of spins based on the molar mass.

To confirm the oxygen release, we also performed an indicator reaction. A solution of sodium 3,6-ditert-butylbenzene-1,2-bis(olate) in THF was prepared in an "MBRAUN" glovebox in an inert atmosphere; sodium 3,6-ditert-butylbenzene-1,2-bis(olate) was obtained via the reduction of 3,6-ditert-butyl-*o*-benzoquinone with metallic sodium. This solution was placed in a microbubbler connected with an ampule containing a $[Cu(hfac)_2L_2]$ sample (20 mg) or a solution of $[Cu(hfac)_2L_2]$ (20 mg) in pentan-2-one (1 mL). After the complex or its solution was heated at 45−50 °C for 24 h, the yellow color of the starting solution of sodium 3,6-ditert-butylbenzene-1,2-bis(olate) changed to cyan, as a result of the reaction with oxygen isolated by $[Cu(hfac)_2L_2]$.

Our kinetic measurements showed that the concentration of nitronyl nitroxide L remained constant during its heating in toluene or pentan-2-one (1.0×10^{-3} M and 5×10^{-3} M solutions) at 45 °C for 96 h. The case was different when the solution of $[Cu(hfac)_2L_2]$ in pentan-2-one was thermostatted at 45 °C for 24 h. In the electronic absorption spectrum of the reaction mixture, the intensity of the band with a maximum at 603 nm typical for $[Cu(hfac)_2L_2]$ decreased considerably and the absorption bands with maxima at 437 and 465 nm appeared, because of the accumulation of $[Cu(hfac)_2(L^1)_2]$ in solution. Intermittent recording of the electronic spectra of the reaction mixture showed isosbestic points at 400 and 512 nm. Treatment of the kinetic data indicated that a second-order reaction occurred:

$$2[Cu(hfac)_2L_2] \rightarrow 2[Cu(hfac)_2(L^1)_2] + 2O_2$$

Structure of the Complexes. An X-ray study of $[Cu(hfac)_2L_2]$ at 295 and 305 K did not reveal any polymorphic transformation, and the molecular and crystal structures of the compound remained constant. (To avoid the cracking of the single crystal and its "springing" from the holder needle, we coated it with an epoxide resin.)

The $[Cu(hfac)_2L_2]$ crystals had a deep dark blue color, while the $[Cu(hfac)_2(L^1)_2]$ crystals were orange; in the course of the solid-state reaction, they gradually became light-colored while having various green shades. The transformation of $[Cu(hfac)_2L_2]$ to $[Cu(hfac)_2(L^1)_2]$ in solution was much faster. When stored under the normal conditions for a few days, the solution of $[Cu(hfac)_2L_2]$ also gradually changed color from dark blue to orange and crystallized into $[Cu(hfac)_2(L^1)_2]$. The

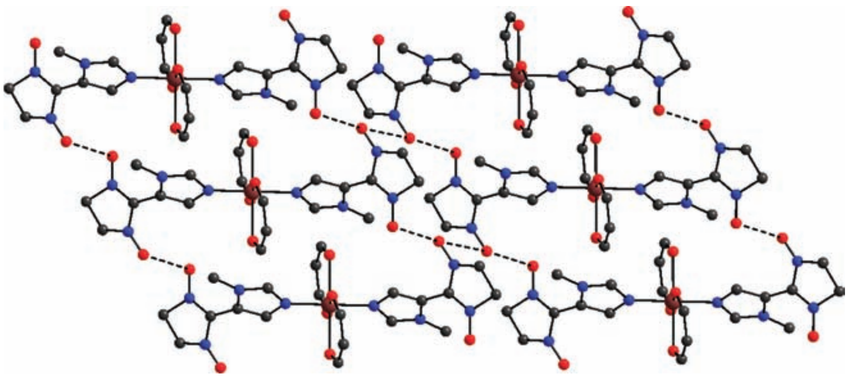


Figure 2. Packing of $[Cu(hfac)_2L_2]$ molecules. (Legend: Cu, brown ball; O, red ball; C, black ball; and N, blue ball.) The H atoms and the CH_3 and CF_3 groups are omitted for clarity.

