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Quenching the Hysteresis in Single Crystals of a 1D Chain Iron(II) Spin Crossover Complex

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The unusual grinding effects observed in the 1D spin crossover polymer $[FeL(bipy)]_n$ (**1**), with L being a tetradentate $N_2O_2^{2-}$ coordinating Schiff base type ligand {(3,3′)-[1,2-phenylenebis(iminomethylidyne)]bis(2,4-pentanedionato)(2–)-$N,N',O^2,O^{2'}$} and bipy = 4,4′-bipyridine, are investigated using magnetic measurements, X-ray powder diffraction and optical reflectivity studies. The observed behaviour can be explained when solvent effects are taken into account.

Introduction

Spin transition (spin crossover, SCO) complexes are an interesting class of compounds that can be switched between two or more states by external perturbations as temperature, pressure or light.[1] Several applications in the field of information technology can be envisioned for this class of substances, especially for complexes that exhibit a wide hysteresis around room temperature (memory effect).[2] The occurrence of hysteresis effects depends on the "communication" between the metal centers during the spin transition, i.e. cooperative effects. Different intermolecular interactions as π-stacking, hydrogen bonds or van der Waals interactions are suitable information transmitters. However, covalent linkers did attract special attention over the last years as the spreading of those interactions can be more easily controlled.[3] This resulted in the synthesis and characterization of several iron(II) spin crossover coordination polymers.[4]

Results and Discussion

In this context, we previously reported the synthesis and magnetic properties of a 1D SCO polymer obtained by combination of an iron(II) complex with an equatorial, tetradentate Schiff base type ligand and 4,4′-bipyridine as bridging axial ligand (compound **1**).[5] The powder sample displays a spin transition with an approximately 18 K wide thermal hysteresis loop ($T_{1/2\uparrow}$ = 237 K and $T_{1/2\downarrow}$ = 219 K). Single crystals of the compound were obtained; however, the quality of the crystals was inferior, and only the conformation of the molecule in the HS state could be determined.[5] Several attempts were made to obtain single crystals of higher quality for the determination of the X-ray structure before and after the spin transition, but they were not successful. Recently, we were able to determine the conformation of the molecule at 130 K. A top-view of the asymmetric unit is given in Figure 1. For this type of complexes, the spin state of the iron centre can be determined by observing the O–Fe–O angle which changes from about 90° in the LS state to about 110° in the HS state.[6] According to the outcome from X-ray structure analysis, the single crystals of **1** appear to remain in the HS state at 130 K with O–Fe–O angles around 110° for all four iron centres in the asymmetric unit. This is quite in contrast to the outcome

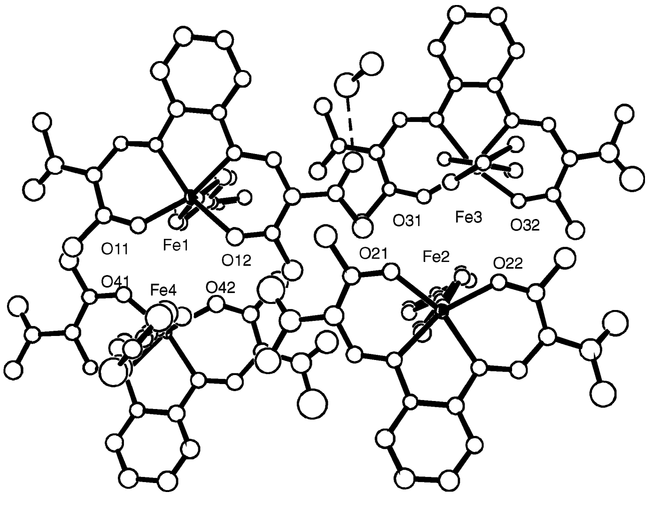

Figure 1. ORTEP drawing of the top-view of the asymmetric unit of compound **1** at 130 K. The O–Fe–O angle is clearly visible for each of the molecules and typical for iron(II) in the HS state (Fe1 110°, Fe2 115°, Fe3 112° and Fe4 112°).

