A Tetranuclear Mixed-Valent $\mathrm{Mn}^{\mathrm{II}}_3\mathrm{Mn}^{\mathrm{IV}}$ Compound with a (μ_4-O)Mn_4 Core[**]

Tereza Afrati, Catherine Dendrinou-Samara,
Catherine P. Raptopoulou, Aris Terzis,
Vassilis Tangoulis,* and Dimitris P. Kessissoglou*

It has become accepted that the water-oxidation catalytic site in the oxygen-evolving complex (OEC) contains four manganese ions that are bridged together by water-derived ligands O^{2-} and OH^-. The crystal structure of OEC confirmed the presence of four manganese atoms, yet a clear image of the manganese cluster still eludes us.[1] Thus, the question whether the natural model acts as a tetranuclear or 1:3 or 2:2 cluster still remains. Working on the 1:3 model we have published some mononuclear and mixed-valent trinuclear manganese compounds.[2–4] Tetranuclear mixed-valent manganese complexes as potential models for the OEC of photosystem II (PSII) have also been reported.[5–30] Most of them also exhibit interesting magnetic behavior as a result of the ground-state spin frustration that is typical for this type of compound.[6, 7] Christou and co-workers[6, 7] and Brudvig, Crabtree, and co-workers.[12, 13] have shown that, under appropriate conditions, monofunctional carboxylato ligands support the formation of the so-called butterfly type tetranuclear clusters. However, these and other carboxylato systems are labile and tend to aggregate further. Higher-nuclearity oxo-carboxylate species with 6, 9, 10, and 12 manganese atoms have been structurally characterized.[15, 16] To date, the lowest-valence tetranuclear clusters, with an average Mn oxidation state of 2.5+ and a II,III,II,III formulation, reported are $[\mathrm{Mn_4O(AcO)_2(H_2O)_2(tphpn)_2}]^{4+}$ (tphpn = $[(o\text{-py})\text{-}\mathrm{CH_2}]_2\mathrm{NCH_2CH(O^-)CH_2N[CH_2}(o\text{-py})]_2$; py = pyridine) with a linear (μ-O)$\mathrm{Mn_2}$ bridging moiety and $[\mathrm{Mn_4O_2(Ph_3\text{-}COO)_6)_2(OEt_2)_2}]$ with a (μ_3-O)Mn bridging moiety.[18, 20] The next lowest average Mn oxidation state of 2.75+ is found in $[\mathrm{Mn^{II}Mn^{III}_3}]$ species such as $[\mathrm{Mn_4O_2(X\text{-}PhCOO)_7(bpy)_2}]$ (X = Cl, Br, bpy = 2,2′bipyridine)[21] with a (μ_3-O)$\mathrm{Mn_3}$ bridging group and the $[\mathrm{Mn^{II}_2Mn^{III}Mn^{IV}}]$ core of the $[\mathrm{Mn_4O_2(H_2O)_2(CF_3SO_3)_2(tphpn)_2}]^{3+}$ ion with a (μ-O)$\mathrm{Mn_2}$ bridging unit.[19] The average Mn oxidation state 3.0+ is only found in the $[\mathrm{Mn^{III}_4}]$ formulation. Typical examples of this structure are $[\mathrm{Mn_4O_2(MeCOO)_6(py)_2(dbm)_2}]$[22] (dbm = dibenzoylmethane) and $(\mathrm{NBu_4})[\mathrm{Mn_4O_2(X\text{-}PhCOO)_9(H_2O)}]$[23] with a ($\mu$-O)$\mathrm{Mn_2}$ bridging group. The average Mn oxidation states 3.25+ and 3.50+ are considered the most in favor of the S_1 state of the OEC and the formulations reported to date are $[\mathrm{Mn^{IV}Mn^{III}_3}]$ and $[\mathrm{Mn^{III}_2Mn^{IV}_2}]$. The compounds $(\mathrm{H_2Im})_2[\mathrm{Mn_4O_3Cl_6(MeCOO)_6(HIm)}]$, $[\mathrm{Mn_4O_3Cl_4\text{-}(MeCOO)_3(py)_3}]$, and $[\mathrm{Mn_4O_3Cl(MeCOO)_3(dbm)_3}]$ (HIm = imidazolium) which have a distorted cubane $[\mathrm{Mn_4O_3Cl}]$ core with a (μ_3-O)$\mathrm{Mn_3}$ bridging group[22, 24, 25] represent the former formulation while the $[(\mathrm{Mn_2O_2})_2(\mathrm{tphpn})_2]^{4+}$ ion with a (μ-O)$\mathrm{Mn_2}$ bridging unit[17, 26, 27] is an example of the latter. Average Mn oxidation states 3.75+ with a $[\mathrm{Mn^{III}Mn^{IV}_3}]$ formulation, the most favorable for the S_2 state, and 4.00+ for $[\mathrm{Mn^{IV}_4}]$ have been reported for the $[\mathrm{Mn_4O_6(bpy)_6}]^{3+}$ and $[\mathrm{Mn_4O_6(bpy)_6}]^{4+}$ ions, respectively.[28]

