



Two-dimensional Manganese(II) Coordination Polymer Complex Containing Aqua, Diethyl Phosphate and Chloride Ligands: Synthesis, Spectroscopic Characterization, Thermal Analyses, and Crystal Structure

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A new two-dimensional manganese(II) coordination polymer, $[\text{Mn}(\mu\text{-DEP})(\mu\text{-Cl})(\text{H}_2\text{O})_2]_n$ (1) (DEP is diethyl phosphate), was prepared from the reaction of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and TEP (TEP is triethyl phosphate) ligand in mixture of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (1:10) at 40 °C. Suitable crystals for crystal structure determination were obtained by slow evaporation of the produced colorless solution at room temperature. Complex 1 was characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction. The X-ray structural analysis indicated that the manganese(II) is six-coordinated in a distorted octahedral configuration by four oxygen atoms from two water and two bridged diethyl phosphate ligands and two bridged chloride anions. Also, the thermal stability of 1 was studied by thermogravimetric and differential thermal analyses.

Keywords: Manganese(II), Crystal structure, Diethyl phosphate, Thermal stability

INTRODUCTION

In recent years, supramolecular coordination polymers, which are one-dimensional (1D) extended chains, two-dimensional (2D) sheets or three-dimensional (3D) frameworks (CPs), porous coordination polymers (PCPs) and metal-organic framework coordination polymers (MOFs), containing manganese(II) ions with organic bridging ligands have been rapidly developed. These coordination polymer complexes are interesting for their application in catalytic processes [1-3] as heavy metal ion removers [4,5], biosensors [6,7], magnetic [8,9], gas sorption [10,11], luminescence materials [12,13], and ion-sensing materials [14,15]. On the other hand, triethyl and diethyl phosphate compounds, $[(\text{EtO})_3\text{P}=\text{O}]$ and $[(\text{EtO})_2\text{PO}_2]^-$, are widely used for metal extraction systems [16-19]. Triethyl phosphate can be coordinated to transition metals through one oxygen atom in neutral mode

and lead to the formation of mononuclear complexes [20-22], while in the anionic form, $[(\text{EtO})_2\text{PO}_2]^-$, it can be coordinated through two oxygen atoms as a bridging ligand and lead to the formation of one-dimensional coordination polymer complexes [23-25]. It must be noted that research on these alkylphosphates has received little attention. Continuing these researches, we wish to report herein the synthesis and crystal structure of a new two-dimensional coordination polymer of $[\text{Mn}(\mu\text{-DEP})(\mu\text{-Cl})(\text{H}_2\text{O})_2]_n$ (1). Structural studies on this complex were performed by elemental analysis, X-ray crystallography and IR spectroscopic technique. Also, the thermal stability of title complex was studied by thermogravimetric and differential thermal analyses.

EXPERIMENTAL

Materials and Physical Methods

All chemicals were purchased from Merck, and used as received. Elemental analysis was performed using an

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Elementar Analysensystem GmbH VarioEL. Infrared spectrum ($4000\text{--}250\text{ cm}^{-1}$) was taken on a Shimadzu-470 spectrometer in CsI pellets. Melting points were obtained on a Kofler Heizbank Rechart type 7841 melting point apparatus. Thermal behavior was measured with a STA 503 Bähr apparatus.

Preparation of Complex $[\text{Mn}(\mu\text{-DEP})(\mu\text{-Cl})(\text{H}_2\text{O})_2]_n$ (1)

Triethyl phosphate (1.32 g, 1.24 ml, 7.2 mmol) in CH_3OH (30 ml) was added to a solution of $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (0.72 g, 3.6 mmol) in H_2O (3 ml) and the resulting colorless solution was stirred at $40\text{ }^\circ\text{C}$ for 30 min. This solution was left to evaporate slowly at room temperature. After two weeks, colorless prismatic crystals of 1 were isolated (yield 0.76 g, 75.5%, m. p. $> 300\text{ }^\circ\text{C}$). Anal. Calcd. for $\text{C}_4\text{H}_{14}\text{O}_6\text{PMnCl}$ (%): C, 17.19; H, 5.01. Found: C, 17.11; H, 4.98. IR (CsI, cm^{-1}): 3445br, 2988m, 2936w, 2902m, 1442w, 1396w, 1206s, 1165m, 1109s, 1091s, 1041s, 968s, 825s, 810s, 754w, 553m, 519s, 442w, 378m, 316m, 252m.

