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# Synthesis of 2-iminonitroxide-substituted phenols and pyridine-3-oles. Copper(II) complexes with imino nitroxides containing 2-hydroxyphenyl substituents

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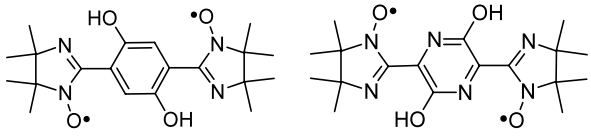
**Abstract**

Methods for the synthesis of a new family of nitronylnitroxides, iminonitroxides, and their precursors with 2-hydroxyphenyl or 3-hydroxypyridin-2-yl substituents in the side chain have been developed. Five heterospin chelates of Cu(II) with deprotonated iminonitroxides have been isolated. Their structure and magnetic properties have been studied. In all complexes, ferromagnetic intramolecular exchange interactions take place ($J \sim 40$–$350$ cm$^{-1}$).


*Keywords:* Imino nitroxide; Nitronyl nitroxide; Cu(II) complexes; Molecular magnets

## 1. Introduction

Molecular ferromagnet design based on complexes of paramagnetic metal ions with nitroxides is becoming an area of active interest, as evidenced by the growing number of experimental works and reviews [1,2]. The necessity of constructing highly dimensional heterospin structures stimulates the development of syntheses of increasingly complex polyfunctional nitroxides. As functional groups it is desirable to use combinations of donor groups leading to stereochemically nonrigid complexes with potentialities for higher coordination numbers of the metal ion. The latter, in turn, opens up extra opportunities to increase the structural dimensionality of the heterospin complex. Among the classical stereochemically nonrigid metal-containing matrices are complexes with Schiff bases [3,4]. It is not surprising, therefore, that procedures are available for syntheses of transition metal complexes with various spin-labeled Schiff bases containing piperidine [5–7], pyrrolidine [8] or 3-imidazoline [9] nitroxides as a paramagnetic fragment. Since the paramagnetic centers in these complexes are separated by a reasonably long chain of chemical bonds, the exchange interactions in the complexes equal several cm$^{-1}$ in magnitude [9]. To enhance the energy of exchange interactions between the odd electrons of the nitroxide and the metal ion we decided to develop methods for the synthesis of a series of spin-labeled Schiff bases based on 2-imidazoline heterocycles as well as metal complexes with them. The aim of our project is to develop synthesis of heterospin polymer compounds from vicinal dihydroxyaryl derivatives of bisiminonitroxides of the type presented below:



A consistent approach to such biradicals demands a preliminary work on synthetic procedures for simpler spin-labeled derivatives. This paper describes synthetic procedures for nitronyl nitroxides **4a**–**g**, **9**, paramag-

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netic Schiff bases with a 2-imidazoline ring $\mathbf{HL}^1$–$\mathbf{HL}^8$, and heterospin complexes of Cu(II) with $\mathbf{L}^1$–$\mathbf{L}^4$. The preliminary results are presented in Ref. [10].

## 2. Experimental

### 2.1. Materials and instruments

All the solvents used were reagent quality. Removal of all solvents was carried out under reduced pressure and all commercial reagents were used without additional purification. Unless otherwise stated, the reactions were monitored by TLC on Silufol® UV-254 plates (Silpearl on aluminium foil, Czecho-Slovakia). Silica gel 'Merck' (Silica gel 60 0.063–0.200 mm for column chromatography) and $Al_2O_3$ (neutral, analytical grade, for chromatography, Russia) were used for column chromatography. $^1$H NMR spectra were recorded at 25 °C using a Bruker Avance 300 spectrometer locked to the deuterium resonance of the solvent. Chemical shifts were calculated relative to solvent signals used as the internal standards: $\delta_H$ 2.05 ppm for acetone-$d_6$, $\delta_H$ 2.50 ppm for DMSO-$d_6$, $\delta_H$ 7.240 ppm for $CDCl_3$. The synthesis of 2,3-bis(hydroxylamino)-2,3-dimethylbutane (**2**) was described previously [11,12]. 2-Hydroxy-3-nitrobenzaldehyde and 5-bromo-2-hydroxy-3-nitrobenzaldehyde were prepared by nitration of correspondingly salicylaldehyde and 5-bromo-2-hydroxy-benzaldehyde. The structures were confirmed by IR and NMR spectra. Other reagents were commercially available, and used without further purification.

### 2.2. Syntheses of compounds

#### 2.2.1. 2-(2-Hydroxy-phenyl)-4,4,5,5-tetramethyl-imidazolidine-1,3-diol (**3a**)

A mixture of **2** (0.45 g, 3.0 mmol) and salicylaldehyde (0.37 g, 3.0 mmol) in MeOH (10 ml) was stirred at ambient temperature for 3 h, and the solvent was evaporated. The residue was washed with hexane, filtered off, and recrystallized from $CHCl_3$. Yield 0.39 g (52%), colourless needles, m.p. 154–155 °C. $^1$H NMR (acetone-$d_6$): $\delta = 1.18$ (s, 6H, Me), 1.24 (s, 6H, Me), 4.78 (s, 1H, H(2)), 6.65–6.79 (m, 2H, H(3′), H(5′)), 7.08–7.23 (m, 2H, H(4′), H(6′)), 7.45 (br. s, 2H, N–OH). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 610, 674, 721, 731, 752, 788, 813, 830, 860, 896, 922, 946, 969, 1005, 1036, 1109, 1151, 1209, 1238, 1263, 1366, 1382, 1496, 1595, 1618, 2904, 2988, 3314 br. *Anal.* Found: C, 61.8; H, 8.2; N, 10.8. Calc. for $C_{13}H_{20}N_2O_3$: C, 61.9; H, 8.0; N, 11.1%.

#### 2.2.2. 2-(5-Bromo-2-hydroxy-phenyl)-4,4,5,5-tetramethyl-imidazolidine-1,3-diol (**3b**)

A mixture of **2** (1.47 g, 10.0 mmol) and 5-bromo-2-hydroxybenzaldehyde (2.01 g, 10.0 mmol) in MeOH (20 ml) was stirred for 12 h at ambient temperature. The resulting precipitate was filtered off and recrystallized from AcOEt. Yield 2.42 g (73%), white powder, m.p. 193–194 °C, $R_f$ (AcOEt) 0.85. $^1$H NMR (acetone-$d_6$): $\delta = 1.18$ (s, 6H, Me), 1.24 (s, 6H, Me), 4.78 (s, 1H, H(2)), 6.67 (d, 1H, $J = 8.6$ Hz, H(3′)), 7.28 (dd, 1H, $J = 8.6$ Hz, $J = 2.5$ Hz, H(4′)), 7.36 (d, 1H, $J = 2.5$ Hz, H(6′)), 7.65 (br. s, 2H, N–OH), 11.0 (br. s, 1H, OH). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 628, 656, 719, 736, 789, 824, 885, 904, 927, 947, 966, 1005, 1039, 1081, 1126, 1150, 1199, 1261, 1352, 1369, 1380, 1392, 1455, 1486, 1585, 1609, 2897, 2979, 2995, 3352 br. *Anal.* Found: C, 47.1; H, 5.9; Br, 24.2. Calc. for $C_{13}H_{19}BrN_2O_3$: C, 47.1; H, 5.8; Br, 24.1%.

#### 2.2.3. 2-(2-Hydroxy-5-nitro-phenyl)-4,4,5,5-tetramethyl-imidazolidine-1,3-diol (**3c**)

A mixture of **2** (0.19 g, 1.32 mmol) and 2-hydroxy-5-nitrobenzaldehyde (0.20, 1.20 mmol) in MeOH (10 ml) was stirred for 24 h at ambient temperature. The solvent was evaporated in vacuum, and the residue recrystallized from a mixture of AcOEt with EtOH. Yield 0.24 g (69%), yellow crystals, m.p. 134–135 °C. IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 744, 796, 862, 916, 943, 991, 1018, 1103, 1143, 1200, 1257, 1298, 1349, 1367, 1379, 1389, 1454, 1540, 1594, 1615, 2917, 2980, 3291 br. *Anal.* Found: C, 52.1; H, 6.3; N, 13.8. Calc. for $C_{13}H_{19}N_3O_5$: C, 52.5; H, 6.4; N, 14.1%.

#### 2.2.4. 2-(5-Bromo-2-hydroxy-3-nitro-phenyl)-4,4,5,5-tetramethyl-imidazolidine-1,3-diol (**3d**)

A mixture of **2** (2.96 g, 20.0 mmol) and 5-bromo-2-hydroxy-3-nitrobenzaldehyde (4.92 g, 20.0 mmol) in MeOH (30 ml) was stirred for 3 h at ambient temperature. Then the reaction mixture was cooled to −10 °C, kept at that temperature for 1 h, and the resulting precipitate was filtered off. Yield 5.14 g (68%), yellow powder, m.p. 198–200 °C (AcOEt). $^1$H NMR (acetone-$d_6$): $\delta = 1.22$ (s, 6H, Me), 1.26 (s, 6H, Me), 5.01 (s, 1H, H(2)), 7.77 (d, 1H, $J = 2.5$ Hz, H(6′)), 8.00 (d, 1 H, $J = 2.5$ Hz, H(4′)). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 626, 651, 696, 723, 767, 810, 823, 845, 882, 907, 920, 952, 988, 1017, 1029, 1095, 1113, 1143, 1197, 1237, 1292, 1344, 1380, 1416, 1454, 1540, 1584, 1610, 2916, 2983, 3099, 3263 br. *Anal.* Found: C, 41.9; H, 5.1; Br, 21.2; N, 11.1. Calc. for $C_{13}H_{18}BrN_3O_5$: C, 41.5; H, 4.8; Br, 21.2; N, 11.2%.

#### 2.2.5. 2-(2-Hydroxy-3-nitro-phenyl)-4,4,5,5-tetramethyl-imidazolidine-1,3-diol (**3e**)

A mixture of **2** (1.51 g, 10.0 mmol) and 2-hydroxy-3-nitrobenzaldehyde (1.70 g, 10.0 mmol) in MeOH (30 ml) was stirred for 2 h at ambient temperature. After evaporation of the solvent, the residue was washed with hexane, and the solvent was decanted. A mixture of AcOEt with hexane (1:1, v/v) was added to the crude product, and the resulting mixture was kept at −10 °C

for 12 h. The precipitate was filtered off. Yield 2.33 g (79%), yellow powder, m.p. 141–142 °C (from a mixture of AcOEt with $C_6H_6$). $^1H$ NMR (acetone-$d_6$): $\delta = 1.21$ (s, 6H, Me), 1.26 (s, 6H, Me), 4.99 (s, 1H, H(2)), 6.96 (dd, 1H, $J = 8.3$ Hz, 7.6 Hz, H(5′)), 7.28 (dd, 1 H, $J =$ 7.6 Hz, 1.4 Hz, H(6′)), 7.82 (d, 1 H, $J = 8.3$ Hz, 1.4 Hz, H(4′)). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 676, 750, 798, 868, 915, 942, 964, 994, 1041, 1071, 1154, 1265, 1330, 1367, 1387, 1457, 1544, 1612, 2914, 2982, 3234 br. *Anal.* Found: C, 52.3; H, 6.3; N, 14.0. Calc. for $C_{13}H_{19}N_3O_5$: C, 52.5; H, 6.4; N, 14.1%.

### 2.2.6. 2-(2-Hydroxy-phenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-3-oxide-1-oxyl (**4a**) [13]

$NaIO_4$ (0.91 g, 4.2 mmol) was added in portions for 20 min to a stirred ice-cooled mixture of **3a** (0.71 g. 2.8 mmol), $CHCl_3$ (10 ml), and water (10 ml). The cooling was removed, and the reaction mixture was stirred for 20 min. The chloroform layer was separated, and the aqueous layer extracted with $CHCl_3$ ($3 \times 10$ ml). The consolidated solutions were dried with $Na_2SO_4$, and the solvent was distilled off in vacuum. The residue was dissolved in $C_6H_6$ (3 ml) and chromatographed on an $Al_2O_3$ column ($1.5 \times 10$ cm, $C_6H_6$ as eluent). The fraction containing **4a** was concentrated to a volume of $\sim 3$ ml, diluted with hexane (10 ml), and cooled. The precipitate was filtered off. Yield 0.51 g (74%), blue needles, m.p. 119–120 °C. IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 637, 766, 804, 833, 874, 1034, 1133. 1148, 1163, 1213, 1256, 1307, 1338, 1373, 1392, 1429, 1449, 1470, 1526, 1572, 1609, 2993, 3439 br. *Anal.* Found: C, 62.4; H, 6.8; N, 11.0. Calc. for $C_{13}H_{17}N_2O_3$: C, 62.6; H, 6.9; N, 11.2%.