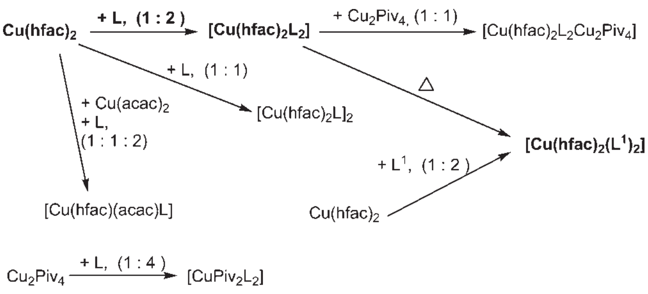
physicochemical characteristics of the thus-obtained $[Cu(hfac)_2(L^1)_2]$ were identical to those of the authentic $[Cu(hfac)_2(L^1)_2]$ sample obtained by an alternative synthesis from $Cu(hfac)_2$ and L^1. Similar transformations of $[M(hfac)_2L_2]$ into $[M(hfac)_2(L^1)_2]$ were also recorded for complexes with other metals (Ni, Co, and Mn).

The structure of the centrosymmetric $[Cu(hfac)_2L_2]$ molecule is shown in Figure 1b. In the distorted octahedron around the metal ion, the N_{Im} atoms of the imidazole ring lie in the equatorial plane (d_{Cu-N} = 1.992(6)−2.001(3) Å), shifting two O_{hfac} atoms to the axial positions (d_{Cu-O} = 2.276(4)−2.301(5) Å). In the L molecule, the angle between the planes of the imidazole and CN_2 fragments of the imidazoline rings is ~45°. The interatomic distances in the N−O groups of the paramagnetic ligands are typical for nitroxides: 1.261(8)-1.278(4) Å. We have not found any distinctions in the packing of $[Cu(hfac)_2L_2]$ molecules relative to the packing described in the literature.[10] The shortest intermolecular distances between the O_{NO} atoms of the NO groups are 3.67−3.77 Å. The molecular packing is such that the O_{NO} atoms form groups of four atoms with a short O···O central distance, longer terminal distances, and still longer distances between the quadruples (Figure 2). The only distinction of the packing in $[Cu(hfac)_2L_2]$ is an almost linear arrangement of the O atoms of the nitronyl nitroxyl fragments in these quadruples. However, it was difficult to trace the relationship between the microstructure and the macrostructural consequences, such as that for the "jumping crystals"[9] described earlier[9f] (e.g., "the reason for the 'jumping' effect is not obvious from the crystal structure";[9b] "virtually no experimental evidence exists on the atomic-scale mechanisms driving these transition"[9i]). The molecular structure of $[Cu(hfac)_2(L^1)_2]$ (see Figure 1c) was very similar to that of $[Cu(hfac)_2L_2]$.

Nitronyl nitroxides can spontaneously lose oxygen, and this process always occurs (at a definite rate).[11] Even when stored at low temperatures for some time, the solid nitronyl nitroxide samples contained the corresponding imino nitroxide impurities.[11] Although large numbers of nitronyl nitroxides and their metal complexes were studied and more than a thousand structural solutions for the given class of compounds are found in the Cambridge Structural Databank[10] alone, the chemofragmentation of the crystals of nitronyl nitroxides or their metal complexes inherent in $[Cu(hfac)_2L_2]$ has never been reported. Therefore, we made an attempt to understand the reason for the chemomechanical activity of the crystals.

Since chemical reactions are known to be initiated most actively on metal centers, we initially tried to vary the metal. For this purpose, we synthesized $[M(hfac)_2L_2]$, where M = Ni, Co, or Mn. All these complexes were prepared as crystals of good quality. For all of them, the molecular structure of $[M(hfac)_2L_2]$ and the packing of molecules in the solid complex were similar to those in $[Cu(hfac)_2L_2]$. Similar to $[Cu(hfac)_2L_2]$, all $[M(hfac)_2L_2]$ crystals showed a mechanical activity similar to that of $[Cu(hfac)_2L_2]$ under the same conditions. Consequently, the ability of crystals to undergo specific fragmentation accompanied by crystal jumping was not related to the nature of the metal; rather, it was determined by the molecular packing of $[M(hfac)_2L_2]$ complexes (for the individual L crystals, this effect was not observed).

Scheme 1



As mentioned above, it was impossible to trace an unambiguous relationship between the microstructure and the macrostructural consequences for $[Cu(hfac)_2L_2]$. This problem requires separate studies. Now, we tried to determine if it was possible to observe this effect for other Cu(II) complexes with L, to confirm that the ability to experience the mechanical motion was determined exactly by the packing of $[M(hfac)_2L_2]$.

