Metal complex with the enaminoketone derivative of 2-imidazoline nitroxide

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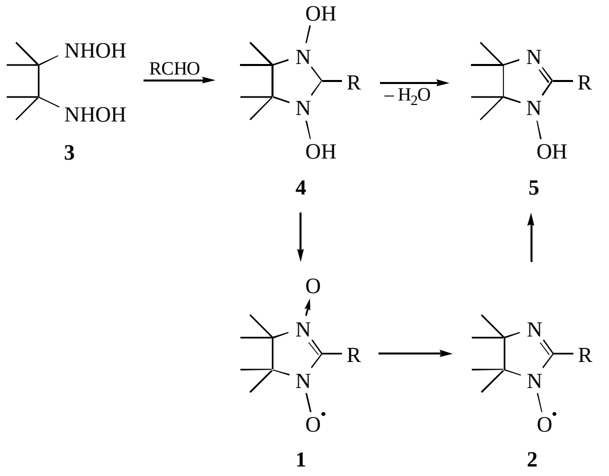
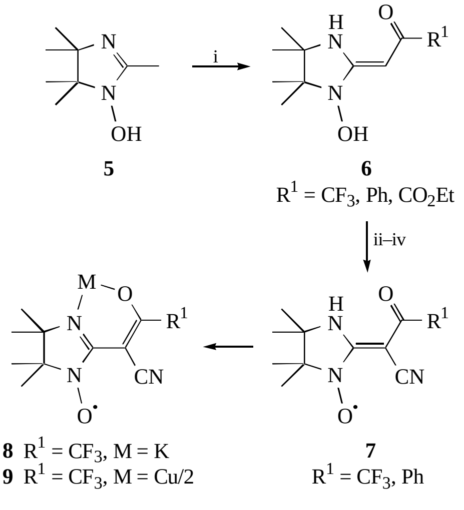
Functional derivatives of iminonitroxides were prepared by introducing a functional group into the side chain of 1-hydroxy-2-methyl-2-imidazoline; a K$^+$ salt and a Cu^{2+} bischelate with the first enaminoketone derivative of 2-iminonitroxide were synthesised and structurally characterised.

Heterospin systems based on metal complexes with 2-imidazoline nitroxides are widely used in molecular magnet design.[1] However, the syntheses of nitronyl nitroxides **1** and iminonitroxides **2** containing functional groups R (Scheme 1), which are favourable for metal complex formation, were confined to only one synthetic procedure. This method, which was proposed by Ullman, involves the condensation of dihydroxyamine **3** with aldehydes or their synthetic equivalents and the subsequent oxidation of dihydroxyimidazolidines **4**. Iminonitroxides **2** were generated by the reduction of **1**.[2] In this work, a donor group R (enaminoketone fragment) was introduced at the 2-position of a heterocyclic ring using another approach, the modification of 1-hydroxy-2-methyl-2-imidazoline (**5**, R = Me).



Scheme 1



Scheme 2 *Reagents and conditions*: i, LDA, R^{1}CO$_2$Et, Et$_2$O, 0 °C; ii, NCS, CHCl$_3$, room temperature; iii, NaCN, DMSO, room temperature; iv, PbO$_2$, CHCl$_3$.

First, we found an effective approach to the synthesis of **5**. The process looks like the ‘thermal dehydration’ of **4** to **5** (Scheme 1). It proceeds with a high yield in boiling heptane (or toluene at 100 °C).† We found that the dehydration was not accelerated in the presence of *para*-toluenesulfonic acid. The conversion of **4** to **5** by thermal dehydration does not proceed in an inert atmosphere. The presence of atmospheric oxygen is indispensable. Thermal dehydration of **4** is a very effective one-pot synthesis of **5**.

