Indian Journal of Chemistry
Vol. 60A, May 2021, pp. 669-675

Synthesis, crystal structure, thermal analysis and molecular interactions of bis(3,5-dimethyl-3H-1,2,4-triazole)octamolybdate

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Received 27 October 2020; revised and accepted 10 March 2021

This paper describes the synthesis of {bis(3,5-dimethyl-3H-1,2,4-triazole)octamolybdate}(2:1) molecule by mixing bis(acetylacetonato)dioxo molybdenum(VI) and 3-(E)-{1-(furan-2-yl)ethylidene)amino]-1-phenylurea. The structure of the molecule was determined by using single crystal X-ray diffraction technique. Structure determination reveals that the title complex $Mo_8O_{26}.2(C_4H_9N_3)$ contains two moieties namely an octamolybdate $[Mo_8O_{26}]$ complex, and 3,5-dimethyl-1,2,4-triazole $[2(C_4H_9N_3)]$ in the unit cell. The $[Mo_8O_{26}]$ unit consists of two $\{Mo_4O_{13}\}$ subunits linked together by bridging oxygen atoms with an approximate C_{2h} symmetry under Triclinic system, $P\overline{1}$ space group with lattice parameters a = 10.1007(2), b = 10.3887(2), c = 13.0380(3) Å, α = 66.921(3) β = 69.466(3) γ = 62.892(2)°. The octamolybdate units are linked by methylmethanamine as chains via N-H…O interactions. The ^1H-^1H COSY NMR recorded in DMSO-d_6 spectral data indicates the absence of the coupling between the protons. The thermal analysis indicates that the complex is thermally stable. The Hirshfeld surface of the compound mapped with d_{norm} (-1.0 a.u. to 1.0 a.u.) and the deep red spot on the Hirshfeld surface depicts the formation of strong N-H···O hydrogen bond.

Keywords: 3,5-Dimethyl-4H-1,2,4-triazole, Octamolybdate, Triclinic system, Hirshfeld surface analysis

Today heterocyclic compounds play an important role in various fields of science such as medical, agriculture and industries etc.[1]. In addition, heterocyclic compounds also essential in day-to-day life for all the living organisms. For example, Deoxyribo nucleic acid, haemoglobin, vitamin B_{12} etc. contain nitrogenous heterocycles. The five-membered heterocyclic ring compounds focused a special attention due to their wide range of biological activities. A literature survey reveals that among five- membered ring compounds, 1,2,4-triazoles have pulled in much consideration as they have turned out to be genuinely available and have diverse biological activities[2-13]. The significance of 1,2,4-triazole lies in the way that they can be viably utilized as anti-inflammatory[3], analgesic[3], anti-HIV and anti-viral, anti-tuberculosis[4,5], anticonvulsant activity[6], anti-microbial[7], anti-proliferative agents[8], neurotropic activity[9], anti-cancer activity[10], anti-fungal[11,12], anti-bacterial agents[13], anti-leishmanial activity, and anti-depression[14].

Various therapeutic molecules also have been available in market such as fluconazole, voriconazole[15], alprazolam[16], etinolam[17] interesting drugs candidates which containing 1,2,4-triazole moieties. In this aspect, various transition metal complexes of 1,2,4-triazole were reported in literature[18-21] but the molybdenum complexes are limited[22-24] in particularly octa-molybdenum complexes. As, molybdenum is abundant and non-noble, metal-organic coordination complexes containing molybdenum and 1,2,4-triazole moieties attracted considerable interest due to their various applications, prompt us attempt to prepare octa-molybdenum$[(Mo_8O_{26})^{4-}]$ complexes with 1,2,4-triazole. In addition, due to the presence of nitrogen and/or oxygen atoms and aromatic and/or heterocyclic moieties, the molecule exhibit building block self-assembled through intermolecular interactions[25]. Hence, it is essential to investigate and analyze the molecular interactions, crystal packing behaviour and also novel tool such as Hirshfeld surface analysis[26-28]. The surface analysis data provides a molecular fingerprint 2D map that gives the information of visualization and quantification about the distribution of interactions in environments.

In the light of the above and in continuation of our ongoing research work[28] on octa-molybdates with nitrogen containing organic moieties[29-34], herein reporting the synthesis and crystal structure of an octa-molybdate, 3,5-dimethyl-1,2,4-triazole (1:2) (Fig. 1) and its molecular interactions.