Herein the first example of a tetranuclear cluster $[\mathrm{Mn^{II}_3Mn^{IV}(O)(pko)_4(3,4\text{-}D)_4}]\cdot 2.5\,\mathrm{CH_3OH}$ (pko = di(2-pyridyl)ketonoxime, 3,4-D = 3,4-dichlorophenoxy acetic acid) containing a (μ_4-O)$\mathrm{Mn_4}$ bridging moiety is presented. The most interesting features of this compound are: 1) it is the only example of a manganese tetranuclear cluster with a $2e^-$ difference between the oxidation states of the metal ions and 2) it is the first example of a manganese tetranuclear cluster with four metal centers interacting through a μ_4-O bridging atom.

The central $[\mathrm{Mn_4}(\mu_4\text{-O})]^{8+}$ core is best described as a distorted $\mathrm{Mn_4}$ tetrahedron with the $\mathrm{Mn^{IV}}$ ion Mn1 and the $\mathrm{Mn^{II}}$ ions Mn2, Mn3, Mn4 in octahedral environments (Figure 1). A μ_4-O atom bridges the four manganese ions. The four ketonoximato N–O groups link the $\mathrm{Mn^{IV}}$ ion with the three $\mathrm{Mn^{II}}$ ions, while each $\mathrm{Mn^{II}}$ ion is bridged with the other two $\mathrm{Mn^{II}}$ ions through carboxylato bridges. The Mn ⋯ Mn separations fall in the range of 3.185 – 3.607 Å with the shortest one being between $\mathrm{Mn^{II}}$ ions Mn2 and Mn4, which are bridged by a unidentate, double bound carboxylato ligand and a bidentate chelate carboxylato ligand, and the

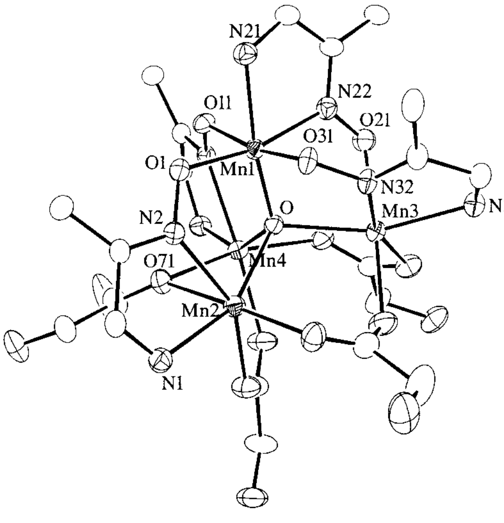

Figure 1. An ORTEP diagram of **1** with thermal ellipsoids set at 30% probability, showing the coordination environment of the tetranuclear cluster.

---

[*] Prof. D. P. Kessissoglou, T. Afrati, Dr. C. Dendrinou-Samara
Department of General and Inorganic Chemistry
Aristotle University of Thessaloniki
Thessaloniki 54124 (Greece)
Fax: (+30) 310997738
E-mail: kessisog@chem.auth.gr

Dr. V. Tangoulis
Department of Materials Science
University of Patras
Patras 26500 (Greece)
Fax: (+30) 610996358
E-mail: vtango@upatras.gr

Dr. C. P. Raptopoulou, Dr. A. Terzis
NCSR "Demokritos", Institute of Materials Science
15310 Aghia Paraskevi Attikis (Greece)

[**] This work was carried out in the frame of WG0010 of D21 COST action. The authors thank Prof. V. L. Pecoraro for his valuable suggestions. V.T. thanks Dr. Claudio Sangregorio and the Department of Chemistry, Florence, Italy for taking the magnetic measurements.

