

Spin-Crossover Fe^{II}_4 Squares: Two-Step Complete Spin Transition and Reversible Single-Crystal-to-Single-Crystal Transformation**

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Molecular bistability plays a very important role in developing modern advanced devices and thus has attracted much attention in recent years.^[1] Toward this end, spin-crossover (SCO) compounds, in which the high-spin (HS) and low-spin (LS) states can be interconverted by heat, pressure, or light irradiation, are potential candidates for futuristic applications such as the development of miniature molecule-based display devices or data storage elements.^[2] To date over 200 SCO systems,^[3] many of which are interesting mononuclear compounds,^[4] have been reported. It has been recognized that direct linking of the mononuclear SCO centers (e.g. into binuclear or polynuclear clusters) could significantly enhance the interactions between SCO centers that play an important role in enhancing bistable behavior.^[5] For example, square-shaped SCO compounds are one such interesting system, which not only possesses inherent structural beauty but also contributes a rich range of unique, magnetically accessible structures: the [HS-HS-HS-HS], *cis*-[HS-HS-LS-LS]/*trans*-[HS-LS-HS-LS], and [LS-LS-LS-LS] states.

Since the first square Fe^{II}_4 compound exhibiting both thermal and light-induced but incomplete spin transition was reported by Lehn, Güthlich, and co-workers in 2000,^[6] the number of tetranuclear Fe^{II} squares exhibiting SCO bi- or multistability is still quite low,^[6–8] and all of them underwent incomplete spin transition.^[6,7] Two cyanide-bridged square Fe^{II}_4 compounds show interesting two-step spin transitions, but only two of the four Fe^{II} centers show SCO behavior.^[8] In fact, no square Fe^{II}_4 compound showing complete spin transition of all four Fe^{II} centers has been reported to date. Moreover, a guest-responsive effect based on single crystals has not yet been taken into account for those square-shaped compounds, which actually is a convenient and significant avenue for investigating SCO phenomena in the solid state.^[9] During our studies on SCO compound $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ (tpa = tris(2-pyridylmethyl)amine),^[4c,9f] we notice that the $[\text{Fe}(\text{tpa})]^{2+}$ entity possesses two accessible coordination sites. We proposed that square or chain structures would be

achieved by using linear bridging ligands. Herein, we report such a novel square Fe^{II}_4 compound $[\text{Fe}(\text{tpa})\{\text{N}(\text{CN})_2\}]_4 \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ ($1 \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$) constructed from $[\text{Fe}(\text{tpa})]$ and dicyanamide.^[10] This compound undergoes both thermal and light-induced two-step spin transition and reversible single-crystal-to-single-crystal (SCSC) transformations between $1 \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ and its solvent-free forms $1 \cdot (\text{BF}_4)_4$ induced by guest desorption and resorption.

Complete and rapid desorption of guest molecules occurred upon heating of the as-prepared sample of $1 \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ to 340 K. The resulting guest-free form, $1 \cdot (\text{BF}_4)_4$, is stable up to approximately 550 K (Figure S1 in the Supporting Information). To investigate structures associated with different SCO phases identified by the magnetic studies (see below) before and after guest-desorption-induced SCSC transformation from $1 \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ to $1 \cdot (\text{BF}_4)_4$, single-crystal X-ray diffraction data were collected in situ on one crystal of $1 \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ in a successive heating/cooling cycle at 150, 250, 350, 250, and 150 K.^[11] During this cycle, no phase transition was observed. Selected bond lengths, angles, and structural parameters are given in Table S1 in the Supporting Information. Compound $1 \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ crystallized in the monoclinic space group $P2_1/c$. The asymmetric unit contains one half complex 1^{4+} ion (two crystallographically distinct Fe1 and Fe2 ions), two BF_4^- anions (denoted as B1 and B2, respectively) and one water molecule. Each distorted $[\text{FeN}_6]$ octahedron is formed by four nitrogen atoms provided by the tpa ligand and two from the $\text{N}(\text{CN})_2^-$ groups. The four Fe^{II} centers are linked by $\mu\text{-N}(\text{CN})_2^-$ groups in a square arrangement adopting an alternating Fe1-Fe2-Fe1-Fe2 geometric configuration, as shown in Figure 1.