Materials and Methods

The reagents and solvents used were commercially available and used as received without further purification. $(NH_4)_6Mo_7O_{24}H_2O$, acetylacetone (acacH), 2-acetyl furan, and acetyl hydrazine were purchased from Sigma-Aldrich chemicals. Fourier-Transform Infrared (FTIR) spectrum of the complex recorded using ATR ALPHA FTIR (BRUKER, Germany) in the range 4000-400 cm^{-1}. ^1H-NMR was recorded on a BRUKER 400 MHz NMR in deuterated dimethylsuphoxide solvent and TMS as internal standard. Chemical shifts δ are quoted in ppm. The NETZSCH STA 449F5 instrument was used to carry out TG-DSC analysis of metal complex in nitrogen atmosphere (30–900 °C) at a heating rate of 10 °C min^{-1} using alumina powder as reference.

Synthesis and crystallization

The starting materials, Schiff base, 2-acetylfuran-4-phenyl-3-semicarbazone (AFPS)[35] and metal complex precursor, $MoO_2(acac)_2$ were prepared as described in literature[36]. The following reaction was carried out expecting the step 1, MoO_2L_2 complex, (where, L = 2-acetylfuran-4-phenyl-3-semicarbazone) (Scheme 1) but circumstantially achieved step II, which is a formation of $[Mo_8O_{26}\cdot 2(C_4H_9N_3)]$.

In a 250 mL round bottom flask, $MoO_2(acac)_2$ (0.54 gm dissolved in 20 mL of ethanol, 16 mmol) and 0.4 g (24 mmols) of 2-acetylfuran-4-phenyl-3-semicarbazone (AFPS) ligand dissolved in 15 mL of ethanol were combined and heated under reflux on a water bath for 1h. The reaction mixture was cooled to room temperature and filtered. On slow evaporation

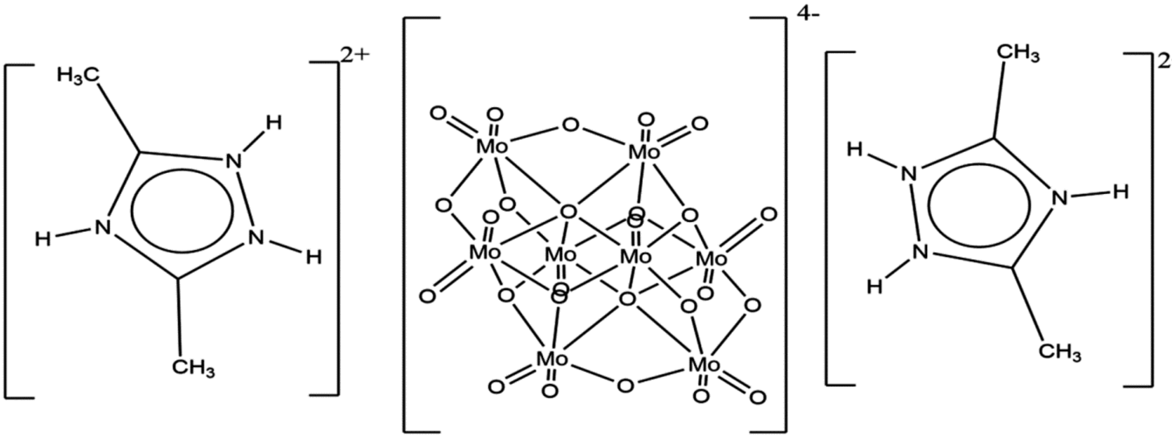
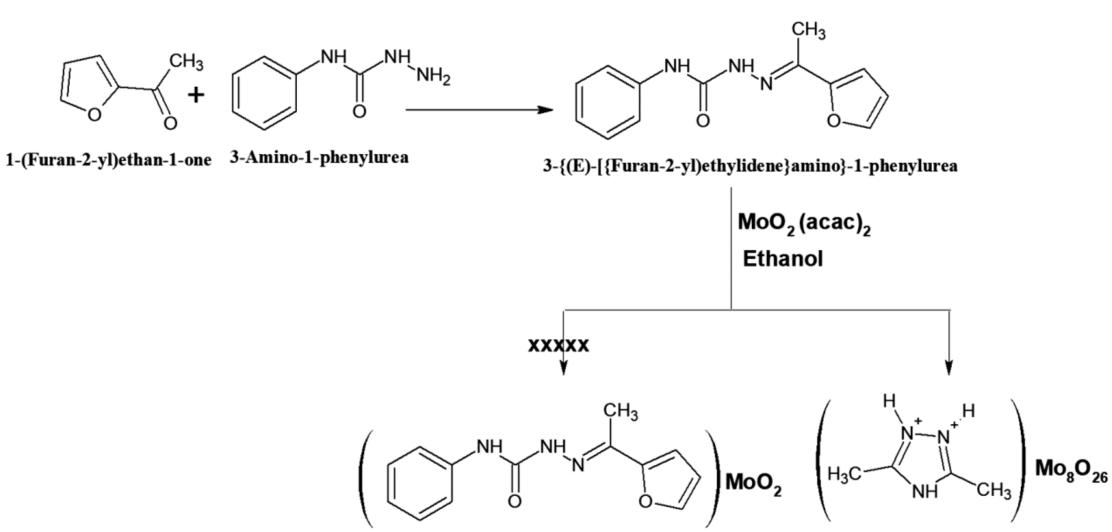