X-Ray Structure Analysis

The X-ray diffraction measurements for single crystal of $[\text{Mn}(\mu\text{-DEP})(\mu\text{-Cl})(\text{H}_2\text{O})_2]_n$ (1) was made on a Bruker APEX II CCD area-detector diffractometer at 293 K using graphite mono-chromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The structure of 1 was solved by SHELX-97 and absorption correction was applied using the SADABS program [26]. Data collection, cell refinement, and data reduction were performed by applying APEX II, SAINT, SHELXTL, and PLATON program packages [26-31]. The ORTEP and crystal packing diagram for title complex were drawn with the Mercury 2.4 program [32].

RESULTS AND DISCUSSION

Synthesis of Complex $[\text{Mn}(\mu\text{-DEP})(\mu\text{-Cl})(\text{H}_2\text{O})_2]_n$ (1)

Complex 1 was prepared from the reaction of one equivalent of $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ with one equivalent of triethyl phosphate in mixture of $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ (1:10) at $40\text{ }^\circ\text{C}$. Suitable crystals of title complex for X-ray diffraction measurement were obtained by slow evaporation of the resulted colorless solution at room temperature. The synthetic route of title complex is shown in Scheme 1.

Spectroscopic Characterization of $[\text{Mn}(\mu\text{-DEP})(\mu\text{-Cl})(\text{H}_2\text{O})_2]_n$ (1)

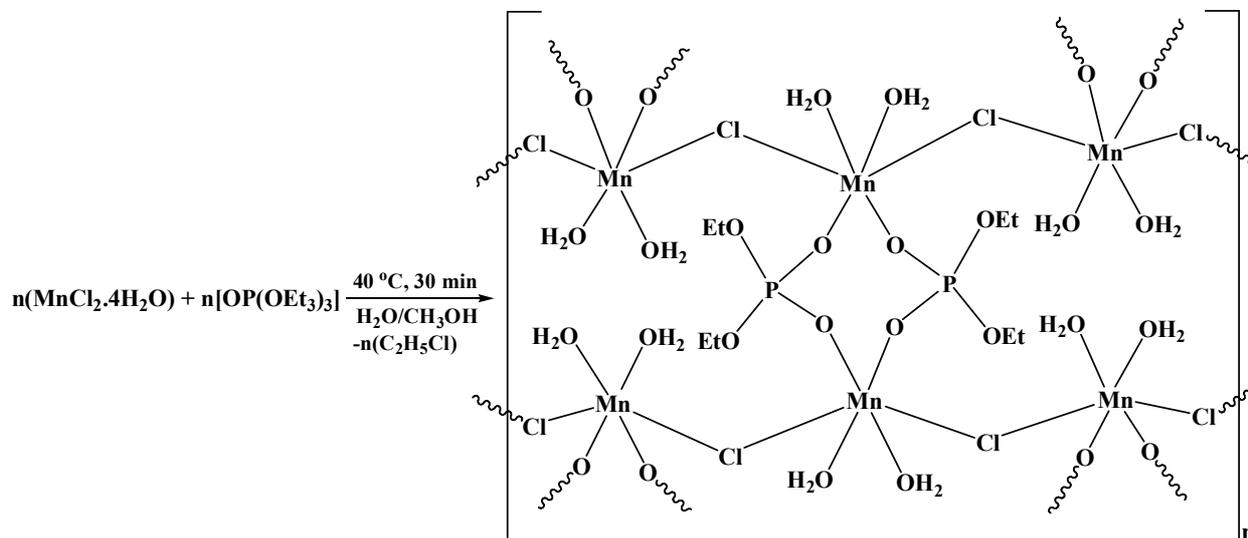
The IR absorption bands for title complex are listed in the experimental section. The infrared spectrum of title complex show a broad absorption band at around 3445 cm^{-1} , which is assigned to the O-H stretching vibrations for coordinated of H_2O molecules. Three weak and medium absorption bands at 2988, 2936 and 2902 cm^{-1} , and two weak absorption bands at 1442 and 1396 cm^{-1} are assigned to the C-H stretching and bending vibrations of the ethyl groups of diethyl phosphate ligands, respectively. Bands within the region of $1206\text{--}810\text{ cm}^{-1}$ are attributed to C-O, P-O, C-C and P-O-C stretching vibrations. The strong to weak absorption bands observed in the range $754\text{--}442\text{ cm}^{-1}$ are assigned to the P-O, C-O, C-C and P-O-C bending vibrations [25,33-36]. Furthermore, in the infrared spectrum of this complex, the Mn-O_{water} and Mn-O_{DEP} stretching vibrations were observed at 378 and 316 cm^{-1} , respectively, and the Mn-($\mu\text{-Cl}$)-Mn stretching vibration was observed at 252 cm^{-1} [37-40].

