# Porous Nitrogen Rich Cadmium-Tetrazolate Based Metal Organic Framework (MOF) for H2 and CO2 Uptake

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# Porous Nitrogen Rich Cadmium-Tetrazolate Based Metal Organic Framework (MOF) for $H_2$ and $CO_2$ Uptake

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**S** *Supporting Information*

**ABSTRACT:** The highly porous nitrogen rich metal organic framework $[Cd_3(4\text{-}TP)_6]$ (Cd-4TP-1) was synthesized solvothermally from the predesigned organic building block 4-tetrazole pyridine (4-TP) and Cd(II) as metal center using DMF as solvent. Cd-4TP-1 has a three-dimensional porous architecture where all the binding sites of Cd(II) are exclusively occupied by the nitrogen atoms from the $\mu_2$-tetrazolyl group or the pyridyl functionality of the 4-TP ligands. Cd-4TP-1 has Brunauer−Emmett−Teller (BET) and Langmuir surface areas of 472.2 and 728.6 $m^2$/g, respectively, and shows 1.1 wt % $H_2$ (77 K) and 2.7 mmol/g $CO_2$ uptake (273 K).
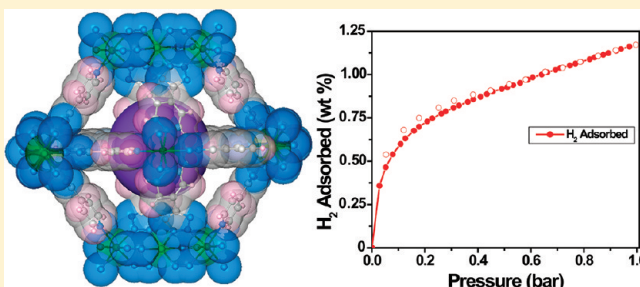
In the past few years, research on crystalline metal organic frameworks (MOFs) has expanded rapidly.[1] A variety of synthetic strategies that allow the preparation of a given framework structure with specific physicochemical properties, such as gas storage, separation,[2] catalysis,[3] multiferroics,[4] and drug delivery,[5] have been perceived. Using ligands containing carboxylate group's a large number of MOFs have been synthesized in the past few years with different topologies, porosities, and framework architecture.[6] Recently, MOFs having heterocyclic functionalities, such as pyrazole, imidazole, triazole, and tetrazole, in their frameworks have caught researchers' attention due to their diverse modes of attachment.[7] Heteroaromatic compounds such as tetrazolates in their anionic forms have wider applications in MOF synthesis because of their ability to bridge multiple metal sites and their facile derivatization to provide bridging ligands with additional functionality. These ligands aroused particular interest due to their applications in coordination chemistry as ligands,[8] in medicinal chemistry as stable substitutes for the carboxylate functionality,[9] and as energy related materials.[10] Also, it is anticipated that metal−tetrazole complexes could produce some unusual extended structures because substituted 1H-tetrazoles have relatively low p$K_a$ values (in the range 3−5), similar to common bridging ligands such as di-, tri-, and tetracarboxylic acids.[11] Moreover, the concept of synthesis of highly porous MOFs designed from supramolecular building blocks (SBBs) has been developed using tetrazolate ligands.[12] Although these kinds of 5-substituted tetrazolate ligands proved to be very interesting and useful in various applications, particularly in the extended 2D and 3D MOF family, these systems are less explored compared to the other five membered aromatic heterocycles such as imidazole, pyrazole, triazole, and their derivatives.

Herein as a part of our ongoing investigations synthesizing MOFs with tetrazolate ligands,[13] we report the synthesis, structure,

**Scheme 1. Schematic Diagram Showing the Synthesis of 4-Tetrazole Pyridine by Click Reaction of 4-Cyanopyridine to 4-Tetrazole Pyridine and the Synthesis of the Cd-4TP-1 MOF by the Solvothermal Method**
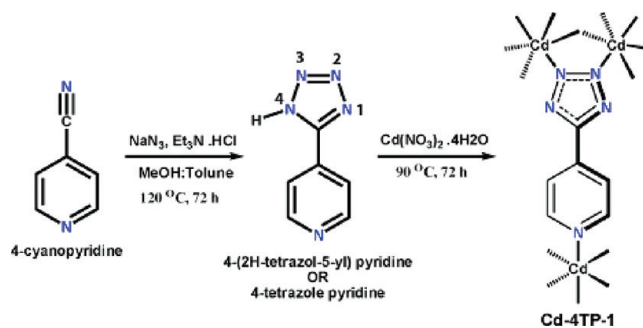


