

Supporting information

Oxidation-induced control of self-assembly using a bis-dipyrromethyl substituted phenanthroline building block

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General methods: All solvents were of reagent grade quality and purchased commercially. 2,3-Dichloro-5,6-dicyano quinone (DDQ) was purchased from Aldrich and used without further purification. Phenanthroline-2,9-dicarbaldehyde¹ and 3,4-dimethyl-5-ethyloxycarbonylpyrrole² were prepared as reported previously. NMR spectra were recorded on a Varian Mercury 400 instrument. The NMR spectra were referenced to solvent and the spectroscopic solvents were purchased from Cambridge Isotope Laboratories. Chemical ionization (CI) and electro spray ionization (ESI) mass spectra were recorded on a VG ZAB-2E and a VG AutoSpec apparatus, respectively. TLC analyses were carried out using Sorbent Technologies neutral alumina (200 μm) sheets.

Bis-2,9-[di-(3,4-dimethyl-5-ethyloxycarbonyl-2-pyrrolyl)-methyl]-phenanthroline (1): Under an argon atmosphere phenanthroline-2,9-dicarbaldehyde (82 mg, 0.34 mmol) and 3,4-dimethyl-5-ethyloxycarbonylpyrrole (224 mg, 1.30 mmol) in 20 mL acetonitrile were heated to reflux for 2 h in the presence of 3 drops of concentrated hydrochloric acid. After cooling to room temperature, the volume was reduced to 5 mL, the precipitate was filtered off and washed with 3 \times 3 mL acetonitrile. The product was purified by flash column chromatography over neutral alumina, using a 9:1 mixture of dichloromethane and methanol as the eluent. Removal of the solvents yielded 158 mg (56 %) of **1** as a pale yellow powder. ¹H NMR (400 MHz, CDCl₃): δ 1.17 (t, J = 7.2 Hz, 12 H, OCH₂CH₃), 1.95 (s, 12 H, CH₃), 2.27 (s, 12 H, CH₃), 3.97 (m, 4 H, OCH₂CH₃), 4.10 (m, 4 H, OCH₂CH₃), 5.80 (s, 2 H, CH), 6.93 (s, 2 H, phen-H), 7.33 (d, J = 8.4 Hz, 2 H, phen-H), 7.83 (d, J = 8.4 Hz, 2 H, phen-H), 11.43 (br s, 4 H, NH); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 8.99, 10.62, 14.22, 41.29, 59.47, 116.75, 117.75, 123.99, 125.62, 126.37, 127.12, 132.14, 137.25, 143.75, 159.83, 161.57; MS(CI⁺): m/z calcd for C₅₀H₅₇N₆O₈, [M+H]⁺, 869.4; found 869.4. Crystals of **1** suitable for X-ray diffraction analysis were grown as colorless needles from chloroform solution via evaporations at room temperature.

Bis-2,9-[di-(3,4-dimethyl-5-ethyloxycarbonyl-2-pyrrolyl)-hydroxymethyl]-phenanthroline

(2): DDQ 65 mg (290 μmol) was added to **1** (50 mg, 58 μmol) in 30 mL of dichloromethane and the dark red mixture was stirred at room temperature for 15 min. The mixture was washed with 10 mL of a saturated aqueous sodium bicarbonate solution and the organic phase was dried over sodium sulfate. The solvent was evaporated off, and the product was purified by column chromatography over neutral alumina, using 0.3 % methanol in dichloromethane as the eluent. Evaporation of the solvent yielded 18 mg (34 %) of **2** as a colorless solid. ^1H NMR (400 MHz, CDCl_3): δ 1.37 (t, $J = 7.2$ Hz, 12 H, OCH_2CH_3), 1.56 (s, 12 H, CH_3), 2.21 (s, 12 H, CH_3), 4.22 (m, 8 H, OCH_2CH_3), 6.25 (s, 2 H, OH), 7.21 (d, $J = 8.4$ Hz, 2 H, phen-H), 7.84 (s, 2 H, phen-H), 8.23 (d, $J = 8.4$ Hz, 2 H, phen-H); $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl_3): δ 8.63, 10.45, 14.44, 29.71, 59.98, 71.63, 116.50, 122.24, 126.46, 127.59, 127.90, 134.22, 137.99, 144.55, 162.47, 163.31; MS(ESI+): m/z calcd for $\text{C}_{50}\text{H}_{57}\text{N}_6\text{O}_{10}$, $[\text{M}+\text{H}]^+$, 901.4; found 901.4. Crystals of **2** suitable for an X-ray diffraction analysis were grown as colorless needles by slow diffusion of *n*-pentane into a saturated solution of the molecule in dichloromethane.

