

Hydrogen bonded homodimetallic compounds of the formula $[M(H_2O)_5M(dipic)_2] \cdot 2H_2O$, $M = Co^{II}$ or Ni^{II} and dipic = dipicolinate anion

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Abstract: Two homodimetallic dipicolinate compounds of the formulae $[Co(H_2O)_5Co(dipic)_2] \cdot 2H_2O$ (**1**) and $[Ni(H_2O)_5Ni(dipic)_2] \cdot 2H_2O$ (**2**) have been synthesized and their crystal structures have been determined by single-crystal X-ray diffraction analysis. The prepared isostructural compounds consist of cationic $\{MO_5O\}^{2+}$ and anionic $\{MN_2O_4\}^{2-}$ moieties, where Co^{II}/Co^{II} or Ni^{II}/Ni^{II} metal centers are connected together by bridging μ -carboxylate oxygen atoms from dipicolinate anions. H-bond interactions involving aqua ligands, dipicolinate oxygens and lattice solvent molecules stabilize the dimeric units by linking them into 3-D polymeric networks.

Keywords: dipicolinate compounds, H-bond, 3-D polymeric networks

Introduction

Compounds containing dipicolinates (anions of pyridine-2,6-dicarboxylic acid, also well-known as dipicolinic acid *abbr.* H_2dipic) exhibit a large structural variability (Das and Baruah, 2012). Dipicolinates are versatile N,O-chelating ligands with a large number of coordination modes varying from bidentate or tridentate chelating to bridging via one or more carboxylate oxygen atoms, capability to stabilize water clusters (Das and Baruah, 2013) and function as hydrogen-bond acceptors as well as hydrogen-bond donors (Sharif et al., 2012; Ucar et al., 2007). Moreover, dipicolinates in combination with metal aqua ions, which have high affinity towards the formation of strong H-bonds, may result into the formation of 2-D or 3-D H-bonded metaloorganic frameworks with diverse topologies and interesting properties (Kirillova et al., 2007).

A series of homodimetallic aqua dipicolinate complexes with the general formulae $[M(H_2O)_5M(dipic)_2] \cdot 2H_2O$ and $[M(H_2O)_6][M(dipic)_2] \cdot 2H_2O$ ($M = Fe^{II}$, Co^{II} , Ni^{II} , Cu^{II} or Zn^{II}) were spectroscopically and structurally investigated (Laine et al., 1995; Wang et al., 2004; Wen et al., 2002; Qi et al., 2004). A family of dinuclear heterodimetallic dipicolinate compounds of the type $[M(H_2O)_5M'(dipic)_2] \cdot mH_2O$ (where $M/M' = Cu^{II}/Co^{II}$, Cu^{II}/Ni^{II} , Cu^{II}/Zn^{II} , Zn^{II}/Co^{II} , Ni^{II}/Co^{II} and $m = 2-3$) were characterized by IR and UV/Vis spectroscopy, elemental analysis and single-crystal X-ray diffraction analysis (Kirillova et al., 2008). In addition, crystal structures and properties of some new aqua dipicolinate compounds of lanthanide metals, e.g. polymeric homodimetallic complexes $\{[Nd_2(dipic)_3(H_2O)_3] \cdot 0.5H_2O\}_n$ and

$\{[Gd_2(dipic)_3(H_2O)_3] \cdot H_2O\}_n$ (Gao et al., 2006), complex $\{[La(dipic)_2(H_2O)_2] \cdot 4H_2O\}_n$ (Sharif et al., 2012) and similar dipicolinate compounds with lanthanides (Brayshaw et al., 2005; Ghosh and Bharadwaj, 2004; Mooibroek et al., 2010; Reinhard and Güdel, 2002;), were also studied.

Compounds of this type, due to their crystal structures and the resulting interesting properties, can find their applications in the fields of aqueous chemistry, catalysis, supramolecular medicinal chemistry (Yang et al., 2002), crystal engineering (Mirzaei et al., 2014; Pramanik & Das, 2009), bioinorganic chemistry, material chemistry and magnetic materials (Brayshaw et al., 2005; Parent et al., 2007), in bleaching and bactericidal compositions, etc.

Hence, we report herein the synthesis and structural characterization of two isostructural homodimetallic dipicolinate complexes of the type $[M(H_2O)_5M(dipic)_2] \cdot 2H_2O$, (where $M = Co^{II}/Co^{II}$ or Ni^{II}/Ni^{II} and dipic = dipicolinate anion) which form 3-D hydrogen bonded metaloorganic frameworks in the solid state.