Thermal Studies of $[\text{Mn}(\mu\text{-DEP})(\mu\text{-Cl})(\text{H}_2\text{O})_2]_n$ (1)

The thermal stability of complex 1 between 30 and $780\text{ }^\circ\text{C}$ has been determined by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on single crystal samples in a static air atmosphere with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ (Fig. 1). The TGA curve shows that the structure is stable up to $222\text{ }^\circ\text{C}$, and the weight loss of 1 can be divided into two steps in the range $222\text{--}670\text{ }^\circ\text{C}$. The weight loss of 12.5% during the first step from $222\text{ to }245\text{ }^\circ\text{C}$ corresponds to the loss of two coordinated water molecules (calcd. 12.9%). In the last step between $335\text{ and }670\text{ }^\circ\text{C}$, the one diethyl phosphate ligand and the two chloride anions are lost and the framework decomposes (63.3%, calcd.: 61.7%). The final residual weight is 24.2% corresponding to one MnO (calcd. 25.4%) [41]. The differential thermal analysis (DTA) of 1 displays one distinct endothermic peak at $228\text{ }^\circ\text{C}$ and two distinct exothermic peaks at 380 and $463\text{ }^\circ\text{C}$.

Description of the Molecular Structures of $[\text{Mn}(\mu\text{-DEP})(\mu\text{-Cl})(\text{H}_2\text{O})_2]_n$ (1)

Crystallographic data for 1 are given in Table 1 and selected bond lengths and angles are presented in Table 2.



Scheme 1. The preparation method for complex 1

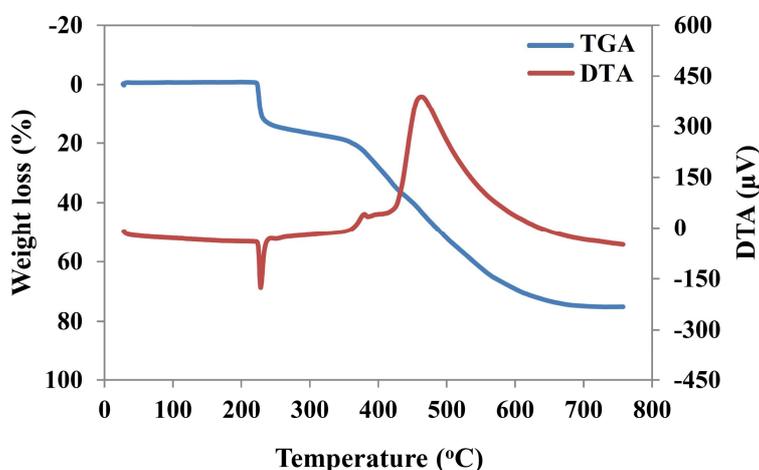


Fig. 1. Thermal behavior of 1.