and gas adsorption properties of a nitrogen rich tetrazolate based MOF $[Cd_3(4\text{-}TP)_6]$ (Cd-4TP-1) [4-TP = 4-tetrazole pyridine]. In the typical synthesis, solvothermal reaction of predesigned 4-TP[14] with Cd(NO$_3$)$_2$·4H$_2$O at 90 °C resulted in the formation of Cd-4TP-1, where DMF is used as the solvent (Scheme 1). The resulting colorless plate crystals of Cd-4TP-1 were characterized by X-ray single crystal diffraction analysis. The structure of Cd-4TP-1 was further identified by elemental analysis and IR, the phase purity was confirmed by PXRD, and thermal stability was analyzed by thermogravimetric analyses. The permanent porosity and the $H_2$ and $CO_2$ uptake properties were analyzed by gas adsorption studies.
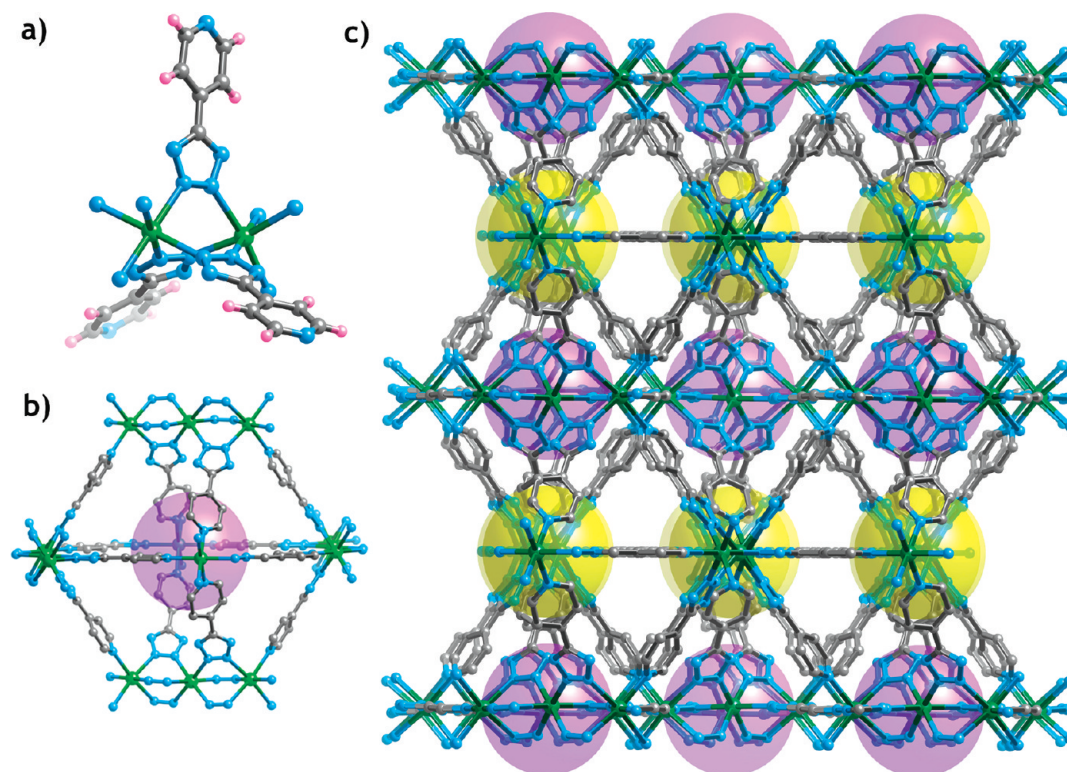
**Figure 1.** Crystal structure of Cd-4TP-1 MOF. (a) Secondary binding units of Cd-4TP-1, where all the binding sites of Cd(II) are coordinated to the nitrogen atoms from the N2, N3-donors of the tetrazolate moiety and the pyridyl nitrogen atoms of the ligands. (b) Single hollow cage of 7.5 Å diameter observed in Cd-4TP-1 which is accessible through the windows of dimensions 3.92 Å × 5.2 Å. (c) Packing diagrams of Cd-4TP-1 showing cages of 7.5 Å diameter present in the Cd-4TP-1 MOF through the $b$ axis. Color code: N (blue), C (gray), H (pink), Cd (green).