This easy route to **5** permits one to use 2,4,4,5,5-pentamethyl-1-hydroxy-2-imidazoline (**5**, R = Me) as a starting compound for the syntheses of persistent enaminoketones of 2-imidazoline nitroxide. The reactions of **5** (R = Me) with esters in the presence of lithium diisopropylamide give enaminoketones **6** (Scheme 2). The introduction of the nitrile substituent into enaminoketones **6** (R^1 = Ph, CF$_3$) and further oxidation led to relatively persistent nitroxides **7** (MS, *m*/*z*: 276 [M$^+$] R^1 = CF$_3$; *m*/*z*: 284 [M$^+$] R^1 = Ph). Nitroxide analogues of **7** with hydrogen substituted for the nitrile group are unstable and quickly decompose in solution. Nitroxide **7** (R^1 = CF$_3$) turned out to be the most long-living. However, we converted it every time to potassium salt **8** persistent under normal conditions. Single crystals of potassium salt **8**‡ and Cu^{2+} complex **9**§ with nitroxide **7** (R^1 = CF$_3$) were obtained, whose structures are shown in Figures 1 and 2, respectively. Synthesis¶ of **9** is actually a logical end of the chain of transformations presented in Scheme 2.

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† A typical procedure includes the boiling of a suspension of 1 g of **4** in 30–40 ml of heptane for 10–12 h. The precipitate of 1-hydroxy-2-imidazoline **5** was filtered off (85% yield for R = Me, 70% for R = Et and 50% for R = Ph) after recrystallization from hexane–ethyl acetate.

5 (R = Me): mp 104–106 °C. ^{1}H NMR ([^{2}H$_6$]DMSO) δ: 1.08 (s, 6H), 1.09 (s, 6H, 4,5-Me$_2$), 1.93 (s, 3H, 2-Me), 8.08 (br. s, OH). ^{13}C NMR ([^{2}H$_6$]DMSO) δ: 13.5 (2-Me), 18.6, 23.4 (4,5-Me$_2$), 65.1, 69.8 (C-4, C-5), 162.1 (C-2). IR (KBr, ν/cm^{-1}): 3160, 2900–2600, 1616. Found (%): C, 61.5; H, 10.5; N, 17.9. Calc. for $C_8H_{16}N_2O$ (%): C, 61.5; H, 10.3; N, 17.9.

5 (R = Et): mp 121–123 °C. ^{1}H NMR (CD$_3$OD) δ: 1.15 (t, 3H, CH$_2$*Me*), 1.21 (s, 6H), 1.24 (s, 6H, 4,5-Me$_2$), 2.45 (q, 2H, C*H*$_2$Me). IR (KBr, ν/cm^{-1}): 3110, 2900–2600, 1613. Found (%): C, 62.9; H, 11.1; N, 16.3. Calc. for $C_9H_{18}N_2O$ (%): C, 63.5; H, 10.7; N, 16.5.

5 (R = Ph): mp 190–191 °C. ^{1}H NMR (CDCl$_3$) δ: 1.36 (s, 6H), 1.43 (s, 6H, 4,5-Me$_2$), 7.25, 7.49 (2m, 5H, Ph), 8.33 (br. s, 1H, OH). IR (KBr, ν/cm^{-1}): 3110, 2900–2600, 1611, 1591, 1573. Found (%): C, 71.3; H, 8.2; N, 12.6. Calc. for $C_{13}H_{18}N_2O$ (%): C, 71.5; H, 8.3; N, 12.8.