Materials and Methods

Synthesis

The above-mentioned title compounds, $[Co(H_2O)_5Co(dipic)_2] \cdot 2H_2O$ (**1**) and $[Ni(H_2O)_5Ni(dipic)_2] \cdot 2H_2O$ (**2**), were formed as by-products in similar syntheses by the following procedure: to an aqueous solution (40 cm³) of cobalt(II) acetate tetrahydrate (for compound **1**) or nickel(II) acetate tetrahydrate (for compound **2**; both 0.25 g; 1.00 mmol), a stoichiometric amount of bathocuproine (0.36 g; 1.00 mmol) was added, the reaction mixture was

stirred and heated for approximately 30 minutes and then treated with 2,6-pyridinedicarboxylic acid (dipicolinic acid; 0.17 g; 1.00 mmol) in the molar ratio of 1:1:1, heated to the boiling point and cooled down to the laboratory temperature. The resulting solutions were filtered and left to slowly evaporate at ambient temperature. After a few days, dark red (complex **1**) or light green (complex **2**) single-crystals suitable for X-ray diffraction analysis were separated.

X-ray Crystallography

Crystal data and conditions of data collection and refinement are reported in Table 1. Data collection and cell refinement were carried out using a Stoe StadiVari diffractometer with a PILATUS3S 300K HPAD detector and a microfocused source Xenocs FOX3D (CuK α radiation) at 100 K. Crystal structures were solved by direct or charge-flipping methods using SHELXT (Sheldrick, 2015a) or SuperFlip (Palatinus and Chapuis, 2007) and refined by the full-matrix least-squares procedure with SHELXL (ver. 2016/4, Sheldrick, 2015b). Geometrical analyses were performed using the program SHELXL. Crystal structures were drawn with OLEX2 (Dolomanov et al., 2009).

Results and Discussion

Basic structure features of [Co(H₂O)₅Co(dipic)₂] \cdot 2H₂O (**1**) and [Ni(H₂O)₅Ni(dipic)₂] \cdot 2H₂O (**2**) are depicted in Figs. 1–2, the main information about crystal structures (crystal systems, space groups, unit cell parameters, experimental details etc.) are shown in Table 1 and the selected bond distances are collected in Table 2.

Compound [Co(H₂O)₅Co(dipic)₂] \cdot 2H₂O (**1**) crystallizes in the monoclinic crystal system with the space group *P*2₁/*c* and its crystal structure consists of two lattice water molecules and a complex molecule, which can be divided into two parts, cationic and anionic, with different coordination environments. In the cationic part, Co^{II} center is coordinated by five terminal aqua ligands [Co2—OW distances are in the range of 2.056(2)–2.170(2) Å (Table 2)] and one μ -carboxylate oxygen atom of a bridging dipicolinate anion [Co2—O2 = 2.088(2) Å], which interconnects cationic and anionic moieties. The anionic part of the complex comprises of a hexacoordinated Co^{II} center with two dipicolinate anions acting as tridentate chelating ligands by pyridine nitrogen atoms [Co1—N1 = 2.023(2) Å, Co1—N2 = 2.021(2) Å] and carboxylate oxygen atoms [Co1—O are in

Tab. 1. Experimental details.

	1	2
Chemical formula	C ₁₄ H ₂₀ Co ₂ N ₂ O ₁₅	C ₁₄ H ₂₀ Ni ₂ N ₂ O ₁₅
<i>M_r</i>	574.18	573.74
Crystal system, space group	Monoclinic <i>P</i> 2 ₁ / <i>c</i>	Monoclinic <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.3535(2) 27.1247(8) 9.5973(2)	8.2966(3) 27.0138(6) 9.6313(3)
α , β , γ (°)	90 98.179(2) 90	90 98.574(3) 90
<i>V</i> (Å ³)	2152.50(9)	2134.47(11)
<i>Z</i>	4	4
Radiation type	Cu <i>K</i> α	Cu <i>K</i> α
ρ_{calc} (g cm ⁻³)	1.772	1.785
<i>F</i> (000)	1068.0	1176.0
Crystal size (mm)	0.29 \times 0.12 \times 0.08	0.45 \times 0.35 \times 0.15
2 θ range for data collection (°)	6.518 to 142.500	6.544 to 142.526
Reflections collected	27702	20641
Independent reflections	3999	4016
Restraints/parameters	0/317	0/318
<i>R</i> _{int}	0.0594	0.0298
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²),	0.0287, 0.0455	0.0383, 0.1020
<i>S</i>	0.932	1.050
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.36, -0.47	0.89, -0.83
CCDC	1572828	1572827

Tab. 2. Selected bond lengths.