### 2.2.7. 2-(5-Bromo-2-hydroxy-phenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-3-oxide-1-oxyl (**4b**)

$NaIO_4$ (0.64 g, 3.0 mmol) was added to a stirred mixture of **3b** (0.66 g, 2.0 mmol), $CHCl_3$ (10 ml), and water (10 ml) at 5 °C. The cooling was removed, and the reaction mixture stirred for 30 min. The organic layer was separated, and the aqueous layer extracted with $CHCl_3$ ($2 \times 10$ ml). The consolidated solutions were dried with $Na_2SO_4$, filtered through an $Al_2O_3$ layer ($1.5 \times 5$ cm), and concentrated. The residue was ground with hexane, the solvent was decanted, and the residue recrystallized from a mixture of $C_6H_6$ with hexane. Yield 0.49 g (75%), blue needles, m.p. 142–143 °C. IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 614, 641, 664, 696, 735, 763, 806, 832, 867, 884, 945, 976, 1013, 1101, 1137, 1162, 1215, 1251, 1300, 1340, 1374, 1396, 1427, 1469, 1494, 1523, 1566, 1602, 1667, 2941, 2982, 3018, 3076, 3428 br. *Anal.* Found: C, 47.8; H, 4.9; Br, 23.9; N, 8.5. Calc. for $C_{13}H_{16}BrN_2O_3$: C, 47.6; H, 4.9; Br, 24.4; N, 8.5%.

### 2.2.8. 2-(2-Hydroxy-5-nitro-phenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-3-oxide-1-oxyl (**4c**)

$NaIO_4$ (0.50 g, 2.3 mmol) was added to a stirred mixture of **3c** (0.20 g, 0.68 mmol), $CHCl_3$ (10 ml), and water (10 ml). The reaction mixture was then stirred for 1 h. The product was isolated as in procedure **4b**. Yield 0.16 g (80%), blue needles, decomp. at 160 °C. IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 627, 642, 677, 704, 723, 748, 828, 885, 904, 1080, 1139, 1165, 1209, 1260, 1323, 1351, 1374, 1429, 1473, 1524, 1578, 1621, 2947, 2995, 3447 br. *Anal.* Found: C, 52.8; H, 5.4; N, 14.1. Calc. for $C_{13}H_{19}N_3O_5$: C, 53.1; H, 5.5; N, 14.3%.

### 2.2.9. 2-(5-Bromo-2-hydroxy-3-nitro-phenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-3-oxide-1-oxyl (**4d**)

$NaIO_4$ (1.29 g, 6.0 mmol) was added to an ice-cooled stirred mixture of **3d** (1.50 g, 4.0 mmol), $CH_2Cl_2$ (30 ml), and water (30 ml). The reaction mixture was then stirred for 2 h, while the temperature was gradually raised to room temperature. The organic layer was separated, dried over $Na_2SO_4$, and filtered through a $SiO_2$ ($1.5 \times 10$ cm) layer. After the solvent was removed in vacuum, the residue was recrystallized from $C_6H_6$ with charcoal (bath temperature 50–60 °C). Yield 1.26 g (84%), blue–violet needles, decomp. at 130–135 °C. IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 655, 697, 729, 765, 811, 878, 920, 979, 1133, 1158, 1204, 1269, 1356, 1375, 1397, 1449, 1532, 1594, 2995, 3098, 3450 br. *Anal.* Found: C, 41.6; H, 3.9; Br, 21.3; N, 10.9. Calc. for $C_{13}H_{15}BrN_3O_5$: C, 41.8; H, 4.1; Br, 21.4; N, 11.3%.

### 2.2.10. 2-(2-Hydroxy-3-nitro-phenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-3-oxide-1-oxyl (**4e**)

$NaIO_4$ (0.30 g, 1.40 mmol) was added to a mixture of **3e** (0.15 g, 0.51 mmol), $CHCl_3$ (10 ml), and water (10 ml), and the reaction mixture was stirred for 30 min at ambient temperature. The organic layer was separated, and the water layer extracted with $CHCl_3$ ($1 \times 10$ ml). The combined organic solutions were dried with $Na_2SO_4$, the solvent was evaporated, and the residue recrystallized from a mixture of $C_6H_6$ with hexane. Yield 86 mg (58%), blue needles, decomp. at 125–128 °C. IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 650, 684, 750, 806, 838, 876, 913, 971, 1136, 1163, 1215, 1287, 1354, 1396, 1432, 1450, 1520, 1537, 1579, 1609, 2940, 2974, 2992, 3088, 3441 br. *Anal.* Found: C, 53.2; H, 5.3; N, 14.1. Calc. for $C_{13}H_{19}N_3O_5$: C, 53.1; H, 5.5; N, 14.3%.

### 2.2.11. 2-(4,4,5,5-Tetramethyl-3-oxy-4,5-dihydro-1H-imidazol-2-yl)-phenol (**5a**)

A mixture of **3a** (0.25 g, 1.0 mmol), $SeO_2$ (20 mg, 0.2 mmol), and MeOH (15 ml) was stirred with boiling for 2 h (TLC monitoring; the spot of **3a** vanished, and a spot

with $R_f$ (AcOEt) 0.1 appeared; treatment of the latter with aqueous $NaIO_4$ led to orange coloring). The reaction mixture was cooled, and the solvent distilled off in vacuum. To the residue was added benzene ( ~ 10 ml), the mixture was heated to boiling and filtered (the spot with $R_f$ (AcOEt) 0.1 vanished, and a spot with $R_f$ (AcOEt) 0.31 appeared; treatment of the latter with aqueous $NaIO_4$ gave orange coloring). The resulting solution was concentrated and chromatographed on $SiO_2$ (AcOEt as eluent). The fractions containing **5a** were consolidated and evaporated; the residue was recrystallized from a mixture of AcOEt with hexane (1:1 v/v). Yield 91 mg (40%), cream crystals, m.p. 126–127 °C. $^1$H NMR (acetone-$d_6$): $\delta = 1.36$ (s, 6H, Me), 1.38 (s, 6H, Me), 6.41 (br. s, 1H, N–OH), 6.73–6.84 (m, 2H, H(3), H(5)), 7.35–7.43 (m, 2H, H(4), H(6)). IR (KBr): $\tilde{\nu}$ (cm$^{-1}$) 666, 695, 753, 781, 860, 896, 943, 958, 1034, 1085, 1122, 1151, 1168, 1228, 1256, 1314, 1371, 1395, 1447, 1492, 1611, 2750, 2857, 2968, 3065, 3400 br. MS, *m/z* (%): 234.1380 ($M^+$, 42, calcd. for $C_{13}H_{18}N_2O_2$ 234.1368), 217 $[M-OH]^+$ (11), 161 (7), 160 (8), 146 (15), 120 (32), 119 (5), 114 (13), 100 (12), 98 (45), 91 (6), 84 (66), 83 (6), 70 (6), 69 (100). *Anal.* Found: C, 66.8; H, 7.7; N, 11.9. Calc. for $C_{13}H_{18}N_2O_2$: C, 66.6; H, 7.7; N, 12.0%.

### 2.2.12. 4-Bromo-2-(4,4,5,5-tetramethyl-3-oxy-4,5-dihydro-1H-imidazol-2-yl)-phenol (**5b**)

A mixture of **3b** (0.33 g, 1.0 mmol), $SeO_2$ (30 mg, 0.27 mmol), and MeOH (20 ml) was stirred with boiling for 3 h. The reaction mixture was cooled, and the solvent distilled off in vacuum. To the residue was added benzene (5 ml). The mixture was heated to boiling (as in the case of **5a**, TLC showed mutual transformation of the compounds), placed on a $SiO_2$ (1.5 × 10 cm) column, and eluted with $CHCl_3$ (TLC monitoring; treatment of spot **5b** with aqueous $NaIO_4$ led to orange coloring). The fractions containing **5b** were consolidated and evaporated; the residue was recrystallized from a mixture of AcOEt with hexane (1:1, v/v). Yield 0.18 g (58%), cream crystals, m.p. 210–211 °C, $R_f$ ($CHCl_3$) 0.11, $R_f$ (AcOEt) 0.61. $^1$H NMR (acetone-$d_6$): $\delta = 1.38$ (s, 6H, Me), 1.41 (s, 6H, Me), 6.67 (d, 1H, $J = 9.3$ Hz, H(3)), 7.28 (dd, 1H, $J = 9.3$ Hz, $J = 2.8$ Hz, H(4)), 7.36 (d, 1H, $J = 2.8$ Hz, H(6)). IR (KBr): $\tilde{\nu}$ (cm$^{-1}$) 658, 701, 739, 767, 786, 827, 883, 898, 936, 972, 1058, 1082, 1129, 1228, 1249, 1300, 1371, 1392, 1482, 1606, 1653, 2987, 3114, 3447 br. MS, *m/z* (%): 312.0456 ($M^+$, 39, calcd. for $C_{13}H_{17}BrN_2O_2$ 312.0474), 295 $[M-OH]^+$ (14), 226 (13), 224 (15), 200 (23), 198 (24), 100 (33), 98 (100). *Anal.* Found: C, 49.8; H, 5.3; Br, 24.3; N, 9.1. Calc. for $C_{13}H_{17}BrN_2O_2$: C, 49.9; H, 5.5; Br, 25.5; N, 8.9%.

### 2.2.13. 4-Nitro-2-(4,4,5,5-tetramethyl-3-oxy-4,5-dihydro-1H-imidazol-2-yl)-phenol (**5c**)

A mixture of **3c** (0.50 g, 1.7 mmol) and $SeO_2$ (50 mg, 0.45 mmol) was refluxed in MeOH (20 ml) for 1 h. The reaction mixture was cooled, and the solvent distilled off in vacuum. The residue was ground with ether, and hexane was added. The residue was filtered off and recrystallized from a mixture of AcOEt with a small amount of EtOH. Yield 0.38 g (81%), yellow crystals, decomp. at 195 °C. $^1$H NMR (acetone-$d_6$): $\delta = 1.43$ (s, 6H, Me), 1.46 (s, 6H, Me), 6.78 (d, 1H, $J = 8.6$ Hz, H(3)), 7.50 (dd, 1H, $J = 8.6$ Hz, $J = 2.5$ Hz, H(4)), 7.53 (d, 1H, $J = 2.5$ Hz, H(6)). IR (KBr): $\tilde{\nu}$ (cm$^{-1}$) 637, 667, 694, 758, 814, 834, 922, 954, 1012, 1068, 1135, 1166, 1213, 1241, 1277, 1326, 1354, 1396, 1462, 1489, 1543, 1615, 1834, 2970, 3130, 3426 br. *Anal.* Found: C, 55.8; H, 6.3; N, 15.0. Calc. for $C_{13}H_{17}N_3O_4$: C, 55.9; H, 6.1; N, 15.1%.

### 2.2.14. 4-Bromo-2-nitro-6-(4,4,5,5-tetramethyl-3-oxy-4,5-dihydro-1H-imidazol-2-yl)-phenol (**5d**)

A mixture of **3d** (3.76 g, 10 mmol) and $SeO_2$ (0.10 g, 0.90 mmol) was refluxed in MeOH (50 ml) for 2 h. The reaction mixture was cooled, the red residue filtered off, and the solvent distilled off in vacuum. The residue was dissolved in boiling AcOEt (30 ml), the solution was filtered to remove the insoluble yellow precipitate, and the solvent distilled off. The product was ground with hexane, and the resulting lemon yellow powder filtered off. Yield 2.63 g (73%), yellow crystals, m.p. 197–198 °C (AcOEt–hexane mixture). $^1$H NMR (acetone-$d_6$): $\delta =$ 1.44 (s, 6H, Me), 1.48 (s, 6H, Me), 7.79 (dd, 1H, $J = 2.8$ Hz, H(6)), 8.05 (d, 1H, $J = 2.8$ Hz, H(4)). IR (KBr): $\tilde{\nu}$ (cm$^{-1}$) 696, 744, 788, 820, 889, 1026, 1123, 1165, 1247, 1299, 1373, 1394, 1523, 1614, 2982, 3426 br. *Anal.* Found: C, 43.7; H, 4.3; Br, 22.3; N, 11.8. Calc. for $C_{13}H_{16}BrN_3O_4$: C, 43.6; H, 4.5; Br, 22.3; N, 11.7%.