This complex crystallizes in the orthorhombic crystal system with *Ibam* space group. The molecular structure of this complex together with the atomic labeling scheme is shown in Fig. 2. As shown in this figure, the asymmetric units of 1 consist of one manganese(II) cation, one bridged dimethyl phosphate anion, one bridged chloride anion and two coordinated H_2O molecules. Also, the structure of 1 consists of a $[\text{Mn}(\mu\text{-DEP})(\mu\text{-Cl})(\text{H}_2\text{O})_2]$ fragment and a

repetition unit in this two-dimensional polymer. In this complex, each Mn(II) cation is six-coordinated in a distorted octahedral configuration by two bridged chloride anions and four O atoms from two bridged bidentate dimethyl phosphate and two O atoms from two water molecules. As depicted in Fig. 3, the manganese atoms are linked by two bridged chloride anions to form one-dimensional stair-stepped coordination polymers of $[\text{Mn}(\mu\text{-$

Table 1. Crystallographic and Structural Refinement Data for 1

Formula	C ₄ H ₁₄ ClMnO ₆ P
Formula weight	279.51
Temperature (K)	298(2)
Wavelength λ (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Ibam</i>
Crystal size (mm ³)	0.50 × 0.05 × 0.50
<i>a</i> (Å)	8.8876(19)
<i>b</i> (Å)	10.917(3)
<i>c</i> (Å)	22.517(6)
Volume (Å ³)	2184.7(10)
<i>Z</i>	8
Density (calcd.) (g cm ⁻³)	1.700
θ ranges for data collection	3.47-26.78
F(000)	1144
Absorption coefficient (mm ⁻¹)	1.596
Index ranges	-11 ≤ <i>h</i> ≤ 8 -11 ≤ <i>k</i> ≤ 13 -26 ≤ <i>l</i> ≤ 28
Data collected	3432
Unique data (<i>R</i> _{int})	1153, (0.0293)
Parameters, restraints	72, 0
Final <i>R</i> ₁ , <i>wR</i> ₂ (Obs. data)	0.0240, 0.0603
Final <i>R</i> ₁ , <i>wR</i> ₂ (All data)	0.0245, 0.0607
Goodness of fit on <i>F</i> ² (S)	1.116
Largest diff peak and hole (e Å ⁻³)	0.279, -0.235
CCDC No.	2010793

Cl)(H₂O)₂]_n in a-direction, which are further bridged by the two bridged bidentate dimethyl phosphate ligands to form a two-dimensional layer network. The neighboring Mn...Mn distances through bridged chloride anion and bridged bidentate dimethyl phosphate ligands are 4.476 and

5.035 Å, respectively. Also, in this two-dimensional polymer, six manganese centers are connected by four dimethyl phosphate ligands and four μ -Cl⁻ anions to form 16-membered rings, Mn₆O₂P₄Cl₄.

In this complex, the Mn-O_{DEP} bond length is

Table 2. Selected Bond Lengths (Å) and Angles (°) for 1

Mn1-C11	2.6020(9)	O1-Mn1-O1 ⁱⁱ	93.27(4)
Mn1-O1	2.1099(12)	O1-Mn1-O3 ⁱⁱ	90.53(5)
Mn1-O3	2.2074(16)	C11 ^{iv} -Mn1-O1	92.61(3)
Mn1-C11 ^{iv}	2.6133(9)	O3-Mn1-O3 ⁱⁱ	85.54(6)
P1-O1	1.4951(11)	C11 ^{iv} -Mn1-O3	84.42(4)
P1-O2	1.5728(13)	Mn1-C11-Mn1 ⁱⁱⁱ	118.25(2)
C11-Mn1-O1	96.74(3)	O1-P1-O2	103.75(6)
C11-Mn1-O3	85.58(4)	O1-P1-O1 ⁱ	118.90(7)
C11-Mn1-C11 ^{iv}	166.35(2)	O1 ⁱ -P1-O2	111.51(6)
O1-Mn1-O3	175.29(5)	O2-P1-O2 ⁱ	107.04(7)

Symmetry codes: (i) 2-x,2-y,z; (ii) x,y,1-z; (iii)-1/2+x,3/2-y,1-z; (iv)1/2+x,3/2-y,1-z.

