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Formation, structures and magnetic properties of M(hfac)$_2$ (M = Cu or Mn) complexes of 4-amino-TEMPO and its derivative

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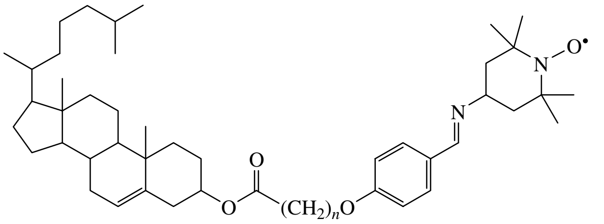
The reactions of TEMPO derivatives having a benzylideneamine unit with Cu(hfac)$_2$ revealed unexpected formation of a complex consisting of 4-amino-TEMPO and Cu(hfac)$_2$ and its crystal structure and magnetic properties showed marked difference from those of the corresponding Mn(hfac)$_2$ complex and a complex derived from bis-TEMPO-substituted-ethylenediamine.

Considerable attention has recently been paid to the development of organic-inorganic hybrid molecular-based magnets, in which the coordination of paramagnetic metal ions with pure organic radicals plays a significant role.[1] In the course of the development of organic multifunctional spin systems,[2] we prepared a series of glass-forming 2,2,6,6-tetramethylpyperidyloxy (TEMPO) derivatives having a cholesterol, as well as a benzylideneamine unit **1**, which exhibited apparent changes of their intermolecular magnetic interactions by heating over thermal phase transition temperatures.[3] We tried to prepare the corresponding metal complexes derived from TEMPO derivatives **1** and M(hfac)$_2$ (M = Cu or Mn, hfac = hexafluoroacetylacetonato) to obtain possible metallomesogens with elongated molecular structures.[4] However, the product was not the expected complex solely coordinated at the TEMPO moiety but an unexpected (1:2) complex consisting of 4-amino-TEMPO and Cu(hfac)$_2$. Here, we report on the unexpected formation of the complex, its structure and magnetic properties together with those of the related Mn(hfac)$_2$ complexes derived from 4-amino-TEMPO and its derivative.



1a $n = 3$
1b $n = 4$
1c $n = 5$

When benzylideneamine **1** ($n = 1$)[3] was treated with Cu(hfac)$_2$ in a dichloromethane solution, greenish crystals were obtained from the reaction mixture and the investigation of a crystal by X-ray analysis revealed that the compound was not expected complex **2** ($n = 1$) but a degraded complex. Closer inspection of the analysis showed it to be a 1:2 complex **3** composed of 4-amino-TEMPO and Cu(hfac)$_2$ [$Cu_2(C_5HF_6O_2)_4(C_9H_{19}N_2O)$], and the yield was 45%. Although there is no evidence that the complex preserved its structure in solution, the structuring is considered to occur during crystallizaion. The result also indicates the occurrence of bond cleavage reaction at the C–N double bond of the imine group by a trace amount of water and the participation of Cu(hfac)$_2$ not only as a ligand but also as a Lewis acid catalyst (Scheme 1). The same complex was similarly obtained by the treatment of **1** ($n = 4, 5$)[3] with Cu(hfac)$_2$ in 23 and 41% yields and, moreover, the complex could also be prepared by the reaction of 4-amino-TEMPO and Cu(hfac)$_2$ in dichloromethane with higher yield (84%).

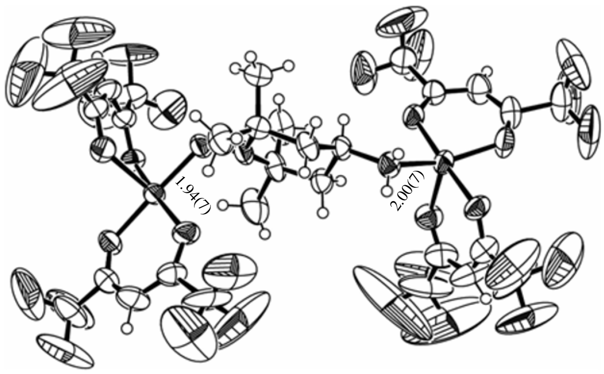


Figure 1 Crystal structure of Cu(hfac)$_2$ complex **3**.