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from susceptibility measurements on the powder sample. We, therefore, decided to grow a large enough amount of crystals for detailed investigations including magnetic measurements, X-ray powder diffraction and optical reflectivity studies to investigate this phenomenon.

Firstly we recorded the magnetic susceptibility of the crystals in the temperature range from 300 K to 5 K. The result is given as solid squares in Figure 2A. The room-temperature moment of 3.32 $cm^3K^{-1}mol^{-1}$ it typical for iron(II) in the HS state and does not change significantly as a function of temperature. Only very small devations between the cooling and the heating curves (Figure 2B) were observed which could be due to a spin change of a small part of the molecules. The heating and cooling curves were repeated; however, no changes were observed. Two parts of the crystals were then pulverised using mortar and pistil (sample I) or a vibrating sample mill (sample II). The resulting curves of the magnetic measurements are given in Figure 2A as open circles (I) and open squares (II). For comparison purposes the results of the magnetic measurements of the powder sample (open triangles) are included as well.

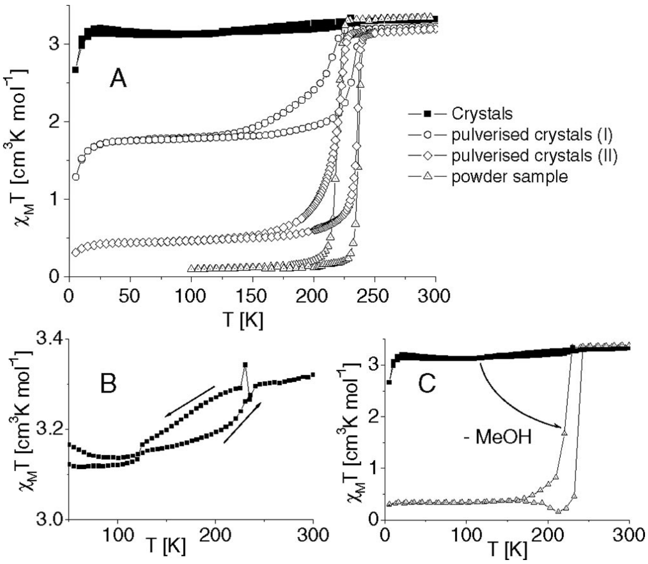

Figure 2. Thermal variation of $\chi_M T$ for the different samples of compound **1**. A: magnetic properties of the crystals (solid squares), pulverised crystals (open circles and open squares) and a separately prepared powder sample (triangles) of **1**. B: Extract of the $\chi_M T$ vs. T plot of the crystal sample of **1**. C: $\chi_M T$ vs. T plot of freshly prepared crystals of **1**$(MeOH)_{0.25}$ (solid squares) and decomposed crystals of **1** (open triangles).

The room-temperature moments of both samples of the pulverised crystals are with 3.23 $cm^3K^{-1}mol^{-1}$ (sample I) and 3.19 $cm^3K^{-1}mol^{-1}$ (sample II) in the range typical for an iron(II) HS complex. Upon cooling, an incomplete, cooperative spin transition into the LS state takes place with a residual HS molar fraction (γ_{HS}) of $\gamma_{HS} = 0.56$ ($\chi T = 1.80\ cm^3K^{-1}mol^{-1}$) for sample I and $\gamma_{HS} = 0.14$ ($\chi T = 0.46\ cm^3K^{-1}mol^{-1}$) for sample II. With increasing grinding (or alternatively with smaller particle size) an increasing reappearance of the hysteresis can be observed. This effect is completely opposite to the grinding effects reported so far for spin transition compounds where hysteresis effects disappear with increasing grinding and higher residual HS and/or LS molar fractions are observed.[7] Until now this was explained by the destruction of the domains responsible for the cooperative interactions during the spin transition in agreement with the domain model by Sorai and Seki.[8] In case of compound **1**, a first explanation of the observed behaviour could be that because of a too rigid packing of the molecules in the crystals the spin transition is quenched except for a small layer on the surface which is more flexible. With increasing grinding the ratio of surface layer/bulk sample increases, and the spin transition reappears with a decreasing remaining HS molar fraction until the particles are small enough for a complete spin transition. As the grinding appears to have no negative effect on the quality of the thermal hysteresis loop, this implicates that the domain model is not applicable for compound **1** or alternatively the domains are very small.