X-ray diffraction analysis of 1·CHCl₃

X-ray Experimental for C₅₀H₅₆N₆O₈·CHCl₃: Crystals grew as pale yellow prisms by slow evaporation from chloroform. The data crystal was cut from a larger crystal and had approximate dimensions; 0.35 x 0.32 x 0.11 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoK α radiation ($\lambda = 0.71073\text{\AA}$). A total of 434X frames of data were collected using ω -scans with a scan range of 1.5° and a counting time of 126 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S1. Data reduction were performed using DENZO-SMN.³ The structure was solved by direct methods using SIR97⁴ and refined by full-matrix least-squares on F² with anisotropic displacement parameters for the non-H atoms using SHELXL-97.⁵ The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms on nitrogen were observed in a ΔF map and refined with isotropic displacement parameters. The function, $\sum w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.091*P)^2 + (3.3455*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. R_w(F²) refined to 0.206, with R(F) equal to 0.0748 and a goodness of fit, S, = 1.03. Definitions used for calculating R(F), R_w(F²) and the goodness of fit, S, are given below.⁶ The data were corrected for secondary extinction effects. The correction takes the form: $F_{\text{corr}} = kF_c/[1 + (1.3(3)\times 10^{-6}) * F_c^2 \lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁷ All figures were generated using SHELXTL/PC.⁸ A list of observed and calculated structure factors are located in table S1.

Table S1. Crystal data and structure refinement for **1**·CHCl₃.

Empirical formula	C ₅₁ H ₅₇ Cl ₃ N ₆ O ₈	
Formula weight	988.38	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 17.4821(2) Å	α = 97.040(1)°.
	b = 17.7345(2) Å	β = 109.612(1)°.
	c = 17.8705(3) Å	γ = 102.223(1)°.
Volume	4986.68(12) Å ³	
Z	4	
Density (calculated)	1.316 Mg/m ³	
Absorption coefficient	0.243 mm ⁻¹	
F(000)	2080	
Crystal size	0.35 x 0.32 x 0.11 mm	
Theta range for data collection	1.80 to 27.52°.	
Index ranges	-22 ≤ h ≤ 22, -23 ≤ k ≤ 22, -23 ≤ l ≤ 23	
Reflections collected	36894	
Independent reflections	22761 [R(int) = 0.0385]	
Completeness to theta = 27.52°	99.1 %	
Absorption correction	None	
Refinement method	Full-matrix-block least-squares on F ²	
Data / restraints / parameters	22761 / 31 / 1290	
Goodness-of-fit on F ²	1.033	
Final R indices [I > 2σ(I)]	R1 = 0.0748, wR2 = 0.1805	
R indices (all data)	R1 = 0.1561, wR2 = 0.2165	
Extinction coefficient	1.3(3) × 10 ⁻⁶	
Largest diff. peak and hole	0.868 and -0.837 e.Å ⁻³	

Figure S1. View of the molecule 1 in 1 showing the atom labeling scheme. Displacement ellipsoids are scaled to the 30% probability level. Most hydrogen atoms have been removed for clarity. Dashed lines are indicative of H-bonding interactions. The geometry of these interactions is listed in Table S2.

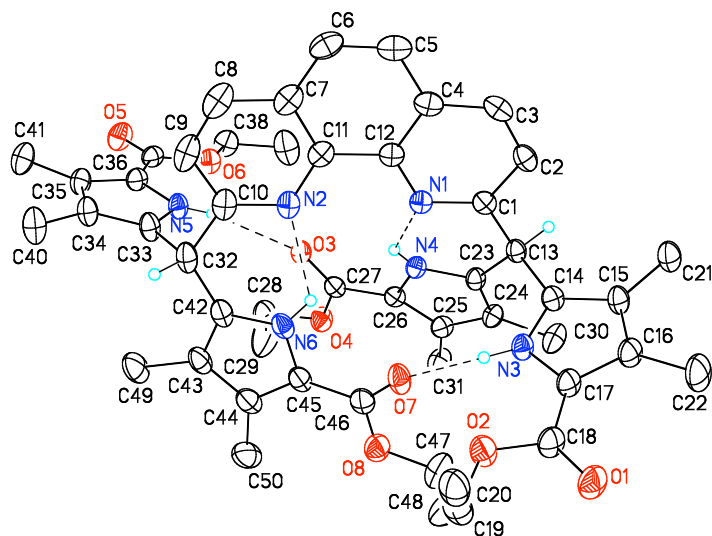


Figure S2. View of the molecule 2 in 1 showing the atom labeling scheme. Displacement ellipsoids are scaled to the 30% probability level. Most hydrogen atoms have been removed for clarity. Dashed lines are indicative of H-bonding interactions. The geometry of these interactions is listed in Table S2.