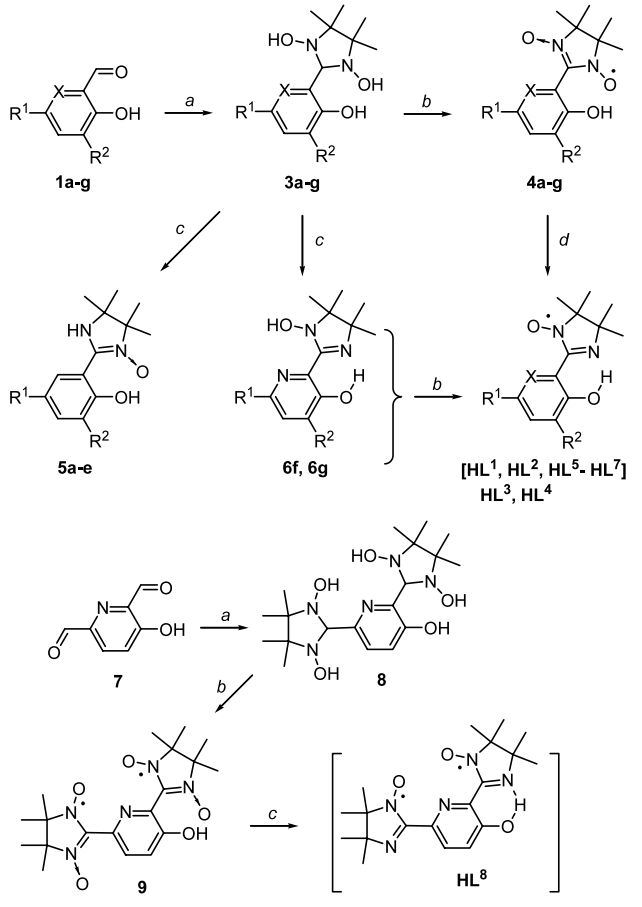
### 2.2.15. 2-Nitro-6-(4,4,5,5-tetramethyl-3-oxy-4,5-dihydro-1H-imidazol-2-yl)-phenol (**5e**)

A mixture of **3e** (0.30 g, 10 mmol), $SeO_2$ (30 mg, 0.27 mmol), and MeOH (15 ml) was stirred at ambient temperature for 10 h. The solvent was distilled off in vacuum, and $C_6H_6$ (5 ml) was added to the residue. The mixture was heated on a water bath to boiling, and the solution was decanted on a $SiO_2$ (1.5 × 15 cm) column. This procedure was repeated eight times. The mixture was eluted with $CHCl_3$ (TLC monitoring, development with aqueous $NaIO_4$, spot **5e** gives orange coloring). The fractions containing **5e** were consolidated and evaporated, and the residue was recrystallized from a mixture of AcOEt with hexane (1:1, v/v). Yield: 0.21 g (75%), yellow crystals, m.p. 97–98 °C, $R_f$ ($CHCl_3$) 0.38. $^1$H NMR (acetone-$d_6$): $\delta = 1.41$ (s, 6H, Me), 1.44 (s, 6H, Me), 6.72 (t, 1H, $J = 7.9$ Hz, H(5)), 7.28 (dd, 1H, $J = 7.9$ Hz, $J = 1.7$ Hz, H(6)), 7.36 (dd, 1H, $J = 7.9$ Hz, $J = 1.7$

Hz, H(4)). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 675, 699, 753, 804, 823, 864, 915, 941, 1008, 1123, 1172, 1222, 1265, 1290, 1364, 1448, 1530, 1552, 1621, 2935, 2983, 3186 br., 3404 br. *Anal.* Found: C, 55.8; H, 6.3; N, 15.0. Calc. for $C_{13}H_{17}N_3O_4$: C, 55.9; H, 6.1; N, 15.1%.

### 2.2.16. Preparation in solution of 2-(2-hydroxyphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl (HL[1]), 2-(2-hydroxy-5-bromophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl (HL[2]) and 2-(2-hydroxy-3-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl (HL[5])

Method *d* (Scheme 1). A mixture of nitroxide **4a**, **4b**, or **4e** (0.61 mmol), $NaNO_2$ (0.20 g, 2.90 mmol), AcOH (0.5 ml), water (0.5 ml), and $CHCl_3$ (10 ml) was stirred at ambient temperature till the starting nitronylnitroxide (30–50 min) disappeared. To the reaction mixture was added water (0.5 ml) and $NaHCO_3$ in an amount required for acetic acid neutralization. The resulting mixture was dried by mixing it with $Na_2SO_4$ for 5–10 min, and then filtered through a $NaHCO_3$ (1.5 × 1 cm) and $Al_2O_3$ (1.5 × 8 cm) layers (**HL**[1], **HL**[2], **HL**[5] decompose on $SiO_2$!). The iminonitroxide was eluted with $CHCl_3$ (10 ml). $R_f$ ($CHCl_3$) is 0.87 for **HL**[1], 0.84 for **HL**[2], 0.52 for **HL**[5]; the spots are orange–red, or brown after drying. In an alternative procedure *b* (Scheme 1), **HL**[1], **HL**[2], and **HL**[5] were prepared by oxidation of **5a**, **5b**, and **5e**, respectively, with $NaIO_4$.




Scheme 1. **a**, **HL**[1]: $R^1 = R^2 = H$, X = CH; **b**, **HL**[2]: $R^1 = Br$, $R^2 = H$, X = CH; **c**, **HL**[3]: $R^1 = NO_2$, $R^2 = H$, X = CH; **d**, **HL**[4]: $R^1 = Br$, $R^2 = NO_2$, X = CH; **e**, **HL**[5]: $R^1 = H$, $R^2 = NO_2$, X = CH; **f**, **HL**[6]: $R^1 = R^2 = H$, X = N; **g**, **HL**[7]: $R^1 = CH_3$, $R^2 = H$, X = N. (*a*) 2,3-bis(hydroxylamino)-2,3-dimethylbutane (**2**), MeOH; (*b*) $NaIO_4$, $CHCl_3$, $H_2O$; (*c*) $SeO_2$, MeOH; (*d*) $NaNO_2$, AcOH, $H_2O$, $CHCl_3$.

Importantly, other products formed when a $CHCl_3$ solution of **HL**[1] was stored for 15–25 min at ambient temperature; in this case, the color of the solution became increasingly deep brown. Concentration of a solution of **HL**[1] on a rotary evaporator led to increased rate of decomposition of **HL**[1]. No other products were observed on storage of a cooled $CHCl_3$ solution of **HL**[2]. Evaporation of the solution of **HL**[2] led to red oil, which converted, within a few minutes, into a mixture of brown products containing **5b**. Evaporation of the $CHCl_3$ solution of **HL**[5] formed **5e**.

### 2.2.17. Isolation of by-products in synthesis of HL[2]

The reaction mixture obtained from nitroxide **4b** (0.40 g) was dried with $Na_2SO_4$, the solvent was distilled off, and the residue chromatographed on $SiO_2$ (AcOEt as eluent). This gave two major fractions. TLC showed that the first fraction contains **5b**. The second, yellow-colored fraction was evaporated, and the residue recrystallized from a mixture of petroleum ether with AcOEt. The resulting orange powder was dissolved in $CH_2Cl_2$ (5 ml), heptane (10 ml) was added, and the solution was allowed to stay overnight in an open flask in a thermostat. The crystalline product was filtered off and X-ray investigated. This gave 5-bromo-3-(4,4,5,5-tetramethyl-imidazolidin-2-ylidene)-cyclohex-5-ene-1,2,4-trione (**12**). Yield 130 mg (33%), m.p. 190–191 °C, $R_f$ ($CHCl_3$) 0.12. IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 654, 697, 729, 808, 846, 872, 905, 986, 1061, 1185, 1252, 1302, 1351, 1373, 1397, 1579, 1605, 1690, 2982, 3052, 3308. Satisfactory elemental analysis data were not obtained.

### 2.2.18. 2-(2-Hydroxy-5-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl (HL[3])

Method *d* (Scheme 1). A mixture of **4c** (0.10 g, 0.34 mmol), $NaNO_2$ (0.10 g, 1.45 mmol), AcOH (0.2 ml), water (0.2 ml), and $CHCl_3$ (10 ml) was stirred with boiling for 40 min (until the starting **4c** disappeared). The reaction mixture was cooled and filtered through an $Al_2O_3$ layer (1.5 × 8 cm, $CHCl_3$ as eluent). The solvent was distilled off, and the residue was ground with cold hexane, filtered off, and recrystallized from hexane (bath temperature 60–65 °C). Yield 40 mg (43%), red–brown crystals, decomp. at 135 °C. IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 600, 639, 664, 681, 737, 754, 787, 836, 863, 899, 923, 957, 1070, 1129, 1143, 1159, 1229, 1273, 1298, 1342, 1379, 1398, 1433, 1449, 1485, 1523, 1592, 1622, 2932, 2989, 3121, 3431 br. *Anal.* Found: C, 56.1; H, 5.8; N, 15.2. Calc. for $C_{13}H_{16}N_3O_4$: C, 56.1; H, 5.8; N, 15.1%.

Method *b* (Scheme 1). $NaIO_4$ (0.10 mg, 0.47 mmol) was added to a stirred mixture of **5c** (0.20 g, 0.72 mmol), $CHCl_3$ (15 ml), and water (15 ml). The reaction mixture was stirred for 1 h at ambient temperature. The organic layer was separated, and the aqueous layer extracted with $CHCl_3$ ($3 \times 10$ ml). The combined solutions were dried with $Na_2SO_4$, and the solvent distilled off in vacuum. The residue was recrystallized from petroleum ether with charcoal (5 ml). Yield 0.17 g (85%).

### 2.2.19. 2-(5-Bromo-2-hydroxy-3-nitro-phenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl (*HL*$^4$)

Method *b* (Scheme 1). $NaIO_4$ (0.48 mg, 2.26 mmol) was added in portions for 20 min to a stirred mixture of **5d** (0.81 g, 2.26 mmol), $CHCl_3$ (20 ml), and water (15 ml). The reaction mixture was stirred for 2 h at ambient temperature. The chloroform layer was separated, and the aqueous layer extracted with $CHCl_3$ ($2 \times 10$ ml). The combined solutions were dried with $Na_2SO_4$ and filtered through an $Al_2O_3$ layer ($1.5 \times 8$ cm, $CHCl_3$ as eluent). The solvent was distilled off before the product started to crystallize, and hexane (10 ml) was added. Yield 0.53 g (66%), red–brown crystals, decomp. at 168 °C. IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 633, 673, 691, 719, 773, 789, 876, 897, 960, 1109, 1139, 1163, 1219, 1257, 1345, 1372, 1427, 1479, 1528, 1588, 1614, 2980, 3095, 3436 br. *Anal.* Found: C, 44.1; H, 4.6; Br, 22.6; N, 11.5. Calc. for $C_{13}H_{15}BrN_3O_4$: C, 43.7; H, 4.2; Br, 22.4; N, 11.8%.