Our next experiment was to find out what happens on the surface. Optical reflectivity spectra are one possibility to monitor the spin transition on the surface of the sample, and the reflectivity spectra of the crystalline and of the powder samples were therefore investigated in dependence of the temperature. The observed changes in the optical spectra when going from room temperature to 100 K are similar for both samples of compound **1**. The absorption band around 850 nm, which is characteristic for the d-d transition in the HS state, decreases, and at the same time the absorption bands in the visible region (d-d and MLCT transitions of the LS state) increase. To illustrate this phenomenon, Figure 3 shows the temperature dependence of the reflectivity recorded at one fixed wavelength (e.g. 880 nm). For both samples a thermal spin transition occurs with an about 20 K wide thermal hysteresis loop, in good agreement with the magnetic measurements on the powder sample. Consequently, at the surface of the crystals clearly a spin transition does take place.

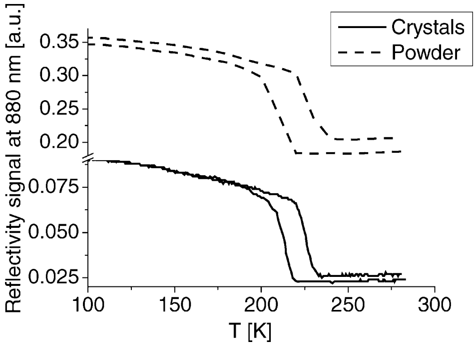

Figure 3. Dependency of the reflectivity signal at 880 nm as a function of the temperature for **1** in the crystalline and powder samples.

As a next step to a better understanding of the system, the X-ray powder patterns of the different samples were investigated in dependence of the temperature. The general idea was to estimate the particle size of the different samples as further proof for the above-mentioned assumptions.

The results are given in the 2θ range of 14–20° in Figure 4A. The spin transition is accompanied by a change in the X-ray powder pattern which is most likely due to a phase transition, as frequently observed for cooperative spin transition compounds. Surprisingly, for the more crystalline samples of compound **1** the same temperature-dependent changes were observed independent of the grinding grade and with no indications for a remaining HS molar fraction (Figure 4B). In contrast to this, in the calculated patterns of the single-crystal X-ray structure analysis only minor changes are found for the different temperatures (298 K, 200 K, 130 K). Additionally, the calculated powder patterns of the single crystals do not agree with those of the powder or the ground crystal samples of **1** (HS or LS state), indicating differences in the composition of the substance and/or a further phase transition.

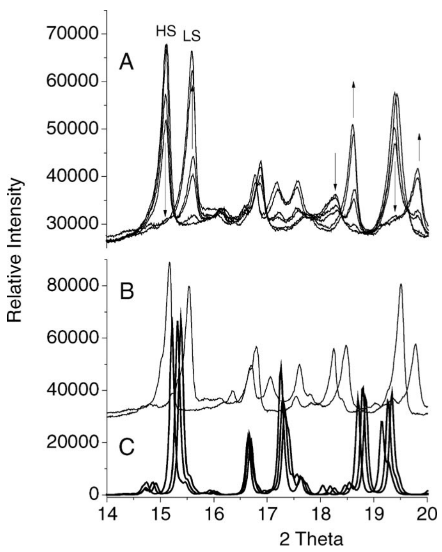

Figure 4. Temperature dependence of the X-ray powder pattern of different samples of **1**. A: powder sample at 200 K, 225 K, 230 K, 235 K, 240 K and 250 K; B: crystalline sample at 100 K and 280 K; C: calculated pattern from the single-crystal X-ray structure analysis at 130 K, 200 K and 300 K.