Cd-4TP-1 crystallizes in the $Cmc2_1$ space group (orthorhombic crystal system),[20] where all Cd(II) metal centers are in an octahedral coordination state. The three-dimensional structure of Cd-4TP-1 is constructed from the linkage of simple octahedral Cd(II) secondary building units (SBUs)[15] and 4-TP ligands. The fundamental building unit is a trinuclear assembly of octahedral Cd(II) centers, bridging through the N2, N3-nitrogen atoms of the tetrazolate moiety (Figure S9 of the Supporting Information) and through the pyridyl nitrogen atoms of the 4-TP ligands (Figure 1a). The $[Cd_3(4\text{-TP})_6]$ is a common repeating unit in this structure. All the Cd(II) sites in the trinuclear moiety are equivalent and connected exclusively to the nitrogen atoms of the $\mu_2$-tetrazolyl group or the pyridyl functionality of the 4-TP ligand. Although all of the Cd(II) metal centers are equivalent (coordinating to six nitrogen atoms) in the trinuclear moiety, the central Cd(II) is sandwiched between two outer Cd(II) metal centers and is connected to six N2/N3 nitrogen atoms from $\mu_2$-tetrazolyl groups (Scheme S2 of the Supporting Information), while the outer Cd metal centers are connected to the three N2/N3 nitrogen atoms from $\mu_2$-tetrazolyl groups and three nitrogen atoms from the pyridyl functionality of 4-TP ligands. Each octahedral Cd metal site in Cd-4TP-1 is formed through the coordination of three N2/N3 nitrogen atoms from the tetrazolyl group and three from the pyridyl group or exclusively connected to the six N2/N3 nitrogen atoms from tetrazolyl groups. It is noteworthy that no other coordinating aqua or hydroxo species are connected to the Cd metal centers. This type of nitrogenous framework is new and interesting among this series of compounds synthesized using a 4-TP ligand with Cd metal centers. Although there are seven previously reported MOFs synthesized

using a 4-TP ligand with a Cd metal center, all of them have the metal coordination with either oxygen (from either water or DMF) or chlorine (from either HCl or CdCl$_2$) or phosphorus (from H$_3$PO$_4$) atoms. Out of 12 tetrazolyl groups connecting to each trinuclear SBU, six are bridging between Cd(II) metal centers through the N2/N3 of the tetrazolyl groups and six are coordinated through the pyridyl nitrogen atoms of the 4-TP ligands. Each trinuclear Cd building block is thus associated with 12 4-TP ligands, 8 of which are directed to the neighboring trinuclear subunits to form $\{Cd_3(4\text{-TP})_6\}_6$ cages (Figure 1b), enclosing a cavity of 7.5 Å diameter that is occupied by DMF molecules (Figure 1c). As shown in Figure 1c, in Cd-4TP-1 two types of identical pores are present. These pores are identical in diameter but vary in position. Each trinuclear SBU unit directs in three-dimensions through the pyridyl and tetrazolyl groups of 4-TP ligands, so as to link 1 given cage to 12 adjacent cages. Each individual cage communicates to the next adjacent cages through the windows of dimensions 3.92 Å × 5.2 Å (Figure 1c).