We isolated the binuclear $[Cu(hfac)_2L]_2$ complex into the following components (see Scheme 1): the $[Cu(hfac)(acac)L]\cdot EtOH$ complex, where acac is acetylacetonate, with a "partially" modified ligand shell of the initial chelate fragment; the $[CuPiv_2L_2]\cdot 2CH_2Cl_2$ complex, in which the hfac ligands were replaced by pivalates; and the polymer chain $[Cu(hfac)_2L_2Cu_2Piv_4]\cdot 3C_7H_8$ complex, in which (in contrast to $[Cu(hfac)_2L_2]$) one of the O atoms of the nitronyl nitroxyl fragment is coordinated to the metal ion. The structure of the heterospin molecules of these complexes is shown in Figure 3. Unlike $Cu(hfac)_2L_2$, these complexes did not demonstrate any specific mechanical motion. Therefore, we again draw the conclusion that this motion is related to the peculiarities of the molecular packing of solid $[Cu(hfac)_2L_2]$.

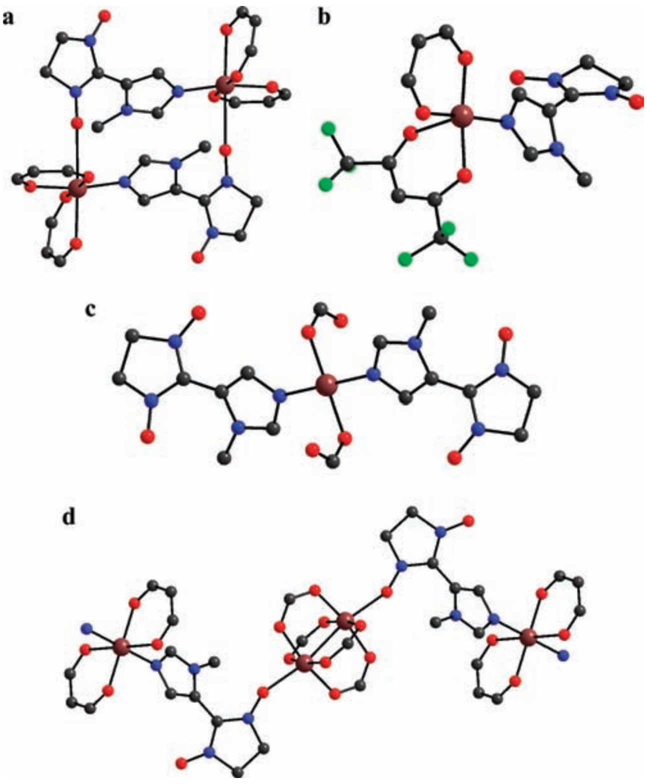


Figure 3. Structure of heterospin molecules: (a) $[Cu(hfac)_2L]_2$, (b) $[Cu(hfac)(acac)L]$, (c) $[CuPiv_2L_2]$, and (d) $[Cu(hfac)_2L_2Cu_2Piv_4]$. (Legend: Cu, brown ball; O, red ball; C, black ball, N, blue ball; and F, green ball.) The $(CH_3)_3C$ groups of trimethylacetates, the CH_3 groups of the imidazoline ring and acetylacetonate, the CF_3 groups of hexafluoroacetylacetonate (except the $[Cu(hfac)(acac)L]$ molecule), and the H atoms are omitted for clarity.

CONCLUSION

To summarize, our study has revealed the first heterospin coordination compounds $[M(hfac)_2L_2]$ (where M = Cu, Ni, Co, or Mn), whose crystals can experience mechanical motions upon warming. These motions (jumps, propulsions) were accompanied by the spontaneous elimination of oxygen. $[M(hfac)_2L_2]$ crystals are certainly too expensive to be used as sources of oxygen. However, these compounds were reported[9i] to be of interest as a prospective material basis for the fabrication of efficient actuators (mechanical devices that are capable of converting thermal or light energy into motion or mechanical work at a macroscopic level).[12] Information regarding the jumping crystals will be gradually accumulated and become useful to understand, with time, how changes at the molecular level are transformed into a process at the macro level. It is interesting that, in the series of isostructural $[M(hfac)_2L_2]$, the packing determined the crystal jumping ability, while variation of the transition metal did not affect the possibility of a macroscopic motion.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Structural determination parameters, crystal and structure refinement data, atomic coordinates, and isotropic displacement parameters for L^1, $[Cu(hfac)_2L_2]$, $[Mn(hfac)_2L_2]$, $[Co(hfac)_2L_2]$, $[Cu(hfac)_2(L^1)_2]$, $[Cu(hfac)_2L]_2$, $[Cu(hfac)(acac)L]\cdot EtOH$, $[CuPiv_2L_2]\cdot 2CH_2Cl_2$, and $[Cu(hfac)_2L_2Cu_2Piv_4]\cdot 3C_7H_8$ (in CIF form). This material is available free of charge via Internet at http://pubs.acs.org.

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