### 2.2.20. 2-(5-Bromo-2-hydroxy-3-nitro-phenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-3-oxide-1-ol (*10*)

$NaIO_4$ (0.21 mg, 1.0 mmol) was added to a stirred mixture of **3b** (0.33 g, 0.72 mmol), $CHCl_3$ (10 ml), and water (10 ml). The reaction mixture was stirred for 20 min, and hexane (10 ml) was added. The precipitate was filtered off, dried in air, and recrystallized from $CHCl_3$. Yield 0.28 g (85%), colorless crystals, m.p. 135–136 °C, $R_f$ (AcOEt) 0.75. $^1$H NMR (acetone-$d_6$): $\delta = 1.40$ (s, 12H, Me), 6.67 (d, 1H, $J = 8.6$ Hz, H(3′)), 7.28 (dd, 1H, $J = 8.6$ Hz, $J = 2.5$ Hz, H(4′)), 7.36 (d, 1H, $J = 2.5$ Hz, H(6′)), 8.90 (br. s, 0.3H). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 611, 675, 826, 853, 883, 938, 970, 1019, 1081, 1134, 1221, 1244, 1296, 1369, 1389, 1420, 1495, 1569, 2897, 2982, 3238 br. *Anal.* Found: C, 47.9; H, 5.1; Br, 24.4; N, 8.5. Calc. for $C_{13}H_{17}BrN_2O_3$: C, 47.4; H, 5.2; Br, 24.3; N, 8.5%.

### 2.2.21. 3-Hydroxy-pyridine-2-carbaldehyde (*1f*)

A solution of KOH (1.12 g, 20.0 mmol) in EtOH (20 ml) was added dropwise for 30 min to a stirred suspension of 2-hydroxymethyl-pyridin-3-ol hydrochloride (3.23 g, 20.0 mmol) in EtOH (20 ml). The reaction mixture was stirred for 30 min and then filtered. The solvent was distilled off. The resulting viscous colorless oil was ground with ether, and the finely crystalline precipitate was filtered off to give 2-hydroxymethyl-pyridin-3-ol. Yield 2.31 g (92%), m.p. 183–185 °C. $^1$H NMR (acetone-$d_6$): $\delta = 4.77$ (s, 2H, $CH_2$), 7.19 (dd, 1H, $J = 8.1$ Hz, $J = 4.3$ Hz, H(5′)), 7.21 (dd, 1H, $J = 8.1$ Hz, $J = 1.5$, H(4′)), 8.06 (dd, 1H, $J = 4.3$ Hz, $J = 1.5$ Hz, H(6)). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 613, 704, 744, 794, 810, 866, 882, 958, 1014, 1067, 1119, 1171, 1219, 1246, 1292, 1346, 1375, 1462, 1489, 1537, 1582, 1605, 2637, 2813, 3050, 3312 br.

A mixture 2-hydroxymethyl-pyridin-3-ol (1.25 g, 10.0 mmol), $SeO_2$ (0.56 g, 5 mmol), and *p*-dioxane (30 ml) was stirred with boiling for 6 h. After cooling, the reaction mixture was filtered, and the solvent distilled off in vacuum. To the residue was added AcOEt (15 ml), and the solution was filtered through $SiO_2$ ($1.5 \times 5$ cm, AcOEt as eluent). The solvent was distilled off, and the crude product (**1f**) was purified by vacuum sublimation (90 °C/1 torr). Yield 0.58 g (47%), m.p. 79–80 °C (Ref. [14] 81–82 °C). $^1$H NMR (acetone-$d_6$): $\delta = 7.48$ (dd, 1H, $J = 8.7$ Hz, $J = 1.4$ Hz, H(4′)), 7.63 (dd, 1H, $J = 8.7$ Hz, $J = 4.9$ Hz, H(5′)), 8.06 (dd, 1H, $J = 4.9$ Hz, $J = 1.4$ Hz, H(6′)), 10.05 (s, 1H, CHO). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 647, 735, 810, 872, 1063, 1113, 1149, 1234, 1312, 1354, 1408, 1467, 1579, 1680, 2543, 3087, 3436 br. *Anal.* Found: C, 57.9; H, 4.2; N, 11.3. Calc. for $C_6H_5NO_2$: C, 58.5; H, 4.1; N, 11.4%.

### 2.2.22. 3-Hydroxy-6-methylpyridine-2-carbaldehyde (*1g*)

Compound **1g** was prepared in exactly the same manner as **1f**. Yield 68%, m.p. 106–107 °C, the substance completely corresponds to the compound described in Ref. [15].

### 2.2.23. 2-(3-Hydroxypyridin-2-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (*3f*)

To a solution of **2** (0.30 g, 2.03 mmol) in MeOH (5 ml) and $C_6H_6$ (5 ml) was added **1f** (0.25 g, 2.03 mmol), and the reaction mixture was stirred for 30 min at ambient temperature. The solvent was evaporated, and the residue treated with ether and filtered off. Yield 0.42 g (83%), yellow powder, m.p. 196–197 °C (AcOEt). $^1$H NMR (acetone-$d_6$): $\delta = 1.23$ (s, 6H, Me), 1.26 (s, 6H, Me), 5.05 (s, 1H, H(2)), 7.48 (dd, 1H, $J = 7.8$ Hz, $J = 1.4$ Hz, H(4′)), 7.63 (dd, 1H, $J = 7.8$ Hz, $J = 4.4$ Hz, H(5′)), 7.99 (dd, 1H, $J = 4.4$ Hz, $J = 1.4$ Hz, H(6′)), 7.53 (br. s, 1.2 H), 11.3 (br. s, 0.15 H). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 647, 711, 740, 799, 835, 894, 912, 933, 961, 980, 1060, 1114, 1162, 1223, 1271, 1382, 1449, 1482, 1583, 2888, 2966, 2995, 3180 br., 3374 br. *Anal.* Found: C, 56.7; H, 7.7; N, 16.2. Calc. for $C_{12}H_{19}N_3O_3$: C, 56.9; H, 7.6; N, 16.6%.

### 2.2.24. 2-(3-Hydroxy-6-methylpyridin-2-yl)-4,4,5,5-tetramethylimidazolidine-1,3-diol (*3g*)

Compound **3g** was prepared from **1g** in exactly the same manner as **3f**. Yield 90%, white crystals, m.p. 182–183 °C (from a mixture of AcOEt with EtOH). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 655, 705, 746, 770, 790, 849, 923, 1003,

1021, 1127, 1142, 1159, 1249, 1319, 1370, 1477, 1590, 2923, 2979, 3347 br. *Anal.* Found: C, 58.2; H, 8.1; N, 15.6. Calc. for $C_{13}H_{21}N_3O_3$: C, 58.4; H, 7.9; N, 15.7%.

### 2.2.25. 2,6-Bis-(1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine-2-yl)-3-hydroxypyridin (**8**)

Compound **8** was prepared from *3-hydroxy-2,6-dicarbaldehyde* (**7**) [16]. Yield 72%, yellow powder, decomp. At 200 °C (AcOEt). $^1$H NMR (acetone-$d_6$): $\delta = 1.13$ (s, 6H, Me), 1.19 (s, 6H, Me), 1.23 (s, 6H, Me), 1.27 (s, 6H, Me), 4.84 (s, 1H, H($2_{Im.}$)), 5.06 (s, 1H, H($2_{Im.}$)), 7.03 (d, 1H, $J = 8.0$ Hz, H($4_{Py}$)), 7.14 (br. s, 1.3 H), 7.43 (d, 1H, $J = 8.0$ Hz, H($5_{Py}$)), 7.60 (br. s, 1.3H), 11.3 (br. s, 0.16H). Because of the low solubility of the substance, satisfactory elemental analysis data were not obtained.

### 2.2.26. 2-(3-Hydroxypyridin-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-3-oxide-1-oxyl (**4f**)

To a stirred mixture of **3f** (0.51 g, 2.0 mmol), $CHCl_3$ (15 ml), and water (10 ml) was added $NaIO_4$ (0.69 g, 3.2 mmol), and the reaction mixture was stirred for 1 h at ambient temperature. The organic layer was separated, and the aqueous layer extracted with $CHCl_3$ (3 × 10 ml). The combined organic solutions were dried with $Na_2SO_4$, the solvent was evaporated, and the residue recrystallized from a mixture of $C_6H_6$ with hexane. Yield 0.43 g (86%), vinous powder; at 134–136 °C, the colour of the crystals changes to orange and melting occurs. IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 654, 748, 810, 873, 1070, 1111, 1136, 1174, 1214, 1255, 1301, 1371, 1411, 1465, 1508, 1534, 1580, 1684, 1717, 2998, 3446 br. *Anal.* Found: C, 57.7; H, 6.2; N, 16.5. Calc. for $C_{12}H_{16}N_3O_3$: C, 57.6; H, 6.4; N, 16.8%.

### 2.2.27. 2-(3-Hydroxy-6-methylpyridin-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-3-oxide-1-oxyl (**4g**)

Compound **4g** was prepared in exactly the same manner as **4f**. Yield 73%, vinous crystals, decomp. at 198–200 °C (from a mixture of $C_6H_6$ with hexane). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 663, 746, 778, 842, 873, 927, 970, 1044, 1117, 1135, 1169, 1225, 1247, 1283, 1368, 1416, 1448, 1493, 1529, 1576, 2944, 2995, 3436 br. *Anal.* Found: C, 58.8; H, 6.8; N, 15.8. Calc. for $C_{13}H_{18}N_3O_3$: C, 59.1; H, 6.7; N, 15.9%.

### 2.2.28. 2-(1-Hydroxy-4,4,5,5-tetramethyl-3-oxy-4,5-dihydro-1H-imidazol-2-yl)-6-(4,4,5,5-tetramethyl-3-oxy-1-oxyl-4,5-dihydro-1H-imidazol-2-yl)-3-hydroxypyridin (**11**)

Compound **11** was prepared in exactly the same manner as **4f** except that the molar ratio **8**/$NaIO_4$ was 1/3. The product was purified by column chromatography on $SiO_2$ (elution with $CHCl_3$). Yield 68%, green crystals, decomp. at 168 °C (from a mixture of $C_6H_6$ with hexane). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 680, 774, 849, 1020, 1133, 1290, 1371, 1421, 1456, 1522, 1598, 2942, 2996, 3229 br., 3450 br. Anal. Found: C, 61.0; H, 7.6; N, 14.6. Calc. for $C_{13}H_{18}N_3O_3$: C, 59.1; H, 6.7; N, 15.9%.

### 2.2.29. 2,6-Bis-(4,4,5,5-tetramethyl-3-oxy-1-oxyl-4,5-dihydro-1H-imidazol-2-yl)-3-hydroxypyridin (**9**)

Compound **9** was prepared in exactly the same manner as **4f** except that the molar ratio **8**/$NaIO_4$ was 1/6, and reaction time was 6 h. Yield 76%, violet crystals, decomp. at 168 °C (from a mixture of $C_6H_6$ with $CH_2Cl_2$). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 596, 846, 871, 1111, 1138, 1170, 1220, 1253, 1303, 1370, 1416, 1454, 1523, 1583, 2989, 3423 br. *Anal.* Found: C, 56.0; H, 6.7; N, 17.2. Calc. for $C_{19}H_{27}N_5O_5$: C, 56.3; H, 6.7; N, 17.3%.

### 2.2.30. 2-(1-Hydroxy-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-2-yl)-pyridin-3-ol (**6f**)

A mixture of **3f** (0.51 g, 2.0 mmol) and $SeO_2$ (22 mg, 0.2 mmol), was refluxed in MeOH (30 ml) for 1 h. After cooling, the reaction mixture was filtered, and the solvent evaporated. The residue was treated with ether, washed with hexane, filtered off, and recrystallized from AcOEt. Yield 0.35 g (74%), yellow crystals, m.p. 150–151 °C $R_f$ (AcOEt) 0.12. $^1$H NMR (acetone-$d_6$): $\delta = 1.40$ (s, 6H, Me), 1.42 (s, 6H, Me), 6.82 (br. s, 0.68H), 7.15 (dd, 1H, $J = 7.8$ Hz, $J = 1.4$ Hz, H(4′)), 7.38 (dd, 1H, $J = 7.8$ Hz, $J = 4.4$ Hz, H(5′)), 7.99 (dd, 1H, $J = 4.4$ Hz, $J = 1.4$ Hz, H(6′)). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 644, 757, 808, 829, 896, 1002, 1057, 1127, 1151, 1251, 1301, 1366, 1415, 1468, 1513, 1545, 1595, 1613, 2977, 3002, 3179 br. *Anal.* Found: C, 61.0; H, 7.5; N, 17.6. Calc. for $C_{12}H_{17}N_3O_2$: C, 61.3; H, 7.3; N, 17.9%.