As shown in Figure 2, in all the previously reported MOFs[16] with the 4-TP ligand and the Cd(II) metal center, the Cd(II) center is coordinated either to the oxygen (from either water or DMF) or to the chlorine (from either HCl or CdCl$_2$) or to the phosphorus (from H$_3$PO$_4$) atom. Among these MOFs, except $[Cd_4Cl_3(4\text{-pt})_4\cdot(OH)(DMF)_3]\cdot 8DMF\cdot 14MeOH\text{-}(2\cdot 8DMF\cdot 14MeOH)$,[16a] all the Cd(II) metal centers are in an octahedral coordination state. These MOFs are synthesized either by an *in situ* synthetic procedure using the Sharpless–Demko reaction[16b–d] or by using the predesigned 4-TP ligand. The SBUs observed in these MOFs are with one, two, three, or four metal centers (Figure 2). In most of the hydrothermal
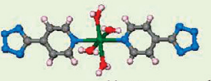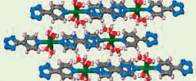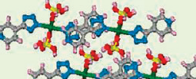
**Figure 2.** Comparison between previously reported MOFs synthesized using 4-tetrazole pyridine (4-TP) and Cd(II) metal center, solvothermally or via a hydrothermal synthetic route (4PTZ, 4-pt, Hpytz, and 4-TP stand for 4-tetrazole pyridine used as a ligand). Color Code: N (blue), C (gray), H (pink), O (red), P/Cl (yellow), Cd (green).

synthetic cases where the solvent used is water, the secondary building unit is monometallic with coordinating water molecules. On the other hand, in solvothermal synthetic procedures with solvents such as DMF/MeOH/DEF, the resulting SBUs are with two, three, or four metal centers in nature. We choose the *ex-situ* solvothermal synthesis method, for the synthesis of Cd-4TP-1, as from the previous reports it is clear that most of the time the structures resulting from *in situ* reaction of 4-cyanopyridine with $CdCl_2$ and/or $NaN_3$ are one-dimensional in nature. In a few cases, the structure adopts a three-dimensional architecture, but

the resulting framework becomes nonporous due to complex coordination nature of the 4-TP ligand.[16b] The reports by Zubieta et al. confirm that, for the synthesis of porous MOFs with 4-tetrazole pyridine as a single ligand system with Cd(II) as metal center, solvothermal reactions using solvents such as DMF are fruitful. Using a similar approach, we could also achieve porous Cd-4TP-1, synthesized using a solvothermal synthetic route, with 4-TP ligand and Cd(II) as metal center. Here, it should be noted that, using 4-TP ligand and Cd(II) metal, seven structural isomers have been reported, including Cd-4TP-1. This

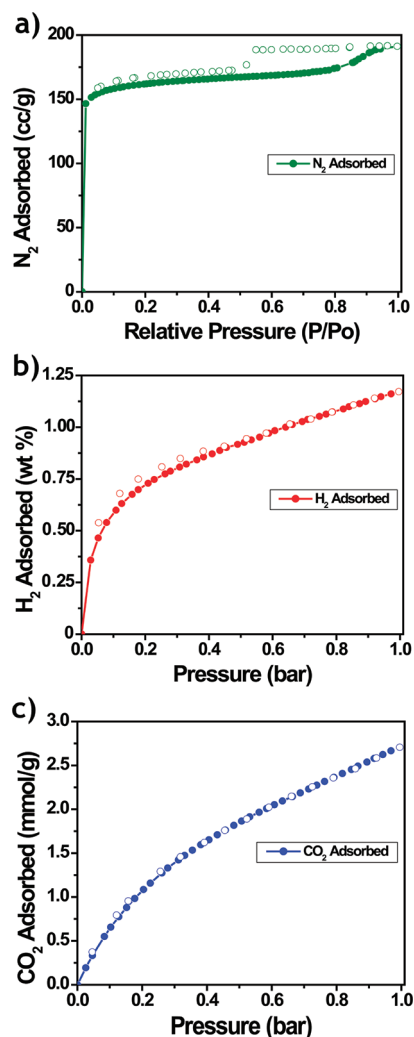**Figure 3.** Gas adsorption isotherms of Cd-4TP-1. (a) Nitrogen adsorption isotherms for Cd-4TP-1 at 77 K and 1 atm pressure. (b) $H_2$ adsorption isotherms for Cd-4TP-1 at 77 K and 1 atm pressure. (c) $CO_2$ adsorption isotherms for Cd-4TP-1 at 273 K and 1 atm pressure. The filled and open circles represent adsorption and desorption, respectively.

system produces one of the highest structural isomers with the same ligand and metal center.