longest one being between the Mn^{II} ions Mn2 and Mn3, which are bridged only by a bidentate chelate carboxylato ligand. For the $Mn^{IV}\cdots Mn^{II}$ separations the shortest (3.259 Å) is between Mn1 and Mn3 which are bridged by two ketonoximato moieties (Table 1). The angles around the $(\mu_4\text{-O})Mn_4$ center vary from 94.2(1) to 120.1(2)° consistent with a distorted tetrahedral geometry and an O^{2-} ion rather than a square-pyramidal geometry which is expected for a μ_4-OH group and for which the Mn atoms should have a square-planar arrangement. All the Mn centers have distorted octahedral coordination environments. The coordination sphere of the Mn^{IV} ion (Mn1), comprises four O atoms, three of which are from the ketonoximato ligands and the fourth from the μ_4-O^{2-} ion, and two N atoms, one from the ketonoximato moiety and the second is a pyridyl nitrogen. Two of the Mn^{II} ions, (Mn2 and Mn4, have $Mn(N_{ketonoximato})(N_{pyridyl})(O_{chelate\text{-}carboxylato})_2(O_{unidentate\text{-}carboxylato})(\mu_4\text{-O})$ coordination spheres, whereas for the third Mn^{II} ion (Mn3), the unidentate carboxylato oxygen is replaced by a ketonoximato oxygen atom. Considering the oxidation states of the manganese atoms, the three of them, Mn2, Mn3, and Mn4, can be easily assigned as Mn^{II}, based on the lengths of the Mn–O bonds which fall in the range of 2.11–2.36 Å, while the bonds around Mn1 of 1.800(4)–2.083(5) Å and the lack of a Jahn–Teller distortion along any of the three axes support an Mn^{IV} oxidation state. Further support for the oxidation state of the Mn1 ion is the tetrahedral coordination environment of the μ_4-O atom (with this geometry the charge balance of the cluster is only satisfied with an Mn(IV) oxidation state). To elucidate more clearly whether the oxidation state of the Mn1 ion is Mn^{IV} or Mn^{III} we have to examine closer the coordination environment of Mn1. This center has a distorted octahedral geometry with a very short Mn1–O bond 1.80 Å and the longest bond is along the same axis to the opposite apex Mn1–N21 2.083 Å. The sum of the axial bonds O-Mn1-N21 3.883 Å, O1-Mn1-N22 3.935 Å, and O11-Mn1-O31 3.815 Å does not suggest any bond elongation or depression along any axis. The presence of the Mn–O bond of 1.8 Å could suggests an $Mn{=}O^{-}$ moiety, but this is unlikely and is not supported by the IR data which do not show the anticipated strong bands at about 1000 and/or 750 cm^{-1} proposed by Groves and Stern.[31] To elucidate the bonding situation further we have synthesized the compound $[Zn_4(OH)_2(pko)_4Cl_2]$ that has a metallacrown structure with zinc ions interacting through OH groups.[32] The IR patterns of Mn and Zn clusters in the range 1000–650 cm^{-1} are almost identical, not showing any additional band which could be assigned to an Mn=O bond.

Table 1. Selected interatomic distances [Å] and angles [°] of **1**.

	Distances [Å]		Distances [Å]
$Mn1\cdots Mn2$	3.351	$Mn2\cdots Mn3$	3.607
$Mn1\cdots Mn3$	3.259	$Mn2\cdots Mn4$	3.185
$Mn1\cdots Mn4$	3.471	$Mn3\cdots Mn4$	3.522
Angles [°]		Angles [°]	
Mn1-O-Mn2	115.9(2)	Mn2-O-Mn4	94.33(13)
Mn1-O-Mn3	108.1(2)	Mn3-O-Mn4	105.98(14)
Mn1-O-Mn4	120.1(2)	Mn4-O71-Mn2	88.53(13)
Mn2-O-Mn3	111.64(14)		

Additional support to the oxidation state of Mn1 as Mn^{IV} is based on variable-temperature magnetic measurements. The temperature dependence of χT of $Mn^{IV}Mn^{II}_3$ in a field of 0.1 T is shown in Figure 2. At room temperature χT is 11.3 $cm^3mol^{-1}K$, smaller than expected for three uncoupled $S = 5/2$ and one $S = 3/2$ spins (15 $cm^3mol^{-1}K$) and steadily increases with decreasing temperature, reaching a maximum of $\chi T = 18.86$ $cm^3mol^{-1}K$, at about 4.5 K. Below this point, it rapidly decreases with decreasing temperature, reaching 18 $cm^3mol^{-1}K$ at around 2 K, possibly a result of zero-field effects. To define the exchange interactions[*] the exchange model in Equation (1) was used which is shown in Figure 3 based on crystallographic criteria.