### 2.2.31. 2-(1-Hydroxy-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-2-yl)-pyridin-6-methyl-3-ol (**6g**)

Compound **6g** was prepared in exactly the same manner as **6f**. Yield 61%, yellow crystals, m.p. 170–171 °C (from a mixture of $C_6H_6$ with hexane 1:1, v/v). $^1$H NMR ($CDCl_3$): $\delta = 1.40$ (s, 6H, Me), 1.46 (s, 6H, Me), 2.47 (s, 3H, Me), 5.86 (br. s, 1H), 7.18–7.30 (m, 2H, H(4′), H(5′)). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 658, 696, 754, 772, 836, 891, 918, 1004, 1106, 1127, 1254, 1290, 1330, 1369, 1506, 1575, 2934, 2979, 3349 br. *Anal.* Found: C, 62.8; H, 7.7; N, 16.7. Calc. for $C_{13}H_{19}N_3O_2$: C, 62.6; H, 7.7; N, 16.9%.

Solutions of 2-(3-hydroxypyridin-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl (**HL**$^6$) and 2-(3-hydroxy-6-methylpyridin-2-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl (**HL**$^7$) 2,6-bis-(4,4,5,5-tetramethyl-1-oxyl-4,5-dihydro-1*H*-imidazol-2-yl)-3-hydroxypyridin and (**HL**$^8$) were prepared in exactly the same manner as the solution of **HL**$^1$. Alternatively, solutions of **HL**$^6$, **HL**$^7$ were prepared by oxidation of **6f** and **6g** with $NaIO_4$ by the standard procedure.

Evaporation of the solution of **HL**$^6$ [$R_f$ (AcOEt) 0.68; $R_f$ (aluminium oxide on aluminium sheets, 60 $F_{254}$

neutral, Merck, $CHCl_3$) 0.85] gave 6-methyl-2-(4,4,5,5-tetramethyl-3-oxy-4,5-dihydro-1*H*-imidazol-2-yl)-pyridin-3-ol (**5f**) [$R_f$ (AcOEt) 0.55; $R_f$ (aluminium oxide on aluminium sheets, 60 $F_{254}$ neutral, Merck, $CHCl_3$) 0.42]. M.p. 153–154 °C. $^1$H NMR (acetone-$d_6$): $\delta = 1.40$ (s, 6H, Me), 1.47 (s, 6H, Me), 5.84 (br. s, 1H, NH), 7.30 (br. s, 1H H(4′)), 7.35 (br. s, 1H, H(5′)), 8.02 (br. s, 1H, H(6′)). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 658, 709, 757, 772, 813, 894, 1086, 1121, 1144, 1224, 1253, 1313, 1369, 1464, 1497, 1542, 1593, 2940, 2982, 3320 br. *Anal.* Found: C, 61.5; H, 7.3; N, 18.0. Calc. for $C_{12}H_{17}N_3O_2$: C, 61.3; H, 7.3; N, 17.9%.

### 2.2.32. $CuL^1_2$ (*I*)

$Et_3N$ (two drops) was added to a solution of freshly synthesized red-colored ligand $\mathbf{HL}^1$ in $CHCl_3$ (10 ml). A solution of $CuCl_2 \cdot 2H_2O$ (60 mg, 0.35 mmol) in MeOH (3 ml) was poured in with stirring. The resulting transparent green solution was dried in a flow of air. $CH_2Cl_2$ (10 ml) was poured to the residue. The mixture was stirred and filtered. MeOH (9 ml) was added to the filtrate in such a way that a second layer formed. After 6 h, dark green crystals shaped as parallelepipeds suitable for an X-ray diffraction analysis formed on the walls of the flask. After their separation, the mother solution was kept at ambient temperature for 1 day, and an additional amount of I was filtered off. Yield 100 mg (62% based on **4a**). Decomp. at 190 °C. IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 765, 880, 1135, 1248, 1344, 1429, 1466, 1525, 1552, 1600, 2929, 2986. *Anal.* Found: C, 57.3; H, 5.8; N, 10.3. Calc. for $C_{26}H_{32}CuN_4O_4$: C, 59.1; H, 6.1; N, 10.6%.

### 2.2.33. $CuL^2_2$ (*II*)

$CuL^2_2$ (**II**) was prepared by the same procedure as $CuL^1_2$ (**I**). Yield 105 mg (52% based on **4b**). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 667, 823, 1135, 1242, 1322, 1463, 1517, 1594, 2927, 2980. *Anal.* Found: C, 45.6; H, 4.5; Br, 23.0; N, 8.2. Calc. for $C_{26}H_{30}Br_2CuN_4O_4$: C, 45.5; H, 4.4; Br, 23.3; N, 8.2%.

### 2.2.34. $CuL^3_2$ (*III*)

A mixture of $\mathbf{HL}^3$ (50 mg, 0.18 mmol), $CuCl_2 \cdot 2H_2O$ (15 mg, 0.09 mmol), $CH_2Cl_2$ (5 ml), $CH_3OH$ (3 ml), and $Et_3N$ (two drops) was stirred for 10 min. The resulting dark brown solution was dried in a flow of air. The residue was extracted with $CH_2Cl_2$ (7 ml). The solution was filtered, and MeOH (4 ml) was added to the filtrate. The mixture was stirred for 10–15 min, whereupon the solvent was evaporated in a flow of air to the amount of 2–3 ml. The brown crystals were filtered off and washed with MeOH (3 ml). Yield 50 mg (90%). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 675, 832, 920, 1128, 1314, 1467, 1604, 2927, 2979, 3439. *Anal.* Found: C, 49.5; H, 4.9; N, 13.1. Calc. for $C_{26}H_{30}CuN_6O_8$: C, 50.5; H, 4.9; N, 13.6%.

### 2.2.35. $CuL^4_2 \cdot 0.5\ CHCl_3$ (*IV*)

A mixture of $\mathbf{HL}^4$ (100 mg, 0.28 mmol), $CuCl_2 \cdot 2H_2O$ (25 mg, 0.14 mmol), $CH_2Cl_2$ (5 ml), $CH_3OH$ (5 ml), and $Et_3N$ (two drops) was stirred until a transparent brownish green solution formed, whereupon the solvent was removed by drying the solution in air, and the residue extracted with $CH_2Cl_3$ (7 ml). The resulting solution was filtered. MeOH (5 ml) was added to the filtrate in such a way that a second layer formed. The mixture was allowed to stay at ambient conditions. After 10 h, dark-green crystals shaped as parallelepipeds formed on the walls and bottom of the flask. Yield 55 mg (47%), decomp. at 230 °C. IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 539, 668, 729, 824, 833, 1138, 1251, 1430, 1450, 1533, 1601, 2982. *Anal.* Found: C, 37.7; H, 3.3; N, 9.6. Calc. for $C_{26.5}H_{8.5}Br_2Cl_{1.5}CuN_6O_8$: C, 38.1; H, 3.4; N, 10.1%. The crystals suitable for an X-ray analysis were prepared by slow diffusion of MeOH to a $CH_2Cl_2$ solution of **IV**.

### 2.2.36. $[Cu(hfac)L^3]_2 \cdot CH_2Cl_2$ (*V*)

A mixture of $Cu(hfac)_2$ (85 mg, 0.18 mmol), $\mathbf{HL}^3$ (50 mg, 0.18 mmol), and $CH_2Cl_2$ (7 ml) was stirred for 20 min. Petroleum ether (8 ml) was added to the reaction mixture. The solution was allowed to stay for 10 h at ambient temperature, whereupon dichroic greenish-brown single crystals shaped as parallelepipeds formed in the flask. Yield 70 mg (65%). IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) 448, 674, 755, 831, 846, 919, 1127, 1257, 1313, 1466, 1492, 1566, 1604, 2979, 3125. *Anal.* Found: C, 39.0; H, 2.9; N, 6.6. Calc. for $C_{37}H_{34}Cl_2Cu_2F_{12}N_6O_{12}$: C, 37.6; H, 2.9; N, 7.1%.

## 2.3. X-ray structure determination

Single crystal data were collected on P4 and SMART APEX Bruker AXS automatic diffractometers at ambient temperature using the standard procedure (Mo radiation, $2 < \theta < 25°$). The structures were solved by direct methods. The full-matrix least-squares refinement was performed anisotropically for nonhydrogen atoms and isotropically for hydrogens. Some H atoms were localized in difference electron density syntheses; the others were generated theoretically. All structure solution and refinement calculations were carried out with SHELX-97 software. The crystal data for the compounds and details of experiment, as well as selected bond lengths and angles are gives in Tables 1–4.

## 2.4. Magnetic measurements

All measurements were carried out on an MPMS-5s Quantum Design SQUID magnetometer (2–300 K, magnetic field 5 kOe). The calculation of molar magnetic susceptibility ($\chi$) was carried out with allowance for atomic diamagnetism. The effective magnetic mo-

Table 1
Crystallographic data for 1,3-dihydroxyimidazolidines **3b**, **3g**; nitrones **5b**, **5f**, and quinone **12**

| Formula | **3b** | **3g** | **5b** | **5f** | **12** |
|---|---|---|---|---|---|
| | $C_{13}H_{18}BrN_2O_3$ | $C_{13}H_{21}N_3O_3$ | $C_{13}H_{17}BrN_2O_2$ | $C_{12}H_{17}N_3O_2$ | $C_{13}H_{15}BrN_2O_3$ |
| Diffractometer | Smart APEX | Smart APEX | Smart APEX | P4 | Smart APEX |
| $T$ (K) | 295 | 295 | 295 | 295 | 295 |
| Space group | $C2/c$ | $P2_1/n$ | $Pccn$ | $C2/c$ | $P\bar{1}$ |
| $Z$ | 8 | 4 | 8 | 8 | 2 |
| Unit cell | | | | | |
| $a$ (Å) | 23.433(7) | 11.429(3) | 22.397(2) | 16.331(3) | 6.059(2) |
| $b$ (Å) | 11.960(3) | 11.639(3) | 10.8753(9) | 16.546(3) | 11.270(3) |
| $c$ (Å) | 11.960(3) | 12.012(3) | 11.714(1) | 11.356(2) | 11.687(3) |
| $\alpha$ (°) | | | | | 112.052(4) |
| $\beta$ (°) | 120.692(1) | 115.175(4) | | 123.01(3) | 103.847(4) |
| $\gamma$ (°) | | | | | 99.452(4) |
| $V$ (Å$^3$) | 2882(1) | 1446.0(7) | 2853.3(4) | 2573.2(9) | 688.9(3) |
| $D_c$ (g cm$^{-3}$) | 1.522 | 1.228 | 1.458 | 1.215 | 1.577 |
| $\mu$ (mm$^{-1}$) | 2.858 | 0.088 | 2.878 | 0.085 | 2.989 |
| $I_{hkl}$ meas/uniq | 6009/2091 | 8602/3396 | 11 406/2046 | 2304/2272 | 2978/1968 |
| $R_{int}$ | 0.1929 | 0.0328 | 0.1062 | 0.0299 | 0.0938 |
| $I_{hkl}/N$ | 2091/240 | 3396/248 | 2046/232 | 2272/223 | 1968/233 |
| Goodness-of-fit | 0.996 | 1.073 | 0.630 | 1.010 | 0.858 |
| $R_1$ ($I_{hkl} > 2\sigma_I$) | 0.0626 | 0.0440 | 0.0350 | 0.0378 | 0.0516 |
| $wR_2$ | 0.1588 | 0.1289 | 0.0866 | 0.0930 | 0.1222 |
| $R_1$ | 0.0695 | 0.0496 | 0.0490 | 0.0592 | 0.0711 |
| $wR_2$ | 0.1654 | 0.1331 | 0.0944 | 0.1040 | 0.1358 |
| N–O | 1.435(4) | 1.440(1) | 1.354(3) | 1.351(2) | |
| | 1.442(4) | 1.433(1) | | | |
| C–N | 1.471(5) | 1.485(1) | 1.305(3) | 1.302(2) | 1.349(6) |
| | 1.483(5) | 1.468(1) | 1.357(4) | 1.346(2) | 1.317(7) |
| $\angle CN_2$–Ph | 75.7(1) | 76.1(3) | 32.2(2) | 25.8(2) | 5.0(6) |

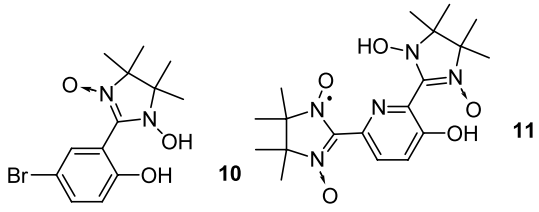
ment was calculated by the formula $\mu_{eff} = [(3k/N_A\beta^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$.