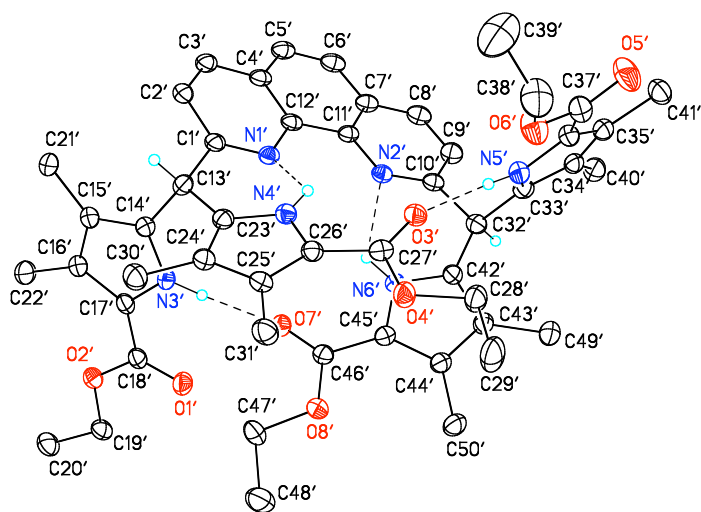


Figure S3. Unit cell packing diagram for **1**·CHCl₃. The view is approximately down the **b** axis. Molecules **1** are shown in wireframe form in the middle of the cell. Molecules **2** are in ball-and-stick format.

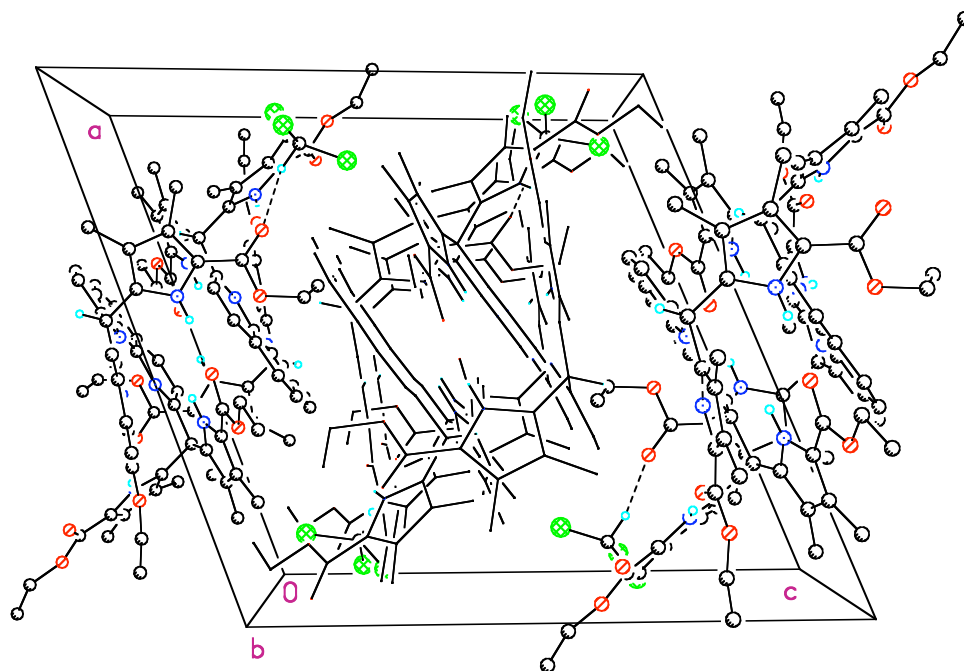


Table S2. Hydrogen bonds for **1**. [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N3'-H3'N...O7'	0.79(3)	2.06(3)	2.849(4)	175(3)
N4'-H4'N...N1'	0.87(4)	2.16(4)	2.748(4)	125(3)
N5'-H5'N...O3'	0.86(4)	2.04(4)	2.900(4)	174(3)
N6'-H6'N...N2'	0.79(3)	2.16(3)	2.756(4)	132(3)
N3-H3N...O7	0.83(4)	1.95(4)	2.777(4)	169(4)
N4-H4N...N1	0.78(4)	2.13(4)	2.672(4)	126(4)
N5-H5N...O3	0.80(3)	2.22(4)	3.001(4)	165(3)
N6-H6N...N2	0.91(4)	2.12(4)	2.729(5)	123(3)
C1A-H1AA...O1	1.00	2.11	3.058(4)	157.6
C1B-H1BA...O5'	1.00	2.20	3.099(6)	149.3