We have prepared the Cd-4TP-1 in gram scale to allow detailed investigation of the aforementioned properties and to examine the architectural and thermal stability reported in this paper. Thermal gravimetric analysis (TGA) performed on as-synthesized Cd-4TP-1 revealed that these compounds have high thermal stability up to 400 °C (section S3 of the Supporting Information). The TGA trace for as synthesized Cd-4TP-1 showed a sharp weight-loss step of 19.5% (90−140 °C) corresponding to escape of guest *N,N*-dimethylformamide (DMF) solvent molecules in pores. As shown in Figure S3 of the Supporting Information after removal of guest solvent molecules and also the framework of Cd-4TP-1, the framework is stable (140−400 °C), as all the coordination sites of Cd-4TP-1 are occupied by nitrogen atoms from 4-TP ligands. This is followed by the sharp weight loss, possibly because of framework decomposition at higher temperature (400−430 °C). In order to confirm the phase purity of the bulk materials, powder X-ray

diffraction (PXRD) experiments were carried out on Cd-4TP-1. All major peaks in experimental PXRD of Cd-4TP-1 match well with simulated PXRD, indicating reasonable crystalline phase purity (Figure S1 of the Supporting Information). In the experimental PXRD pattern of Cd-4TP-1, some diffraction lines are broadened compared to the simulated pattern, possibly because of grinding of samples during analysis.

The single crystal structure analysis of Cd-4TP-1 shows that this MOF has hollow cages of 7.5 Å diameter with slits of dimensions 3.92 Å × 5.2 Å for accessibility to these cages. Also from the TGA analysis, it was revealed that the free guest DMF molecules present in the cages can be removed from the framework by the evacuation at elevated temperature (higher than 140 °C). From the previous reports, it is clear that for reversible gas uptake in the MOFs free and coordinated solvent molecules need to be removed to achieve the solvent free framework. This can be achieved by solvent exchange followed by thermal activation at high temperature at dynamic vacuum. The microcrystals of Cd-4TP-1 were soaked in a 1:1 dry dichloromethane and methanol mixture for 12 h. Fresh 1:1 dry dichloromethane and methanol mixture was subsequently added, and the crystals were allowed to stay for an additional 48 h to remove free solvates (DMF) present in the framework. The sample was dried under a dynamic vacuum ($<10^{-3}$ Torr) at room temperature overnight. Prior to gas sorption experiments, thermal activation at an optimized temperature of 140 °C, for 48 h, has been done to remove free solvent molecules (DMF) present in the framework. However, we acknowledge that the crystallinity of the evacuated sample got diminished significantly (from PXRD analysis) during the evacuation process. A structural change at high temperature and under high vacuum could be a possible reason for this phenomenon. The permanent porosity of Cd-4TP-1 was confirmed by the $N_2$ adsorption isotherm over the activated sample (90 mg). The $N_2$ adsorption isotherms of the activated sample of Cd-4TP-1 exhibit type-I sorption behavior (Figure 3a) with Langmuir and BET surface areas of 728.6 m$^2$/g and 472.2 m$^2$/g, respectively (refer to Figures S5 and S6 of the Supporting Information for more information on BET and Langmuir plots). The surface area shown by the Cd-4TP-1 is well-defined, as this MOF has hollow cages of 7.5 Å with 52.5% solvent accessible voids calculated using *PLATON*.[17]

The $H_2$ and $CO_2$ adsorption properties of Cd-4TP-1 are shown in Figure 3b and c. All these MOFs show reversible type-I $H_2$ and $CO_2$ adsorption isotherms at 77 and 273 K, respectively. In addition, the absence of adsorption−desorption hysteresis indicates that $H_2$ and $CO_2$ is reversibly adsorbed by the MOF reported here. It should be noted that the repeatability of the $H_2$ and $CO_2$ adsorption behavior was confirmed by reproducing the same isotherm three times at 77 and 273 K, respectively. At 77 K, Cd-4TP-1 shows 1.17 wt % of $H_2$ uptake as the pressure approaches 1 atm. Similarly, at 273 K, Cd-4TP-1 shows 2.70 mmol/g of $CO_2$ uptake at 1 atm pressure. As discussed earlier, $H_2$ and $CO_2$ uptake shown by Cd-4TP-1 is well-defined, as this MOF has the moderate BET surface area 472.2 m$^2$/g. The $H_2$ uptake shown by Cd-4TP-1 is lower than those of the previously reported MOFs named $[Cd_4Cl_3(4\text{-pt})_4 \cdot (OH)(DMF)_3] \cdot$ 8DMF·14MeOH($2 \cdot$8DMF·14MeOH), and $[Cd_5Cl_6(4\text{-pt})_4$-$(DMF)_2 (H_2O)_2] \cdot$10DMF($3 \cdot$10DMF)[16a] constructed using the 4-tetrazole pyridine as building block and Cd(II) as metal center. The $H_2$ uptakes shown by $1 \cdot$12DMF (surface area 2043 m$^2$/g), $2 \cdot$8DMF·14MeOH (surface area 1753 m$^2$/g), and $3 \cdot$10DMF (surface area 1409 m$^2$/g) are 2.24, 1.83, and

