ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

2016. Том 57, № 6 *Июль – август* *С. 1230 – 1235*

UDC 548.73:541.49:546.711

CRYSTAL STRUCTURES OF TWO ONE-DIMENSIONAL COORDINATION POLYMERS CONSTRUCTED FROM Mn^{2+} IONS, CHELATING HEXAFLUORO-ACETYLACETONATE ANIONS, AND FLEXIBLE BIPYRIDYL BRIDGING LIGANDS

M.J. Plater, B.M. De Silva, M.R. St J. Foreman, W.T.A. Harrison

Department of Chemistry, University of Aberdeen, Aberdeen, Scotland
E-mail: w.harrison@abdn.ac.uk

Received April, 30, 2015

The syntheses and crystal structures of two one-dimensional coordination polymers, $[Mn(C_5HO_2F_6)_2(C_{16}H_{20}N_2)]_n$ (**1**) and $[Mn(C_5HO_2F_6)_2(C_{20}H_{20}N_2)]_n$ (**2**), are described, where $C_5HO_2F_6^-$ is the hexafluoro acetylacetonate anion, $C_{16}H_{20}N_2$ is 1,6-bis(4-pyridyl)-hexane, and $C_{20}H_{20}N_2$ is 1,4-bis[2-(3-pyridyl)ethyl]-benzene. In both phases, the metal ion lies on a crystallographic twofold axis and is coordinated by two chelating $C_5HO_2F_6^-$ anions and two bridging bipyridyl ligands to generate a *cis*-MnN_2O_4 octahedron. The bridging ligands, which are completed by crystallographic inversion symmetry in both compounds, connect the metal nodes into zigzag $[20\bar{1}]$ chains in **1** and contorted [001] chains in **2**. Intrachain C—H···O interactions occur in **1** but not in **2**, which may be correlated with the relative orientations of the ligands. Crystal data: **1**, $C_{26}H_{22}F_{12}MnN_2O_4$, $M_r = 709.40$, monoclinic, $C2/c$ (No. 15), $a = 9.3475(2)$ Å, $b = 16.6547(3)$ Å, $c = 18.3649(4)$ Å, $\beta = 91.1135(8)°$, $V = 2858.50(10)$ Å^3, $Z = 4$, $R(F) = 0.030$, $wR(F^2) = 0.075$. **2**, $C_{30}H_{22}F_{12}MnN_2O_4$, $M_r = 757.44$, monoclinic, $C2/c$ (No. 15), $a = 19.9198(2)$ Å, $b = 10.6459(2)$ Å, $c = 16.8185(3)$ Å, $\beta = 119.8344(8)°$, $V = 3093.91(9)$ Å^3, $Z = 4$, $R(F) = 0.032$, $wR(F^2) = 0.078$.

DOI: 10.15372/JSC20160616

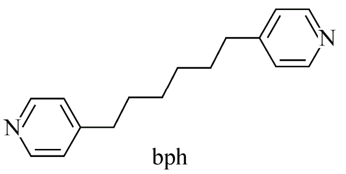
Keywords: manganese, coordination polymer, flexible ligand.

INTRODUCTION

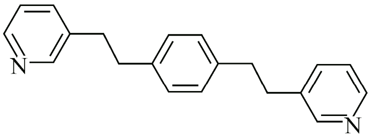
Flexible metal-organic frameworks or MOFs, which can respond to physical and chemical stimuli by structural reorganisation while maintaining crystallinity, are an important family of phases [1] with applications in many areas such as catalysis [2], electrochemistry [3], and drug delivery [4].

Our studies in this area have focused on bipyridyl ligands in which the pyridine rings are connected by a flexible —$(CH_2)_n$— (n = 3—7) alkyl chain, which can adopt different conformations and lead to a variety of polymeric structures in combination with different metal ions [5, 6] and counter ions such as nitrate or perchlorate ions. These "long" ligands, which can bridge metal ions over a separation of 15—20 Å, allow for the formation of various types of interpenetrated networks [7, 8].

