H_2O as a Chemical Link for Ferromagnetic Interactions Between Aminoxyl Units

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A bis(radical) derivative based on a triphenylphosphane core substituted by two nitronyl nitroxide units is reported. This compound was isolated in two forms. One consists of an H_2O adduct where H_2O is hydrogen-bonded to the radical units, whereas the second lacks this bridging unit. Magnetic studies revealed that the presence of the H_2O bridge induces ferromagnetic exchange interaction between the spin carriers.

Purely organic magnets are desirable materials and the design of open-shell supramolecular architectures is currently attracting an increasing interest.[1,2] The approach involving molecular crystals of aminoxyl radicals is certainly the most investigated. It has quickly become evident that to reach the objective it is essential to gain control over the construction of the supramolecular network as well as over the exchange pathways between the spin carriers. Indeed, the bulk magnetic properties will depend on the dimensionality of the system. The basic tools of organic supramolecular chemistry provide solutions for a directed material synthesis.[3,4] Among them, the hydrogen-bonding strategy attracts special interest because it has been suggested from both theoretical[5−7] and experimental[8−11] results that a hydrogen bond might mediate the intermolecular magnetic communication.

An increasing number of supramolecular frameworks consisting of H-bonded paramagnetic subunits bearing either OH,[12−14] NH,[15−17] or acetylenic CH[18] groups as H-donor moieties were found to exhibit long-range magnetic correlation. However, whereas the chemical dimensionality of the solid-state structure and the intermolecular links between the subunits can be controlled by the means of the molecular synthon, it remains difficult to anticipate the final properties of the supramolecular material. In these homomolecular architectures, the exchange interactions between the paramagnetic units proceed through the supramolecular links and the core of the molecules. The resulting dominant exchange will depend on several parameters related both to the building block (such as the chemical nature of the molecule itself, the substitution pattern i.e. aminoxyl unit versus H-donor or -acceptor group positions, and the main exchange pathway among several intermolecular connections) and to the crystal lattice organization. Consequently, it is difficult to manage the dominant exchange between the magnetic centers.

An alternative approach is to link the paramagnetic centers by an independent molecule which allows for ferromagnetic exchange. Obtaining materials with a remnant magnetization by a homo-spin strategy requires a ferromagnetic interaction between the molecular units. A prominent example of this approach involves the use of phenylboronic acid.[19,20] In this report, we show that a simple hydrogen-bonded water molecule may be the driving force behind ferromagnetic interaction between aminoxyl radical units.

Results and Discussion

Synthesis and Crystal Structures

The bis(radical) derivative **5** considered in this study was synthesized as outlined in Scheme 1. The synthesis of bis(aldehyde) **2** was adapted from original procedures,[21,22] except for the deprotection step (Scheme 1, step 3), which was modified to improve the yield (up to 97%). The condensation of phosphane oxide **3** and 2,3-bis(hydroxyamino)-2,3-dimethylbutane, affording **4**, gave best results in refluxing methanol. This reaction should not exceed 6 h as a longer reaction time results in decomposition of the product. The crystalline bis(radical) was obtained by diffusion of either Et_2O or hexane into a solution of **5** in CH_2Cl_2. Either red prismatic or needle-like crystals (**5a** and **5b**, respectively) were formed depending on whether dry or "wet" solvent was used, i.e. dried (see Exp. Sect.) or "for synthesis" qual-

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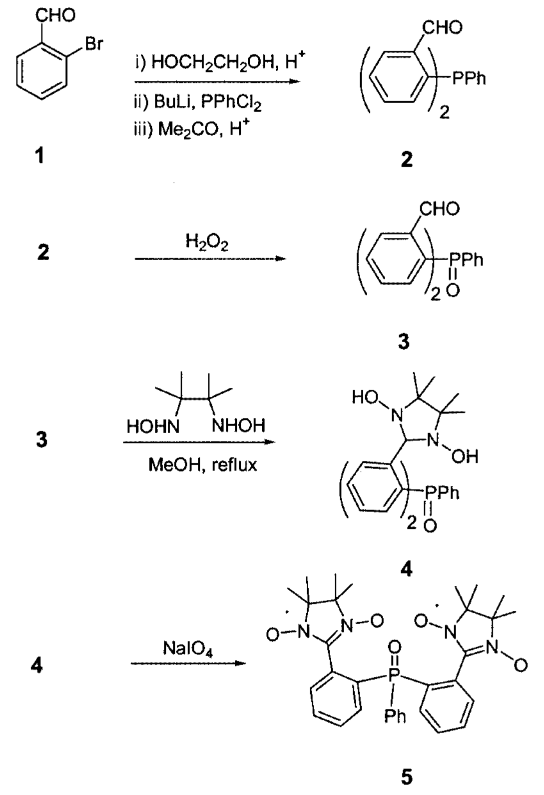

