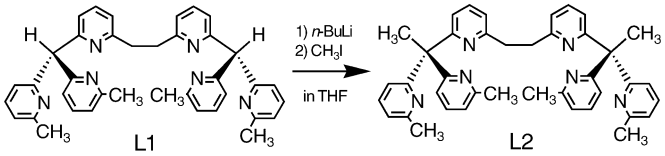
Bioinorganic Chemistry

Synthesis, Structure, and Greatly Improved Reversible O_2 Binding in a Structurally Modulated μ-η^2:η^2-Peroxodicopper(II) Complex with Room-Temperature Stability**

Masahito Kodera, Yuuji Kajita, Yoshimitsu Tachi, Kou Katayama, Koji Kano, Shun Hirota, Shuhei Fujinami, and Masatatsu Suzuki*

Some thermally stable μ-η^2:η^2-peroxodicopper(II) complexes (Cu_2O_2)[1,2] have been reported as models of oxyhemocyanin (oxyHc),[3] and the room-temperature-stable μ-η^2:η^2-Cu_2O_2 complex $[Cu_2(O_2)(L1)](PF_6)_2$ (**1**, where L1 is the sterically hindered hexapyridine ligand 1,2-bis[2-(bis(6-methyl-2-pyridyl)methyl)-6-pyridyl]ethane) is the first example of a μ-η^2:η^2-Cu_2O_2 complex that binds O_2 reversibly in homogeneous solution around room temperature.[2b] However, heating the solution at 80 °C was required for release of O_2 from **1**.[2b] Hence, the next target is to make a functional model of the tense form of oxyHc (low O_2 affinity),[4] which releases O_2 more easily.

It is known that structural modulation of copper complexes by subtle structural perturbation of ligands dramatically affect the Cu/O_2 reactivity.[1] We have synthesized a new sterically hindered hexapyridine ligand having bridgehead methyl groups, namely L2 (Scheme 1), and its μ-η^2:η^2-Cu_2O_2 complexes $[Cu_2(O_2)(L2)](X)_2$ (**3**-X_2, X = PF_6, CF_3SO_3, ClO_4). The structural modulation of the μ-η^2:η^2-Cu_2O_2 complex by the bridgehead methyl groups facilitates release of O_2 and results in an almost perfectly reversible CO/O_2 binding cycle simply by exchanging the gas phase between O_2 and CO. Here, we report greatly improved reversible O_2 binding by **3**, which may provide some insight into the mechanism of Hc, on the basis of the crystal structure and detailed spectral analysis of **3**.



Scheme 1. Synthesis of L2.

Ligand L2 forms Cu^I complexes $[Cu_2(CH_3CN)_2(L2)](X)_2$ (**2**-X_2; X = PF_6, CF_3SO_3, and ClO_4). The structure of **2**-$(CF_3SO_3)_2$ was determined by X-ray analysis[5,7] (Figure 1). The Cu^I ions have a trigonal-pyramidal coordination geometry formed by three pyridyl N atoms of L2 coordinated in a facial mode and a CH_3CN ligand. The Cu···Cu distance in **2** (6.616(1) Å) is large because the CH_2CH_2 spacer connecting the two tripyridyl units adopts an energetically more stable *anti* conformation. The sharp singlet signal of the CH_2CH_2 spacer in the ^{1}H NMR spectrum of **2** (see Experimental Section) indicates free rotation about the C–C single bond in solution.

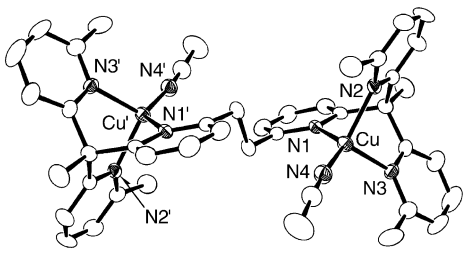


Figure 1. Structure of the cation of **2**-$(CF_3SO_3)_2$ (ORTEP plot, 50% probability; unlabeled open ellipses represent carbon atoms). Selected interatomic distances [Å] and angles [°]: Cu-N1, 2.052(6), Cu-N2, 2.042(7), Cu-N3, 2.070(7), Cu-N4, 1.884(7); Cu···Cu′, 6.616(1), N1-Cu-N2, 88.8(2), N1-Cu-N3, 90.4(3), N1-Cu-N4, 128.9(3), N2-Cu-N3, 93.7(3), N2-Cu-N4, 126.7(3), N3-Cu-N4, 118.1(3).