One possible explanation for these contradictory results is a change in the composition of the crystals in the time interval of the experiments (approximately two months). The only kind of decomposition imaginable causing the observations made so far is the loss of solvent molecules in the crystals. Indeed, the results from X-ray structure analysis indicate the presence of one methanol molecule in the asymmetric unit that is hydrogen-bonded to one of the carbonyl substituents of the equatorial ligand. Due to the low quality of the data this information is not very reliable; however, it is supported by comparison of the elemental analysis of freshly prepared crystals and the powder sample.[9] The magnetic measurements of the crystals were repeated on an "decomposed" batch of the sample, and the results are given in Figure 2c. A complete spin transition with hysteresis is observed for the "decomposed" crystals, and the magnetic properties therefore strongly depend on the presence of lattice solvent. The observations made during the grinding process are (most likely) not due to a change in the particle size but due to a loss of included solvent during the grinding process. As for the reflectivity – since the methanol will first evaporate on the surface, the temperature dependence of the reflectivity should be the same for both samples of the compound.

Conclusions

There are several examples for the influence of additional solvent molecules on the spin transition of SCO complexes.[1h] It has often been observed that the loss of protic solvent molecules destabilizes the LS state,[10] while the loss of aprotic solvent molecules leads to a systematic increase of the transition temperature and continuous decrease of the hysteresis loop width.[11] In contrast to this, in compound **1** the loss of the protic solvent molecule methanol stabilizes the LS state. Similar grinding effects as in **1** were observed for a dinuclear complex; however, only a gradual spin transition is obtained in the powder sample.[12] Technologically attractive SCO complexes should exhibit high transition temperatures with wide thermal hysteresis loops which are stable with respect to grinding effects and/or solvent exclusion. All those properties are unified in compound **1**, where the spin transition properties improve when solvent molecules are lost and/or the crystals are pulverised. This is of great importance when future applications for SCO materials are envisioned, and the results raise our hopes that it will be finally possible to prepare technologically attractive spin transition compounds.

Experimental Section

Compound **1** was prepared as described in the literature.[5] Magnetic measurements were performed with a Quantum Design MPMSR-XL SQUID magnetometer in a temperature range from 5 K to 295 K at 0.02 T and 0.05 T in the settle mode. Data corrections were made as described previously. The intensity data of **1**$(MeOH)_{0.25}$ were collected with a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarisation effects. The structure was solved by direct methods (Sir97[13]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[14]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. ORTEP-III was used for structure representations.[15] The qualtity of the data of **1** was inferior; therefore, the atoms were not refined anisotropically. Only the conformation of the molecule and the crystallograpic data are published.[16] The data will not be deposited with the Cambridge Crystallographic Data Centre. The measurements of the reflectivity signal were performed by using a custom-built setup equipped with an SM240 spectrometer (Opton Laser International). X-ray powder patterns were recorded with an imaging plate detector (HUBER G670, Cu-$K_{\alpha1}$, Guinier technique, SiO_2 as external standard) equipped with a helium closed-cycle cryostat.

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[1] a) H. A. Goodwin, *Coord. Chem. Rev.* **1976**, *18*, 293; b) P. Gütlich, *Struct. Bonding (Berlin)* **1981**, *44*, 83; c) E. König, *Prog. Inorg. Chem.* **1987**, *35*, 527; d) P. Gütlich, A. Hauser, *Coord. Chem. Rev.* **1990**, *97*, 1; e) E. König, *Struct. Bonding (Berlin)* **1991**, *76*, 51; f) P. Gütlich, A. Hauser, H. Spiering, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2024, and references cited therein; g) P. Gütlich, J. Jung, H. Goodwin, *Molecular Magnetism: From Molecular Assemblies to the Devices* (Eds.: E. Coronado, P. Delhaes, D. Gatteschi, J. S. Miller), NATO ASI Series E: Applied Sciences, Kluwer Academic Publishing, **1996**, vol. 321, p. 327; h) P. Gütlich, H. A. Goodwin (Eds.), "Spin Crossover in Transition Metal Compounds I–III", in *Topics in Current Chemistry*, Springer-Verlag, Berlin, Heidelberg, New York, **2004**; i) J. A. Real, A. B. Gaspar, M. C. Munoz, *Dalton Trans.* **2005**, 2062; j) O. Sato, J. Tao, Y.-Z. Zhang, *Angew. Chem.* **2007**, *119*, 2200; *Angew. Chem. Int. Ed.* **2007**, *46*, 2152–2187.