As part of our ongoing studies in this area [9], we now describe the interfacial syntheses and single crystal structures of the new coordination polymers $[Mn(C_5HO_2F_6)_2(C_{16}H_{20}N_2)]_n$ (**1**) and $[Mn(C_5HO_2F_6)_2(C_{20}H_{20}N_2)]_n$ (**2**), where $C_5HO_2F_6^-$ is the hexafluoro acetylacetonate (hfac$^-$) anion, $C_{16}H_{20}N_2$ (bph) is 1,6-bis(4-pyridyl)hexane, and $C_{20}H_{20}N_2$ (bpeb) is 1,4-bis[2-(3-pyridyl)ethyl]-benzene (see schemes below).



bph



bpeb

Manganese has been shown to form MOFs with unusual structures and properties [10, 11]. The addition of a chelating ligand such as hfac$^-$ to the synthesis can modify the dimensionality of coordination networks and alter their properties as recent studies [12, 13] have demonstrated.

MATERIALS AND METHODS

Syntheses. 1,6-Bis(4-pyridyl)hexane (0.10 g, 0.35 mmol), prepared as described previously [6], was dissolved in ethanol (5 ml) and mixed with a solution of $Mn(hfac)_2 \cdot 2H_2O$ (0.184 g, 0.35 mmol) in ethanol (5 ml). The solution was left to stand for 2 weeks after which time a few pale orange blocks of **1** were recovered by vacuum filtration and rinsing with acetone. There was insufficient amount of sample to carry out elemental analysis.

Pyridine-3-carboxaldehyde (2.72 g, 25.4 mmol) was added to a solution of 1,4-*bis*(methyl-triphenylphosphonium)benzene dibromide (10 g, 12.7 mmol) in dry ethanol (50 ml). A fresh solution of sodium ethoxide was slowly added to the stirred mixture over 30 min. After a further 3.5 h the ethanol was removed and water (80 ml) followed by CH_2Cl_2 (8 ml) was added. The triphenylphosphine oxide that remains as a precipitate was filtered off and washed with water. The aqueous washings were combined and neutralized with sodium hydroxide (2M) and the mixture was extracted with CH_2Cl_2 (2×50 ml). CH_2Cl_2 was removed *in vacuo* to give a brown solid that was dissolved in ethanol (15 ml) to which 10 % palladium on carbon (200 mg) was added. This vigorously stirred mixture was hydrogenated at 1 atmosphere pressure and at 24 °C until no more hydrogen was absorbed. The ethanol was removed and the crude product was purified by column chromatography (silica gel; eluent 90 % EtOH : 10 % EtOAc) to give 1,4-bis[2-(3-pyridyl)ethyl]benzene (2.6 g, 72 %) as a white solid, m.p. 125—126 °C. ν_{max} (KBr)/cm^{-1} 3017w, 2924w, 1570w, 1511w, 1419s, 1189w, 1142w, 1023w, 816s, 715s and 534s; δ_H (250 MHz; $CDCl_3$) 2.8 (8H, s), 6.9 (4H, s), 7.1—7.2 (2H, m), 7.36—7.39 (2H, m), 8.35 (2H, s) and 8.38—8.40 (2H, m); δ_c (62.9 MHz; $CDCl_3$) 34.8, 36.9, 123.2, 128.5, 135.9, 136.8, 138.5, 147.2 and 149.8; *m*/*z* 289 (CI) ($[M+H]^+$, 100 %) $C_{20}H_{21}N_2$ requires 289.1699 Found 289.1698).

1,4-Bis[2-(3-pyridyl)ethyl]benzene (0.10 g, 0.35 mmol) was dissolved in the ethanol (5 ml) and mixed with a solution of $Mn(hfac)_2 \cdot 2H_2O$ (0.184 g, 0.35 mmol) in the ethanol (5 ml). The solution was left to stand for 2 weeks after which a few pale orange blocks of **2** were collected.

Crystallographic studies. The intensity data for **1** and **2** were collected using a Nonius Kappa CCD diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å, $T = -153$ °C). For **1**, a pale orange block of dimensions 0.15×0.15×0.10 mm was chosen for data collection; for **2**, a pale orange bock, 0.20×0.15×0.15 mm was used. Empirical (multi-scan) absorption corrections were applied at the data reduction stage.