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The μ-η^2:η^2-Cu_2O_2 complexes **3**-X_2 were prepared by addition of O_2 to dicopper(I) complexes **2**-X_2 in CH_2Cl_2 and isolated as purple crystals by cooling the solution at −30 °C with slow diffusion of $PhCH_3$. Measurements of O_2 uptake with a gas-burette system showed that one equivalent of O_2 is bound to **2**-$(PF_6)_2$ in CH_2Cl_2 at various concentrations and temperatures. Spontaneous decomposition of **3**-$(PF_6)_2$ in solution in CH_2Cl_2, monitored at 350 nm, obeys first-order kinetics with $k = 7.0 \times 10^4\ \text{min}^{-1}$ at 25 °C (half-life time $\tau_{1/2} =$ 2.5 h). The thermal stability of **3** is affected by the counter-anion: the $\tau_{1/2}$ values of **3**-$(ClO_4)_2$ and **3**-$(CF_3SO_3)_2$ are 3.0 and 3.6 h, respectively.

Reversible binding of O_2 was observed in CH_2Cl_2/acetone (3/0.002) (Figure 2a): **3** releases O_2 under argon simply on heating the solution to 40 °C and is easily regenerated at 0 °C by replacing the gas phase over the solution by O_2. The small amount of acetone assists release of O_2 from **3** by coordination to the copper(I) center. Replacing the O_2 atmosphere with argon is sufficient to release O_2 from **3**. After three cycles of reversible O_2 binding, irreversible decomposition of **3** amounted to less than 10%. Heating at 80 °C in vacuo and addition of a small amount of CH_3CN are necessary for releasing O_2 from **1**. Thus, the reversible O_2 binding of **3** is greatly improved over that of **1**. Moreover, we prepared the CO/L2 complex $[Cu_2(CO)_2(L2)](PF_6)_2$ (**4**-$(PF_6)_2$) and achieved completely reversible O_2/CO binding (Scheme 2) with a solution of **4** in CH_2Cl_2 at 25 °C without addition of any coordinating solvent and without heating (Figure 2b). In this system, **4** is easily converted to **3** by addition of O_2 and regenerated quantitatively when the gas phase is replaced by CO. After several O_2/CO cycles, **4** was quantitatively recovered from the solution. The reason for the greatly improved reversibility is the easy release of O_2 from **3**.

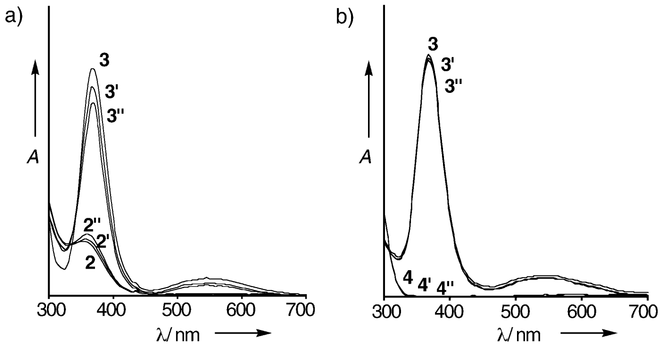
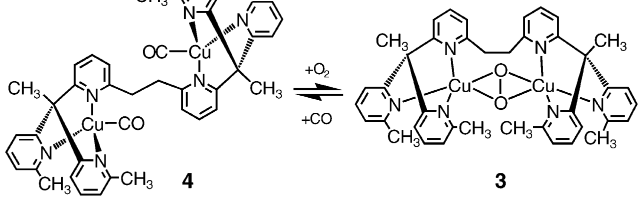