1.58 wt %, respectively at 1 atm pressure, and these $H_2$ uptakes are higher compared to that of Cd-4TP-1 (surface area 472 m$^2$/g). The higher $H_2$ uptake values of these MOFs are well justified, as these MOFs have a higher surface area than Cd-4TP-1. Although Cd-4TP-1 has a very low surface area, the $H_2$ uptake shown is still comparable with those of reported MOFs, such as MOF-177,[18a] MOF-5,[18a] and CPM-5,[18b] and ZIFs, such as ZIF-8, −11 at 1 atm pressure.[7e] Since Cd-4TP-1 has limited surface area compared to those of MOF-177, MOF-5, and CPM-5, we acknowledge that high pressure $H_2$ and $CO_2$ uptake will be lower for Cd-4TP-1 than for these MOFs. It is now commonly believed that carbon dioxide emissions from burning of fossil fuels in power plants and automobiles are altering the temperature of the atmosphere and the acidity of the oceans with undesirable consequences for the Earth's environment. We studied the $CO_2$ uptake of Cd-4TP-1, as it contains free nitrogen, which according to a recent theoretical study should enhance the adsorption energy of $CO_2$. $CO_2$ uptake of Cd-4TP-1 is seen to be comparable to that of some well-known MOFs, such as MOF-5, MOF-177, and IRMOF-3,[18a] and ZIFs, such as ZIF-96,[18c] -78,[2g] and -69,[2g] and it outperforms ZIF-100[2g] and BPL carbon at 1 atm pressure.[19] Although some zeolite materials outperform BPL carbon in terms of selective $CO_2$ adsorption, regeneration difficulties mean that their suitability for practical use is uncertain and they were therefore not included in the comparative adsorption measurements.

In summary, by using the predesigned heterocyclic ligand 4-tetrazole pyridine, for the first time we have synthesized a nitrogen rich porous metal organic framework, where all the coordination sites of Cd(II) are exclusively occupied by the nitrogen atoms from N2, N3-donors of the tetrazolate terminus and pyridyl nitrogen atoms of the ligands. Interestingly, Cd-4TP-1 contains only nitrogen atoms as the coordinating centers, and the framework is totally free from oxygen, phosphorus, and halogen atoms. Cd-4TP-1 has large hollow cages of 7.5 Å diameter which are accessible through slits of dimensions 3.92 Å × 5.2 Å. Although Cd-4TP-1 has a low surface area, the $H_2$ and $CO_2$ uptake shown is comparable with those of some well-known MOFs and it outperforms zeolites and activated carbons.

## ■ ASSOCIATED CONTENT

**ⓢ Supporting Information.** Description of experimental details, including synthetic methods and crystallography, supplementary figures, including TGA, infrared spectroscopy, and powder XRD profiles, tables of crystallographic data, CIF files, and anisotropic thermal ellipsoids for the Cd-4TP-1 MOFs reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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## ■ ACKNOWLEDGMENT

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(20) Crystal data for Cd-4TP-1: $C_{138}H_{92}N_{115}Cd_{12}$, $M_r$ = 4710.19, orthorhombic, space group $Cmc2_1$, $a$ = 34.311 (10) Å, $b$ = 40.539 (10) Å, $c$ = 20.326 (11) Å, $V$ = 28273.5(15) Å$^3$, $Z$ = 4, $\rho_{calcd}$ = 1.107 g cm$^{-3}$, final $R1$ = 0.0531 and $wR2$ = 0.1478 for 19425 independent reflections $[I > 2\sigma(I)]$. CCDC-838792.