## 3. Results and discussion

### 3.1. Syntheses of ligands

In the first step, we synthesized nitronylnitroxides **4a**–**g**, **9**, which were prepared by coupling of aldehyde **1a**–**g**, **7** with 2,3-bis(hydroxylamino)-2,3-dimethylbutane (**2**) [11,12] followed by oxidation as described by Ullman et al. [17] (Scheme 1). The structures of nitroxides **4b**, **4c**, **4g**, **9** and 1,3-dihydroxyimidazolidines **3b**, **3g** obtained as single crystals were confirmed by X-ray analysis (Figs. 1 and 2).

Note that oxidation of 1,3-dihydroxyimidazolidines **3b**–**e** initially quickly gives a yellow solid precipitate, whose further oxidation leads to nitroxides **4b**–**c**. As an example we isolated a yellow intermediate, which formed on oxidation of **3b**; this product was identified as 1-hydroxy-2-imidazoline-3-oxide (**10**). Oxidation of bis(1,3-dihydroxyimidazolidine) derivative **8** is a special case; at first it leads to a green monoradical **11**, whose structure was proven by X-ray investigation (Fig. 2). Further oxidation of **11** to **9** is hindered, taking much more time and demanding an excess of oxidant.



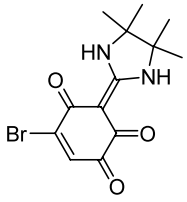

Treatment of nitroxides **4a**–**e** with $NaNO_2$ by the standard procedure [17] led to the desired $\mathbf{HL}^1$–$\mathbf{HL}^8$. Isolation of each $\mathbf{HL}^n$, however, had its own specific features.

Because of its instability on storage for 1–2 h in solution or on concentration, $\mathbf{HL}^1$ was introduced in the reaction leading to the Cu(II) complex, which is much more stable, immediately after purification by column chromatography on $Al_2O_3$ (Fig. 6). Referring to decomposition of $\mathbf{HL}^1$ in solution, one can note that one of the decomposition products is **5a**, whose formation was confirmed by TLC by comparing with the authentic sample obtained by interaction of **3a** with $SeO_2$.

Table 2
Crystallographic data for nitroxides **4b**, **4c**, **4g**, **9**, **11**, **HL**$^3$, **HL**$^4$

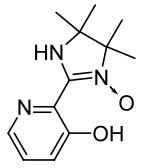
| Formula | **4b** | **4c** | **4g** | **9** | **11** | **HL**$^3$ | **HL**$^4$ |
|---|---|---|---|---|---|---|---|
| | $C_{13}H_{16}BrN_2O_3$ | $C_{13}H_{16}N_3O_5 \cdot {}^1/_4 C_7H_8$ | $C_{13}H_{18}N_3O_3$ | $C_{20}H_{24}N_5O_5 \cdot CH_2Cl_2$ | $C_{20}H_{28}N_5O_5 \cdot CH_2Cl_2 \cdot H_2O$ | $C_{13}H_{16}N_3O_4$ | $C_{13}H_{15}BrN_3O_4$ |
| Diffractometer | SMART APEX | SMART APEX | SMART APEX | P4 | P4 | SMART APEX | SMART APEX |
| $T$ (K) | 295 | 295 | 295 | 295 | 295 | 240 | 240 |
| Space group | $P2_1/n$ | $P\bar{1}$ | $Pbca$ | $P2_1/c$ | $P\bar{1}$ | $P2_1/n$ | $P2_12_12$ |
| $Z$ | 4 | 4 | 8 | 4 | 2 | 4 | 8 |
| Unit cell | | | | | | | |
| $a$ (Å) | 9.712(2) | 7.3336(8) | 15.066(1) | 12.338(2) | 1.810(2) | 9.137(3) | 20.569(4) |
| $b$ (Å) | 11.806(3) | 11.829(1) | 11.479(1) | 16.533(3) | 11.934(2) | 11.394(3) | 21.857(4) |
| $c$ (Å) | 13.256(3) | 17.879(2) | 15.820(2) | 11.786(2) | 11.945(2) | 13.731(4) | 6.623(1) |
| $\alpha$ (°) | | 84.419(2) | | | 116.70(3) | | |
| $\beta$ (°) | 111.174(3) | 85.948(2) | | 92.38(1) | 116.61(3) | 107.846(6) | |
| $\gamma$ (°) | | 89.310(2) | | | 92.68(3) | | |
| $V$ (Å$^3$) | 1417.3(6) | 1539.8(3) | 2736.0(4) | 2402(2) | 1278.2(4) | 1360.7(7) | 2978(1) |
| $D_c$ (g cm$^{-3}$) | 1.538 | 1.369 | 1.283 | 1.353 | 1.324 | 1.358 | 1.594 |
| $\mu$ (mm$^{-1}$) | 2.906 | 0.104 | 0.093 | 0.310 | 0.297 | 0.102 | 2.780 |
| $I_{hkl}$ meas/uniq | 5770/2032 | 6681/4400 | 15 615/3278 | 4438/4216 | 3432/3188 | 5709/1965 | 12 979/4303 |
| $R_{int}$ | 0.1057 | 0.0787 | 0.2003 | 0.0397 | 0.0389 | 0.1918 | 0.1060 |
| $I_{hkl}/N$ | 2032/232 | 4400/558 | 3278/245 | 4216/415 | 3188/427 | 1965/246 | 4303/492 |
| Goodness-of-fit | 0.929 | 1.278 | 1.057 | 0.955 | 0.993 | 0.868 | 0.862 |
| $R_1$ ($I_{hkl} > 2\sigma_I$) | 0.0529 | 0.0660 | 0.0800 | 0.0657 | 0.1029 | 0.0914 | 0.0584 |
| $wR_2$ | 0.1195 | 0.1832 | 0.1824 | 0.1421 | 0.2656 | 0.1529 | 0.1169 |
| $R_1$ | 0.0790 | 0.0787 | 0.1136 | 0.1581 | 0.1582 | 0.2407 | 0.0817 |
| $wR_2$ | 0.1530 | 0.1943 | 0.2038 | 0.1842 | 0.3130 | 0.2040 | 0.1274 |
| N–O (nitroxide) | 1.306(5) | 1.304(3) | 1.269(2) | 1.280(5) | 1.382(3) | 1.308(7) | 1.267(6) |
| | 1.278(4) | 1.268(3) | 1.276(2) | 1.293(4) | 1.337(3) | | 1.272(8) |
| | | 1.299(3) | | 1.276(5) | 1.292(3) | | |
| | | 1.275(3) | | 1.285(5) | 1.273(2) | | |
| C–N | 1.327(6) | 1.321(3) | 1.341(3) | 1.332(5) | 1.374(3) | 1.355(8) | 1.402(8) |
| | 1.362(6) | 1.348(3) | 1.334(3) | 1.334(6) | 1.314(3) | 1.276(8) | 1.401(8) |
| | | 1.317(3) | | 1.320(5) | 1.341(3) | | 1.276(7) |
| | | 1.345(3) | | 1.347(5) | 1.352(3) | | 1.252(9) |
| $\angle CN_2$–Ph | 34.7(2) | 37.2(1) | 74.0(2) | 77.1(2) | 15.4(3) | 0.7(9) | 4.7(1) |
| | | 38.5(1) | | 60.5(2) | 19.1(3) | | 6.5(1) |

Reduction of **4b** leads to solution of nitroxide **HL**$^2$; removing of the solvent gave hydroxyimidazoline **5b**, and benzoquinone **12** as major products. The structure of **5b** and **12** was confirmed by X-ray analysis (Figs. 1 and 4); structure analysis of **HL**$^2$ was carried out for its Cu(II) complex (Fig. 6).



**12**

Spin-labeled Schiff bases **HL**$^3$, **HL**$^4$ were isolated individually (Fig. 3). Nitroxide **HL**$^5$ and hydroxypyridinyl derivatives **HL**$^6$–**HL**$^8$ as well as **HL**$^1$ and **HL**$^2$ may not be isolated from solution. For example, evaporation of a solution of **HL**$^5$ or **HL**$^6$ leads to nitrones **5e**, **f**. The structure of **5f** was proven by direct X-ray investigation.



**5f**

For synthesis of **HL**$^3$, one can effectively use route *b*, *d* as well as the alternative route *c*, *b* [18] (Scheme 1). **HL**$^4$ was only isolated in the case of *c*, *b*. The yields of **HL**$^1$ and **HL**$^2$ in reaction *c*, *b* were much lower. Note that treatment of **3a**–**e** with $SeO_2$ forms **5a**–**e**; the structure of one of these compounds (**5b**) was confirmed by X-ray analysis (Fig. 1). Dehydration of hydroxypyridyl derivatives **3f**, **3g** by $SeO_2$ forms hydroxylamines **6f**, **6g**, differing widely in their spectral characteristics from nitrone **5f**.

Since **HL**$^1$, **HL**$^2$, **HL**$^5$–**HL**$^8$ could not be isolated as solids, for syntheses of their complexes we used their

Table 3
Crystallographic data for complexes **I**–**V**

| Compound | $CuL^1{}_2$ (**I**) | $CuL^2_2$ (**II**) | $CuL^3_2$ (**III**) | $CuL^4_2 \cdot CH_2Cl_2$ (**IV**) | $[CuL^3(hfac)]_2 \cdot CH_2Cl_2$ (**V**) |
|---|---|---|---|---|---|
| Space group | $P\bar{1}$ | $C2/c$ | $P2_1/n$ | $P\bar{1}$ | $C2/c$ |
| $Z$ | 2 | 4 | 4 | 2 | 4 |
| Unit cell | | | | | |
| $a$ (Å) | 10.154(2) | 27.145(4) | 12.561(3) | 11.063(1) | 18.457(3) |
| $b$ (Å) | 10.388(2) | 10.138(1) | 12.300(3) | 11.930(1) | 19.490(2) |
| $c$ (Å) | 13.340(3) | 10.600(1) | 17.889(5) | 12.656(3) | 14.998(2) |
| $\alpha$ (°) | 70.46(3) | | | 89.96(1) | |
| $\beta$ (°) | 71.02(3) | 109.61(1) | 98.24(2) | 80.73(1) | 117.310(10) |
| $\gamma$ (°) | 86.77(3) | | | 82.69(1) | |
| $V$ (Å$^3$) | 1251.8(4) | 2747.9(6) | 2735(2) | 1634.7(5) | 4793.8(11) |
| $D_c$ (g cm$^{-3}$) | 1.401 | 1.658 | 1.501 | 1.662 | 1.636 |
| $\mu$ (mm$^{-1}$) | 0.912 | 3.742 | 0.859 | 3.249 | 1.109 |
| $\theta$-Range (°) | 2.08–24.99 | 2.16–25.00 | 2.02–25.00 | 1.88–25.00 | 1.80–25.00 |
| $I_{hkl}$ meas/uniq | 4591/4333 | 2389/2388 | 4826/4593 | 6048/5724 | 4352/4215 |
| $R_{int}$ | 0.0371 | 0.1178 | 0.0686 | 0.0358 | 0.0292 |
| $I_{hkl}/N$ | 4333/440 | 2388/229 | 4593/491 | 5724/462 | 4215/393 |
| Goodness-of-fit | 0.997 | 1.038 | 0.920 | 0.978 | 0.870 |
| $R_1$ ($I_{hkl} > 2\sigma_1$) | 0.0539 | 0.0674 | 0.0703 | 0.0692 | 0.0604 |
| $wR_2$ | 0.1161 | 0.1800 | 0.0952 | 0.1794 | 0.1584 |
| $R_1$ | 0.1048 | 0.0879 | 0.2145 | 0.1187 | 0.1219 |
| $wR_2$ | 0.1365 | 0.1992 | 0.1337 | 0.2126 | 0.2064 |

*N-parameters.

solutions. $HL^3$, $HL^4$ were isolated as solids because the 2-hydroxyphenyl derivatives of iminonitroxides are stabilized by the introduction of an acceptor substituent in the aromatic ring.