Scheme 1

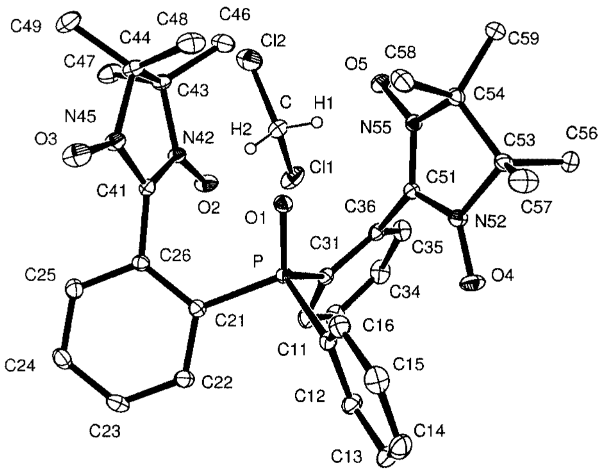

Figure 1. ORTEP drawing for compound **5a** (30% probability ellipsoids); selected bond lengths [Å] and angles [°]: O2−N42 1.287(2), O3−N45 1.281(2), O4−N52 1.275(2), O5−N55 1.283(2), C41−N42 1.343(2), C41−N45 1.338(2), C26−C41 1.473(2), C21−C26 1.408(2), P−O1 1.486(1), P−C11 1.810(2), P−C21 1.825(2), P−C31 1.822(1); O1−P−C11 112.41(7), O1−P−C21 111.75(7), O1−P−C31 112.88(7); mean plane angles: radical−phenyl 68.22(5) and 78.99(5), radical−radical 67.28(6)

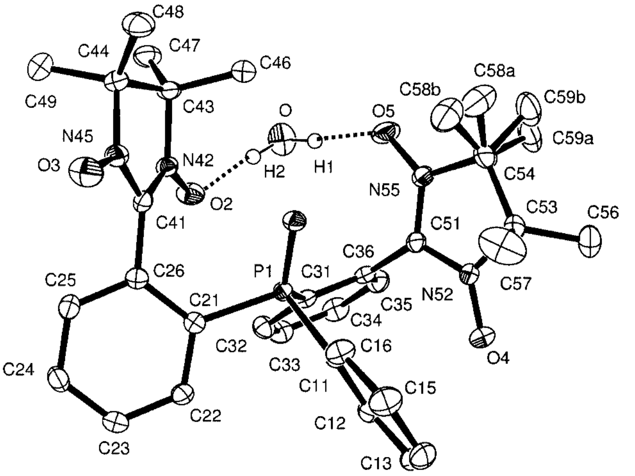

Figure 2. ORTEP drawing for compound **5b** (30% probability ellipsoids); selected bond lengths and distances [Å] and angles [°]: O2−N42 1.288(2), O3−N45 1.278(2), O4−N52 1.283(2), O5−N55 1.280(2), C41−N42 1.334(2), C41−N45 1.351(3), C26−C41 1.476(3), C21−C26 1.409(3), C51−N52 1.341(2), C51−N55 1.341(3), C36−C51 1.477(3), P−O1 1.480(2), P−C11 1.811(2), P−C21 1.821(2), P−C31 1.827(2) O2···H2 2.03(3), O5···H1, 1.94(3); O2−O−O5 94.35(7), O1−P−C11 110.74(8), O1−P−C21 113.96(8), O1−P−C31 114.79(9); mean plane angles: radical−phenyl 51.56(7) and 87.26(7), radical−radical 77.09(8)

ity solvent. These crystals were suitable for X-ray structural analysis.

