Single-Molecule Magnets

A Nonanuclear Iron(II) Single-Molecule Magnet**

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Single-molecule magnets (SMMs) have attracted considerable interest in recent times.[1] Although molecular, these species display superparamagnetic properties normally seen in mesoscale magnetic particles and thus can function as magnetizable entities below their blocking temperature. As a consequence, they represent the ultimate limit of miniaturization for data-storage domains in magnetic media.[1] Quantum tunneling of magnetization (QTM) effects[2] have led to the proposal that SMMs could be exploited as qubits in quantum computing.[3] The existence of SMM behavior was first noted ten years ago in the complex $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$ ($S=10$, $D=-0.50\ \mathrm{cm^{-1}}=-0.72\ \mathrm{K}$),[4] which represents the most extensively studied SMM.[1] Another compound that has been investigated for its SMM behavior is $[\{Fe_8O_2(OH)_{12}(tacn)_6\}Br_7{\cdot}H_2O]Br{\cdot}8\,H_2O$ (tacn = 1,4,7-triaza-

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[**] This work was supported by the Greek Secretariat of Research and Technology (Grant 99ED139) and the European Community within the framework of the TMR contract FMRX-CT980174.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200353147

cyclononane), characterized by an $S = 10$ ground state.[1] Since the first discovery, other oxidation levels[5] in the Mn_{12} family and other Mn_x[1,6] and M_x ($M = V^{III}$,[7] Fe^{III},[8] Co^{II},[9] $Ni^{[10]}$) SMMs, including mixed-metal systems,[11] have been prepared with S values ranging from 3 to 13. Recently Cornia et al.[12] presented a method to deposit suitably derivatized Mn_{12}-type SMMs on a gold film and observed them directly at the single-molecule level using STM.

Because a SMM derives its unusual properties from a combination of large ground-state spin (S) and large, easy-axis-type anisotropy due to a negative axial zero-field splitting (ZFS), D,[1] a primary goal in this area is to maximize S and $|D|$. Large S values arise from ferromagnetic or competing antiferromagnetic exchange, and there are many competing contributions to D such as single-ion ZFS, anisotropic and dipolar exchange, and relative orientations of the single ions and the cluster magnetic axes.[13]

Herein we report the first member of a new class of iron(II)-based SMMs obtained by a rational synthetic route: $[Fe_9(N_3)_2(O_2CMe)_8\{(2\text{-py})_2CO_2\}_4]$, where $[(2\text{-py})_2CO_2]^{2-}$ is the doubly deprotonated *gem*-diol form of di-2-pyridyl ketone. This Fe^{II} complex is the second example of SMMs in iron(II) chemistry, after the cubane complex $[Fe_4(sae)_4(MeOH)_4]$ (sae^{2-} = the dianion of 2-salicylidene-amino-1-ethanol).[14] Iron SMMs are of considerable interest, because it is known[15] that the nuclear spin of the transition metal in a polynuclear SMM affects the rate of QTM (Mn has a nuclear spin of $I = 5/2$, whereas ^{56}Fe has $I = 0$). Moreover, Fe^{II} centers are known to exhibit moderate-to-large single-ion anisotropy in high-spin ferrous complexes.[16]

We had previously reported the synthesis of the nonanuclear cobalt(II) complex $[Co_9(OH)_2(O_2CMe)_8\{(2\text{-py})_2CO_2\}_4]$ (**1**),[17] which comprises two μ_4-OH^- ions, and the replacement of these two bridges by two μ_4:η^1 (that is, end-on) N_3^- ions to yield the related azido complex[18] $[Co_9(N_3)_2(O_2CMe)_8\{(2\text{-py})_2CO_2\}_4]$(**2**). The latter retains all the structural features of the former, but exhibits a ground-state spin seven times that of **1**, due to dominant ferromagnetic interactions introduced by the end-on azido ligands. Later,[19] we extended the above reactivity pattern to nickel(II) chemistry by synthesizing $[Ni_9(N_3)_2(O_2CMe)_8\{(2\text{-py})_2CO_2\}_4]$ (**3**); magnetic studies revealed that the ground-state spin value for **3** ($S = 9$) is nine times that of its precursor $[Ni_9(OH)_2(O_2CMe)_8\{(2\text{-py})_2CO_2\}_4]$ (**4**). No SMM behavior above 2 K has been observed in **2** and **3**. Synthesis of the iron(II) analogue of **1** and **4** and incorporation of the end-on azido bridge into the Fe_9 cage skeleton in place of the hydroxo anion were designed to introduce ferromagnetic superexchange interactions aimed at generating a ground state of the Fe_9 core characterized by a total spin S of either $(8\times2)-2 = 14$ or $9\times2 = 18$ (for high-spin Fe^{II}, $S = 2$), as a result of the topology of the cluster.[18,19] In addition, we attempted to introduce significant magnetic anisotropy of the Fe_9 core through single-ion anisotropy of Fe^{II} (if $D < 0$, it would be possible to prepare an iron(II) SMM).