Fig. 1 — Chemical structure of bis(3, 5-dimethyl-3H-1,2,4-triazole)octamolybdate



Scheme 1 — Synthesis of ligand and its Mo compound of the filtrate, crystals of the title compound were obtained that are suitable for X-ray crystallography analysis.

Crystal structure determination

Single-crystal X-ray diffraction data collected using a Bruker APEX II diffractometer equipped with a CCD detector using monochromated Mo Kα radiation (λ = 0.71073 Å) in phi(ϕ) and omega(ω) scan. The unit cell measurement, data collection, integration, scaling and absorption corrections were done using Bruker Apex II software[37]. The intensity data were processed by using the Bruker SAINT[38] suite of programs. Further the refinements were performed by using Olex2 1.2[39]. The crystal structure was determined by direct methods and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-squares refinements on F2 Scattering factors for neutral atoms were employed in the refinements.

All non-hydrogen atoms were refined anisotropically and all hydrogen atoms isotropically using Olex2 1.2[39]. Empirical absorption correction was applied using SADABS[40]. The molecular Plots and the crystal packing diagrams were generated using CAMERON programs[41]. The crystallographic data and the structure refinement parameters were summarized in Table 1.

Refinement

Table 1 — Experimental details of X-ray crystallography

Chemical formula	$Mo_8O_{26}\cdot 2(C_4H_9N_3)$
CCDC number	2011124
M_r	1381.77
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	203
a, b, c (Å)	10.1007 (2), 10.3887 (2), 13.0380 (3)
α, β, γ (°)	66.921 (3), 69.466 (3), 62.892 (2)
V (Å^3)	1095.33 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.29
No. of measured, independent and observed [I>2u(I)] reflections	36223, 5436, 4326
R_{int}	0.029
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.668
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.029, 0.074, 1.08
No. of reflections	5436
No. of parameters	220
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.60, -0.94