The X-ray crystal structure of **5a** confirmed that the molecule is indeed the anticipated bis(radical) and revealed that the crystal lattice includes CH_2Cl_2. An ORTEP view is presented in Figure 1 with selected bond lengths and angles. The main interatomic distances are very similar to those found for the related mono(radical) derivative.[23] The distance between the two nitronyl nitroxide units in the molecule can be evaluated by the C41−C51 separation, which is 5.220(2) Å; the shortest separation involving the NO units of the two radical moieties is found for O2−O5 which is 4.213(2) Å. The angle between the mean plane of the radical moieties is 67.28(6)°. The shortest intermolecular contacts involving the aminoxyl O atoms are O2 to the CH_2Cl_2 solvate [O2···H2C, 2.33(2) Å], O3 and O4 to the phenyl rings of neighboring molecules [O3···HC22, 2.45(2) Å; O4···HC24, 2.32(2) Å], and O5 to a methyl group [O5···HC46, 2.44(3) Å].

The X-ray crystal structure analysis for the needle-shaped crystals of **5b** revealed that an H_2O molecule had co-crystallized with compound **5**. No other solvate molecules were found in the crystal lattice. Interestingly, the H_2O molecule is actually linked to **5**, as depicted in the ORTEP view of this adduct (Figure 2). Two hydrogen bonds are established between the H_2O molecule and an O atom of one NO unit of each radical moiety, H1−O5 [1.94(3) Å] and H2−O2 [2.03(3) Å]. Despite the presence of the H_2O in **5b**, the separation of the two aminoxyl units [4.170(2) Å for O2···O5], and the angle between the mean plane of the radical moieties [77.09(8)°] remain very similar to those found in **5a**. Most of the intramolecular geometric characteristics are also similar for the two compounds **5a** and **5b** (see caption to Figure 2). The shortest intermolecular contacts involving the aminoxyl O atoms of **5b** (containing the bridging H_2O), are found for O2···HC56 [2.70(2) Å], O3···HC49 [2.79(2) Å], O4···HC14 [2.37(3) Å], and

O5···HC47 [2.47(3) Å]. The crystal structure shows two close, statistically disordered positions for two methyl groups (C58 and C59) of one radical moiety.

Magnetic Properties

The solid-state temperature dependence of the molar magnetic susceptibilities, χ_M, for **5a** and **5b** were investigated on polycrystalline samples with a SQUID magnetometer in the temperature range 2−300 K. The plot of $\chi_M T$ versus T for both derivatives is shown in Figure 3. In the temperature region of 50−300 K, the $\chi_M T$ value for each compound is 0.75 $cm^3 \cdot K \cdot mol^{-1}$ and remains almost invariant as expected for two $S = 1/2$ spins in a Curie regime. At lower temperatures, however, compounds **5a** and **5b** behave quite differently. For **5a**, the $\chi_M T$ value decreases with temperature and reaches 0.67 $cm^3 \cdot K \cdot mol^{-1}$ at 2 K, indicating antiferromagnetic interaction between the spin carriers. For **5b**, the value of $\chi_M T$ steadily increases up to 0.91 $cm^3 \cdot K \cdot mol^{-1}$ as T is lowered to 2 K, a feature characteristic for ferromagnetic interactions between the aminoxyl units.

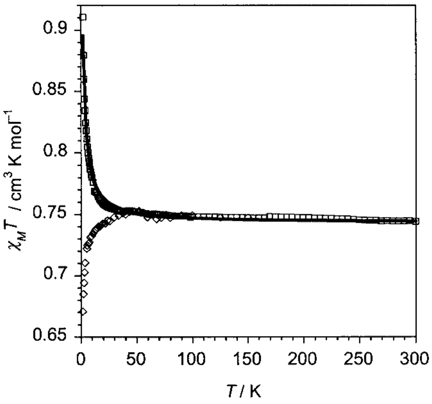

Figure 3. Experimental $\chi_M T$ versus T behavior for compounds **5a** (tilted squares) and **5b** (squares); the solid line represents the calculated best fit to the experimental data for **5b**