### 3.2. Crystal structure of organic molecules

In molecules **3b** and **3g**, the 5-membered heterocycles are shaped as an envelope; the deviation of one of their

Table 4
Selected bond lengths (Å) and angles (°) for complexes **I**–**V**

| Compound | $CuL^1{}_2$ (**I**) | $CuL^2_2$ (**II**) | $CuL^3_2$ (**III**) | $CuL^4_2 \cdot CH_2Cl_2$ (**IV**) | $[CuL^3(hfac)]_2 \cdot CH_2Cl_2$ (**V**) |
|---|---|---|---|---|---|
| CN | 4 | 4 | 4 | 4 | 5 |
| Cu–O | 1.882(3) | 1.868(5) | 1.878(4) | 1.893(2) | 1.917(4) 2.258(4) |
| | 1.870(3) | | 1.890(5) | 1.899(2) | 1.929(4) 2.027(5) |
| Cu–N | 1.988(3) | 1.989(5) | 1.946(6) | 1.982(3) | 1.981(5) |
| | 1.976(3) | | 1.945(5) | 1.970(2) | |
| N–O (nitroxide) | 1.264(4) | 1.262(7) | 1.286(7) | 1.273(3) | 1.293(7) |
| | 1.270(4) | | 1.265(6) | 1.284(3) | |
| ∠ OCuN | 90.5(1) | 91.2(2) | 93.2(2) | 90.96(9) | 90.0(2) |
| | 91.8(1) | | 92.6(2) | 92.29(8) | |
| ∠ (OCuN–OCuN) | 41.1(1) | 35.4(2) | 53.6(2) | 40.47(9) | 28.8(3) |
| –·O···O·– | 3.825 | 3.393 | 5.955 | 3.913 | > 5 Å |
| ∠ $CN_2$–Ph | 27.9(4) | 16.5(6) | 19.5(6) | 29.0(3) | 26.8(4) |
| | 9.8(5) | | 16.7(8) | 23.7(3) | |
| ∠ $NO_2$–Ph | | | 6.7(9) | 58.6(3) | 15.3(7) |
| | | | 4.7(1.3) | 52.6(2) | |
| –·O···$O_{NO_2}$ | | | 3.026 | | 3.180 |
| | | | 3.236 | | |
| Cu···–·O | 5.238 | 5.277 | 5.228 | 5.212 | 5.253 |
| | 5.300 | | 5.255 | 5.233 | |
| Cu··O·– | | | 4.628 | | 4.499 |
| Cu···Cu | | | | | 3.257 |

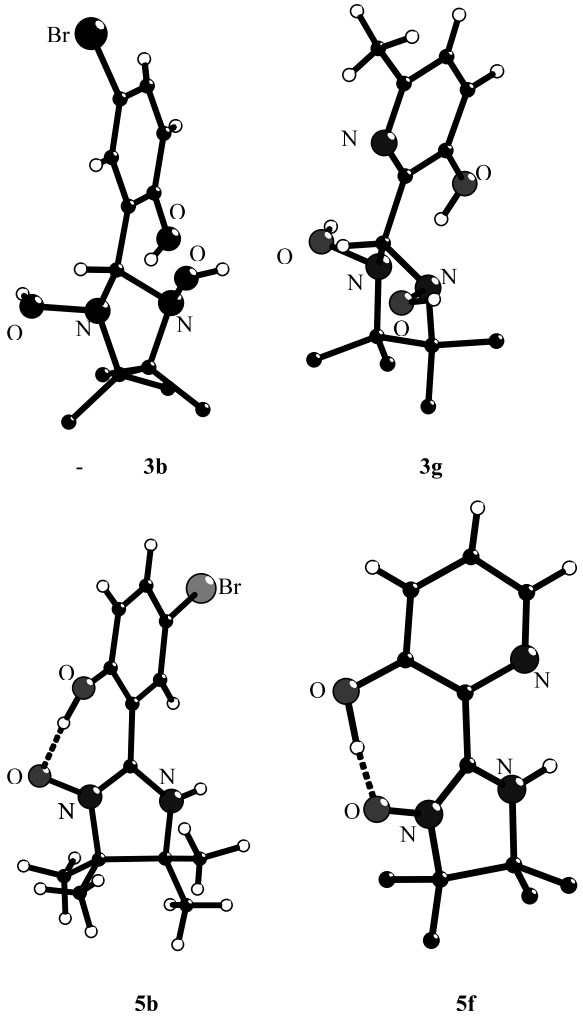



Fig. 1. Structure of 1,3-dihydroxyimidazolidines **3b**, **3g** and nitrones **5b**, **5f**.

N atoms is ~0.7 Å, and the C–N and N–O distances are close to single bond lengths (1.471–1.485 and 1.433–1.435 Å, respectively). The phenyl ring lies at an angle of ~75° to the plane of the $CN_2$ fragment of the heterocycle, leading to the formation of two nonequivalent intramolecular hydrogen bonds between the hydroxyl group and the nitrogen atoms in **3b** (O···N 2.668 and 2.943 Å) and of one intramolecular hydrogen bond in **3g** (N···O 2.616 Å). Localization of the H atom on the N atom of the imidazolidine ring in **5b** and **5f** suggests that the molecule is of nitrone form. In the O–N–C–N–H fragment, the O and H atoms deviate from the $CN_2$ plane by −0.15 and +0.26 Å (**5b**) and 0.05 and −0.20 Å (**5f**), respectively. In **5b**, the NH group forms an intermolecular hydrogen bond with the O atom of the NO group of the neighboring molecule, linking molecules in chains. In **5f**, this role is performed by the H-bond between the NH groups and the pyridine nitrogen atom. The angles between the planes of the phenyl or pyridine cycle and the $CN_2$ fragment are much smaller than those in **3b** and **3g** (Table 1). The N–O bond lengths are 1.351–1.354 Å, and the C–N bonds are nonequivalent: C=N(→O) 1.302–1.305 and C–N(–H) 1.346–1.357 Å.

In iminonitroxides $\mathbf{HL}^3$ and $\mathbf{HL}^4$ and nitronylnitroxides **4b**, **4c**, **9**, **4g**, **11**, the N–O bonds are still shorter, up to 1.308. The $O^{\bullet}$–N–C=N and $O^{\bullet}$–N–C=N→O fragments are virtually planar. The angle between the plane of the $CN_2$ fragment and the phenyl ring is ~35° in nitronylnitroxides and up to 7° in iminonitroxides (Table 2). In molecule **11**, the N–O bond lengths differ: 1.273 and 1.292 Å in the 'nitronylnitroxide' moiety and 1.382 and 1.337 Å in the hydroxylamine moiety.

In quinone **12**, the conformation of the imidazolidine ring is close to that in nitronylnitroxides and iminonitroxides. The sum of the angles at the N atoms is 350.0 and 348.4° versus 330° in **3b** and **3g**. The C=O distances are in the range 1.194–1.226 Å.

### 3.3. Magnetic properties of ligands and their precursors

For radicals **4a**–**g**, $\mathbf{HL}^3$, $\mathbf{HL}^4$, **11**, $\mu_{eff}$ at room temperature is close to the theoretical value (1.73 B.M.); for biradical **9** $\mu_{eff}$ is 2.45 M. For **4e**–**g**, $\mathbf{HL}^3$, $\mathbf{HL}^4$, **9**, **11**, the value of $\mu_{eff}$ is constant up to 10 K.

For radicals **4a**, **4b**, **4c**, $\mathbf{HL}^4$, the dependences $\mu_{eff}(T)$ and $\chi(T)$ are shown in Fig. 5.

A description of these dependences using the Bleaney–Bowers model [19] gave optimal parameters presented in Table 5 (in Fig. 5, the theoretical curves are shown as solid lines).

### 3.4. Syntheses of complexes

Complexes **I**–**IV** were prepared by addition of a methanolic solution of $CuCl_2 \cdot 2H_2O$ to the solution of freshly synthesized ligand in $CHCl_3$ or $CH_2Cl_2$ in the presence of $Et_3N$. Single crystals of the compounds were grown under conditions of slow diffusion of methanol into the $CHCl_3$ or $CH_2Cl_2$ solution of the complex. Compound **V** was obtained by the reaction of $Cu(hfac)_2$ with $\mathbf{HL}^3$ in $CH_2Cl_2$. The crystals were grown from a mixture of $CH_2Cl_2$ with petroleum ether.

### 3.5. Crystal structure of the complexes

In $CuL^n_2$ (**I**–**IV**), the environment of the copper atom is a flattened tetrahedron (Fig. 6), whose distortion depends on the substituent in the benzene ring ($\angle$(OCuN–OCuN) 35.4° for $CuL^2_2$, 40.5° for $CuL^4_2$, 41.1° for $CuL^1_2$, 53.6° for $CuL^3_2$). The ligand is cyclic bidentate and is coordinated by the imine nitrogen atom of the imidazoline ring and the oxygen atom of the deprotonated hydroxyl group. The Cu–O and Cu–N distances in $CuL^n_2$ are 1.868–1.899 and 1.945–1.989 Å, respectively. The mixed-ligand complex **V** is formed by

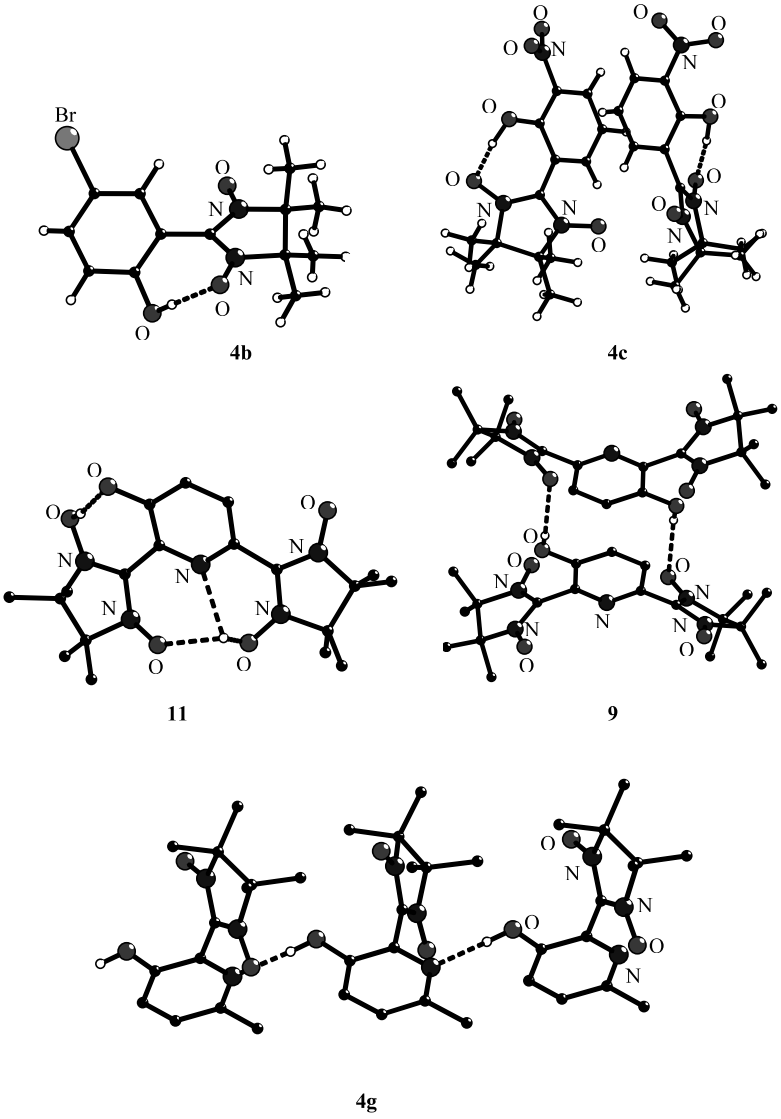



Fig. 2. Structure of nitronylnitroxides **4b**, **4c**, **4g**, **9**, **11**.

the centrosymmetric molecules of composition $[CuL^3(hfac)]_2$. The environment of the copper atom is a distorted trigonal bipyramid (Fig. 7), where the base is formed by the donor atoms $O_{hfac}$ (Cu–$O_{hfac}$ 2.027 Å), $N_L$ (1.981 Å), and $O_L$ of the neighboring $\mathbf{L}^3$ (Cu–$O_L$ 2.258 Å) and the apices are occupied by the O atoms (Cu–$O_L$ 1.917 Å and Cu–$O_{hfac}$ 1.929 Å). Thus $\mathbf{L}^3$ performs a cyclic tridentate bridging function. The Cu···Cu distance in the dimer is 3.258 Å. The 6-membered chelate ring formed by the paramagnetic ligand is nonplanar due to the rotation of the phenyl ring with respect to the $CN_2$ fragment of the imidazoline cycle, the rotation angle being from 9.8 to 29.0°. Also, note the difference in the arrangement of the $NO_2$ groups relative to the plane of the phenyl ring in **III**–**V**; in the complex with $\mathbf{L}^4$, the angle between the planes is as high as 52°. The N–O distances in the nitroxyl groups are typical of nitroxides: 1.262–1.293 Å. The shortest intermolecular distances between the oxygen atoms of the nitroxyl groups are found in $CuL_2^2$.