Figure 2. a) Reversible O_2 binding by **2**-$(PF_6)_2$ in CH_2Cl_2/acetone (3/0.002). A solution of **2**-$(PF_6)_2$ was oxygenated at 0 °C under O_2 to give **3**-$(PF_6)_2$ (**2**→**3**). Compound **2**-$(PF_6)_2$ was regenerated from **3**-$(PF_6)_2$ by warming at 40 °C under argon (**3**→**2'**). Three cycles are shown. b) Reversible O_2 binding by **4**-$(PF_6)_2$ in CH_2Cl_2. A solution of **4**·$(PF_6)_2$ was oxygenated at 25 °C under O_2 to form **3**-$(PF_6)_2$ (**4**→**3**). Compound **4**-$(PF_6)_2$ was regenerated form **3**-$(PF_6)_2$ at 25 °C under CO (**3**→**4'**). Three cycles are shown.



Scheme 2. Reversible O_2/CO binding by **3**.

The X-ray structure analysis of **3**-$(PF_6)_2$[6,7] revealed two independent molecules **3a** and **3b**, which are similar to each other (Figure 3). Though the overall structure of **3** is similar to

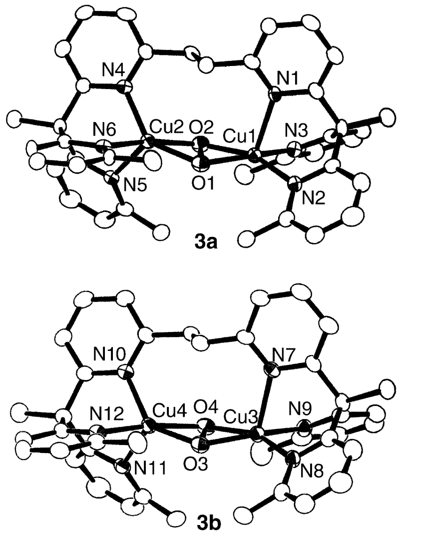


Figure 3. Structures of **3a** and **3b** (ORTEP plots, 50% probability; unlabeled open ellipses represent carbon atoms). Selected interatomic distances [Å] and angles [°]: Cu1-O1, 1.918(4), Cu1-O2, 1.913(3), Cu1-N1, 2.262(4), Cu1-N2, 1.962(4), Cu1-N3, 1.968(4), Cu2-O1, 1.961(4), Cu2-O2, 1.894(4), Cu2-N4, 2.030(4), Cu2-N5, 2.125(4), Cu2-N6, 1.968(4), Cu3-O3, 1.920(4), Cu3-O4, 1.903(4), Cu3-N7, 2.245(4), Cu3-N8, 1.966(4), Cu3-N9, 1.978(4), Cu4-O3, 1.953(4), Cu4-O4, 1.894(4), Cu4-N10, 2.033(4), Cu4-N11, 2.122(4), Cu4-N12, 1.962(4); Cu1···Cu2, 3.523(8), Cu3···Cu4, 3.516(8), O1-O2, 1.491(5), O3-O4, 1.487(5), Cu1-O1-Cu2, 130.5(2), Cu1-O2-Cu2, 135.4(2), Cu3-O3-Cu4, 130.4(2), Cu3-O4-Cu4, 135.7(2); the dihedral angle between the Cu1-O1-O2 and Cu2-O1-O2 planes is 168.22°, and that between the Cu3-O3-O4 and Cu4-O3-O4 planes 168.45.

that of **1**,[2b] in the former steric repulsion between the bridgehead methyl groups and 3-py H atoms of L2 cause significant structural differences. This so-called pyridine shift[8] enhances the steric hindrance of the 6-Me groups and thus elongates the Cu−O and Cu···Cu distances of **3**. The average Cu−O bond lengths of 1.922 and 1.918 Å and Cu···Cu separations of 3.523 and 3.516 Å for **3a** and **3b**, repectively, are larger than those of 1.910 and 3.477 Å, respectively, for **1**. The Cu−O bond of **3** is the longest of all structurally characterized μ-η^2:η^2-Cu_2O_2 complexes (1.89–1.915 Å[2,9]). The μ-η^2:η^2-Cu_2O_2 core of **3** is more planar than that of **1**; the Cu-O-O′-Cu′ dihedral angles of 168.22 and 168.45° of **3a** and **3b**, respectively, are larger than that of **1** (163.3°). The more planar μ-η^2:η^2-Cu_2O_2 core in **3** may be due to the elongation of the Cu···Cu separation.[10] The copper coordination geometry of **3** is less distorted from square-pyramidal