[2] a) O. Kahn, C. Jay Martinez, *Science* **1998**, *279*, 44–48; b) O. Kahn, C. Jay, J. Kröber, R. Claude, F. Grolière, Patent EP0666561, **1995**; c) J.-F. Létard, O. Nguyen, N. Daro, Patent FR0512476, **2005**; d) J.-F. Létard, P. Guionneau, L. Goux-Capes, *Topics in Current Chemistry* (Eds.: P. Gütlich, H. A. Goodwin), Springer, Wien, NewYork, **2004**, vol. 235, p. 221; e) A. Galet, A. B. Gaspar, M. C. Munoz, G. V. Bukin, G. Levchenko, J. A. Real, *Adv. Mater.* **2005**, *17*, 2949–2953.

[3] a) O. Kahn, E. Codjovi, *Philos. Trans. R. Soc. London, Ser. A* **1996**, *354*, 359; b) O. Kahn, Y. Garcia, J.-F. Létard, C. Mathoniére, *NATO ASI Ser. Ser. C* **1998**, *518*, 127.

[4] a) C. Genre, G. S. Matouzenko, E. Jeanneau, D. Luneau, *New J. Chem.* **2006**, *30*, 1669; b) P. J. van Koningsbruggen, Y. Garcia, O. Kahn, L. Fournés, H. Kooijman, A. L. Spek, J. G. Haasnoot, J. Moscovici, K. Provost, A. Michalowicz, F. Renz, P. Gütlich, *Inorg. Chem.* **2000**, *39*, 1891; c) N. Moliner, M. C. Munoz, S. Létard, L. Salmon, J.-P. Tuchagues, A. Bousseksou, J. A. Real, *Inorg. Chem.* **2002**, *41*, 6997; d) J. A. Real, E. Andrés, M. C. Munoz, M. Julve, T. Granier, A. Bousseksou, F. Varret, *Science* **1995**, *268*, 265; e) N. Moliner, M. C. Munoz, S. Létard, X. Solans, N. Menéndez, A. Goujon, F. Varret, J. A. Real, *Inorg. Chem.* **2000**, *39*, 5390; f) G. S. Matouzenko, G. Molnár, N. Bréfuel, M. Perrin, A. Bousseksou, S. A. Borshch, *Chem. Mater.* **2003**, *15*, 550; g) Y. Garcia, V. Niel, M. C. Munoz, J. A. Real, *Top. Curr. Chem.* **2004**, *233*, 229; h) G. S. Matouzenko, M. Perrin, B. Le Guennic, C. Genre, G. Molnár, A. Bousseksou, S. A. Borshch, *Dalton Trans.* **2007**, 934–942; i) J. A. Real, A. B. Gaspar, V. Niel, M. C. Munoz, *Coord. Chem. Rev.* **2003**, *236*, 121–141; j) S. M. Neville, B. A. Leita, D. A. Offermann, M. B. Duriska, B. Moubaraki, K. W. Chapman, G. J. Halder, K. S. Murray, *Eur. J. Inorg. Chem.* **2007**, 1073–1085; k) K. S. Murray, C. J. Kepert, *Top. Curr. Chem.* **2004**, *233*, 195–228.

[5] B. Weber, R. Tandon, D. Himsl, *Z. Anorg. Allg. Chem.* **2007**, *633*, 1159–1162.

[6] a) E.-G. Jäger, *Chemistry at the Beginning of the Third Millenium* (Eds.: by L. Fabbrizzi, A. Poggi), Springer Verlag, Berlin, Heidelberg, **2000**, pp. 103–138; b) G. Leibeling, Ph. D. Thesis, Universiy of Jena, Germany, **2003**; c) B. R. Müller, G. Leibeling, E.-G. Jäger, *Chem. Phys. Lett.* **2000**, *319*, 368–374; d) B. Weber, E. Kaps, J. Weigand, C. Carbonera, J.-F. Letard, K. Achterhold, F.-G. Parak, *Inorg. Chem.* **2008**, *47*, 487–496; e) B. Weber, C. Carbonera, C. Desplances, J.-F. Létard, *Eur. J. Inorg. Chem.* **2008**, 1589–1598.