At 150 K, the average Fe–N bond lengths of Fe1 and Fe2 ions are 1.973 and 1.967 Å, respectively, both in the range

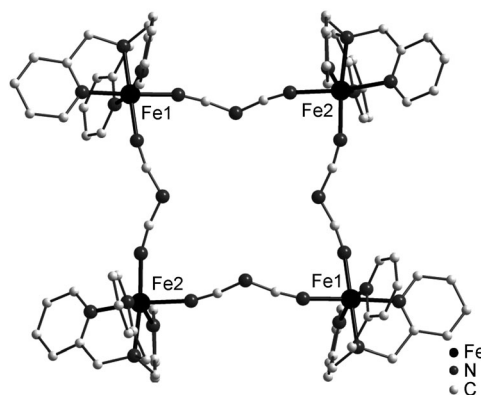


Figure 1. Molecular structure of the Fe^{II}_4 square in $1 \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$. Anions, water molecules, and hydrogen atoms are omitted for clarity.

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expected for a LS Fe^{II} -N bond. Upon warming to 250 K, the value for Fe1 increases to 2.130 Å, whereas that associated with Fe2 varies slightly from 1.967 to 1.988 Å. The change in the Fe1-N bond length (0.15 Å) suggests that a LS-to-HS transition occurs at the Fe1 center upon temperature increase. In other words, the Fe^{II}_4 square of $\mathbf{1} \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ shows an intermediate $[\text{HS}_{\text{Fe1}}\text{-LS}_{\text{Fe2}}\text{-HS}_{\text{Fe1}}\text{-LS}_{\text{Fe2}}]$ phase at 250 K. The HS and LS states can also be distinguished from geometries around Fe^{II} ions with distortion parameter Σ .^[12] HS Fe^{II} ions tend to form more distorted octahedra and thus have larger Σ values than their LS counterparts. At 150 and 250 K, the Σ values are 60.2° (LS) and 90.6° (HS) for Fe1 ion and 54.1° (LS) and 57.5° (LS) for Fe2 ion, respectively, thus the transition from LS $(\text{Fe}^{\text{II}}_{\text{LS}})_4$ square to the mixed-spin intermediate species is suggested in this temperature range.

Upon further heating to 350 K, the guest molecules were removed and SCSC transformation occurred from $\mathbf{1} \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ to its guest-free form $\mathbf{1} \cdot (\text{BF}_4)_4$, as shown in Figure 2. The average Fe-N bond lengths of 2.151 and 2.138 Å and Σ

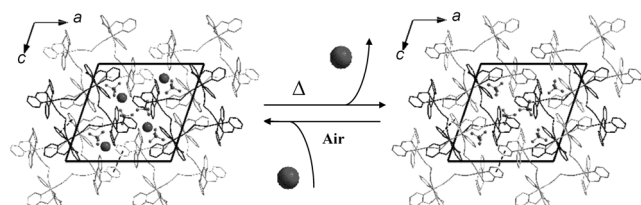


Figure 2. Schematic representation of the reversible SCSC transformations between $\mathbf{1} \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ (left) and its guest-free form $\mathbf{1} \cdot (\text{BF}_4)_4$ (right) induced by guest desorption/resorption.