	1 (M = Co)	2 (M = Ni)
M1—O1	2.212(2)	2.171(2)
M1—O3	2.183(2)	2.162(2)
M1—O5	2.175(2)	2.153(2)
M1—O7	2.116(2)	2.101(2)
M1—N1	2.023(2)	1.969(2)
M1—N2	2.021(2)	1.960(2)
M2—O2	2.088(2)	2.034(2)
M2—O1W	2.060(2)	2.046(2)
M2—O2W	2.056(2)	2.030(2)
M2—O3W	2.088(2)	2.047(2)
M2—O4W	2.170(2)	2.119(2)
M2—O5W	2.081(2)	2.052(2)

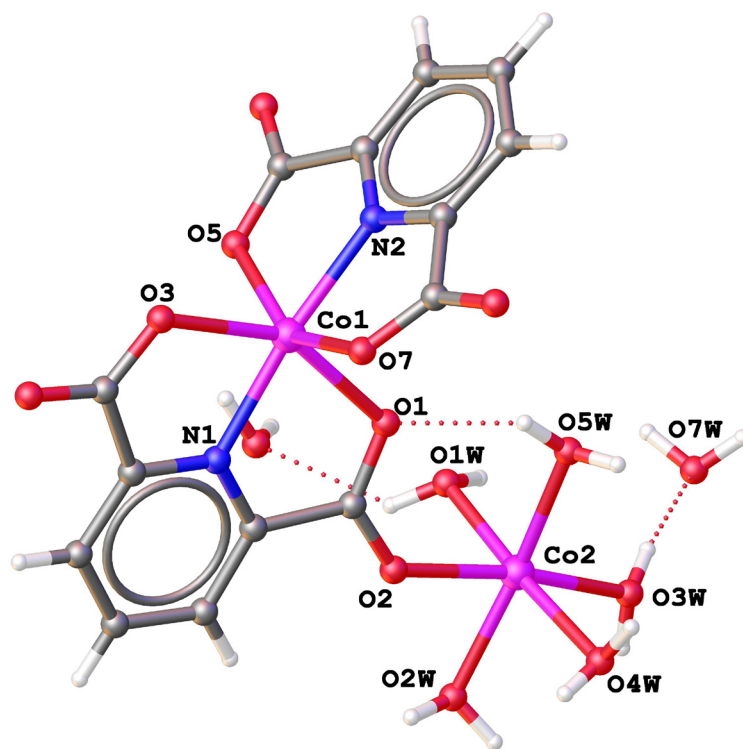
the range of 2.116(2)–2.212(2) Å (Table 2)]. Coordination polyhedra around the Co^{II} metal centers are of a distorted octahedral shape with {CoO₅O'} and {CoN₂O₄} coordination chromophores.

Complex [Ni(H₂O)₅Ni(dipic)₂].2H₂O (**2**) is isostructural to complex (**1**), it has similar unit cell parameters (given in Table 1), and therefore is not discussed further in detail.

Fig. 3 represents π - π stacking interactions (Janiak, 2000) between two symmetrically equivalent pyridine rings [N1/C2—C6] in the crystal structure of **1**. The centroid...centroid distances (Janiak, 2000)

are 3.73 Å for **1** and 3.71 Å for **2**. The shift distances (Janiak, 2000) are 1.39 Å and 1.42 Å, respectively. The distances between two planes of pyridine rings are exactly 3.46 Å and 3.43 Å, respectively.

Figs. 4 and 5 show enriched hydrogen bond networks in the crystal packing of complex **1**. The complex molecules of **1** (or **2**) and uncoordinated water molecules are connected by O—H...O hydrogen bonds into 3-D supramolecular networks. Uncoordinated water molecules, O6W, are linked by multicentered O—H...O hydrogen bonds to coordinated carboxylate oxygen atoms, O3 and O7 [O6W—H6WA...O3 and O6W—H6WA...O7, with $d(O...O)$ distances in the region of 3.003(2)–3.197(3) Å, (Tables 3 and 4)], and O—H...O hydrogen bonds to coordinated water molecules, O4W [O6W—H6WB...O4W, with $d(O6W...O4W)$ distance of 2.896(2) and 2.920(2) Å, respectively]. The complex molecules of **1** (or **2**) are interconnected with uncoordinated water molecules O6W and O7W by O—H...O hydrogen bonds between coordinated water molecules O1W and uncoordinated water molecules O6W, between coordinated water molecules O2W and solvent water molecules O6W, and between water molecules of the complex O3W and solvent water molecules O7W [O1W—H1WA...O6W, O2W—H2WA...O6W and O3W—H3WB...O7W with $d(O...O)$ distances in the range of 2.641(3)–2.938(2) Å, (Tables 3 and 4)]. Uncoordinated water