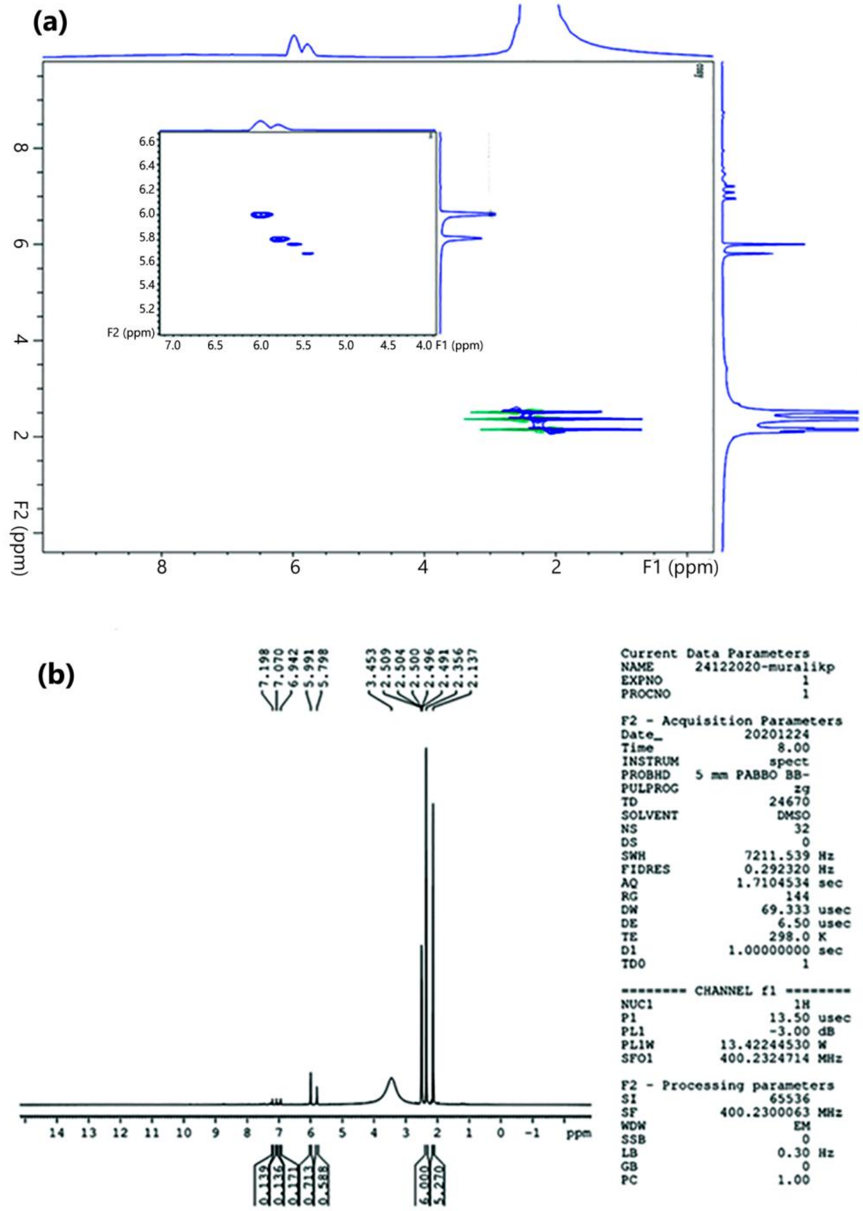
The H atoms were positioned geometrically with d(C-H) = 0.93 Å and d(N-H) = 0.86 Å, and were refined as riding with $U_{iso}(H) = 1.2\ U_{eq}(N)$ and $U_{iso}(H) = 1.5\ U_{eq}(O)$. There were two significant regions of disordered electron density detected in the residual Fourier difference map after the refinement of atoms. None of these lattice solvent molecules could be reasonably modelled, and the remaining electron density had its contribution to the diffraction data accounted for with the SQUEEZE routine within PLATON. Analyses of these voids from SQUEEZE results in a total electron count of 11.6 and 14.6e$^-$ within the voids per unit cell, with a void volume of 339 Å^3 and 11.4Å^3, respectively.

Hirshfeld surface analysis

The Hirshfeld surfaces and two-dimensional fingerprint plots[26,27] were generated using CrystalExplorer17.5[42], to obtain the information on crystal packing. The derivation of the Hirshfeld surface and a representation of the corresponding 2D fingerprint-plots provides a convenient means of quantifying the interactions in crystal structures.

Results and Discussion

The title compound, $[Mo_8O_{26}\cdot 2(C_4H_9N_3)]$ was prepared using 2-acetylfuran-4-phenyl-3-semicarbazone and $MoO_2(acac)_2$ as shown in the Scheme 1. In this reaction, ligand, 2-acetylfuran-4-phenyl-3-semicarbazone underwent cyclization and as a result 3,5-dimethyl-1, 2, 4-triazole was formed[43]. In the formation of complex, the cyclized 1, 2, 4-triazole shows a rare system of H_2 and on deprotonation act as anionic bidentate ligand and coordinated with metal ion that led to poor crystalline nature[18]. In the FT-IR spectrum of complex, >C=N- and >NH groups showed characteristic peaks at 1588 and 3184 cm^{-1}, respectively. Bands in the range 1114-1149 cm^{-1} are due to ν(N–N) stretching[44]. In the IR spectrum of metal complex, the $[\beta\text{-}Mo_8O_{26}]^{-4}$ cluster is characterized by two absorption bands at 897 and 943 cm^{-1} corresponding to the $\nu(Mo{=}O)_{(terminal)}$ absorption vibration. The absorption bands in the range of 500-866 cm^{-1} are assigned to $\nu(Mo\text{-}\mu_2\text{-}O)$ and $\nu(Mo\text{-}\mu_3\text{-}O)$ vibrations[28]. The ^{1}H-NMR of the complex recorded in DMSO-d_6 solvent. The ^{1}H-^{1}H COSY NMR spectrum of the complex (Fig. 2a) indicates the absence of the coupling of the protons. However in ^{1}H-NMR (Fig. 2b) in DMSO-d_6 indicates



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PULPROG                  zg
TD                    24670
SOLVENT                DMSO
NS                       32
DS                        0
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FIDRES             0.292320 Hz
AQ                1.7104534 sec
RG                      144
DW                   69.333 usec
DE                     6.50 usec
TE                    298.0 K
D1               1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
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P1                    13.50 usec
PL1                   -3.00 dB
PL1W            13.42244530 W
SFO1            400.2324714 MHz

F2 - Processing parameters
SI                    65536
SF              400.2300063 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
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Fig. 2 — (a) ^{1}H-^{1}H COSY (b) ^{1}H NMR spectrum of [$Mo_8O_{26}\cdot 2(C_4H_9N_3)$] in DMSO-$d_6$

the presence of N-H proton in the downfield (δ 5.798 and 5.991 ppm) due to intramolecular hydrogen bonding and the -CH_3 proton signal appeared at δ 2.137 and 2.356 ppm corresponding to the uncoordinated part of the ligand.