than that of **1**; the τ values (τ varies from 0 for an idealized square pyramid to 1 for an idealized trigonal bipyramid)[11] of 0.00 and 0.37 for **3a** and 0.00 and 0.38 for **3b** are smaller than those of 0.16 and 0.44 for **1**. These data suggest that the easy release of O_2 by **3** is due to the elongation of the Cu–O bond and the Cu···Cu distance, and it is not inhibited by the planar structure of the Cu_2O_2 core and by the less distorted copper coordination geometry.[10b]

The resonance Raman spectrum of **3**, obtained with excitation at 514.5 nm, shows a strong band at 765 cm^{-1}, which shifts to 724 cm^{-1} on labeling with ^{18}O and is assigned to the O–O stretch of peroxide bound in a μ-η^2:η^2-mode on the basis of its frequency and isotopic shift (41 cm^{-1}). Solomon et al. reported that the O–O stretch moves to higher energy as the μ-η^2:η^2-Cu_2O_2 core becomes more bent, and the Cu···Cu distance shortens.[10b] In our systems, in contrast, the ν_{O-O} band of **3** is at higher wavenumber than that of **1** (760 cm^{-1}), in spite of the more planar μ-η^2:η^2-Cu_2O_2 core and longer Cu···Cu distance of **3**. The O–O stretch of **3** is the strongest in the range of 713–765 cm^{-1} for μ-η^2:η^2-Cu_2O_2 complexes, including oxyHc, reported so far.[2,9,10b,12] The strong O–O bond may be favorable for release of O_2. The O_2^{2-}–Cu^{II} charge-transfer bands at 360 (24700) and 532 nm (1530 $M^{-1}cm^{-1}$) in **1** shift to slightly lower energy in **3** (366 (24000) and 537 nm (2100 $M^{-1}cm^{-1}$)). This is consistent with the long Cu–O bond of **3** and suggests that the crystal structure of **3** is retained in solution.

In conclusion, **3** is the best model for reversible O_2 binding among all μ-η^2:η^2-Cu_2O_2 complexes reported so far, and the long Cu–O bond, the large Cu···Cu distance, and strong O–O bond of **3** are favorable for easy release of O_2. Structural modulation by the bridgehead methyl groups provides important structural changes that facilitate release of O_2. Therefore, it can be concluded that **3** is a functional model of the tense form of oxyHc.

Experimental Section

L2: Ligand L1 (1.15 g, 2.0 mmol) was dissolved in dry THF (100 mL) and *n*-butyllithium (1.6 M in hexane, 2.63 mL, 4.2 mmol) was added at −78 °C under argon. The mixture was stirred for 3 h at room temperature. Then methyl iodide (0.60 g, 4.2 mmol) was added with stirring at −78 °C, and the mixture was stirred for 2 h at room temperature. Ligand L2 (0.79 g, 66 %) was isolated after purification by column chromatography on silica gel. M.p. 159.2–160.8 °C; elemental analysis (%) calcd for $C_{40}H_{40}N_6$: C 79.44, H 6.67, N 13.90; found: C 78.92, H 6.69, N 13.48; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.24 (s, 6H; CH_3), 2.40 (s, 12H; py-CH_3), 2.99 (s, 4H; CH_2), 6.53 (d, ^3J(H,H) = 7.8 Hz, 4H; py-3), 6.60 (d, ^3J(H,H) = 7.8 Hz, 2H; py′-5), 6.64 (d, ^3J(H,H) = 7.8 Hz, 2H; py′-3), 6.85 (d, ^3J(H,H) = 7.8 Hz, 4H; py-5), 7.21 (t, ^3J(H,H) = 7.8 Hz, 2H; py′-4), 7.28 ppm (t, ^3J(H,H) = 7.8 Hz, 4H; py-4); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C, TMS), δ = 24.73 (CH_3), 26.87 (py-CH_3), 36.92 (CH_2), 60.24 ($C_{bridgehead}$), 120.28, 120.33, 120.40, 120.91 (py-3, 5, py′-3, 5), 135.53 (py-4, py′-4), 157.06 (py-6), 160.08 (py′-6), 165.36, 165.76 ppm (py-2, py′-2); IR (KBr disk): $\tilde{\nu}$ = 1580, 1565, 1445 cm^{-1} (py ring); FAB MS: *m*/*z*: 605 $[M+H]^+$.