### 3.6. Magnetic properties of the complexes

The experimental dependences $\mu_{eff}(T)$ of the copper complexes are presented in Fig. 8. They point to ferromagnetic exchange interactions in the molecules and antiferromagnetic interactions between the molecules.

The intramolecular interactions are quite effective, so that even at room temperature $\mu_{eff}$ slightly exceeds the theoretical values for uncoupled spins in all complexes under study. Above 100 K, the $\chi(T)$ dependences are well approximated by the Curie–Weiss equation with the parameters given in Table 6. The large value of the $C$ constant for $[CuL^3(hfac)]_2$ corresponds to the ferromagnetically ordered spins of the copper ions and iminoni-

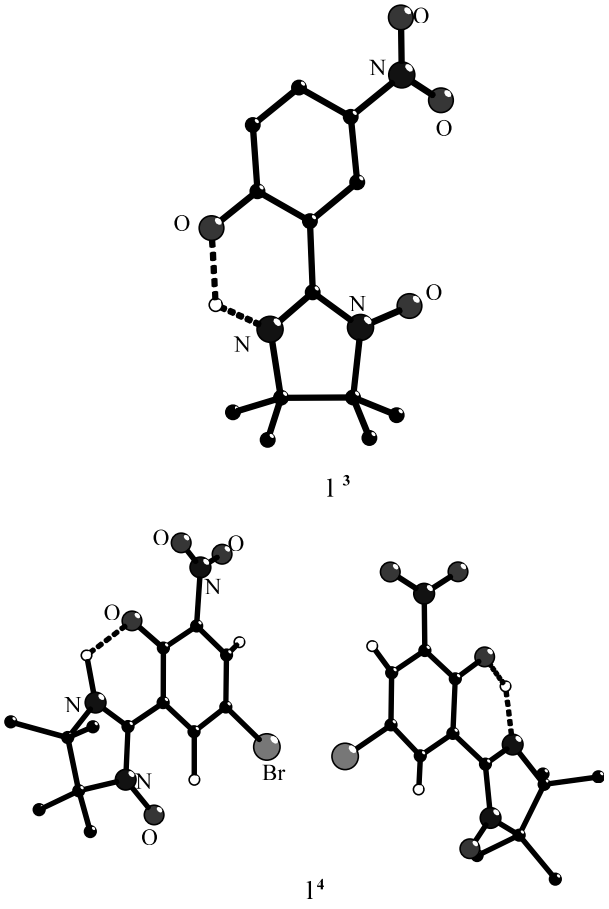



Fig. 3. Structure of iminonitroxides **HL**[3], **HL**[4].

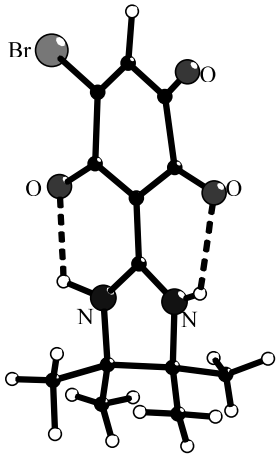



Fig. 4. Structure of quinone **12**.

troxyl fragments coordinated by the imine nitrogen atom. Therefore, $\theta$ in this complex defines the interaction of the copper ions *via* the bridging oxygen atoms. Theoretical analysis of the experimental $\mu_{eff}$(T) dependences for **I**–**V** was carried out in a cluster approximation using the approaches suggested in [20,21]. Optimal descriptions were obtained by using the model clusters: three-center exchange cluster (R–$^{J}$Cu–$^{J}$R) for $CuL_2^3$ and

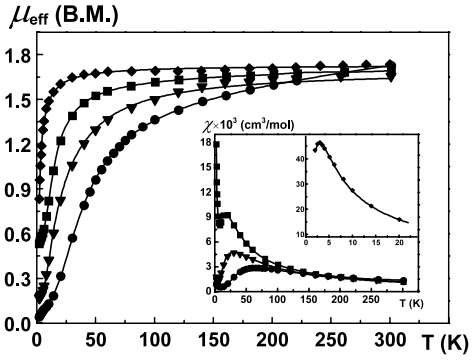



Fig. 5. Experimental dependences $\mu_{eff}$(T) and $\chi$(T) for nitroxides **4a** (■), **4b** (●), **4c** (▼), **HL**[4] (◆). Solid lines—optimal theoretical curves.

Table 5
Magnetic parameters

| Compound | $C$ (cm$^3$ K mol$^{-1}$) | $\theta$ (K) | $J$ (cm$^{-1}$) | $\sigma$ |
|---|---|---|---|---|
| **4a** | 0.375 | −15.5 | −11.8 | 0.00012 |
| **4b** | 0.376 | −67.6 | −36.3 | 0.00176 |
| **4c** | 0.369 | −32.9 | −18.1 | 0.0047 |
| **HL**[4] | 0.373 | −6.2 | −1.6 | 0.00092 |

$CuL_2^4$, four-center exchange cluster (R–$^{J}$Cu–$^{J1}$Cu–$^{J}$R) for $[CuL^3(hfac)]_2$, and alternant magnetic chain cluster ($[–R–Cu–R–^{J1}R–^{J}Cu–^{J}R–^{J1}R–Cu–R]_n$) for $CuL_2^1$ and $CuL_2^2$. The optimal parameters obtained are presented in Table 6, and the corresponding theoretical curves are shown in Fig. 8 by solid lines.

The next step of our research is to use ligands **HL**[5]–**HL**[8] for the preparation of transition metal complexes; this work is now in progress.

## 4. Supplementary material

Crystal data for structural analysis of investigated compounds have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 203058–203074. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## Acknowledgements

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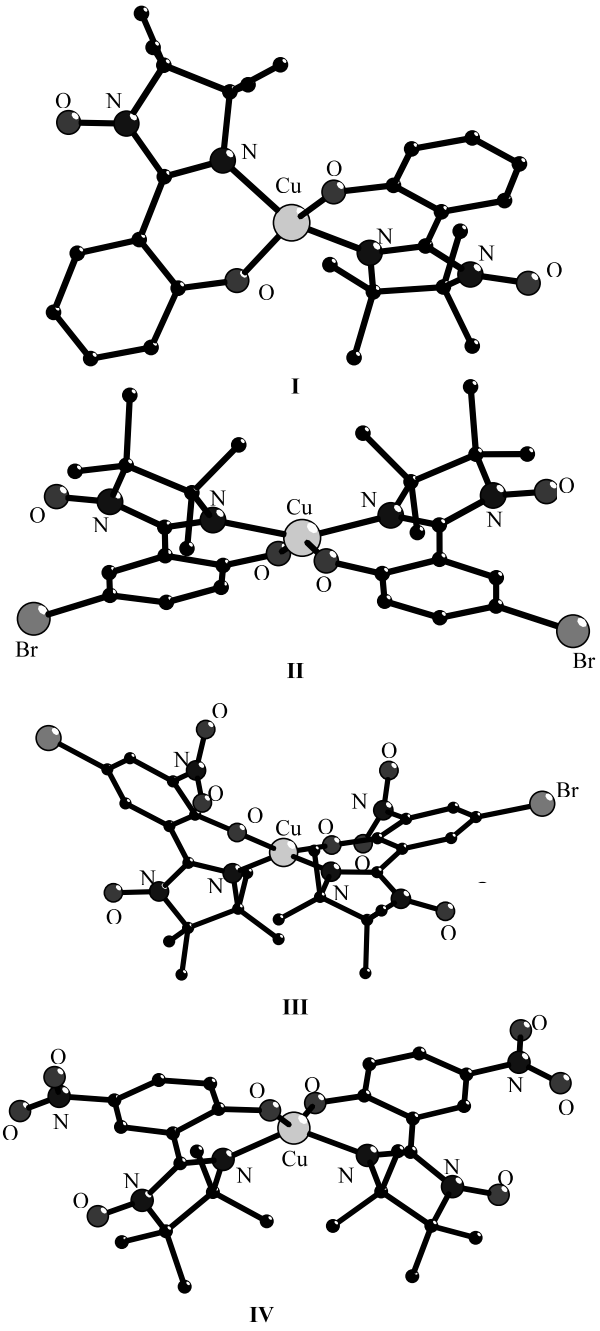


Fig. 6. Structure of complexes **I**–**IV**.

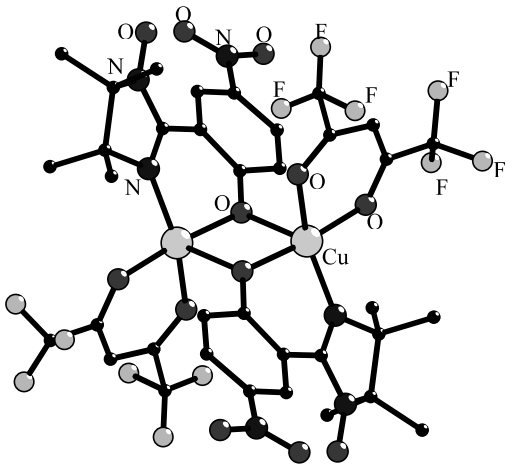

Fig. 7. Structure of $[CuL^3(hfac)]_2$ (**V**).

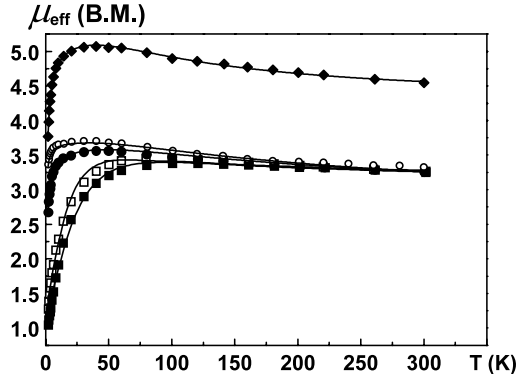


Fig. 8. Experimental dependences $\mu_{eff}$(T) for complexes $CuL^1_2$ (□), $CuL^2_2$ (■), $CuL^3_2$ (●), $CuL^4_2$ (○), $[CuL^3(hfac)]_2$ (◆). Solid lines—optimal theoretical curves.

Table 6
Magnetic parameters

| Complex | $C$ ($cm^3$ K $mol^{-1}$) | $\theta$ (K) | $G$ | $J$ ($cm^{-1}$) | J1 ($cm^{-1}$) | nJ′ ($cm^{-1}$) | $\sigma$ |
|---|---|---|---|---|---|---|---|
| $CuL^1_2$ | 1.208 | 25.7 | 2.15±0.07 | 39±5 | −13±3 | −0.6±0.1 | 0.0048 |
| $CuL^2_2$ | 1.208 | 29.5 | 2.1±0.1 | 51±9 | −25±4 | −0.7±0.1 | 0.0079 |
| $CuL^3_2$ | 1.211 | 35.5 | 2.15±0.05 | 90±30 | 0 | −0.41±0.08 | 0.0026 |
| $[CuL^3(hfac)]_2 \cdot CH_2Cl_2$ | 2.164 | 45.5 | 2.17±0.1 | 350±1 | 110±12 | −0.31±0.02 | 0.00034 |
| $CuL^4_2$ | 1.232 | 49.4 | 2.15±0.05 | 120±10 | 0 | −0.12±0.01 | 0.00082 |

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