values of 98.0 and 88.2° for Fe1 and Fe2, respectively, suggest that each of the Fe^{II} ions is in a HS state, and the crystal is in the $(\text{Fe}^{\text{II}}_{\text{HS}})_4$ phase. The temperature was then decreased from 350 K, and diffraction data were collected using the desolvated sample $[\mathbf{1} \cdot (\text{BF}_4)_4]$ obtained at 350 K. When this sample was cooled to 250 and 150 K, the average Fe-N bond lengths and Σ values for Fe1 and Fe2 of $\mathbf{1} \cdot (\text{BF}_4)_4$ (Table S1 in the Supporting Information) varied only slightly from the corresponding values of the solvated form $\mathbf{1} \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$, thus suggesting that the removal of guest molecules exerts no observable influence on the SCO Fe^{II} centers. Even more interesting is the fact that the desolvated crystal $[\mathbf{1} \cdot (\text{BF}_4)_4]$ is able to re-absorb water molecules and recover to the solvated form, denoted as $\mathbf{1} \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$, by exposure to ambient atmosphere for one week. The crystal data of this compound at 150 K^[11] are almost the same as those of the as-prepared $\mathbf{1} \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ at the same temperature. Reversible SCSC transformations along with guest desorption/resorption are thus inferred.

Beyond the molecular level, the packing of $\mathbf{1} \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ can be viewed as layers of $\mathbf{1}^{4+}$ cations, BF_4^- ions, and water molecules parallel to the *ac* plane (Figure 2). Along the *a* and *c* axes, $\mathbf{1}^{4+}$ cations are stacked through π - π interactions between pyridine rings on adjacent $[\text{Fe}(\text{tpa})]$ entities with aromatic centroid-to-centroid distances of 3.869(1) and 3.906(2) Å at 150 K and 3.876(1) and 3.951(2) Å at 250 K. Between $\mathbf{1}^{4+}$ cations and BF_4^- ions, F...H-C hydrogen bonds

are found, with the closest F...H separation varying from 2.228(2) to 2.346(2) Å and 2.375(1) to 2.436(2) Å when the temperature increases from 150 K to 250 K for B1 and B2, respectively. Water molecules occupy voids between BF_4^- ions and interact with B1 and B2 through F...H-O hydrogen bonds with distances (F...H) of 2.211(2) and 1.908(2) Å at 150 K and 2.191(1) and 1.801(2) Å at 250 K, respectively. At 350 K, the water molecules are removed, but the crystal packing of $\mathbf{1} \cdot (\text{BF}_4)_4$ is similar to that of $\mathbf{1} \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ at 150 and 250 K, except that some intermolecular interactions are elongated because of lattice enlargement in the $(\text{Fe}^{\text{II}}_{\text{HS}})_4$ state. Upon cooling, little changes of π - π interactions and F...H-C hydrogen bonds are found.

Magnetic properties of $\mathbf{1} \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ were studied in two successive cooling/heating cycles, the first 300–100–380 K cycle and the second 380–100–380 K one. The corresponding $\chi_{\text{M}}T$ versus *T* plots are shown in Figure 3. In the first temperature cycle, the $\chi_{\text{M}}T$ value is 11.07 cm³ mol⁻¹ K at 300 K, slightly lower than that expected for four uncoupled

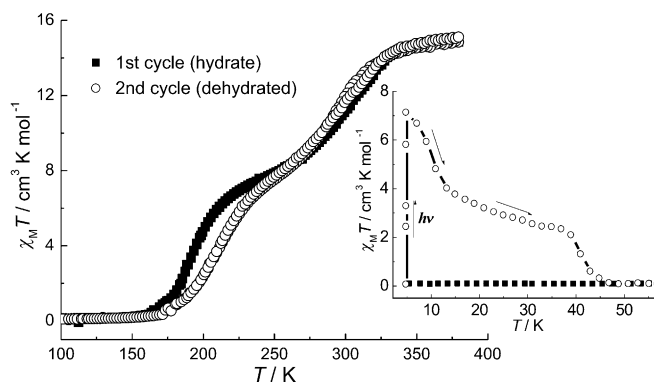


Figure 3. $\chi_{\text{M}}T$ versus *T* plots for $\mathbf{1} \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ in two successive temperature cycles of 300–100–380 K (■) and 380–100–380 K (○). Inset: Light-induced SCO of $\mathbf{1} \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$.