Both structures were solved by direct methods using SHELXS-97 in space group *C*2/*c* (No. 15) and the atomic models were developed and refined against $|F|^2$ with SHELXL-97 [14]. The O-bound H atoms in **1** were found in difference maps and refined as riding atoms in their as-found relative positions with $U_{iso}(H) = 1.2U_{eq}(O)$. The C-bound H atoms were geometrically placed and modelled as riding atoms with C—H = 0.95—0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The structures were verified and analysed with PLATON [15] and the molecular graphics were generated with ORTEP-3 [16] and ATOMS [17]. Crystal data for **1** and **2** are summarized in Table 1.

RESULTS

Structure of 1. The asymmetric unit of **1** consists (Fig. 1) of a Mn^{2+} ion lying on a crystallographic twofold axis, a $C_5HO_2F_6^-$ (hfac$^-$) chelating ligand, and half a $C_{16}H_{20}N_2$ (bph) bridging ligand; the complete bph molecule is generated by crystallographic inversion symmetry. The coordination

Table 1

Key crystallographic data for **1** *and* **2**

Parametr	**1**	**2**
Emp. formula	$C_{26}H_{22}F_{12}MnN_2O_4$	$C_{30}H_{22}F_{12}MnN_2O_4$
MW	709.40	757.44
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a, b, c, Å	9.3475(2), 16.6547(3), 18.3649(4)	19.9198(2), 10.6459(2), 16.8185(3)
β, deg.	91.1135(8)	119.8344(8)
V, Å^3; Z	2858.50(10); 4	3093.91(9); 4
ρ_{calc}, g·cm^{-3})	1.648	1.626
μ, mm^{-1}	0.577	0.539
Data collected / unique	8408 / 2806	8683 / 3034
R_{Int} / $R(F)$ / $wR(F^2)$	0.035 / 0.030 / 0.075	0.036 / 0.032 / 0.078
CCDC code*	223262	223261

---

*Full crystallographic data for these structures including atomic coordinates and geometrical parameters can be accessed at: http://www.ccdc.cam.ac.uk/Community/Requestastructure/Pages/DataRequest.aspx by citing the code number shown.

polyhedron about the metal ion is a fairly regular *cis*-MnN_2O_4 octahedron (Table 2), arising from two O,O-bidentate hfac$^-$ anions and two bph N atoms. The bond valence sum (BVS) [18] for Mn1 is 2.05 (expected value = 2.00), the octahedral volume is 13.99 Å^3, and the angular variance [19] for the X—Mn—Y octahedral bonds is $57.6^{\circ 2}$.

The six-membered chelate ring formed by the anion is well described as an envelope, with the Mn^{2+} ion deviating by 0.3144(19) Å from the mean plane of the ligand atoms (r.m.s. deviation = 0.021 Å). The bond lengths of the hfac$^-$ anion are consistent with previous structural studies and indicate that the usual model of delocalization of its C—O and central C—C single and C=C double bonds is applicable here [20]. The dihedral angle between the hfac$^-$ chelate ring and pyridine (py) ring planes bonded to the metal ion is 15.43(9)°. The py rings bonded to Mn1 subtend a dihedral angle of 88.59(4)° and the dihedral angle between the hfac$^-$ chelate rings is 61.06(5)°. The py rings of the