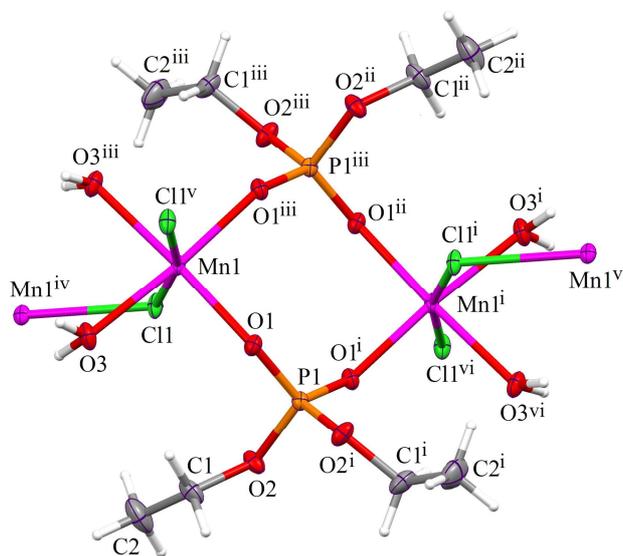


Fig. 2. ORTEP drawing (30% probability displacement ellipsoids) of complex 1 with the atom numbering scheme. Symmetry codes: (i) 2-x,2-y,z; (ii) 2-x,1-y,1-z; (iii) x,y,1-z; (iv) -1/2+x,3/2-y,1-z; (v) 1/2+x,3/2-y,1-z; (vi) 5/2-x,1/2+y,1-z.

2.1099(12) Å and is similar to those in $[\text{Mn}_2(\mu_3\text{-DMP})_2(\mu\text{-DMP})_2]$ (DMP is dimethyl phosphate) [34] and $\{[\text{Mn}_2(\mu\text{-DMP})_3(\mu\text{-DMSO})_2(\text{DMSO})(\text{H}_2\text{O})]\text{NO}_3\cdot\text{H}_2\text{O}\}_n$ [42], but

the Mn-O_{water} bond length is 2.2074(16) Å and is slightly longer than found in $\{[\text{Mn}_2(\mu\text{-DMP})_3(\mu\text{-DMSO})_2(\text{DMSO})(\text{H}_2\text{O})]\text{NO}_3\cdot\text{H}_2\text{O}\}_n$ (2.143(3) Å) [42]. The