The magnetic behavior for compound **5a** indicates that, overall, weak antiferromagnetic interactions are operative between the radical units. These may originate either from the intramolecular exchange interaction between the two aminoxyl groups or from intermolecular exchange interactions through the close contacts to neighboring molecules. Most probably both take place concomitantly. More importantly, it reveals that the intramolecular exchange through the phosphane core in bis(radical) **5a** is rather weak. This observation can be attributed to the large dihedral angles (68.22 and 79.00°) between the nitronyl nitroxide heterocycles and phenyl rings to which these are linked. It has been shown that this reduces the spin density on the atoms linking the aminoxyl moieties and, consequently, reduces the exchange interaction through the molecular core.[24]

No significant differences in the geometrical features distinguish the bis(radical) unit in **5a** from that of **5b**. Thus, the ferromagnetic behavior found for **5b** may be attributed to the H_2O molecule linking the two aminoxyl moieties, providing an alternative pathway for the intramolecular exchange interaction between the two radical units. The field dependence of the magnetization for **5b**, measured at 2 K, compares favorably to the calculated value for an $S = 1$ spin state (as calculated by the Brillouin function; Figure 4). An estimate of the intramolecular exchange parameter, J, for **5b** was obtained by analyzing the magnetic data with a dimer-model derived from the spin Hamiltonian $H = -J\mathbf{S}_1 \cdot \mathbf{S}_2$. Least-square fitting to the experimental data led to $J = 1.58 \pm 0.02$ cm^{-1} with $g = 2.00$ (Figure 3). This ferromagnetic interaction between the aminoxyl units via the H_2O molecule is accounted for by the mechanism based on electron spin polarization. Indeed, an alternate polarization on the atom sequence NO···H−O−H···ON results in the same polarization on each of the aminoxyl groups, a situation for which ferromagnetic interaction between both spin carriers is anticipated.

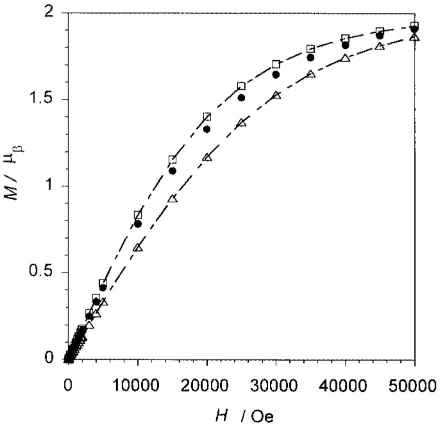

Figure 4. Experimental (black dots) field dependence of the magnetization for compound **5b** at 2 K compared to the magnetization given by the Brillouin function for one $S = 1$ spin (squares) and two uncorrelated $S = 1/2$ spins (triangles) for the same temperature (the lines are just eye guides)

Concluding Remarks

Crystal engineering based on the self-assembly of molecular subunits utilizing hydrogen bonds has proven to be a valuable approach for the preparation of magnetic supramolecular materials. A possible strategy consists of linking the paramagnetic subunits by using an independent molecule which allows for ferromagnetic exchange between the magnetic centers. The results gathered with the bis(radical) derivatives **5a**,**b** show that a hydrogen-bonded water molecule may be the driving force behind ferromagnetic interaction between aminoxyl radical units. These two compounds demonstrate the usefulness hydrogen bonds in the propagation of exchange interactions.

Experimental Section

General: Unless otherwise specified, commercially available solvents and reagents were used without further purification. Dry

THF was obtained by distillation from Na/benzophenone, CH_2Cl_2 was distilled from CaH_2, MeCN was dried with P_2O_5, DMF was dried with $MgSO_4$ and distilled under vacuum, MeOH was dried with $Mg(OMe)_2$ prior to distillation. Reactions involving *n*BuLi were carried out under N_2 in oven-dried glassware. $PPhCl_2$ was distilled prior to use. NMR spectra were recorded with a Bruker instrument operating at 200 MHz for ^1H. IR spectra were recorded in the range 4000−400 cm^{-1} using a Perking Elmer FT-IR Pergamon 1000. Elementary analyses were performed by the "Service Central d'Analyse du CNRS" at Vernaison, France.