HS Fe^{II} ions, which indicates that some of the Fe^{II} ions in the Fe^{II}_4 square of $\mathbf{1} \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ have undergone spin transition at room temperature. Upon cooling, the $\chi_{\text{M}}T$ value decreases gradually to reach a declined plateau between 260 and 220 K, corresponding to the $[\text{HS}_{\text{Fe1}}\text{-LS}_{\text{Fe2}}\text{-HS}_{\text{Fe1}}\text{-LS}_{\text{Fe2}}]$ state revealed by crystallographic studies. The $\chi_{\text{M}}T$ value then abruptly decreases and attains a constant value of 0.17 cm³ mol⁻¹ K below 156 K, indicating a spin transition from $[\text{HS}_{\text{Fe1}}\text{-LS}_{\text{Fe2}}\text{-HS}_{\text{Fe1}}\text{-LS}_{\text{Fe2}}]$ to the $(\text{Fe}^{\text{II}}_{\text{LS}})_4$ state. This profile indicates that compound $\mathbf{1} \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$ undergoes a two-step, complete spin transition with critical temperatures of 302 and 194 K, respectively. Upon heating, the $\chi_{\text{M}}T$ versus *T* plot overlays completely that of the cooling mode and reaches a value of 14.47 cm³ mol⁻¹ K at 340 K, corresponding to the $(\text{Fe}^{\text{II}}_{\text{HS}})_4$ state.

Based on thermogravimetric analysis (Figure S1 in the Supporting Information), we deduce that desolvation is complete at the conclusion of heating process of the first temperature cycle, so magnetic studies can be carried out in a further cooling/heating cycle (380–100–380 K) by using the obtained guest-free sample $\mathbf{1} \cdot (\text{BF}_4)_4$. Upon cooling, the $\chi_{\text{M}}T$ value decreases in a two-step process that is more abrupt than

that of $1\cdot(\text{BF}_4)_4(\text{H}_2\text{O})_2$, with the critical temperatures of 294 and 211 K. The corresponding heating process gives a $\chi_{\text{M}}T$ versus T curve that is similar to that from the above cooling process, except that there is 6 K wide hysteresis (Figure 3) in the high-temperature range. The slight differences in abruptness and hysteresis between $1\cdot(\text{BF}_4)_4(\text{H}_2\text{O})_2$ and $1\cdot(\text{BF}_4)_4$ obviously originated from the alteration of hydrogen-bond interactions induced by guest desorption.^[9f] Magnetic measurements were also carried out for the products obtained by exposure of $1\cdot(\text{BF}_4)_4$ to air (Figure S2 in the Supporting Information), which revealed that the SCO behavior of $1\cdot(\text{BF}_4)_4(\text{H}_2\text{O})_2^{\text{re}}$ was almost the same as that of as-prepared $1\cdot(\text{BF}_4)_4(\text{H}_2\text{O})_2$, thus indicating complete resorption of guest molecules.

The light-induced excited-spin-state trapping (LIESST) effect^[13] of $1\cdot(\text{BF}_4)_4(\text{H}_2\text{O})_2$ was investigated by irradiating a sample at 5 K to saturation with blue light (457 nm, 150 mW) for 30 minutes (Figure 3, inset). The maximum $\chi_{\text{M}}T$ value at 5 K ($7.08\text{ cm}^3\text{ mol}^{-1}\text{ K}$) indicated that a photoexcited population of approximately 47.9% was achieved. When the light was switched off and the sample was heated at 1 K min^{-1} , the light-induced HS state relaxed with a complicated sequence of regimes. The first relaxation of the metastable HS state was rather fast, with an abrupt drop of $\chi_{\text{M}}T$ values between 5 and 13.5 K. After that, the $\chi_{\text{M}}T$ value shows a smooth decrease centered at $3.00\text{ cm}^3\text{ mol}^{-1}\text{ K}$ (13.5–33 K), a value close to half of that at 5 K and indicating a near 1:1 ratio of metastable HS and LS Fe^{II} populations at the intermediate phase. Upon further warming, a second abrupt relaxation between 33 and 49 K took place and made the light-excited species return to the thermally induced LS state. Even though it is difficult to infer the origin of this interesting light-induced two-step SCO process without structural comparison before and after irradiation, a two-step relaxation mechanism can be proposed, which is associated with the existence of two types of Fe^{II} centers in the square. Further investigations, such as Mössbauer spectroscopy^[14] and X-ray studies^[15] after irradiation, are required to fully understand this unusual light-induced SCO behavior.