Anaerobic reaction of di-2-pyridyl ketone ($(2\text{-py})_2CO$) with 2 equiv of iron(II) acetate[20] in boiling MeCN resulted in a dark-red solution from which $[Fe_9(OH)_2(O_2CMe)_8\{(2\text{-py})_2CO_2\}_4]$ (**5**) formed as a precipitate in 30% yield [Eq. (1)]. The double deprotonation of the *gem*-diol form of the ligand (formed in situ in the presence of the metal ion) is a consequence of the high $MeCO_2^-$ to $(2\text{-py})_2C(OH)_2$ ratio (4:1) used in the reaction. Anaerobic treatment of **5** with a slight excess of NaN_3 in boiling MeCN produced orange $[Fe_9(N_3)_2(O_2CMe)_8\{(2\text{-py})_2CO_2\}_4]$ (**6**) in 40% yield [Eq. (2)].

$$9\,Fe(O_2CMe)_2\cdot1.75\,H_2O+4\,(2\text{-py})_2CO \xrightarrow[\Delta]{MeCN} [Fe_9(OH)_2(O_2CMe)_8\{(2\text{-py})_2CO_2\}_4]+10\,MeCO_2H+9.75\,H_2O \tag{1}$$

$$[Fe_9(OH)_2(O_2CMe)_8\{(py)_2CO_2\}_4]+2\,NaN_3 \xrightarrow[\Delta]{MeCN} [Fe_9(N_3)_2(O_2CMe)_8\{(py)_2CO_2\}_4]+2\,NaOH \tag{2}$$

The molecular structure[21] of **6** is shown in Figure 1. The asymmetric unit contains two almost identical nonanuclear molecules. The nine Fe^{II} ions adopt the topology of two square pyramids sharing a common apex at the central metal ion (Fe1 in Figure 1) and are held together by four μ_5:η^1:η^3:η^3:η^1 $(2\text{-py})_2CO_2^{2-}$ ligands (Scheme 1). Each Fe···Fe

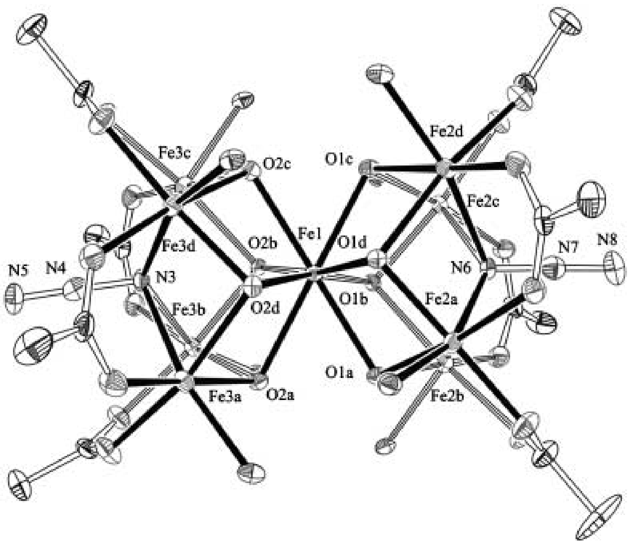
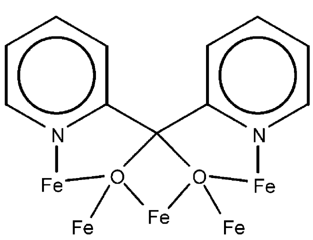


Figure 1. ORTEP plot of one of the two independent nonanuclear molecules of **6** (thermal ellipsoids set at the 30% probability level). All H atoms and all noncoordinated atoms of the $[(2\text{-py})_2CO_2]^{2-}$ ligands are omitted for clarity. Interatomic distance ranges [Å]: Fe-N($[(2\text{-py})_2CO_2]^{2-}$) 2.123–2.160, Fe–N(azido) 2.342–2.449, Fe1-O 2.258–2.317, Fe2(Fe3)-O($[(2\text{-py})_2CO_2]^{2-}$) 2.032–2.249, Fe2(Fe3)-O(acetate) 1.983–2.179. Average esd values: 0.004 Å.