[7] a) Y. Miyazaki, T. Nakamoto, S. Ikeuchi, K. Saito, A. Inaba, M. Sorai, T. Tojo, T. Atake, G. S. Matouzenko, S. Zein, S. A. Borshch, *J. Phys. Chem. B* **2007**, *111*, 12508–12517; b) E. König, G. Ritter, S. K. Kulshreshtha, N. Csatary, *Inorg. Chem.* **1984**, *23*, 1903–1910; c) E. König, G. Ritter, S. K. Kulshreshtha, *Inorg. Chem.* **1984**, *23*, 1144–1148; d) E. W. Müller, H. Spiering, P. Gütlich, *Chem. Phys. Lett.* **1982**, *93*, 567–571; e) M. S. Haddad, W. D. Federer, M. W. Lynch, D. N. Hendrickson, *Inorg. Chem.* **1981**, *20*, 131–139.

[8] M. Sorai, S. Seki, *J. Phys. Chem. Solids* **1974**, *35*, 555.

[9] Crystals: $C_{28}H_{26}FeN_4O_4(CH_3OH)_{0.25}$ (546.39): calcd. C 62.10, H 4.98, N 10.25; found C 62.06, H 4.93, N 10.37. Powder: $C_{28}H_{26}FeN_4O_4$ (538.38): calcd. C 62.47, H 4.87, N 10.41; found C 62.55, H 4.93, N 10.46.

[10] a) P. Gütlich, Y. Garcia, H. A. Goodwin, *Chem. Soc. Rev.* **2000**, *29*, 419–427; b) G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray, J. D. Cashion, *Science* **2002**, *298*, 1762–1765; c) B. A. Leita, B. Moubaraki, K. S. Murray, J. P. Smith, *Polyhedron* **2005**, *24*, 2165–2172; d) V. Niel, A. L. Thompson, M. C. Munoz, A. Galet, A. E. Goeta, J. A. Real, *Angew. Chem. Int. Ed.* **2003**, *42*, 3760–3763.

[11] a) C. Rajadurai, Z. Qu, O. Fuhr, B. Gopalan, R. Kruk, M. Ghafari, M. Ruben, *Dalton Trans.* **2007**, 3531–3537; b) M. Nihei, L. Han, H. Oshio, *J. Am. Chem. Soc.* **2007**, *129*, 5312–5313.

[12] a) C. J. Schneider, J. D. Cashion, B. Moubaraki, S. M. Neville, S. R. Batten, D. R. Turner, K. S. Murray, *Polyhedron* **2007**, *26*, 1764–1772; b) K. Nakano, N. Suemura, S. Kawata, A. Fuyuhiro, T. Yagi, S. Nasu, S. Morimoto, S. Kaizaki, *Dalton Trans.* **2004**, 982–988.

[13] *SIR97*: A. Altomare, M. C. Burla, G. M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115.

[14] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, **1993**.

[15] C. K. Johnson, M. N. Burnett, *ORTEP-III*, Oak-Ridge National Laboratory, Oak-Ridge, **1996**; L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

[16] Crystal data for $\mathbf{1}(\mathrm{MeOH})_{0.25}$: $C_{113}H_{108}Fe_4N_{16}O_{17}$, M_r = 2185.56 g mol^{-1}, size 0.26 × 0.12 × 0.06 mm, triclinic, space group $P\bar{1}$, a = 11.5638(2), b = 19.6799(6), c = 23.3958(7) Å, α = 79.759(1), β = 87.859(2), γ = 79.830(2)°, V = 5157.0(2) Å^3, Z = 2, $\rho_{\mathrm{calcd.}}$ = 1.404 g cm^{-3}, μ (Mo-K_α) = 0.71073 Å, $F(000)$= 2266, 44624 reflections in h (–15/13), k (–25/25), l (–30/30), measured in the range 3.17° ≤ θ ≤ 27.57°, 23592 independent reflections, 10861 reflections with $F_o > 4\sigma(F_o)$, 639 parameters, 0 restraints $R_{1\mathrm{all}}$ = 0.2995, $wR_{2\mathrm{all}}$ = 0.5320.

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