2-$(PF_6)_2$: L2 (120.8 mg, 0.20 mmol) was dissolved in MeCN (10 mL) and added to $[Cu(MeCN)_4](PF_6)$ (149.0 mg, 0.40 mmol) under argon. The mixture was stirred for 1 h at room temperature under argon. On addition of Et_2O (30 mL) to the resultant solution, a pale yellow solid precipitated. The solid was purified by recrystallization from MeCN/Et_2O under Ar. Yield: 183 mg (83 %). Elemental analysis (%) calcd for $C_{44}H_{46}N_8P_2F_{12}Cu_2 \cdot 0.5\,CH_2Cl_2$: C 46.67, H 4.14, N 9.79, Cu 11.00; found: C 46.60, H 4.05, N 9.79, Cu 11.18; ^{1}H NMR (400 MHz, CD_3CN, 25 °C, TMS): δ = 2.48 (s, 6H; CH_3), 2.65 (s, 12H; py-CH_3), 3.45 (s, 4H, CH_2), 7.03 (d, ^3J(H,H) = 7.6 Hz, 2H; py′-5), 7.30 (d, ^3J(H,H) = 7.6 Hz, 4H; py-5), 7.54 (br, 2H; py′-3), 7.65 (br, 4H; py-3), 7.68 (t, ^3J(H,H) = 7.6 Hz, 2H; py′-4), 7.79 ppm (t, ^3J(H,H) = 7.6 Hz, 4H; py-4); IR (KBr disk): $\tilde{\nu}$ = 1590, 1565, 1450 (py ring), 840 cm^{-1} (PF_6); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 257 (15000), 269 (16000), 340 nm (2800 $M^{-1}cm^{-1}$); FAB MS: *m*/*z*: 957 $[M-PF_6]^+$, 749 $[M-2PF_6-2MeCN+H_2O]^+$, 731 $[M-2PF_6-2MeCN]^+$, 667 $[M-2PF_6-2MeCN-Cu]^+$. **2**-$(CF_3SO_3)_2$ and **2**-$(ClO_4)_2$ were obtained by the same method as **2**-$(PF_6)_2$, by using $[Cu(MeCN)_4](CF_3SO_3)$ and $[Cu(MeCN)_4](ClO_4)$, respectively, in place of $[Cu(MeCN)_4](PF_6)$.

3-$(PF_6)_2$ was obtained from **2**·$(PF_6)_2$ as described in the text. Elemental analysis (%) calcd for $C_{40}H_{40}N_6O_2P_2F_{12}Cu_2$: C 45.62, H 3.83, N 7.99, Cu 11.96; found: C 45.35, H 3.79, N 7.78, Cu 11.95; ^{1}H NMR (400 MHz, $(CD_3)_2CO$, −30 °C, TMS): δ = 2.95 (s, 6H; $C_{bridgehead}$–CH_3), 3.24 (s, 12H; py-CH_3), 4.42 (bs, 4H; CH_2), 7.67 (d, ^3J(H,H) = 7.3 Hz, 4H; py-5), 7.84 (d, ^3J(H,H) = 7.3 Hz, 2H; py′-5), 8.13–8.32 ppm (m, 12H; py-3,4, py′-3,4); Resonance Raman (Me_2CO, 25 °C): 765 (^{16}O–^{16}O), 724 cm^{-1} (^{18}O–^{18}O); UV/Vis (CH_2Cl_2, 0 °C): λ_{max} (ε) = 366 (24000), 537 nm (2100 $M^{-1}cm^{-1}$); ESI MS (CH_2Cl_2, 25 °C): *m*/*z*: 909 $\{[Cu_2O_2(L2)](PF_6)\}^+$. ESR: silent in CH_2Cl_2 at 77 K.