Scheme 1. Bridging characteristics observed in **6**.

basal edge of the pyramids is further bridged by one *syn,syn* $\mu_2{:}\eta^1{:}\eta^1$ acetate ligand. The four acetate ligands create a cavity at the base of each pyramid, into which an extremely rare $\mu_4{:}\eta^1$ azido ligand is trapped, thus capping the square base. This bridging mode has only been observed in the parent Co and Ni nonanuclear complexes.[18,19] The two square bases have a slightly staggered conformation, thus endowing Fe1 with a tetragonal antiprismatic coordination environment ($Fe^{II}O_8$ chromophore). Octacoordination is an extremely rare feature in iron(II) chemistry, having only been observed in four structurally characterized iron(II) complexes.[22] The packing of the molecules in **6** (see Supporting Information) shows large intermetallic separations between iron ions of neighboring molecules, with the closest intermolecular Fe···Fe distance (7.933(1) Å) being between Fe3b and Fe5b (symmetry operation: x, y, z-1). Complex **6** is the first structurally characterized nonanuclear iron(II) cluster.

Preliminary ^{57}Fe Moessbauer studies of **6** revealed two well-resolved quadrupole-split doublets (Figure 2), with parameters typical of HS iron(II) ions, and with an area ratio very close to the theoretically expected 1:8 value. For example, at 80 K, fitting of the data yielded parameters $\delta_1 = 1.369(6)\ \text{mm s}^{-1}$, $\Delta E_{Q1} = 3.12(1)\ \text{mm s}^{-1}$, $\Gamma_{1/2} = 0.12(1)\ \text{mm s}^{-1}$ (13.4 %) and $\delta_2 = 1.203(2)\ \text{mm s}^{-1}$, $\Delta E_{Q2} = 2.433(3)\ \text{mm s}^{-1}$, $\Gamma_{1/2} = 0.166(3)\ \text{mm s}^{-1}$ (86.6 %) attributed to the central and external high-spin iron(II) sites, respectively.

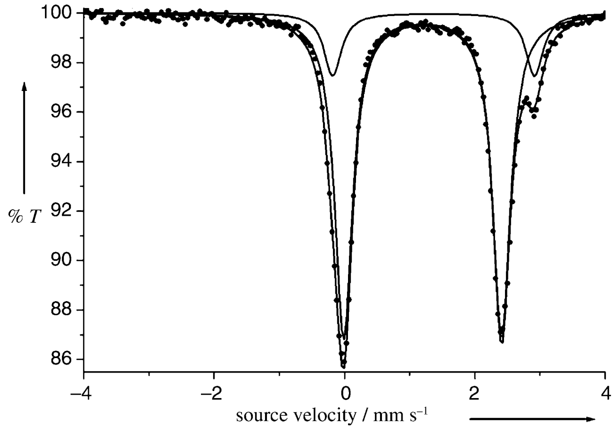


Figure 2. Moessbauer spectrum of **6** at 80 K. The data was least-squares fitted to two quadrupole-split doublets (Lorentzian lines, see text for parameter values).