X-ray diffraction analysis of $2 \cdot C_5H_{12} \cdot CH_2Cl_2$

X-ray Experimental for $C_{50}H_{56}N_6O_{10} \cdot C_5H_{12} \cdot CH_2Cl_2$: Crystals grew as colorless lathes by vapor diffusion of pentane into a dichloromethane solution of **2**. The data crystal was cut from a long lathe and had approximate dimensions; 0.27 x 0.14 x 0.10 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). A total of 258 frames of data were collected using ω -scans with a scan range of 1.9° and a counting time of 218 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S3. Data reduction were performed using DENZO-SMN.³ The structure was solved by direct methods using SIR97⁴ and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.⁵ Most hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to $1.2xU_{eq}$ of the attached atom ($1.5xU_{eq}$ for methyl hydrogen atoms). The hydroxyl group hydrogen atoms were observed in a ΔF map and refined with isotropic displacement parameters. One of the ethyl groups, C14 and C15, were found to be disordered about two orientations. The site occupancy factors for one orientation was assigned the variable x , while the site occupancy factors for the second orientation was assigned to $(1-x)$. The geometry of the group was restrained to be equivalent throughout the refinement. A common isotropic displacement parameter was refined for the affected atoms. In this way, the site occupancy for the major component of the disordered group, atoms C14 and C15, had site occupancies of 67(2)%, while the minor component given by C14a and C15a had site occupancies of 33(2)%. The function, $\sum w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.055*P)^2 + (2.752*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.167, with $R(F)$ equal to 0.0633 and a goodness of fit, S , = 1.02. Definitions used for calculating $R(F)$, $R_w(F^2)$ and the goodness of fit, S , are given below.⁶ The data were corrected for secondary extinction effects. The correction takes the form: $F_{corr} = kF_c/[1 + (4.5(6) \times 10^{-6}) * F_c^2 \lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁷ All figures were generated using SHELXTL/PC.⁸ A list of observed and calculated structure factors are located in table S3.

Table S3. Crystal data and structure refinement for $2 \cdot C_5H_{12} \cdot CH_2Cl_2$.

Empirical formula	C ₅₆ H ₇₀ Cl ₂ N ₆ O ₁₀	
Formula weight	1058.08	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.0307(2) Å	α = 99.633(2)°.
	b = 15.0724(3) Å	β = 99.191(2)°.
	c = 18.4602(4) Å	γ = 111.289(2)°.
Volume	2737.00(9) Å ³	
Z	2	
Density (calculated)	1.284 Mg/m ³	
Absorption coefficient	0.182 mm ⁻¹	
F(000)	1124	
Crystal size	0.27 x 0.14 x 0.10 mm	
Theta range for data collection	1.99 to 27.50°.	
Index ranges	-14 ≤ h ≤ 14, -19 ≤ k ≤ 19, -23 ≤ l ≤ 23	
Reflections collected	22637	
Independent reflections	12451 [R(int) = 0.0383]	
Completeness to theta = 27.50°	99.0 %	
Absorption correction	None	
Refinement method	Full-matrix-block least-squares on F ²	
Data / restraints / parameters	12451 / 3 / 708	
Goodness-of-fit on F ²	1.017	
Final R indices [I > 2σ(I)]	R1 = 0.0633, wR2 = 0.1407	
R indices (all data)	R1 = 0.1164, wR2 = 0.1671	
Extinction coefficient	4.5(6) × 10 ⁻⁶	
Largest diff. peak and hole	0.791 and -0.798 e.Å ⁻³	

Figure S4. View of **2** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. Most hydrogen atoms have been removed for clarity. H-bonding interactions are shown as dashed lines. The geometry of these interactions is listed in Table S4.