In summary, we have reported a novel square Fe^{II}_4 compound that exhibits two-step complete spin transition both thermally and by optical irradiation and the reversible guest desorption/resorption-induced SCSC transformation. The results given by detailed studies on structures and SCO behaviors associated with SCSC transformation may be helpful in developing multistable materials. Further work to syntheses square Fe^{II}_4 compounds with other solvents and anions as well as to investigate solvent and anion exchange is underway.

Experimental Section

Synthesis of $1\cdot(\text{BF}_4)_4(\text{H}_2\text{O})_2$: An aqueous solution (5 mL) of $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ (0.5 mmol), sodium dicyanamide (0.5 mmol), and sodium tetrafluoroborate (0.5 mmol) was poured without stirring into an ethanol solution (1 mL) of tpa (0.5 mmol). The resulting yellow turbid solution with a large amount of precipitate was sealed in a bottle under N_2 atmosphere and left to stand. The precipitate generally turned red in 2 h all grew into large single crystals in four days. Red crystals suitable for X-ray single-crystal diffraction were

collected by filtration. Yield: ca. 60%. Elemental analysis (%) for $\text{C}_{80}\text{H}_{76}\text{B}_4\text{F}_{16}\text{Fe}_4\text{N}_{28}\text{O}_2$: calcd: C 47.28, H 3.77, N 19.30; found: C 47.53, H 3.72, N 19.52. IR (KBr, cm^{-1}): 3432, 2924, 2298, 2174, 1603, 1441, 1382, 1082, 1052, 766, 515.

Guest desorption: Crystals of $1\cdot(\text{BF}_4)_4(\text{H}_2\text{O})_2$ were heated to 340 K in vacuum overnight to produce good quality crystals of $1\cdot(\text{BF}_4)_4$. Elemental analysis (%) for $\text{C}_{80}\text{H}_{72}\text{B}_4\text{F}_{16}\text{Fe}_4\text{N}_{28}$: calcd: C 48.13, H 3.64, N 19.65; found: C 48.21, H 3.65, N 19.64.

Guest resorption: Exposure of $1\cdot(\text{BF}_4)_4$ crystals to air in one week gave high quality crystals of $1\cdot(\text{BF}_4)_4(\text{H}_2\text{O})_2^{\text{re}}$. Elemental analysis (%) for $\text{C}_{80}\text{H}_{76}\text{B}_4\text{F}_{16}\text{Fe}_4\text{N}_{28}\text{O}_2$: calcd: C 47.28, H 3.77, N 19.30; found: C 47.65, H 3.82, N 19.23.