Variable-temperature (2–300 K) dc magnetic susceptibility data (Quantum Design MPMS SQUID magnetometer) were collected on polycrystalline samples of **5** (10 kG) and **6** (1, 5, 10, 25, and 50 kG), molded into a 3 mm diameter pellet inside a glove box. The magnetic study of **5** revealed an overall antiferromagnetic behavior with an $S = 2$ ground state.[23] The $\chi_m T$ product of **6** increases from the room-temperature value of $31.84\ \text{cm}^3\text{mol}^{-1}\text{K}$ reaching a field-dependent maximum of $59.00\ \text{cm}^3\text{mol}^{-1}\text{K}$ at 19 K ($H =$ 1 kG), followed by a sudden drop due to zero-field splitting effects. Considering that the magnetic-field dependence of the $\chi_m T$ product of **6** is effective between 10 and 50 kG, but negligible between 10 and 1 kG (1.5 % on average between 300 and 19 K; Figure 3), and that spin–orbit coupling effects increase with decreasing applied magnetic field, the fitting was carried out on the 10 kG data using an isotropic model based on the spin Hamiltonian [Eq. (3)] that corresponds to exchange pathways shown in Scheme 2.

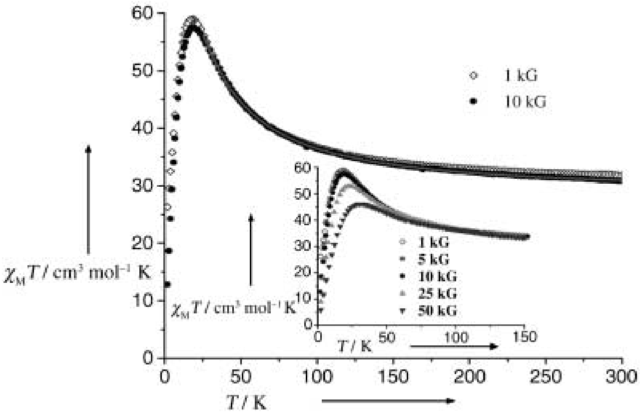
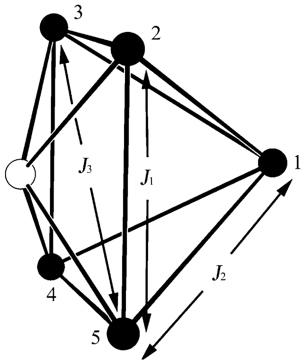


Figure 3. Magnetic susceptibility data of **6** collected at various magnetic fields (1, 5, 10, 25, 50 kG), and shown as $\chi_M T$ versus T plots in the inset. The 10-kG data (300–25 K) have been fitted to the isotropic model described in the text.

$$
\begin{aligned}
\hat{\mathrm{H}} = {} & -2J_1(\hat{S}_2\hat{S}_3+\hat{S}_3\hat{S}_4+\hat{S}_4\hat{S}_5+\hat{S}_5\hat{S}_2+\hat{S}_6\hat{S}_7+\hat{S}_7\hat{S}_8+\hat{S}_8\hat{S}_9+\hat{S}_9\hat{S}_6) \\
& -2J_2(\hat{S}_1\hat{S}_2+\hat{S}_1\hat{S}_3+\hat{S}_1\hat{S}_4+\hat{S}_1\hat{S}_5+\hat{S}_1\hat{S}_6+\hat{S}_1\hat{S}_7+\hat{S}_1\hat{S}_8+\hat{S}_1\hat{S}_9) \\
& -2J_3(\hat{S}_2\hat{S}_4+\hat{S}_3\hat{S}_5+\hat{S}_6\hat{S}_8+\hat{S}_7\hat{S}_9)
\end{aligned}
\tag{3}
$$



Scheme 2. Exchange pathways for **6**.

Owing to the symmetry of the system, the Kambe vector-coupling approach[24] yielded the analytical expression [Eq. (4)] for the energy levels:

$$
\begin{aligned}
E_{(S_A,\,S_B,\,S_C,\,S_D,\,S_E,\,S_F,\,S_G,\,S_T)} = {} & J_1[S_A(S_A+1)+S_B(S_B+1)+S_C(S_C+1)+S_D(S_D+1) \\
& -S_E(S_E+1)-S_F(S_F+1)]+J_2[S_G(S_G+1)-S_T(S_T+1)] \\
& -J_3[S_A(S_A+1)+S_B(S_B+1)+S_C(S_C+1)+S_D(S_D+1)]
\end{aligned}
\tag{4}
$$

where $\hat{S}_A = \hat{S}_2+\hat{S}_4$, $\hat{S}_B = \hat{S}_3+\hat{S}_5$, $\hat{S}_C = \hat{S}_6+\hat{S}_8$, $\hat{S}_D = \hat{S}_7+\hat{S}_9$, $\hat{S}_E = \hat{S}_A+\hat{S}_B$, $\hat{S}_F = \hat{S}_C+\hat{S}_D$, $\hat{S}_G = \hat{S}_E+\hat{S}_F$, and $\hat{S}_T = \hat{S}_1+\hat{S}_G$.