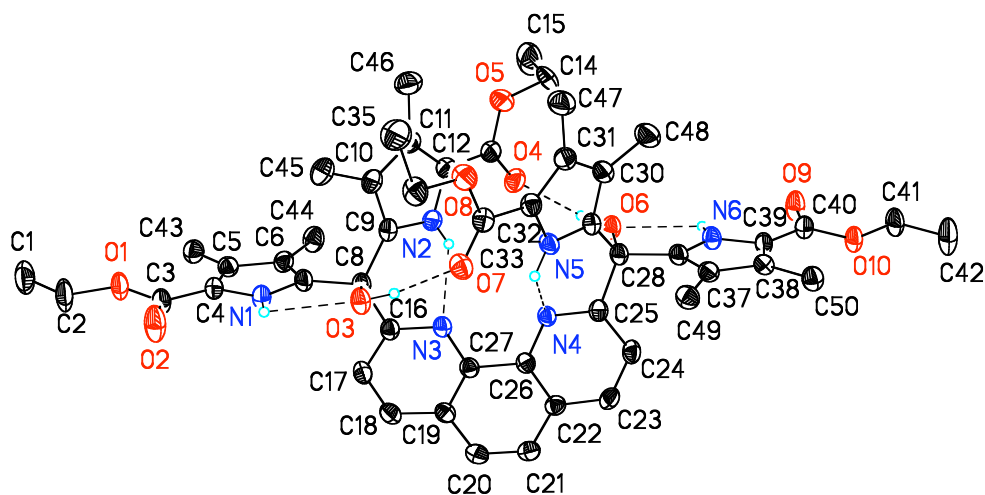


Figure S5. Unit cell packing diagram for **2**. The view is approximately down the *c* axis. H-bonding interactions are shown as dashed lines. The geometry of these interactions is listed in Table S4.

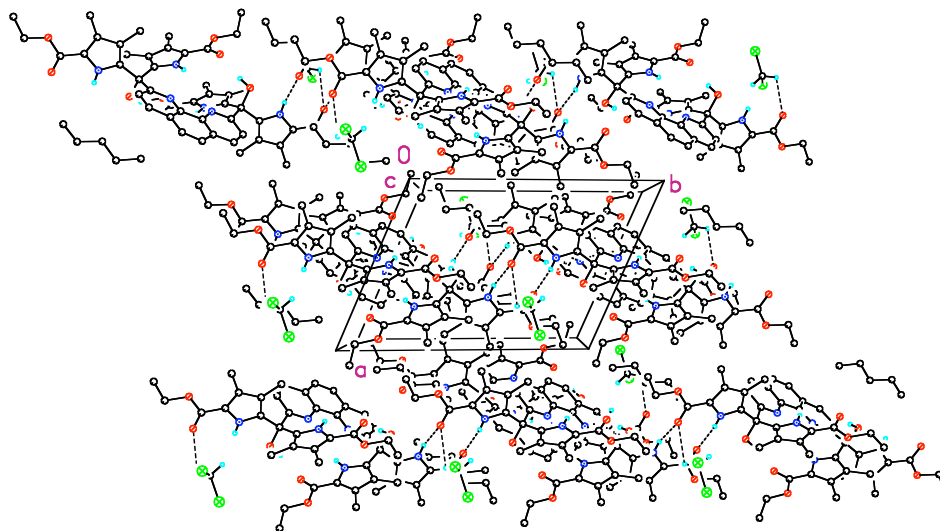


Table S4. Hydrogen bonds for **2** [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N1-H1N...O9#1	0.88	2.15	3.010(3)	164.3
N2-H2N...N3	0.88	2.19	2.709(3)	117.0
N5-H5N...N4	0.88	2.14	2.688(3)	119.8
N6-H6N...O2#2	0.88	2.19	3.067(3)	171.6
O3-H3O...O7	0.86(3)	1.98(3)	2.822(2)	163(3)
O6-H6O...O4	0.85(3)	1.95(3)	2.793(2)	172(3)
C1A-H1AA...O9	0.99	2.67	3.174(4)	111.8
C1A-H1AB...O2#2	0.99	2.84	3.279(4)	107.8

Symmetry transformations used to generate equivalent atoms:

#1 $x, y+1, z$ #2 $x, y-1, z$

References for Supporting Information

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4. SIR97. A program for crystal structure solution. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115-119.
5. G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures. University of Goettingen, Germany, 1994.
6. $R_w(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^4)\}^{1/2}$ where w is the weight given each reflection.
 $R(F) = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$ for reflections with $F_o > 4(\sigma(F_o))$.
 $S = [\sum w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.
7. International Tables for X-ray Crystallography Vol. C, 1992, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson (Ed.), Boston, Kluwer Academic Press.
8. G. M. Sheldrick, SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA, 1994.