Bis(*o*-formylphenyl)phenylphosphane (2)[21,22]

Step 1: 2-(*o*-Bromophenyl)-1,3-dioxolan was prepared from 2-bromobenzaldehyde (**1**), and ethylene glycol according to procedures described in the literature.[21,25]

Step 2: 2-(*o*-Bromophenyl)-1,3-dioxolan (10 g, 44 mmol) was dissolved in freshly distilled THF (120 mL) and cooled to −78 °C. A solution of 1.6 м *n*BuLi in hexane (30 mL; 48 mmol) was added and the resulting mixture stirred at −78 °C for 1 h. Neat PCl_2Ph (3.0 mL; 22 mmol) was then added dropwise and the reaction mixture was stirred at room temperature overnight. Water (15 mL) was cautiously added, the organic and aqueous phases were separated and further extracted and washed with water and benzene respectively. The combined organic fractions were dried with anhydrous $MgSO_4$ and, after filtration, the solvent was removed in vacuo. The residue was recrystallized from MeOH affording white crystals of bis[2-(1,3-dioxolan-2-yl)phenyl](phenyl)phosphane (66%, 5.8 g).

Step 3: A solution of bis[2-(1,3-dioxolan-2-yl)phenyl](phenyl)phosphane (5.9 g, 14 mmol) and *p*-toluenesulfonic acid monohydrate (0.58 g) in acetone (160 mL) was refluxed for 70 min. Water (40 mL) was then added and the acetone evaporated under reduced pressure leading to the formation of a yellow crystalline precipitate (**2**) which was immediately filtered,[26] washed with water and dried (4.45 g, 97%).

Bis(*o*-formylphenyl)(phenyl)phosphane Oxide (3):[22] An aqueous solution of H_2O_2 (0.1 mL, 35%, 3.44 mmol) was added to a solution of **2** (1 g, 3.44 mmol) in acetone (40 mL) and stirred for 1 h. The solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2. This solution was then washed with H_2O until the oxidation test of the aqueous fractions with Mohr's salt proved negative. After drying the organic phase with Na_2SO_4, the solvent was removed in vacuo quantitatively affording **3** as a white powder.

Bis[*o*-1,3-dihydroxy-4,4,5,5-tetramethylimidazol-2-yl)phenyl]-(phenyl)phosphane Oxide (4): A solution of **3** (0.5 g, 1.49 mmol) and 2,3-bis(hydroxyamino)-2,3-dimethylbutane (0.44 g, 3 mmol) in dry MeOH (40 mL) was refluxed under N_2 for 6 h. After reducing the volume in vacuo to ca. 4 mL, H_2O (20 mL) was added leading to the precipitation of a white solid which was filtered, washed with H_2O and dried in vacuo to afford **4** (0.54 g, 60%). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 8.15 (m, 2 H, Ar); 7.65−7.1 (m, 9 H, Ar), 7 (m, 2 H, Ar), 6.35 and 5.12 (2 s, 4 H, OH), 5.38 (s, 2 H, HCN), 1.11, 1.06 and 1.04 (3 s, 24 H, Me) ppm.

Bis(radical) Derivative 5: A solution of $NaIO_4$ (0.58 g, 2.73 mmol) in water (10 mL) was added to a stirred suspension of **4** (0.54 g, 0.91 mmol) in CH_2Cl_2 (35 mL). After 20 min, the violet phases were separated and the aqueous phase further extracted with CH_2Cl_2. The combined organic fractions were washed with H_2O (15 mL) and dried with anhydrous Na_2SO_4. Purification was achieved by flash chromatography under N_2 on silica gel (SiO_2: 35−70 micron, 30 × 2 cm, CH_2Cl_2/Me_2CO (7:3)]. Crystalline bis(radical) **5** was obtained by diffusion of Et_2O into a CH_2Cl_2 solution. IR (KBr): $\tilde{\nu}$ = 1399 (s), 1367 (s), 1197 (m), 1171 (w), 1134 (m), 754 (m), 728 (m), 714 (m), 694 (m), 596 (s) cm^{-1}. EPR (CH_2Cl_2, 295 K): g = 2.006 (1 broad line). **5a:** $C_{33}H_{39}Cl_2N_4O_5P$ (673.5): calcd. C 58.84, H 5.84, N 8.32; found C 58.75, H 5.83, N 8.51. **5b:** $C_{32}H_{39}N_4O_6P$ (606.6): calcd. C 63.35, H 6.48, N 9.23; found C 63.23, H 6.41, N 9.29.