Hydroxylamine precursors of **7** (R^1 = Ph): mp 213–214 °C. ^{1}H NMR ([^{2}H$_6$]DMSO–CD$_3$COCD$_3$) δ: 1.18 (s, 6H), 1.29 (s, 6H, 4,5-Me$_2$), 7.39–7.71 (m, 5H, Ph), 9.6 (br. s, 1H, NH), 10.1 (s, 1H, OH). ^{13}C NMR (CD$_3$OD) δ: 18.5, 23.1 (4,5-Me$_2$), 62.6 (C-4), 71.6 (C-5), 121.7 (C≡N), 128.7, 128.9, 131.6, 141.5 (Ph), 166.3 (C-2), 194.0 (C=O). IR (KBr, ν/cm^{-1}): 3200–2800, 2209 (C≡N), 1600, 1577, 1534. Found (%): C, 67.3; H, 6.8; N, 14.6. Calc. for $C_{16}H_{19}N_3O_2$ (%): C, 67.4; H, 6.7; N, 14.7. (R^1 = CF$_3$): mp 189–191 °C. ^{1}H NMR ([^{2}H$_6$]DMSO) δ: 1.11 (s, 6H), 1.21 (s, 6H, 4,5-Me$_2$), 9.30 (s, NH), 10.4 (s, OH). ^{13}C NMR ([^{2}H$_6$]DMSO) δ: 18.3, 22.2 (4,5-Me$_2$), 61.9 (C-4), 63.6 (=C–CN), 70.3 (C-5), 115.8 (C≡N), 117.2 (q, CF$_3$, $J_{\text{C–F}}$ 291 Hz), 162.8 (C-2), 173.8 (q, C=O, $J_{\text{C–F}}$ 32 Hz). IR (KBr, ν/cm^{-1}): 3400–3200, 2218 (C≡N), 1620, 1547. Found (%): C, 47.7; H, 4.5; N, 14.8. Calc. for $C_{11}H_{14}N_3O_2F_3$ (%): C 47.7; H, 5.1; N, 15.2.

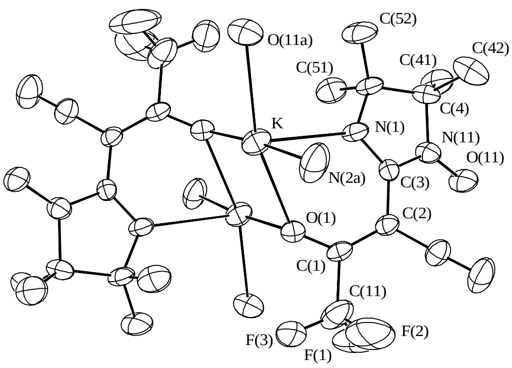

Figure 1 Molecular structure of **8** with displacement ellipsoids drawn at a 35% probability level (hydrogen atoms omitted for clarity). Selected distances (Å) and angles (°): K–O(11a) 2.688(4), K–O(1) 2.719(4), K–N(2a) 2.821(7), K–N(1) 2.854(5), O(1)–C(1) 1.255(7), C(1)–C(2) 1.343(7), C(2)–C(21) 1.407(9), C(2)–C(3) 1.422(7), C(21)–N(2) 1.172(8), O(11)–N(11) 1.281(5), C(3)–N(1) 1.287(6); O(1)–K–N(1) 62.78(13), C(1)–O(1)–K 120.9(4), O(1)–C(1)–C(2) 126.9(6), C(1)–C(2)–C(3) 121.6(6), N(2)–C(21)–C(2) 177.5(8), O(11)–N(11)–C(3) 126.4(5), O(11)–N(11)–C(4) 123.4(4), C(3)–N(11)–C(4) 109.8(5), N(1)–C(3)–C(2) 127.6(5), C(3)–N(1)–K 124.9(4).