4-$(PF_6)_2$: Ligand L2 (120.8 mg, 0.20 mmol) was dissolved in CH_2Cl_2 (10 mL) and $[Cu(MeCN)_4](PF_6)$ (149.0 mg, 0.40 mmol) was added under CO. The mixture was stirred for 2 h at 0 °C under CO. On addition of Et_2O (30 mL), a colorless solid precipitated, which was purified by recrystallization from CH_2Cl_2/Et_2O under CO. Yield: 157 mg (73 %). Elemental analysis (%) calcd for $C_{42}H_{40}N_6O_2P_2F_{12}Cu_2 \cdot 2\,H_2O \cdot 2\,CH_2Cl_2$: C 41.17, H 3.77, N 6.55, Cu 9.9; found: C 41.08, H 3.48, N 6.65, Cu 10.13; ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C, TMS): δ = 2.63 (s, 6H; CH_3), 2.74 (s, 12H; py-CH_3), 3.58 (s, 4H; CH_2), 6.91 (d, ^3J(H,H) = 7.3 Hz, 2H; py′-5), 7.32 (d, ^3J(H,H) = 7.3 Hz, 4H; py-5), 7.71–7.80 ppm (m, 12H; py-3,4, py′-3,4); IR (KBr disk): $\tilde{\nu}$ = 2083 (CO), 1601, 1570, 1466 (py ring), 833 cm^{-1} (PF_6); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 269 nm (30000 $M^{-1}cm^{-1}$); FAB MS: *m*/*z*: 731 $[M-2PF_6-2CO]^+$.

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Keywords: copper · N ligands · O–O activation · peroxo ligands · protein models

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[5] X-ray crystallography on **2** was carried out on a Rigaku Mercury CCD area detector. **2**-$(CF_3SO_3)_2$: $C_{46}H_{46}N_8O_6S_2F_6Cu_2$, $M_r = 1112.12$, colorless crystal, $0.10 \times 0.20 \times 0.45$ mm, triclinic, $P\bar{1}$, $a = 8.180(4)$, $b = 12.194(6)$, $c = 13.149(6)$ Å, $\alpha = 79.153(10)$, $\beta = 81.245(13)$, $\gamma = 89.47(1)°$, $V = 1272.8(11)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.451$ g cm^{-}; $2\theta_{max} = 55.0°$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å), $T = -50\,°C$, 10440 independent reflections, of which 3475 were used, $R = 0.080$ ($I > 3.00\sigma(I)$), $R_w = 0.102$, GOF = 1.294; $\mu = 9.93$ cm^{-1}; full-matrix, least-squares methods on *F*.

[6] X-ray crystallography on **3** was carried out on a Rigaku RAXIS-IV imaging plate diffractometer. A total of 60 (180.00°) oscillation images were collected, each exposed for 22.0 min. **3**-$(PF_6)_2 \cdot 7\,CH_2Cl_2 \cdot 1.5\,C_6H_5CH_3$: $C_{48.75}H_{53}N_6O_2P_2F_{12}Cu_2Cl_7$, $M_r = 1420.19$, dark violet crystal, $0.25 \times 0.20 \times 0.10$ mm, triclinic, $P\bar{1}$, $a = 19.057(4)$, $b = 21.040(3)$, $c = 14.856(2)$ Å, $\alpha = 93.377(6)$, $\beta = 102.387(6)$, $\gamma = 93.30(1)°$, $V = 5792(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.628$ g cm^{-3}; $2\theta_{max} = 51.8°$, $Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å), $T = -120\,°C$, 16943 independent reflections, of which 13735 were used, $R = 0.057$ ($I > 3.00\sigma(I)$), $R_w = 0.096$, GOF = 1.67; $\mu = 11.95$ cm^{-1}; full-matrix, least-squares methods on *F*.

[7] CCDC-218413 (**2**) and CCDC-218414 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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