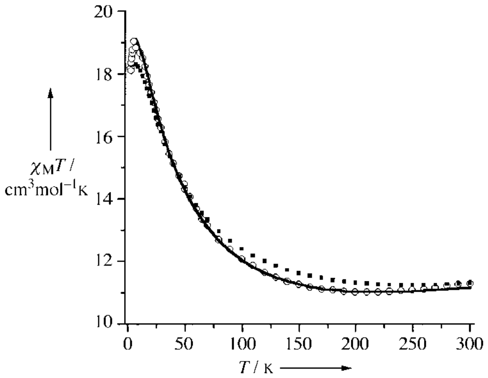

Figure 2. Temperature-dependence of the susceptibility data for $\chi_M T$ of **1** at 0.1 T. ○ is the measured data, —— is the best fit according to Equation (2), ■ is the best fit according to the $Mn^{III}Mn^{II}_3$ model [Eq (3)].

$$\mathcal{H} = J_1S_2S_4 + J_2(S_1S_3 + S_1S_2) + J_3(S_1S_4) \qquad (1)$$

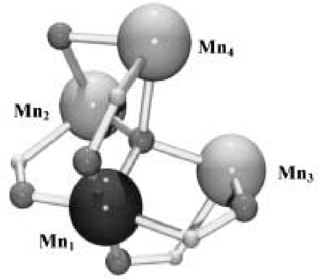

Figure 3. The graphical exchange model according to crystallographic criteria.

The S_2–S_4 exchange interaction is expected to be ferromagnetic while the other two are expected to be antiferromagnetic. To define the valence of the Mn1 (two possibilities exist: Mn^{III} or Mn^{IV}) we used the same magnetic model in the

---

[*] Because of the valence complexity of the complex, various magnetic models were used with more exchange interactions. Even if we take into consideration the interaction S_3–S_4 and S_2–S_3 the fit does not improve while the energy spectrum remains the same with ground state $S = 6$.

two hypothetical cases where the $S_1 = 2$ or $S_1 = 3/2$, respectively, and in the temperature range 5–300 K [Eq. (2) and (3)].

$$\mathrm{Mn^{IV}Mn_3^{II}} \rightarrow J_1 = -4.15\ \mathrm{cm^{-1}}, J_2 = 48.4\ \mathrm{cm^{-1}}, J_3 = 1.33\ \mathrm{cm^{-1}}, g = 1.95 \tag{2}$$

$$\mathrm{Mn^{III}Mn_3^{II}} \rightarrow J_1 = -5.0\ \mathrm{cm^{-1}}, J_2 = 68.9\ \mathrm{cm^{-1}}, J_3 = 0.85\ \mathrm{cm^{-1}}, g = 2 \tag{3}$$

Both fits are superimposable in the low-temperature limit while after 100 K only the model in Equation (2) is closer to the data (Figure 2, solid line). According to the first model the ground state of the system is $S = 6$ while for the second is $S = 11/2$. To define the ground state of the system, magnetization measurements were carried out at two temperatures 2.5 and 4.5 K in the field range 0–6.5 T (Figure 4). The solid lines are the best fits using the Brillouin function for an $S = 6$ system ($g = 2$) with a small $D = 0.025\ \mathrm{cm^{-1}}$ (where D is the zero-field splitting term) while the second case was ruled out because of unrealistic g values. Therefore, the magnetic measurements provide strong evidence that model in Equation (2), that is for an $\mathrm{Mn^{IV}}$ center, is the most appropriate.