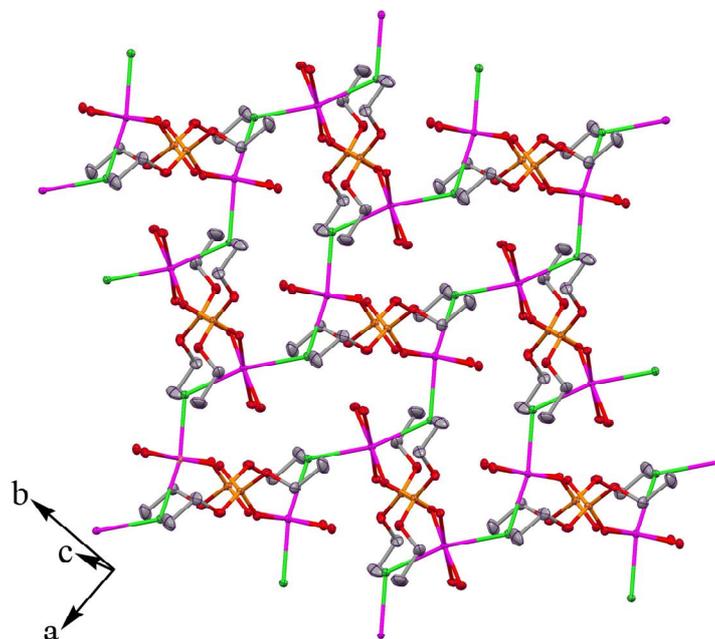


Fig. 3. The two-dimensional layer structure of 1. Hydrogen atoms are omitted for clarity.

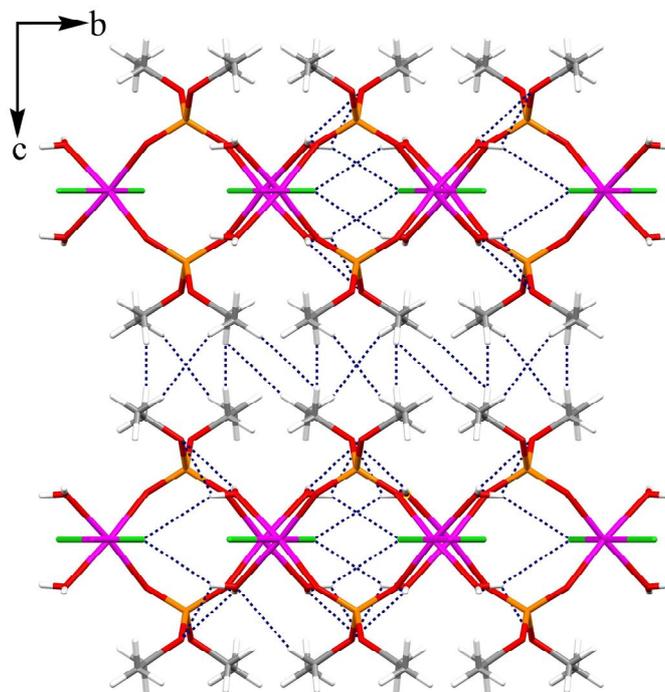


Fig. 4. Crystal packing diagram for 1. Intramolecular C-H...O and C-H...Cl hydrogen bonds and intermolecular C-H...H-C hydrogen-hydrogen interactions are shown as dashed lines.

Table 3. Hydrogen Bond Geometry for 1 in Crystal Packing

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)	Symmetry code
O3-H3A...O1	0.89(4)	1.98(4)	2.8440(19)	164	-1/2+x,3/2-y,1-z
O3-H3A...O2	0.89(4)	2.51(3)	3.074(2)	122	-1/2+x,3/2-y,1-z
O3-H3B...Cl1	0.77(3)	2.70(3)	3.3554(18)	144	3/2-x,-1/2+y,1-z
O3-H3B...Cl1	0.77(3)	2.70(3)	3.3554(18)	144	3/2-x,-1/2+y,z
C1-H1A...O1	0.9700	2.5800	3.034(3)	108	2-x,2-y,z

Mn-Cl bond lengths (2.6020(9) and 2.6133(9) Å) are longer than found in [LMn(μ -Cl)]₂ (2.3909(7) and 2.4603(7) Å), (L is cyclopentadienyl-phosphine) [43].

Figure 4 shows the packing diagram of complex 1 in the unit cell. As shown in this figure, there are intramolecular C-H...O and C-H...Cl hydrogen bonds (Table 3) between the [Mn(μ -DEP)(μ -Cl)(H₂O)₂] fragment in the two-dimensional coordination polymers. Adjacent two-dimensional coordination polymers are linked by weak intermolecular C-H...H-C interactions (C1-H1B...H1B, 2.644 Å, 150° and C1-H1B...H2A, 2.589 Å, 149°) [44-46]. These intramolecular C-H...O and C-H...Cl hydrogen bonds and intermolecular weak hydrogen-hydrogen interactions lead to the formation of a three dimensional supramolecular network.