Fitting of the 10 kG data down to 25 K ($J_1 = 7.0\ \text{cm}^{-1}$, $J_2 = -0.39\ \text{cm}^{-1}$, $J_3 = -3.4\ \text{cm}^{-1}$, $g = 2.015$, $R = 7.3 \cdot 10^{-4}$) yielded an $S = 14$ ground state (see Supporting Information) with low-lying excited states, as expected for a system in which the anisotropic high-spin Fe^{II} centers are weakly coupled. This result is qualitatively corroborated by magnetization measurements: Plots of M versus HT^{-1} at various field strengths (see Supporting Information) show that the magnetization extrapolates to 28 $N_A\mu_B$ above 5 T, suggesting an $S = 14$ ground state. However, models considering population of the only $S = 14$ ground state did not allow us to satisfactorily fit the magnetization data, which indicates an admixture of the ground state of this nonanuclear complex with low-lying excited states (the lowest level of the $S = 14$ state may be slightly above levels of the $S = 13$ and/or $S = 15$ states). The size of the matrix needed to consider the whole system is too large to fit these magnetization data at this time.

To probe the dynamics of the magnetization relaxation in complex **6**, variable-temperature ac SQUID experiments were performed over the 2.0–5.0 K temperature range at frequencies of 1–1000 Hz, with zero applied dc field, on the polycrystalline sample used for the dc studies. The compound exhibits in-phase (χ'_m) and out-of-phase magnetic susceptibility (χ''_m) signals below 3.5 K (Figure 4), due to the inability of **6** to relax sufficiently rapidly to keep up with the oscillating field at these temperatures. The frequency dependence of the χ''_m signal clearly indicates SMM behavior.[1] As determined by fits to Lorentzian lines, the χ''_m peak shifts from 2.34(1) to 2.00(1) K upon decreasing the frequency of the ac field from 1000 to 50 Hz; at lower frequency, the χ''_m peak is shifted below 1.9 K and, thus, is no longer visible. The magnetization relaxation rate data obtained from the ac data were fitted to the Arrhenius equation $\tau = \tau_0 \exp(\Delta E/kT)$, where τ is the relaxation time, ΔE is the energy barrier for the relaxation of the magnetization, k is the Boltzmann constant and τ_0 is the preexponential factor. From the fit, ΔE was found to be 29(1) cm^{-1} (41(1) K) with $\tau_0 = 3.4 \times 10^{-12}$ s. Further studies[23] at lower temperatures and frequencies are planned, as well as investigation of possible hysteresis and quantum tunneling of the magnetization.