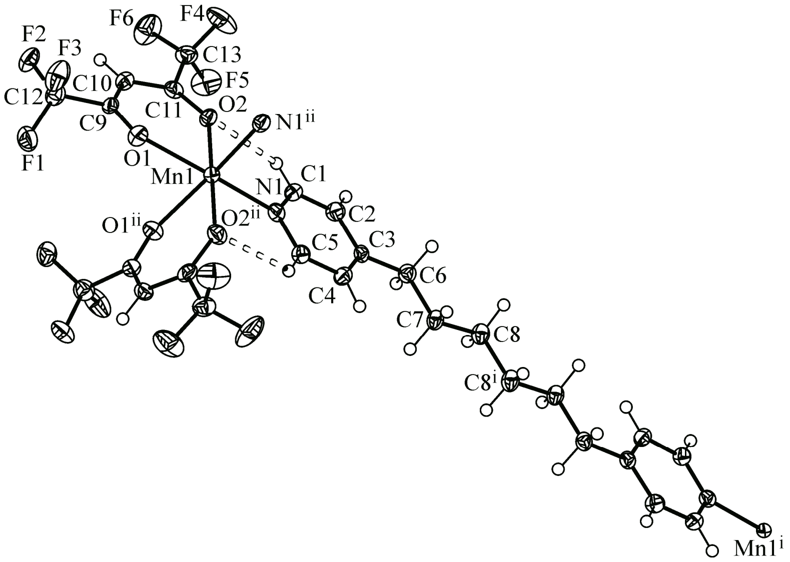


Fig. 1. The asymmetric unit of **1** expanded to show the metal coordination sphere and the complete bph ligand (50 % displacement ellipsoids). The C—H···O interactions are indicated by double-dashed lines.
Symmetry codes: ^{i} $-x$, $2-y$, $1-z$; ^{ii} $1-x$, y, $1/2-z$

Table 2

Selected geometrical data (Å, deg.) *for* **1**

Mn1—O2	2.1566(11)	Mn1—O1	2.2089(11)	O2—Mn1—O1	80.91(4)
Mn1—N1	2.2582(13)	C9—O1	1.2446(18)	C3—C6—C7—C8	–177.91(14)
C11—O2	1.2550(19)	C9—C10	1.400(2)	C7—C8—C8^{i}—C7^{i}	180.0
C10—C11	1.387(2)			C6—C7—C8—C8^{i}	–179.95(17)

C1—H1···O2	0.95	2.43	3.0418(19)	122
C5—H5···O2^{ii}	0.95	2.56	3.2095(19)	126

Symmetry codes: ^{i} $-x, 2-y, 1-z$; ^{ii} $1-x, y, 1/2-z$.

bph ligand in **1** are coplanar by symmetry and the central alkyl chain adopts an almost ideal extended conformation (unique torsion angles = –177.91(14)°, –179.95(17)° and 180°). Both CF_3 groups of the anion are orientated in a staggered arrangement with respect to the C=O groups (O1—C9—C12—F2 = 175.78(13)° and O2—C11—C13—F6 = 170.21(14)°).

In the extended structure of **1**, the bridging bph ligand links the Mn nodes into zigzag chains (Fig. 2), which propagate in the $[20\bar{1}]$ direction. The separation of adjacent Mn ions in the chain is 18.5366 (5) Å; a number of interchain Mn···Mn separations are much shorter than this distance. Two weak C—H···O intrachain interactions link the bph ligand to the O atoms of the anion. The packing for **1** leads to small $[20\bar{1}]$ channels, which are bound by fluorine atoms: it is not known if any guest molecules could be absorbed into these channels.

Structure of 2. The asymmetric unit of **2** has a similar composition to that of **1**: the metal ion, which lies on a twofold axis, is accompanied by a chelating hfac$^-$ anion and half a $C_{20}H_{20}N_2$ (bpeb) bridging ligand (Fig. 3). The complete bpeb ligand is completed by crystallographic inversion symmetry at the midpoint of the central benzene ring. Again, a fairly regular *cis*-MnN_2O_4 octahedron results (Table 3) from the chelating anions and the two bridging bpeb ligands. The Mn^{2+} BVS is 2.14, the octahedral volume is 13.88 Å^3, and the angular variance is 23.3$^{\circ 2}$.

The conformation of the hfac$^-$ chelate ring in **2** is an envelope, with the metal ion deviating by 0.371(2) Å from the plane of the other atoms (r.m.s. deviation = 0.025 Å). The py rings bonded to Mn1 in **2** subtend a dihedral angle of 79.86(4)° and the dihedral angle between the hfac$^-$ chelate rings is 61.17(6)°. The dihedral angle between the py and central rings of the bph ligand in **2** is 41.84(7)° and the conformation of the linking ethyl chain is *gauche* (C2—C6—C7—C8 = 58.41(19)°). Both CF_3 groups of the anion are orientated in a staggered arrangement with respect to the C=O groups (O1—C11—C14—F2 = –162.51(13)° and O2—C13—C15—F4 = –168.29(14)°).