CONCLUSIONS

In this paper, a new two-dimensional manganese(II) coordination polymer, [Mn(μ -DEP)(μ -Cl)(H₂O)₂]_n (1) has been synthesized and characterized by elemental analysis and infrared spectroscopic technique. The structure of this complex was defined by the single crystal diffraction method. The X-ray structural analysis specified that in this complex, the manganese(II) is six-coordinated in a distorted octahedral configuration by four oxygen atoms from two water and two bridged diethyl phosphate ligands and two bridged chloride anions. The crystal structure of this complex has been stabilized by weak intermolecular C-H...H-C interactions between the two-dimensional

coordination polymers. Also, the thermal stability of 1 was studied by thermogravimetric and differential thermal analyses.

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REFERENCES

- [1] G. Zhang, H. Zeng, S. Li, J. Johnson, Z. Mo, M.C. Neary, S. Zheng, *Dalton Trans.* 49 (2020) 2610.
- [2] H. Huang, W. Gao, F. Liu, X.M. Zhang, J.P. Liu, *Inorg. Chim. Acta* 484 (2019) 414.
- [3] J. Chen, M. Chen, B. Zhang, R. Nie, A. Huang, T.W. Goh, A. Volkov, Z. Zhang, Q. Rena, W. Huang, *Green Chem.* 21 (2019) 3629.
- [4] Y. Peng, H. Huang, Y. Zhang, C. Kang, S. Chen, L. Song, D. Liu, C. Zhong, *Nature Comm.* 9 (2018) 187.
- [5] E.R. Engel, J.L. Scott, *Green Chem.* 22 (2020) 3693.
- [6] S.E. Miller, M.H. Teplensky, P.Z. Moghadam, D.F. Jimenez, *Interface Focus* 6 (2016) 20160027.
- [7] P.A. Dhas, N. Deshmukh, P. Caro, C. Patil, P. Luisa García-Martín, M. Padya, B. Nikam, A. Mehta, T. Mutalik, *Coord. Chem. Rev.* 409 (2020) 213212.
- [8] H. Bunzen, M. Grzywa, R. Aljohani, H.A.K. Nidda, D. Volkmer, *Eur. J. Inorg. Chem.* (2019) 4471.
- [9] T. Gong, X. Yang, Q. Sui, Y. Qi, F.G. Xi, E.Q. Gao, *Inorg. Chem.* 55 (2016) 96.