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- [11] X-ray crystallographic data for $\mathbf{1} \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$: $\text{C}_{80}\text{H}_{76}\text{B}_4\text{F}_{16}\text{Fe}_4\text{N}_{28}\text{O}_2$, $M_r = 2032.33 \text{ g mol}^{-1}$, monoclinic, space group $P2_1/c$, $Z = 2$. $T = 150 \text{ K}$, $a = 17.7244(5)$, $b = 14.5192(4)$, $c = 17.2793(6) \text{ Å}$, $\beta = 108.735(4)^\circ$, $V = 4211.1(2) \text{ Å}^3$, $\rho_{\text{calcd}} = 1.603 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.778 \text{ mm}^{-1}$; 17520 data points measured, 8247 unique ($R_{\text{int}} = 0.0471$), 604 parameters, $R_1 = 0.0546$ (6053 with $I > 2\sigma(I)$), $wR_2 = 0.1304$ (all data), $S = 1.059$. $T = 250 \text{ K}$, $a = 18.1190(8)$, $b = 14.6471(7)$, $c = 17.2812(8) \text{ Å}$, $\beta = 106.844(5)^\circ$, $V = 4389.5(4) \text{ Å}^3$, $\rho_{\text{calcd}} = 1.538 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.747 \text{ mm}^{-1}$; 19867 data measured, 8605 unique ($R_{\text{int}} = 0.0542$), 604 parameters, $R_1 = 0.0686$ (5279 with $I > 2\sigma(I)$), $wR_2 = 0.1707$ (all data), $S = 1.023$. X-ray crystallographic data for $\mathbf{1} \cdot (\text{BF}_4)_4$: $\text{C}_{80}\text{H}_{72}\text{B}_4\text{F}_{16}\text{Fe}_4\text{N}_{28}$, $M_r = 1996.30 \text{ g mol}^{-1}$, monoclinic, space group $P2_1/c$, $Z = 2$. $T = 350 \text{ K}$, $a = 18.564(4)$, $b = 14.969(2)$, $c = 17.177(3) \text{ Å}$, $\beta = 107.923(19)^\circ$, $V = 4541.6(14) \text{ Å}^3$, $\rho_{\text{calcd}} = 1.460 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.719 \text{ mm}^{-1}$; 20652 data points measured, 8907 unique ($R_{\text{int}} = 0.0915$), 595 parameters, $R_1 = 0.0785$ (4289 with $I > 2\sigma(I)$), $wR_2 = 0.2228$ (all data), $S = 1.026$. $T = 250 \text{ K}$, $a = 18.0565(17)$, $b = 14.6733(10)$, $c = 17.1896(17) \text{ Å}$, $\beta = 107.415(11)^\circ$, $V = 4345.6(7) \text{ Å}^3$, $\rho_{\text{calcd}} = 1.526 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.751 \text{ mm}^{-1}$; 21255 data points measured, 8528 unique ($R_{\text{int}} = 0.0940$), 595 parameters, $R_1 = 0.0730$ (4107 with $I > 2\sigma(I)$), $wR_2 = 0.1735$ (all data), $S = 0.996$. $T = 150 \text{ K}$, $a = 17.6947(10)$, $b = 14.4946(7)$, $c = 17.2143(11) \text{ Å}$, $\beta = 108.765(7)^\circ$, $V = 4180.4(4) \text{ Å}^3$, $\rho_{\text{calcd}} = 1.586 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.781 \text{ mm}^{-1}$; 20918 data points measured, 8187 unique ($R_{\text{int}} = 0.0940$), 595 parameters, $R_1 = 0.0553$ (5427 with $I > 2\sigma(I)$), $wR_2 = 0.1033$ (all data), $S = 1.010$. X-ray crystallographic data for $\mathbf{1} \cdot (\text{BF}_4)_4(\text{H}_2\text{O})_2$: $\text{C}_{80}\text{H}_{76}\text{B}_4\text{F}_{16}\text{Fe}_4\text{N}_{28}\text{O}_2$, $M_r = 2032.33 \text{ g mol}^{-1}$, monoclinic, space group $P2_1/c$, $Z = 2$. $T = 150 \text{ K}$, $a = 17.7310(7)$, $b = 14.5360(5)$, $c = 17.2826(6) \text{ Å}$, $\beta = 108.722(4)^\circ$, $V = 4218.7(3) \text{ Å}^3$, $\rho_{\text{calcd}} = 1.600 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.777 \text{ mm}^{-1}$; 19627 data points measured, 8260 unique ($R_{\text{int}} = 0.0613$), 604 parameters, $R_1 = 0.0527$ (6017 with $I > 2\sigma(I)$), $wR_2 = 0.1311$ (all data), $S = 1.036$. CCDC 827475, 827476, 827477, 827478, 827479, and 827480 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-request/cif.
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