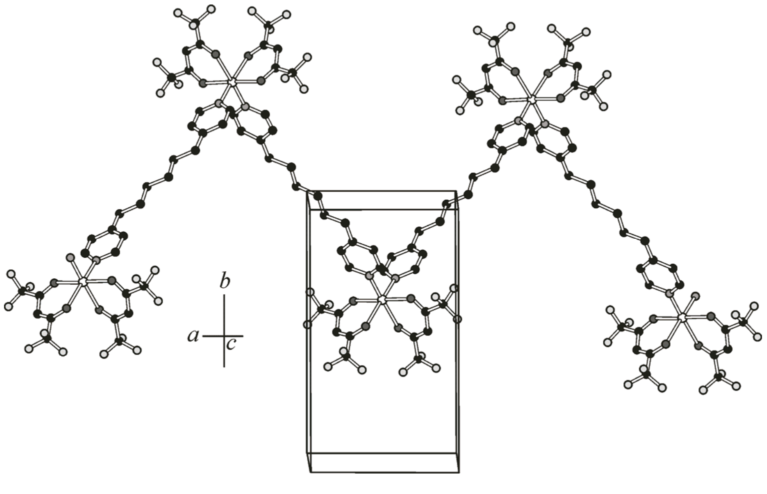


Fig. 2. Part of a $[20\bar{1}]$ polymeric chain in the structure of **1** showing the extended alkyl chains linking the pyridine rings

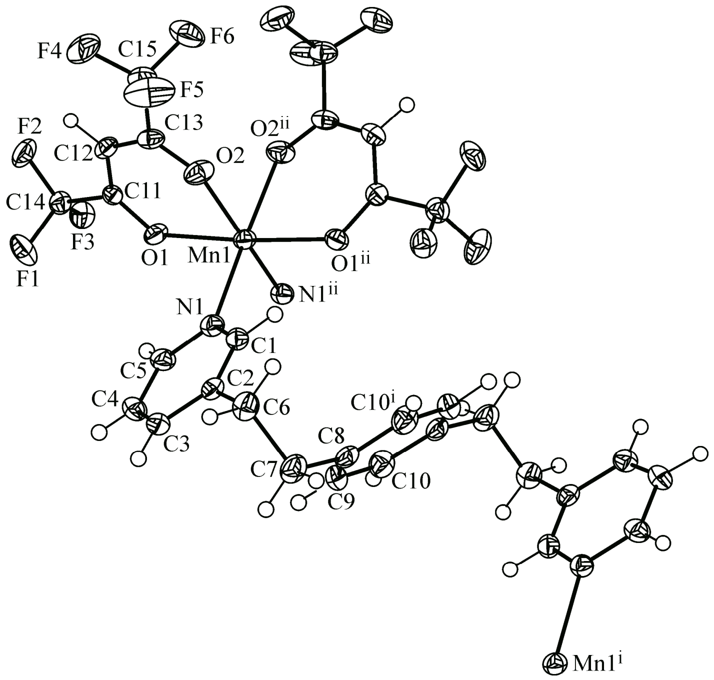


Fig. 3. The asymmetric unit of **2** expanded to show the metal coordination sphere and the complete bpeb ligand (50 % displacement ellipsoids).
Symmetry codes: $^{\mathrm{i}}$ 1–*x*, 2–*y*, –*z*; $^{\mathrm{ii}}$ 1–*x*, *y*, 1/2–*z*

The extended structure of **2** consists of contorted or Z-shaped [001] chains (Mn···Mn separation = 11.3080(4) Å) (Fig. 4), which is quite different to the extended chains seen in **1**. Interestingly, there are no intrachain C—H···O interactions in the structure of **2**. This can be related to the relative orientations of the py rings with respect to the other atoms bonded to the metal atom: in **1**, the dihedral angle between the N1 ring and the best plane of Mn1, the *trans* O1 atom and two bonded O2 atoms (Fig. 1) is 6.11(9)°; the equivalent angle in **2** is 27.21(7)°.