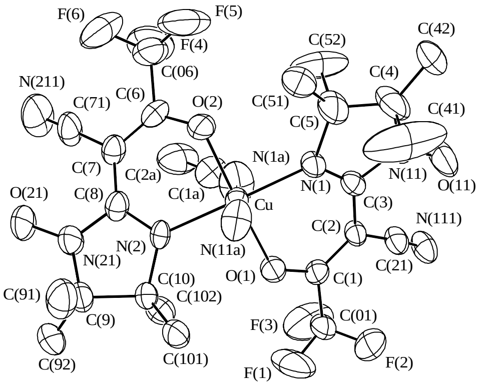

Figure 2 Molecular structure of **9** with displacement ellipsoids drawn at a 35% probability level (hydrogen atoms omitted for clarity). Selected distances (Å) and angles (°): Cu–O(2) 1.953(7), Cu–O(1) 1.963(6), Cu–N(1) 2.024(6), Cu–N(2) 2.033(6), Cu–N(11a) 2.299(9), Cu–N(1a) 2.774(14), O(1)–C(1) 1.290(10), C(1)–C(2) 1.368(11), C(2)–C(3) 1.437(11), C(2)–C(21) 1.441(12), C(21)–N(111) 1.142(11), C(3)–N(1) 1.266(10), N(11)–O(11) 1.264(10), O(2)–C(6) 1.263(11), C(6)–C(7) 1.386(14), C(7)–C(8) 1.409(14), C(7)–C(71) 1.435(15), C(71)–N(211) 1.148(16), C(8)–N(2) 1.296(10), N(21)–O(21) 1.269(10), N(1a)–C(1a) 1.071(17), C(1a)–C(2a) 1.43(2); O(1)–Cu–N(1) 87.9(3), O(2)–Cu–N(2) 88.5(3), N(11a)–Cu–N(1a) 178.0(4), C(1a)–N(1a)–Cu 139.8(13).

The structure of **8** is ionic. The distances between the paramagnetic centres in **8** are at least 6.71 Å, leading to constant μ_{eff} (1.68 B.M.) in the temperature range from 300 to 10 K. In complex **9**, the distorted octahedral environment of the central atom is formed by the O and N atoms of the two deprotonated enaminoketone ligands and by the N atoms of acetonitrile, and the nitrile group of the neighbouring bis-chelate molecule, leading to formation of polymer chains. The temperature dependence of the magnetic susceptibility of **9** is presented in Figure 3. It is adequately approximated by a cluster model with the parameters $g = 2.0$, $J = 90$ cm^{-1} and $nJ' = -0.3$ cm^{-1}. The J value is the highest positive value of the intramolecular exchange interaction energy among the known copper bis-chelates with stable nitroxides. This value points to the presence of highly effective exchange clusters inside the bis-chelate fragments.

Thus, a convenient route to a series of 4,4,5,5-tetramethyl-1-hydroxy-2R-2-imidazolines (**5**, R = Me, Et, Ph) has been found. Derivative **5** (R = Me) may be used as a substrate for syntheses of persistent spin-labeled enaminoketones (**7**, $R^1 = CF_3$, Ph). The first metal complex with the enaminoketone derivative of 2-iminonitroxide **9** has been isolated. A transition from metal complexes with spin-labeled 3-imidazoline enaminoketones, characterised by intramolecular exchange interaction energies of about 5–15 cm^{-1}, to the complex with 2-imidazoline analogue allowed us to achieve noticeably higher intramolecular exchange interaction energies between the unpaired electrons of paramagnetic centres (90 cm^{-1}). Studies are currently under way to synthesise other metal complexes with the enaminoketone derivatives of 2-imidazoline nitroxide and to investigate their structure and magnetic properties.

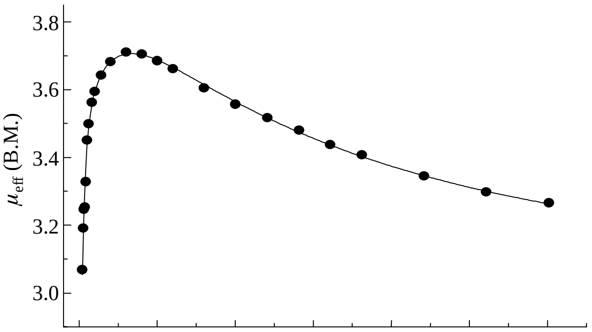

Figure 3 The temperature dependence of μ_{eff} for **9**.