Thermal stability of the title compound, [$Mo_8O_{26}\cdot 2(C_4H_9N_3)$], was examined by thermogravimetric analysis (TGA). As shown in Fig. 3, the first weight loss in the region 210–260 °C corresponding to one organic ligand (observed 7.73%, calculated 7.17%). The second decomposition of the organic ligand molecule occurs from 660–690 °C. The final residue might be related to molybdenum oxide (Mo_2O_3) compound. In DSC curve two exothermic peaks are observed at 230 °C and 670 °C may be due to the decomposition of the organic molecules.

Single crystal structure data

The crystal structure of the title complex $Mo_8O_{26}.2(C_4H_9N_3)$ contains (Fig. 4), two moieties namely an octa-molybdate [Mo_8O_{26}] complex, and 3,5-dimethyl-1,2,4-triazole [$2(C_4H_9N_3)$] in the unit

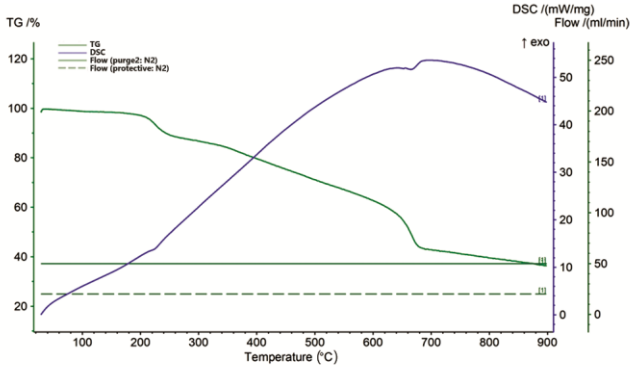

Fig. 3 — TG/DSC analysis of complex, $[Mo_8O_{26}{\cdot}2(C_4H_9N_3)]$

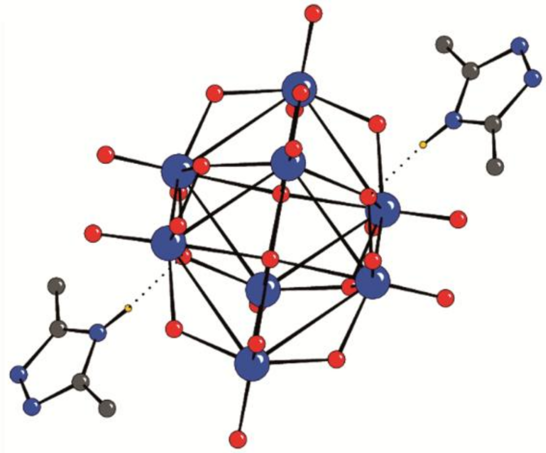

Fig. 4 — A view of the structure of (I), showing the atom-labelling scheme. Symmetry code: (*a*) − *x*, − *y*, − *z*

cell. The $[Mo_8O_{26}]$ unit consists of two $\{Mo_4O_{13}\}$ subunits linked together by bridging oxygen atoms with an approximate C_{2h} symmetry. The Mo—O distances are in rational range, varying between 1.695 to 2.395 Å. The octa-molybdate units are linked by methylmethanamine as chains via N-H…O interactions. Further two ligand molecules held the octa-molybdate units forming three-dimensional supramolecular networks through N-H…O interactions (Fig. 5). The details of the geometric details and hydrogen bond data are given in Supplementary Data, Table S1 & Table S2. Sometimes, as the X-ray crystallography difficult to locate H-atoms and hence their coordinates will miss from crystal structures. The same will be observed in present crystal structure of the titled complex.

The Hirshfeld surface analysis

The Hirshfeld surface of the compound mapped with d_{norm} (-1.0 a.u. to 1.0 a.u.) shown in Fig. 6. The deep red spot on the Hirshfeld surface depicts the formation of strong N-H···O hydrogen bond.