Crystal Structure Analysis of 5a: $C_{32}H_{37}N_4O_5P{\cdot}CH_2Cl_2$ (673.55), red prism, 0.10 × 0.36 × 0.36 mm, monoclinic, *Cc* (no. 9), a = 10.1228(2), b = 29.4913(7), c = 11.5810(3) Å, β = 104.241(1)°, V = 3351.08(14) Å^3, Z = 4, ρ = 1.335 g·cm^{-3}, F_{000} = 1416, μ = 0.288 mm^{-1}. A suitable single crystal for the X-ray diffraction study was obtained by diffusion of Et_2O into a solution of **5** in CH_2Cl_2. The selected crystal was coated with perfluorinated ether, fixed onto a capillary and placed in a cold nitrogen flow (Oxford Cryosystems) in the diffractometer. Preliminary examination and data collection were carried out with a Kappa CCD device (NONIUS MACH3) at the window of a rotating anode (NONIUS FR591) with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection was performed at 143 K within the Θ range of $2.19° < \Theta < 27.48°$.[27] A total of 12904 reflections were integrated and corrected for Lorentz and polarization effects. A correction for absorption effects and/or decay was applied during the scaling procedure.[28] After merging (R_{int} = 0.0175), 6858 [6697: $I_o > 2\sigma(I_o)$] independent reflections remained and were all used to refine 562 parameters. The structure was solved by a combination of direct methods[29] and difference Fourier syntheses.[30] The hydrogen atom positions were found in the difference Fourier map calculated from the model containing all non-hydrogen atoms. The hydrogen positions were refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $w(F_o^2 - F_c^2)^2$ and converged with $R1$ = 0.0258 [$I_o > 2\sigma(I_o)$], $wR2$ = 0.0654 (all data), *GOF* = 1.042 and shift/error < 0.002. The residual electron density between −0.30 and 0.24 e/Å^3 showed no distinctive features. The drawings, listings and checking for correctness were performed with the program PLATON.[31]

Crystal Structure Analysis of 5b: $C_{32}H_{37}N_4O_5P{\cdot}H_2O$, (606.64), red fragment, 0.03 × 0.18 × 0.38 mm, monoclinic, $P2_1/n$ (no. 14), a = 17.6592(2), b = 10.3019(1), c = 18.7393(2) Å, β = 116.8956(5)°, V = 3040.36(6) Å^3, Z = 4, ρ = 1.325 g.cm^{-3}, F_{000} = 1288, μ = 0.142 mm^{-1}. A suitable single crystal for the X-ray diffraction study was obtained by diffusion of Et_2O into a solution of **5** in "wet" CH_2Cl_2. The selected crystal was coated with perfluorinated ether, fixed onto a capillary and placed in a cold nitrogen flow (Oxford Cryosystems) in the diffractometer. Preliminary examination and data collection were carried out with a Kappa CCD device (NONIUS MACH3) at the window of a rotating anode (NONIUS FR591) with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collection was performed at 143 K within the Θ range of $2.14° < \Theta < 25.03°$.[27] A total of 55322 reflections were integrated and corrected for Lorentz and polarization effects. A correction for absorption effects and/or decay was applied during the scaling procedure.[28] After merging (R_{int} = 0.0214), 5378 [4481: $I_o > 2\sigma(I_o)$] independent reflections remained and were all used to refine 571 parameters. The structure was solved by a combination of direct methods[29] and difference Fourier syntheses.[30] The hydrogen atom positions were found in the difference Fourier map calculated from the model containing all non-hydrogen atoms. The hydrogen positions were refined with individual isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $w(F_o^2 - F_c^2)^2$ and converged with $R1$ =

0.0394 [$I_o > 2\sigma(I_o)$], $wR2 = 0.0906$ (all data), $GOF = 1.021$ and shift/error < 0.001. A disorder (51:49) at C58 and C59 clearly resolved. The residual electron density between −0.35 and 0.33 e/ Å^3 showed no distinctive features. The drawings, listings and checking for correctness were performed with the program PLATON.[31]

CCDC-190126 (**5a**) and -190125 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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