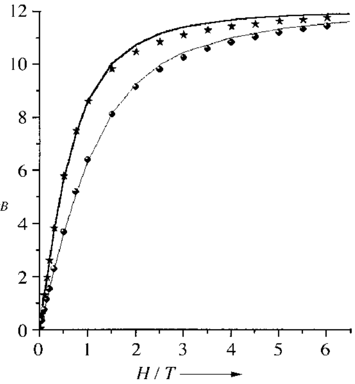

Figure 4. Magnetization measurements, in the reduced form of $M/N\mu_B$, in the field range 0–6.5 T at 2.5 K (solid stars) and 4.5 K (●). The solid lines represent the simulations according to a Brillouin function of a system with an $S = 6$ ground state and $D = 0.025\ \mathrm{cm^{-1}}$.

Experimental Section

The compound $[\mathrm{Mn^{II}Mn^{II}Mn^{II}Mn^{IV}(O)(pko)_4(3,4\text{-}D)_4]\cdot 2.5\,CH_3OH}$ was synthesized by adding the sodium salt of di(2-pyridyl)ketonoxime ligand (10 mmol) to a solution of $\mathrm{MnCl_2 \cdot 4\,H_2O}$ (10 mmol) in methanol (100 mL). The sodium salt of 3,4-D (10 mmol) dissolved in methanol (10 mL) was added. The resulting dark red-brown solution was reduced to a volume of 20 mL after 5 h of stirring. Red/black crystals suitable for X-ray diffraction studies[33] were obtained by slow evaporation. Yield 60%. Elemental analysis (%) calcd for $\mathrm{C_{78.50}H_{62}Cl_8Mn_4N_{12}O_{19.50}}$ (1988.76): C 47.36, H 3.11, N 8.44, Mn 11.06); found: C 47.60, H 3.45, N 8.05, Mn 10.80.

Received: January 14, 2002 [Z18518]

---

[1] A. Zouni, H.-T. Witt, J.; Kern, P. Fromme, N. Krauß, W. Saenger, P. Orth, *Nature* **2001**, *409*, 739.

[2] D. P. Kessissoglou, M. L. Kirk, M. S. Lah, X.-h. Li, C. A. Raptopoulou, W. E. Hatfield, V. L. Pecoraro, *Inorg. Chem.* **1992**, *31*, 5424.

[3] V. Tangoulis, D. A. Malamatari, K. Soulti, V. Stergiou, C. P. Raptopoulou, A. Terzis, T. A. Kabanos, D. P. Kessissoglou, *Inorg. Chem.* **1996**, *35*, 4974.

[4] V. Tangoulis, D. A. Malamatari, G. A. Spyroulias, C. P. Raptopoulou, A. Terzis, D. P. Kessissoglou, *Inorg. Chem.* **2000**, *39*, 2621.

[5] L. Que, Jr., A. E. True, *Prog. Inorg. Chem.* **1990**, *38*, 97.

[6] G. Christou, *Acc. Chem. Res.* **1989**, *22*, 328.

[7] A. R. Schake, E. A. Schmitt, A. J. Conti, W. E. Streib, J. C. Huffman, D. N. Hendrickson, G. Christou, *Inorg. Chem.* **1991**, *30*, 3192.

[8] K. Folting, J. C. Huffman, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1987**, *109*, 5703.

[9] R. D. Guiles, A. McDermott, V. K. Yachandra, J. L. Cole, S. L. Dexheimer, R. D. Britt, K. Wieghardt, U. Bossek, K. Sauer, M. P. Klein, *Biochemistry* **1990**, *29*, 471.

[10] K. Wieghardt, *Angew. Chem.* **1989**, *101*, 1179; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1153.

[11] R. Hotzelmann, K. Wieghardt, U. Florke, H.-J. Haupt, D. C. Weatherburn, J. Bonvoisin, G. Blondin, J.-J. Girerd, *J. Am. Chem. Soc.* **1992**, *114*, 1681.

[12] R. Manchanda, H. H. Thorp, G. W. Brudvig, R. H. Crabtree, *Inorg. Chem.* **1991**, *30*, 494.

[13] G. W. Brudvig, R. H. Crabtree, *Prog. Inorg. Chem.* **1989**, *37*, 99.

[14] J. B. Vincent, G. Christou, *Adv. Inorg. Chem.* **1989**, *33*, 197.

[15] D. Low, D. M. Eichorn, A. Draganescu, W. H. Armstrong, *Inorg. Chem.* **1991**, *30*, 877.

[16] K. S. Hagen, W. H. Armstrong, M. M. Olmstead, *J. Am. Chem. Soc.* **1989**, *111*, 774.