The crystal structure obtained from the X-ray analysis of the complex is shown in Figure 1.[†] Thus, the 4-amino-TEMPO molecule lies between a couple of Cu(hfac)$_2$ units and the oxygen atom of nitroxide and the nitrogen atom of the amino group are coordinated to different copper atoms, giving respective five-coordinate structures. Since a dissimilar structure is reported for 4-amino-TEMPO complex with Ni(hfac)$_2$, in which the oxygen atom of nitroxide is not coordinated to the metal atom but that of solvated methanol is ligated [$Ni(C_5HF_6O_2)_2(C_9H_{19}N_2O)(MeOH)_2$],[5] the structural feature found in the present complex appears to be rather unique in this context.

A paramagnetic behaviour is revealed on the whole from the magnetic data of the complex (see SI) and the Curie constant observed (0.44 emu K mol^{-1}) indicates the cancellation of a couple of spins on the nitroxide and a copper atom by singlet formation. The short contact of 1.94 Å found between the oxygen and copper atoms in the crystal structure is relevant to the singlet formation and the remaining $S = 1/2$ spin on another copper atom is reflecting the Curie constant as the calculated

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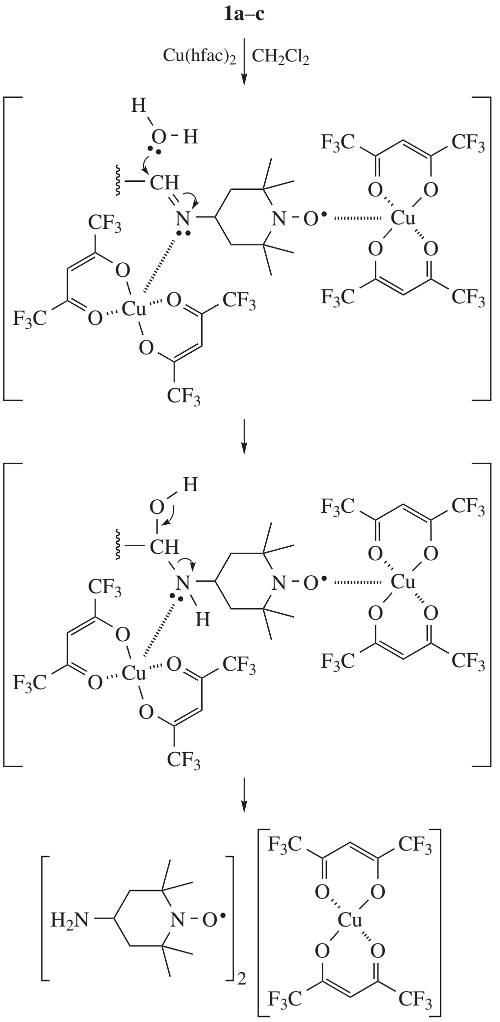
[†] The crystal structures of the radical compounds were solved by the direct methods and refined using the full-matrix least squares method and all non-hydrogen atoms were refined anisotropically. All calculations were performed using the CrystalStructure 3.7.0 crystallographic software package.

Crystallographic data for **3**: $C_{29}H_{23}N_2O_9F_{24}Cu_2$, $M = 1126.56$, triclinic, space group $P1$, $a = 12.9332(16)$, $b = 17.201(2)$ and $c = 10.2000(16)$ Å, $\alpha = 102.289(11)°$, $\beta = 96.352(12)°$, $\gamma = 87.393(10)°$, $V = 2203.0(5)$ Å^3, $T = 294$ K, $Z = 2$, $d_{calc} = 1.698$ g cm^{-3}, $R = 0.0657$, $wR = 0.0586$ [10152 independent reflections and 4324 used reflections, $I > 2\sigma(I)$].

Crystallographic data for **4**: $C_{19}H_{21}N_2O_5F_{12}Mn$, $M = 640.30$, monoclinic, space group $P2_1/n$, $a = 11.170(2)$, $b = 15.292(4)$ and $c = 16.619(3)$ Å, $\beta = 104.145(15)°$, $V = 2752.7(10)$ Å^3, $T = 294$ K, $Z = 4$, $d_{calc} = 1.545$ g cm^{-3}, $R = 0.0611$, $wR = 0.0642$ [6338 independent reflections and 2003 used reflections, $I > 2\sigma(I)$].

Crystallographic data for **5**: $C_{30}H_{42}N_4O_6F_{12}Mn$, $M = 837.60$, orthorhombic, space group $Pna2_1$, $a = 24.696(4)$, $b = 10.837(5)$ and $c = 14.491(6)$ Å, $V = 3878(2)$ Å^3, $T = 294$ K, $Z = 4$, $d_{calc} = 1.434$ g cm^{-3}, $R = 0.0541$, $wR = 0.0592$ [4576 independent reflections and 2477 used reflections, $I > 2\sigma(I)$].