CONCLUSIONS

The syntheses and crystal structures of the one-dimensional coordination polymers $[\mathrm{Mn}(\mathrm{C_5HO_2F_6})_2(\mathrm{C_{16}H_{20}N_2})]_n$ (**1**) and $[\mathrm{Mn}(\mathrm{C_5HO_2F_6})_2(\mathrm{C_{20}H_{20}N_2})]_n$ (**2**) have been described. Although both structures have similar building blocks, the conformations of the bridging ligands are quite different, which to some extent correlates with the different torsion angles for the linking alkyl chains. The presence of C—H···O interactions in one structure, but not the other, can be correlated with subtle differences in the relative orientations of the chelating and bridging ligands with respect to the metal ions.

Table 3

Selected geometrical data (Å, deg.) *for* **2**

Mn1—O1	2.1480(11)	Mn1—O2	2.1969(12)	C2—C6—C7—C8	58.41(19)
Mn1—N1	2.2289(14)	C11—O1	1.2499(19)	O1—Mn1—O2	82.68(4)
C13—O2	1.249(2)	C11—C12	1.393(2)		
C12—C13	1.395(2)				

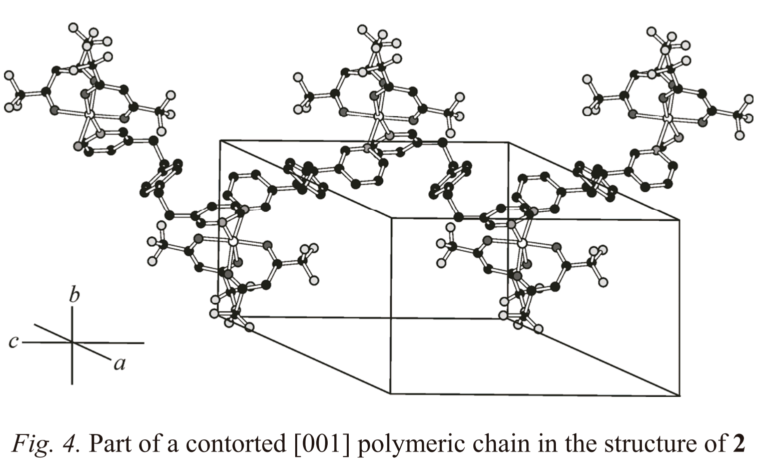


Fig. 4. Part of a contorted [001] polymeric chain in the structure of **2**

A survey of the Cambridge Structural Database (version 5.31) [21] revealed no fewer than 225 structures containing manganese ions and a pair of chelating hfac$^-$ ligands with a wide variety of other ligands and components in the crystal (counter ions if applicable and solvent molecules): most of these structures are molecular rather than polymeric. Two structures closely related to the title compounds are $[Mn(C_5HO_2F_6)_2(C_{13}H_{14}N_2)]_n$ and $[Mn(C_5HO_2F_6)_2(C_{13}H_{14}N_2)]_n \cdot n(C_{14}H_{14})$ [22], where $C_{13}H_{14}N_2$ is 4,4′-trimethylene-dipyridine (tmp) (*i.e.*: a pair of 4-pyrydyl rings bridged by three CH_2 groups) and $C_{14}H_{14}$ is 1,2-diphenylethane. In both these compounds infinite zigzag polymeric chains result, with *cis*-MnN_2O_4 nodes, as also seen in the title compounds. The Mn—N and Mn—O bond lengths and the dimensions of the hfac$^-$ lignads in these compounds are similar to those in the title compounds and the chelate rings adopt envelope conformations. It is notable that the second of these structures can accommodate the bulky 1,2-diphenylethane molecule as a guest species, which appears to wrap itself around the alkyl chain of the tmp ligand. Different syntheses from the same starting materials lead to a large family of compounds of formula $[Mn_2(C_5HO_2F_6)_4(C_{13}H_{14}N_2)_2] \cdot R$ [23] where R is a clathrated species (benzene, toluene, *cis*-stilbene …). In these compounds, both tmp ligands bridge the same pair of metal ions to generate discrete bimetallic species rather than infinite chains. The bond distances and angles in these compounds are similar to those of the title compounds but the chelate rings of the hfac$^-$ ligands are close to planar. Another one-dimensional polymeric species is seen in $[Mn(C_5HO_2F_6)_2(C_9H_9N_3)]_n$ [24], where $C_9H_9N_3$ is *N*-(4-pyridylmethyl)imidazole (npi). Once again, a *cis*-MnN_2O_4 coordination polyhedron is generated by the two chelating hfac$^-$ ligands and the npi bridging ligands.