- [10] Z.B. Han, R.Y. Lu, Y.F. Liang, Y.L. Zhou, Q. Chen, M.H. Zeng, *Inorg. Chem.* 51 (2012) 674.
- [11] H. Furukawa, K.E. Cordova, M. O’Keeffe, O.M. Yaghi, *Science* 341 (2013) 947.
- [12] W.Q. Kan, Y.C. He, Z.C. Zhang, Y.H. Kan, S.Z. Wen, *J. Iran. Chem. Soc.* 16 (2019) 2021.
- [13] F. Yuan, H.S. Yu, C.M. Yuan, C.S. Zhou, F. Li, Y.J. Lu, X.Y. Ling, J. Wang, A. Singh, A. Kumar, *Inorg. Chim. Acta* 449 (2020) 119189.
- [14] Q.Q. Xiao, D. Liu, Y.L. Wei, G.H. Cui, *J. Solid State Chem.* 273 (2019) 67.
- [15] W.P. Lustig, S. Mukherjee, N.D. Rudd, A.V. Desai, J. Li, S.K. Ghosh, *Chem. Soc. Rev.* 46 (2017) 3242.
- [16] H.H. Willard, H. Freund, *Ind. Eng. Chem.* 18 (1946) 195.
- [17] B.S. Fales, N.O. Fujamade, Y.W. Nei, J. Oomens, M.T. Rodgers, *J. Am. Soc. Mass Spectrom.* 22 (2011) 81.
- [18] J. Stangret, R. Savoie, *Canad. J. Chem.* 70 (1992) 2875.
- [19] P. Mäkie, P. Persson, L. Österlund, *J. Colloid and Interface Sci.* 392 (2013) 349.
- [20] A.D. Sutton, I. May, C.A. Sharrad, M.J. Sarsfield, M. Helliwell, *Dalton Trans.* (2006) 5734.
- [21] R. Kanellakopoulos, E. Dornberger, R. Maier, *Z. Anorg. Allg. Chem.* 619 (1993) 593.
- [22] G.H. John, I. May, C.A. Sharrad, A.D. Sutton, D. Collison, M. Helliwell, M.J. Sarsfield, *Inorg. Chem.* 44 (2005) 7606.
- [23] Y. Kyogoku, Y. Iitaka, *Acta Crystallogr.* 21 (1966) 49.
- [24] M. Rafizadeh, V. Amani, *Anal. Sci.* 22 (2006) x211.
- [25] V. Amani, M. Rafizadeh, M. Yousefi, N.S. Zargar, *Anal. Sci.* 22 (2006) x303.
- [26] M. Rafizadeh, V. Amani, N.S. Mortazavi, *Bull. Korean Chem. Soc.* 30 (2009) 489.
- [27] G.M. Sheldrick, *SADABS*. Madison, WI, USA: Bruker AXS, 1998.
- [28] Bruker SMART and SAINT. Madison, WI, USA: Bruker AXS Inc., 1998.
- [29] G.M. Sheldrick, *Acta Crystallogr.* A64 (2008) 112.
- [30] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [31] L.J. Farrugia, *J. Appl. Crystallogr.* 30 (1997) 565.
- [32] A.L. Spek, *Acta Crystallogr.* E76 (2020) 1.
- [33] Mercury 141. Copyright Cambridge Crystallographic Data Center. Cambridge, 2001-2005.
- [34] M. Rafizadeh, R. Tayebee, V. Amani, M. Nasseh, *Cryst. Bull. Korean Chem. Soc.* 26 (2005) 594.
- [35] M. Rafizadeh, V. Amani, H. Farajian, *Z. Anorg. Allg. Chem.* 633 (2007) 1143.
- [36] M. Rafizadeh, V. Amani, *Z. Anorg. Allg. Chem.* 633 (2007) 2738.
- [37] M. Rafizadeh, R. Tayebee, V. Amani, *Turk. J. Chem.* 29 (2005) 385.
- [38] H.A. Chu, W. Hillier, N.A. Law, G.T. Babcock, *Biochim. Biophys. Acta* 1503 (2001) 69.
- [39] V. Amani, N. Faal Hamedani, *Mol. Cryst. Liq. Cryst.* 665 (2018) 207.
- [40] N.K. Jha, B.N. Thakur, *Synt. & React. Inorg. Met. Org. Chem.* 14 (1984) 1057.
- [41] D.A. Thornton, G.M. Watkins, *J. Coord. Chem.* 25 (1992) 299.
- [42] M.B. Zhang, Y.M. Chen, S.T. Zheng, G.Y. Yang, *Eur. J. Inorg. Chem.* (2006) 1423.
- [43] M. Rafizadeh, V. Amani, H. Aghayan, *Acta Crystallogr.* E62 (2006) m2450.
- [44] G.X. Wang, J. Yin, J. Li, Z.B. Yin, W.X. Zhang, Z. Xi, *Inorg. Chem. Front.* 6 (2019) 428.
- [45] T.B. Richardson, S. deGala, R.H. Crabtree, P.E.M. Siegbahn, *J. Am. Chem. Soc.* 117 (1995) 12875.
- [46] A.S. Batsanov, *Acta Crystallogr.* E74 (2018) 570.
- [47] C.F. Matta, J.H. Trujillo, T.H. Tang, R.F.W. Bader, *Chem. Eur. J.* 9 (2003) 1940.