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‡ *Crystal data for* **8**: $C_{11}H_{12}F_3KN_3O_2$, $M = 314.34$, monoclinic, $a = 11.068(2)$ Å, $b = 9.203(2)$ Å, $c = 14.177(3)$ Å, $\beta = 92.19(3)°$, $V = 1443.0(5)$ Å^3, $T = 293$ K, space group $P2_1/c$ (no. 14), $Z = 4$, $d_{\text{calc}} = 1.447$ g cm^{-3}, μ(MoKα) = 0.405 mm^{-1}. 2194 I_{hkl} (2012 unique I_{hkl}, $R_{\text{int}} = 0.1104$) were measured on a Bruker AXS P4 four-circle automatic diffractometer (λMoKα, graphite monochromator, $\theta/2\theta$-scan, $2.64 < \theta < 24.98°$). The structure was solved using the SIR97 program and refined by the full-matrix least-squares technique in an anisotropic approximation for all non-hydrogen atoms. All hydrogen atoms were located in a difference Fourier map and then refined in an isotropic approximation. The final R indexes are: $R_1 = 0.0542$, $wR_2 = 0.1006$ for 2012 unique $I_{hkl} > 2\sigma(I)$, GOOF = 0.664.

§ *Crystal data for* **9**: $C_{24}H_{27}CuF_6N_7O_4$, $M = 655.07$, orthorhombic, $a = 14.045(2)$ Å, $b = 12.342(2)$ Å, $c = 17.259(3)$ Å, $V = 2991.7(8)$ Å^3, $T = 293$ K, space group $Pca2_1$ (no. 29), $Z = 4$, $d_{\text{calc}} = 1.454$ g cm^{-3}, μ(MoKα) = 0.809 mm^{-1}. 2723 I_{hkl} (2723 unique I_{hkl}) were measured on a Bruker AXS P4 four-circle automated diffractometer (λMoKα, graphite monochromator, $\theta/2\theta$-scan, $2.36 < \theta < 24.99°$, empirical absorption correction). The structure was solved by the SIR97 program and refined by the full-matrix least-square technique in an anisotropic approximation for all non-hydrogen atoms. Positions of all hydrogen atoms were located in a difference Fourier map and than refined in an isotropic approximation. The final R indexes for 406 refined parameters are: $R_1 = 0.0576$, $wR_2 = 0.1427$ for $I_{hkl} > 2\sigma(I)$, GOOF = 1.024. All calculations were carried out using the SHELX97 program. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2001. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/98.

¶ For the synthesis of **8**, a solution of KOH (4.0 mmol) in MeOH (5 ml) was added to the solution of **7** ($R^1 = CF_3$) (1 g, 3.6 mmol) in ethyl acetate (100 ml) with stirring. Salt **8** was precipitated from the reaction mixture by adding toluene (50% yield). Single crystals were grown by slow diffusion of benzene into an ethyl acetate solution of **8**. To prepare **9**, a mixture of $Cu(NO_3)_2(H_2O)_3$ (39 mg, 0.16 mmol) and **8** (100 mg, 0.32 mmol) was dissolved in 10 ml of dry acetonitrile, and the solution was allowed to stand at –10 °C. After 2 days, the KNO_3 precipitate was filtered off; after one more day, dark red crystals of the complex were isolated (yield 45%). **8**: mp 257–262 °C (decomp.). IR (KBr, ν/cm^{-1}): 2190 (C≡N), 1603, 1553. Found (%): C, 41.8; H, 3.9; N, 13.1. Calc. for $C_{11}H_{12}N_3O_2F_3K$ (%): C, 42.0; C, 3.9; N, 13.4. **9**: mp 176–179 °C (decomp.). IR (KBr, ν/cm^{-1}): 2220 (C≡N), 1588, 1523. Found (%): C, 43.6; C, 4.0; N, 14.8. Calc. for $C_{24}H_{27}N_7O_4F_6Cu$ (%): C, 44.0; H, 4.2; N, 15.0.

References

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