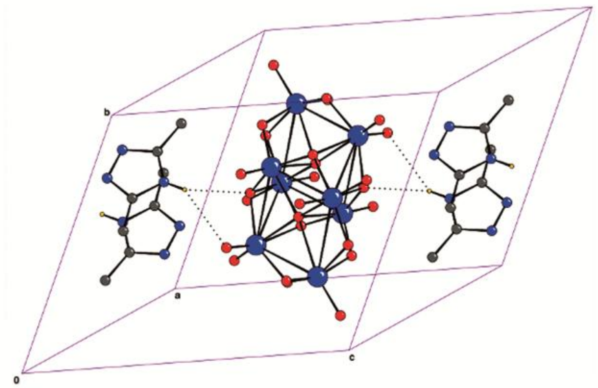

Fig. 5 — Packing of molecules within unit cell with C – H … O intermolecular interactions in dotted lines

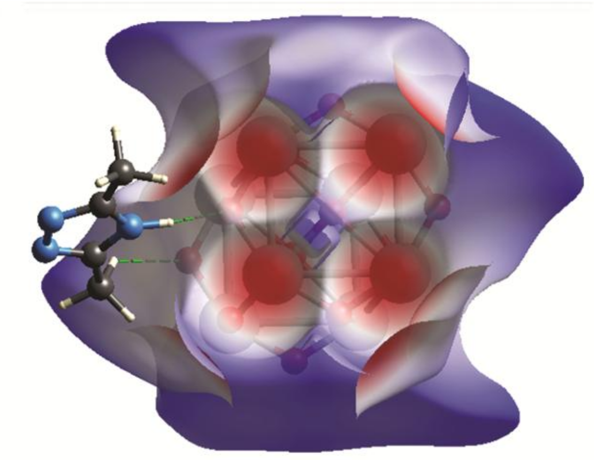

Fig. 6 — Fingerprint plots of compound with different contribution into the total Hirshfeld surface area of the molecules

The Fig. 7 shows the 2D fingerprint plots of compound. The relative contribution of different atom·atom contacts (O…O, O…H, Mo…O and others) in the overall fingerprint. The sharp spikes appear in both the 2D fingerprint plots are due to the presence of short Mo…O contact responsible for the formation of strong Mo…O and weak N-H…O interactions present in the crystal packing. The O…O contact contributes 36.8% and Mo…O contacts 35.1% in the overall interaction in compound.

Hence, the overall fingerprint plot helps to distinguish the differences in the crystal packing of two different molecules as well as to understand the contributions of different type of contacts present. The Hirshfeld details are given in Supplementary Data, Table S3. The relative contribution of different atom-atom contacts in the fingerprint plot given in Fig. 7.