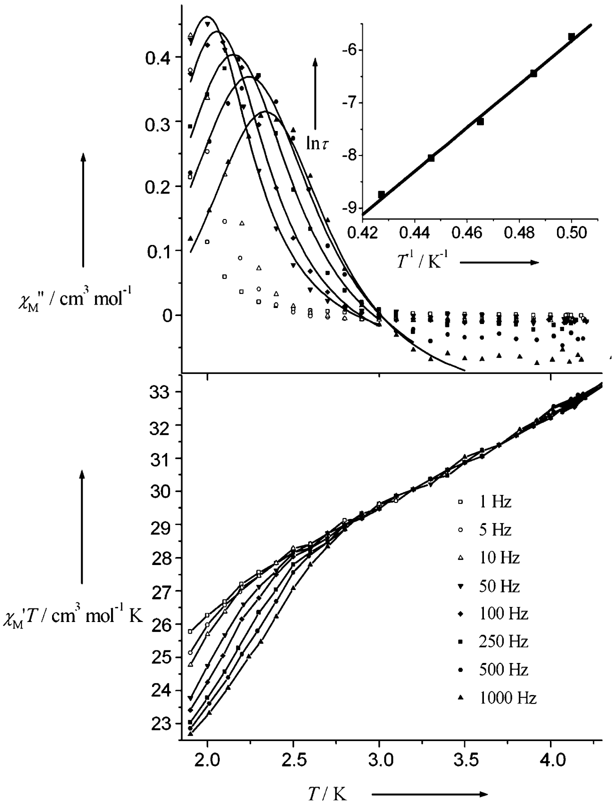


Figure 4. Frequency dependence of the in-phase $\chi'_m T$ product and out-of-phase χ''_m magnetic susceptibility versus T for **6**. Solid lines are fits of the out-of-phase experimental data by Lorentzian lines. An Arrhenius plot of lnτ versus T^{-1} for the values derived from the peak maxima at various frequencies is shown in the inset. The solid line is a least-squares linear fit of the data. Where the χ''_m versus T maxima are not observable, the experimental data have not been fitted.

The azido compound is important to the field of SMMs, as it is a very rare example of iron(II) molecule exhibiting this behavior. The role of the anisotropic Fe^{II} ions in the double square-pyramidal molecular topology appears to be crucial for promoting this magnetic phenomenon. Complex **6** is a totally new type of SMM, being not based on a previously discovered relative. Its structure was designed and the spin of its ground state was modulated. However, the SMM behavior of **6** probably relies on both the single-ion magnetic anisotropy of Fe^{II}, and the favorable size and sign of D for the Fe$_9$ core. This latter aspect remains the point at which there was least "operator control" and the area in which future advances should be made. In conclusion, we believe that the work reported here illustrates a new approach to the synthesis of SMMs, based on detailed analysis of already acquired knowledge, and its use for the rational design of appropriate synthetic schemes.

Experimental Section

5: Treatment of a white slurry of Fe(O$_2$CMe)$_2$·1.75 H$_2$O (0.411 g, 2.00 mmol) in MeCN (50 mL) with (2-py)CO (0.184 g, 1.00 mmol) resulted in a dark blue-green solution. The solution was boiled for 5 min, during which time a noticeable color change to dark red was observed. The red solution was filtered and allowed to stand undisturbed in a capped flask in a glove box. After 2–3 days, red cubes of the product were deposited from the mother liquor, which were then collected by filtration, washed with MeCN, and dried in vacuo (yield ≈30 %). The dried solid analyzed as solvent-free. Elemental analysis (%) calcd for C$_{60}$H$_{58}$Fe$_9$N$_8$O$_{26}$: C 39.82, H 3.23, N 6.19; found: C 39.74, H 2.93, N 5.96.

6: Treatment of a red slurry of **5** (0.651 g, 0.36 mmol) in boiling MeCN (60 mL) with NaN$_3$ (0.066 g, 1.02 mmol) resulted in a dark-red solution. The solution was cooled and filtered, and the filtrate was left to stand undisturbed for one week. Orange crystals of **6**·1.36 H$_2$O·2.16 MeCN suitable for X-ray analysis were obtained, collected by filtration, washed with MeCN, and dried in vacuo (yield ≈40 %). The dried solid analyzed as solvent-free. Elemental analysis (%) calcd for C$_{60}$H$_{56}$Fe$_9$N$_{14}$O$_{24}$: C 38.75, H 3.04, N 10.54; found: C 38.50, H 3.01, N 10.42.

Received: October 24, 2003
Revised: February 23, 2004 [Z53147]

Keywords: azides · cluster compounds · iron · magnetic properties · single-molecule studies

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[21] **6**·1.36 H_2O·2.16 MeCN ($C_{64.32}H_{65.2}Fe_9N_{16.16}O_{25.36}$), $M_r = 1973.12$, triclinic, $P\bar{1}$, $a = 18.864(1)$, $b = 20.177(1)$, $c = 21.752(1)$ Å, $\alpha = 101.015(3)$, $\beta = 97.572(3)$, $\gamma = 90.730(3)°$, $V = 8049.8(5)$ Å^3, $Z = 2$, $T = 160(2)$ K, $F(000) = 4022$, $\rho_{calcd} = 1.637\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 1.657\ mm^{-1}$ ($\lambda = 0.70930$ Å), 44266 reflections measured, 22953 unique ($R_{int} = 0.0407$), 2149 refined parameters, $R_1(F) = 0.0467$ and $wR_2(F^2) = 0.1132$ using 18381 reflections with $I > 2\sigma(I)$. CCDC-222457 (**6**·1.36 H_2O·2.16 MeCN) 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).

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