We thank the EPSRC National Crystallography Service (University of Southampton) for the data collections.

REFERENCES

1. *Schneermann A., Bon V., Schwelder I., Senkovska I., Kaskel S., Fischer R.A.* // Chem. Soc. Rev. – 2014. – **43**. – P. 6062 – 6096.
2. *Fu H.R., Zhang J.* // Chem. Eur. J. – 2015. – **21**. – P. 5700 – 5703.
3. *An T.C., Wang Y.H., Tang J., Wang Y., Zhang L.J., Zheng G.G.* // J. Colloid Interface Sci. – 2015. – **445**. – P. 320 – 325.
4. *Hu Q., Yu J.C., Liu M., Liu A.P., Dou Z.S., Yang Y.* // J. Med. Chem. – 2014. – **57**. – P. 5679 – 5685.
5. *Plater M.J., St J. Foreman M.R., Gelbrich T., Hursthouse M.B.* // J. Chem. Soc., Dalton Trans. – 2000. – P. 1995 – 2000.
6. *Plater M.J., St J. Foreman M.R., Gelbrich T., Coles S.J., Hursthouse M.B.* // J. Chem. Soc., Dalton Trans. – 2000. – 3065 – 3073.
7. *Plater M.J., St J. Foreman M.R., Skakle J.M.S.* // Cryst. Eng. – 2001. – **4**. – P. 293 – 308.
8. *Plater M.J., St J. Foreman M.R., Gelbrich T., Hursthouse M.B.* // Cryst. Eng. – 2001. – **4**. – P. 319 – 328.
9. *Plater M.J., de Silva B.M., St J. Foreman M.R., Harrison W.T.A.* // J. Coord. Chem. – 2015. – in press
10. *Li R.J., Li M., Zhou X.P., Li D., O'Keeffe M.* // Chem. Commun. – 2015. – **50**. – P. 4047 – 4049.
11. *Easun T.L., Jia J.H., Calladine J.A., Blackmore D.L., Stapleton C.S., Vuong K.Q., Champness N.R., George M.W.* // Inorg. Chem. – 2014. – **53**. – P. 2606 – 2612.
12. *Bannerjee S., Rajakannu P., Butcher R.J., Murugavel R.* // CrystEngComm. – 2014. – **16**. – P. 8429 – 8441.
13. *Seco J.M., Calahorro A., Capeda J., Rodriguez-Dieguez A.* // J. Mol. Struct. – 2015. – **1089**. – P. 135 – 145.
14. *Sheldrick G.M.* // Acta Cryst. – 2008. – **A64**. – P. 112 – 122.
15. *Spek A.L.* // Acta Cryst. – 2009. – **D65**. – P. 148 – 155.
16. *Farrugia L.J.* // J. Appl. Cryst. – 1997. – **30**. – P. 565.
17. ATOMS for Windows, version 6.3. Shape Software Inc., Kingsport, Tennessee, USA.
18. *Brown I.D., Altermatt D.* // Acta Cryst. – 1985. – **B41**. – P. 244 – 247.
19. *Robinson K., Gibbs G.V., Ribbe P.H.* // Science (Washington, DC). – 1971. – **172**. – P. 3983.
20. *Malandrino G., Toro R.G., Catalano M.R., Fragalà M.E., Rossi P., Paoli P.* // Eur. J. Inorg. Chem. – 2012. – P. 1021 – 1024.
21. *Allen F.H., Motherwell W.D.S.* // Acta Cryst. – 2002. – **B58**. – P. 407 – 422.
22. *Tabellion F.M., Seidel S.R., Arif A.M., Stang P.J.* // Angew. Chem., Int. Ed. – 2001. – **40**. – P. 1529 – 1532.
23. *Tabellion F.M., Seidel S.R., Arif A.M., Stang P.J.* // J. Amer. Chem. Soc. – 2001. – **123**. – P. 11982 – 11990.
24. *Mago G., Hinago M., Miyasaka H., Matsumoto N., Okawa H.* // Inorg. Chim. Acta. – 1997. – **254**. – P. 145 – 150.