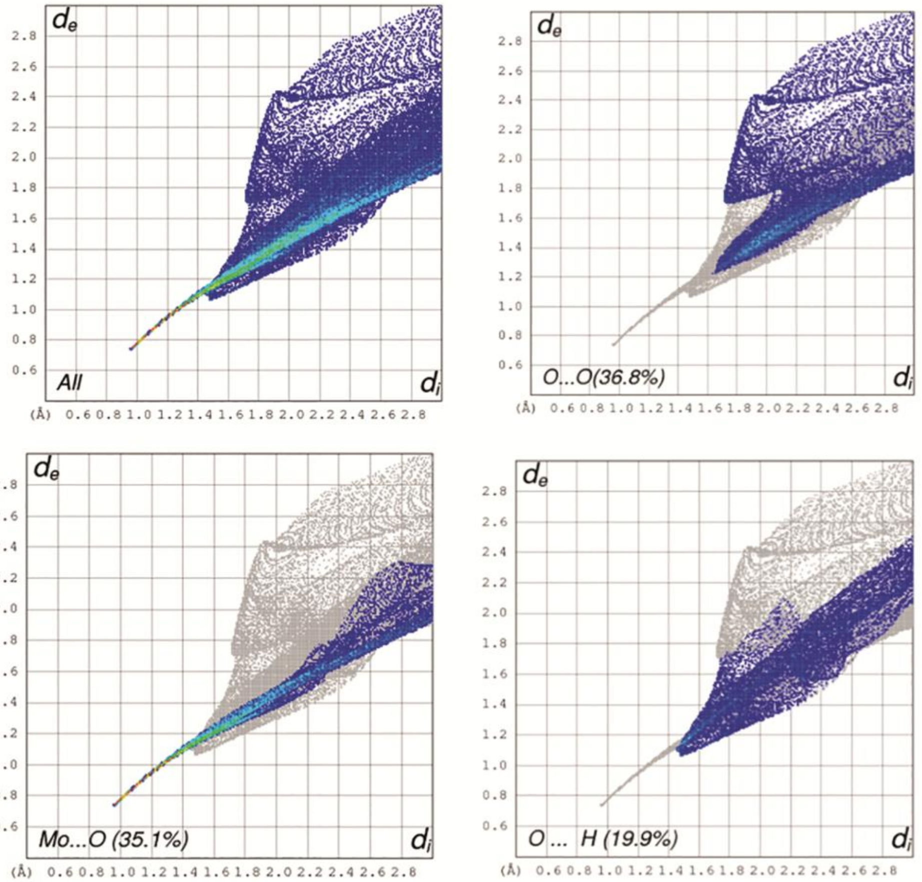

Fig. 7 — Relative contribution of different atom…atom contacts in the fingerprint plot

Conclusions

A new {bis(3,5-dimethyl-4H-1, 2, 4-triazole)octa-molybdate}(1:2) compound was prepared and its structure was determined using the single crystal X-ray diffraction studies. The crystal data indicate the [Mo_8O_{26}] unit consists of two {Mo_4O_{13}} subunits linked together by bridging oxygen atoms with C_{2h} symmetry under triclinic system. The octa-molybdate units are linked by methyl-methanamine as chains *via* N-H…O interactions. The ^{1}H-^{1}H COSY NMR spectral studies in DMSO-d_6 indicate the absence of ^{1}H-^{1}H coupling. The thermal analysis indicates that the complex is thermally stable up to 660 ºC. The Hirshfeld surface of the compound mapped with d_{norm} (-1.0 a.u. to 1.0 a.u.) and the deep red spot on the Hirshfeld surface depicts the formation of strong N-H···O hydrogen bonds.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(05)669-675_SupplData.pdf.

Acknowledgement

KHR is thankful UGC, New Delhi for the award UGC-BSR Faculty Fellowship [Award Lr No. 18-1/2011(BSR)21-12-19] The authors are thankful to SAIF, IIT-Madras, Chennai, India for providing X- ray Crystallographic data, Center for Advanced Material Technology, RIT for TG analysis and NMR Research Center, IISc, Bangalore, for NMR data.

References

1 Yang Hu, Cui-Yun Li, Xiao-Ming Wang, Yong-Hua Yang, & Hai-Liang Zhu, *Chem Rev,* 114 (2014) 572.

2 Sahil Sharma, Devendra Kumar, Gurpreet Singh, Vikramdeep Monga & Bhupinder Kumar, *Eur J Med Chem,* 200 (2020) 112438.

3 Deniz Sarigol, AyseUzgoren-Baran, Banu Cahide Tel, Elif Inci Somuncuoglu, Inci Kazkayasi, Keriman Ozadali-Sari, Oya Unsal-Tan, Gurol Okay, Mevlut Ertan & Birsen Tozkoparan, *Bioorg Med Chem,* 23 (2015) 2518.

4 Shu Zhang, Zhi Xu, Chuan Gao, Qing-Cheng Ren, Le Chang, Zao-Sheng Lv & Lian-Shun Feng, *Eur J Med Chem*, 138 (2017) 501.

5 Keri R S, Patil S A, Budagumpi S & Nagaraja B M, *Chem Biol Drug Des,* 86(4) (2015) 410.

6 Sari S, Kaynak F B & Dalkara S, *Pharmacol Rep,* 70(6) (2018) 1116.

7 Padmaja A, Murali Krishna A, Rajasekhar C & Padmavathi V, *Chem Pharm Bull (Tokyo),* 59(12) (2011) 1509.

8 Zhu X P, Lin G S, Duan W G, Li Q M, Li F Y & Lu S Z, *Molecules*, 25(4) (2020) 986.

9 Ervand G Paronikyan, Anthi Petrou, Maria Fesatidou, Athina Geronikaki, Shushannik Sh Dashyan, Suren S Mamyan, Ruzanna G Paronikyan, Ivetta M Nazaryan & Hasmik H Hakopyan, *Med Chem Comm,* 10(8) (2019) 1399.

10 Abdelrehim E M & El-Sayed D S, *Curr Org Synth*, 17(3) (2020) 211.

11 Lin G S, Duan W G, Yang L X, Huang M & Lei F H, *Molecules,* 22(2) (2017) 193.

12 Hossein Sadeghpour, Soghra Khabnadideh, Kamiar Zomorodian, Keyvan Pakshir, Khadijeh Hoseinpour, Nabiollah Javid, Ehsan Faghih-Mirzaeiand & Zahra Rezaei, *Molecules*, 22 (2017) 1150.