[17] M. K. Chan, W. H. Armstrong, *J. Am. Chem. Soc.* **1991**, *113*, 5055.

[18] M. K. Chan, W. H. Armstrong, *J. Am. Chem. Soc.* **1989**, *111*, 9121.

[19] M. K. Chan, W. H. Armstrong, *J. Am. Chem. Soc.* **1990**, *112*, 4985.

[20] R. J. Kulawiec, R. H. Crabtree, G. W. Brudvig, G. K. Schulte, *Inorg. Chem.* **1988**, *27*, 1309.

[21] B. Albela, M. S. E. Salah, J. Ribas, K. Folting, G. Christou, D. N. Hendrickson, *Inorg. Chem.* **2001**, *40*, 1037.

[22] S. Wang, J. C. Huffman, W. E. Streib, E. A. Schmitt, J. K. McCusker, D. N. Hendrickson, G. Christou, *Angew. Chem.* **1991**, *103*, 314; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 305.

[23] S. Wang, J. C. Huffman, K. Folting, W. E. Streib, E. B. Lobkovsky, G. Christou, *Angew. Chem.* **1991**, *103*, 1681; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1672.

[24] J. S. Bashkin, H.-R. Chang, W. E. Streib, J. C. Huffman, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* **1987**, *109*, 6502.

[25] D. N. Hendrickson, G. Christou, E. A. Schmitt, E. Libby, J. S. Bashkin, S. Wang, H.-L. Tsai, J. B. Vincent, P. D. W. Boyd, J. C. Huffman, K. Folting, Q. Li, W. E. Streib, *J. Am. Chem. Soc.* **1992**, *114*, 2455.

[26] D. W. Randall, B. E. Sturgeon, J. A. Ball, G. A. Lorigan, M. K. Chan, M. P. Klein, W. H. Armstrong, R. D. Britt, *J. Am. Chem. Soc.* **1995**, *117*, 11780.

[27] M. Zheng, G. C. Dismukes, *Inorg. Chem.* **1996**, *35*, 3307.

[28] G. Blondin, R. Davydov, C. Philouze, M.-F. Charlot, S. Styring, B. Akermark, J.-J. Girerd, A. Boussac, *J. Chem. Soc. Dalton Trans.* **1997**, 4069.

[29] W. F. Ruettinger, C. Campana and G. C. Dismukes, *J. Am Chem. Soc.* **1997**, *119*, 6670.

[30] C. Gedye, C. Harding, V. McKee, J. Nelson, J. Patterson, *J. Chem. Soc. Chem. Commun.* **1992**, 392.

[31] J. T. Groves, M. K. Stern, *J. Am. Chem. Soc.* **1988**, *110*, 8628.

[32] M. Alexiou, C. Dendrinou-Samara, C. P. Raptopoulou, A. Terzis, D. P. Kessissoglou, *Inorg. Chem.*, in press.

[33] Empirical formula: $\mathrm{C_{78.50}H_{62}Cl_8Mn_4N_{12}O_{19.50}}$; $M_r = 1988.76$, crystal system: triclinic, space group: $P\bar{1}$, $a = 16.856(9)$, $b = 18.103(9)$, $c = 15.091(9)$ Å, $\alpha = 98.82(2)$; $\beta = 93.27(2)$, $\gamma = 107.24(2)^\circ$, $V = 4320(1)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.529\ \mathrm{Mg\,m^{-3}}$, absorption coefficient = $0.894\ \mathrm{mm^{-1}}$, $F(000) = 2018$; crystal size = $0.10 \times 0.20 \times 0.50$ mm; θ for data collection 1.65 to 22.73°; limiting indices: $0 \leq h \leq 18$, $-19 \leq k \leq 18$, $-16 \leq l \leq 16$, reflections collected/unique 12095/11618 [R(int) = 0.0195], refinement method: Full-matrix-block least-squares on F^2, data/restraints/parameters:11618/0/1292; goodness-of-fit on $F^2 = 1.074$, largest differential peak and hole: 0.850 and $-0.408\ \mathrm{e\,Å^{-3}}$, final R indices: [8096 refs $I > 2\sigma(I)$]: $R1 = 0.0501$, $wR2 = 0.1312$, R indices(all data): $R1 = 0.0860$, $wR2 = 0.1560$. CCDC-177313 contains 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).