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 624669–624671. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2006.



Cu(hfac)$_2$ complex **3**

Scheme 1

constant with observed *g*-value of 2.25 is 0.47 emu K mol^{-1}.

Similar treatment of TEMPO derivative **1** ($n = 3$) with Mn(hfac)$_2$ did not give the corresponding manganese complex with 4-amino-TEMPO but the staring materials were recovered and the result is due probably to weaker Lewis acidity of Mn(hfac)$_2$ than that of Cu(hfac)$_2$. On the contrary, a 1:1 complex of 4-amino-TEMPO with Mn(hfac)$_2$ could be prepared by mixing components in dichloromethane solution in 60% yield [$Mn(C_5HF_6O_2)_2(C_9H_{19}N_2O)$] and the crystal structure and magnetic data are shown in Figures 2 and 3.

Because of the difference in the constitutions of complexes **3** and **4**, it was well anticipated that the crystal structure would be different from each other and actually both the nitroxide oxygen atom in a TEMPO molecule and the nitrogen atom of the amino group in another molecule bind to a manganese atom in a *trans*-apical manner, affording six-coordinate octahedral structure and forming 1-D polymeric chain structure at the same time, as illustrated in Figure 2.†

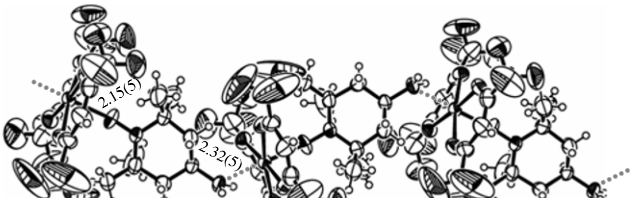


Figure 2 Crystal structure of Mn(hfac)$_2$ complex **4**.

The existence of intermolecular antiferromagnetic interactions is apparent between the spins in complex **4**, as shown in Figure 3, and the χT values of *ca.* 3.0 emu K mol^{-1} at low temperatures correspond to $S = 5/2 - 1/2 = 2$. The gradual increase of the χT values at high temperatures indicates thermal population of a higher spin excited state of $S = 3$, reaching a room temperature value intermediate between those corresponding to $S = 2$ and $S = 3$.‡,6

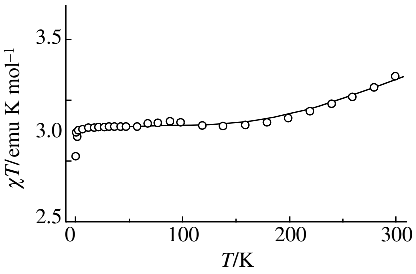


Figure 3 χT–T data of Mn(hfac)$_2$ complex **4**.

Next, we prepared the Mn(hfac)$_2$ complex derived from a 4-amino-TEMPO derivative, *i.e.*, bis-TEMPO-substituted-ethylenediamine[7] [$Mn(C_5HF_6O_2)_2(C_{20}H_{40}N_4O_2)$] and the crystal structure of the complex revealed the complexation of the ethylenediamine moiety with no substantial participation of the TEMPO moiety in this case (SI).† Antiferromagnetic interactions were apparent from the magnetic data of the complex with Curie–Weiss behaviour ($C = 4.9$ emu K mol^{-1}, $\theta = -0.86$ K, see SI) and the value of the Curie constant indicates the existence of an isolated Mn spin ($S = 5/2$) and two non-interacting $S = 1/2$ spins based on TEMPO radicals.

Thus, an unexpected reaction of **1** with Cu(hfac)$_2$ gave rise to the formation of a metal complex of 4-amino-TEMPO with Cu(hfac)$_2$ and the corresponding Mn(hfac)$_2$ complex together with the related one derived from bis-TEMPO-substituted-ethylenediamine could also be prepared to show different structural features and magnetic properties. It is well anticipated that other related metal complexes can also be available by using 4-amino-TEMPO derivatives.

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‡ The following equation is used for the expression of the magnetic data: $\chi T = Ng^2\beta^2/k(28 + 10e^{-3J/T})(7 + 5e^{-3J/T})$, where J is the exchange coupling between Mn and nitroxide spin sites, N is the Avogadro number, g is the average g-factor of spins ($g = 2.00$ is used here), β is the Bohr magneton constant, k is the Boltzmann constant. The J value is estimated to be –274 K from the equation.