13 Feng Gao, Tengfei Wang, Jiaqi Xiao & Gang Huang, *Eur J Med Chem*, 173 (2019) 274.

14 Turan-Zitouni G, Kaplancikli Z A, Kiliç F S & Erol K, *Boll chim farm*, 141 (2002) 192.

15 Haber J, *J Czech Phy*, 140(19) (2001) 596.

16 Coffen L D & Fryer R I, United State Patent, 3,849,434, (1974).

17 Shiroki M, Tahara T & Araki K, Japan Patent 75100096, (1975).

18 Bing Liu, José A Fernandes, João P C Tomé, Filipe A. Almeida Paz & Luís Cunha-Silva, *Molecules,* 20 (2015) 12341.

19 Xiaoqin Si, Linke Li, Liyan Fan, Changhong Wang, Min Qiao & Hongwei Hou, *Synth React Inorg Met-Org Nano-Metal Chem,* 45(6) (2015) 906.

20 Gouranourimi A, Mitra Ghassemzadeh, Samira Bahemmat, Bernhard Neumuller & Ralf Tonner, *Montash Chem*, 146 (2015) 57.

21 Dong Yi, Yaping Wu, Changyou Chen, Li Wang, Qin Wang, Lin Pu & Siping Wei, *Chin Chem Lett,* 30 (2019) 1059.

22 Qian Liu, Yisi Yang, Weidong Hao, Zhihua Xu & Lihong Zhu, *IERI Procedia* 5 (2013) 178.

23 Odularu A T, Ajibade P A & Mbese J Z, *Bioinorg Chem Appl*, 2019 (2019) 6416198.

24 Antunes M M, Amarante T R, Valente A A, Almeida Paz F A, Gonçalves I S & Pillinger M, *Chem Cat Chem,* 10(13) (2018) 2782.

25 Saikat Kumar Seth, Debayan Sarkar, Amalesh Roy & Tanusree Kar, *CrystEngComm,* 13(22) (2011) 6728.

26 McKinnon J J, Jayatilaka D & Spackman M A, *Chem Comm,* 37 (2007) 3814.

27 Spackman M A, McKinnon J J & Jayatilaka D, *Cryst Eng Comm*, 10(4) (2008) 377.

28 Phanimala C, Murali Krishna P, Hussain Reddy K & Anil Kumar G N, *J Mol Struct,* 1193 (2019) 326.

29 Shivakumara N & Murali Krishna P, *J. Mol Struct,* 1199 (2020) 126999.

30 Sennappan M, Murali Krishna P, Ranganathan R & Sivakami Sundari P, *J Mol Struct,* 1179 (2019) 86.

31 Sennappan M, Murali Krishna P & Hari Krishna R, *J Mol Struct*, 1178 (2019) 333.

32 Murali Krishna P, Gopal Reddy N B, Harish B G, Yogesh P. Patil & Nethaji M, *J Mol Struct*, 1175 (2019) 97.

33 Sennappan M, Murali Krishna P, Amar A. Hosamani & Hari Krishna R, *J Mol Struct,* 1164 (2018) 271.

34 Gopal Reddy N B, Murali Krishna P, Shantha Kumar S S, Yogesh P. Patil & Nethaji M, *J Mol Struct*, 1137 (2017) 543.

35 Sulekh Chandra & Anil Kumar, *Spectrochim Acta Part A*, 66(4-5) (2007) 1347.

36 Chen G J, McDonald J W & Newton W E, *Inorg Chem*, 15(11) (1976) 2612.

37 Bruker, APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 2012.

38 SMART & SAINT, Area Detector Control and Integration Software, Siemens Analytical X-ray Instruments Inc. Madison, Wisconsin, USA, 1996.

39 Dolomanov O V, Bourhis L J, Gildea R J, Howard J A K & Puschmann H, *J Appl Crystallogr,* 42 (2009) 339.

40 Sheldrick G M, SHELXS-97 Program for the Solution of Crystal Structures, University of Gottingen, Germany, 1997.

41 Watkin D M, Pearce L, Prout C K, CAMERON-A Molecular Graphics Package. Chemical Crystallography Laboratory, University of Oxford, England, 1993.

42 Wolff S K, Grimwood D J, McKinnon J J, Turner M J, Jayatilaka D & Spackman M J, CrystalExplorer, University of Western Australia, 2012, Version 3.1.

43 Anna Pachuta-Stec, Anna Biernasiuk, Anna Malm & Monika Pituchaa, *J Heterocycl Chem*, 54 (2017) 2867.

44 Kuriakose M, Prathapachandra Kurup M R & Suresh E, *Polyhedron*, 26 (2007) 2713.