**Fig. 1.** Perspective view of **1** with the atom numbering scheme.

molecules, O7W, are connected to uncoordinated carboxylate oxygen atoms (O6, O8) by O—H...O hydrogen bonds [O7W—H7WA...O6 and O7W—H7WB...O8 with $d(\text{O}\cdots\text{O})$ distances within the range of 2.762(2)–2.771(2) Å, (Tables 3 and 4)]. Coordinated water molecules (O1W, O2W, O3W, O4W and O5W) are also linked by O—H...O hydrogen bonds to coordinated

carboxylate oxygen atoms (O1, O3, O5, O7), or to uncoordinated carboxylate oxygen atoms (O4, O6, O8) [O1W—H1WB...O8, O2W—H2WB...O4, O3W—H3WA...O3, O4W—H4WA...O5, O4W—H4WB...O4, O5W—H5WA...O6 and O5W—H5WB...O1 with $d(\text{O}\cdots\text{O})$ distances in the range of 2.631(2)–3.020(2) Å, (Tables 3 and 4)].

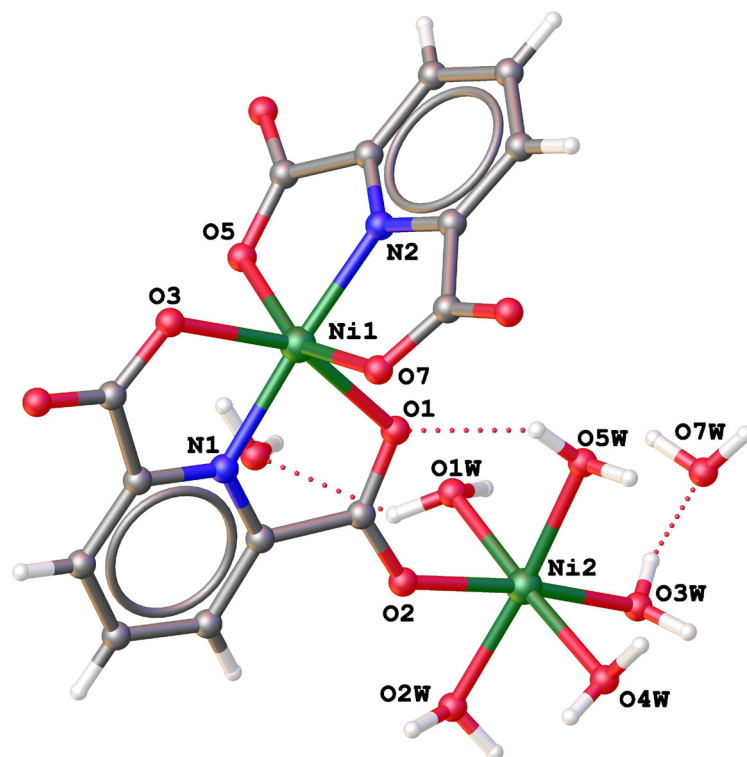


Fig. 2. Perspective view of **2** with the atom numbering scheme.

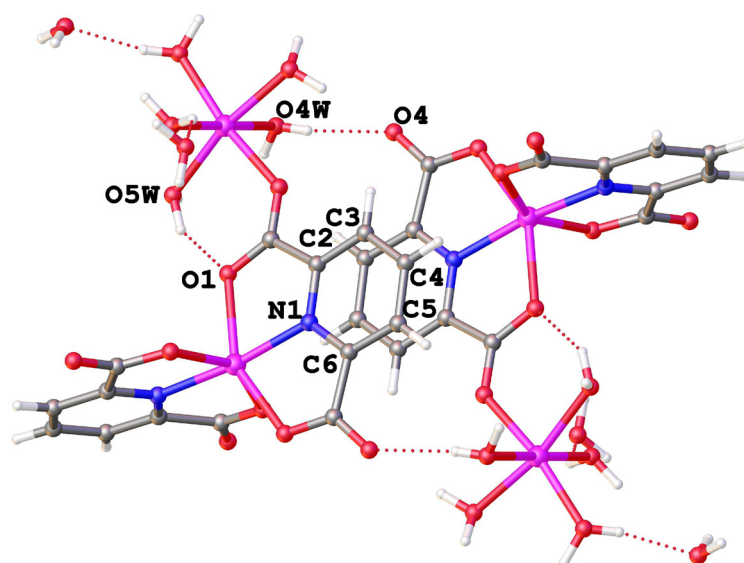


Fig. 3. π - π stacking interactions and hydrogen bonds in the crystal structure of **1**.

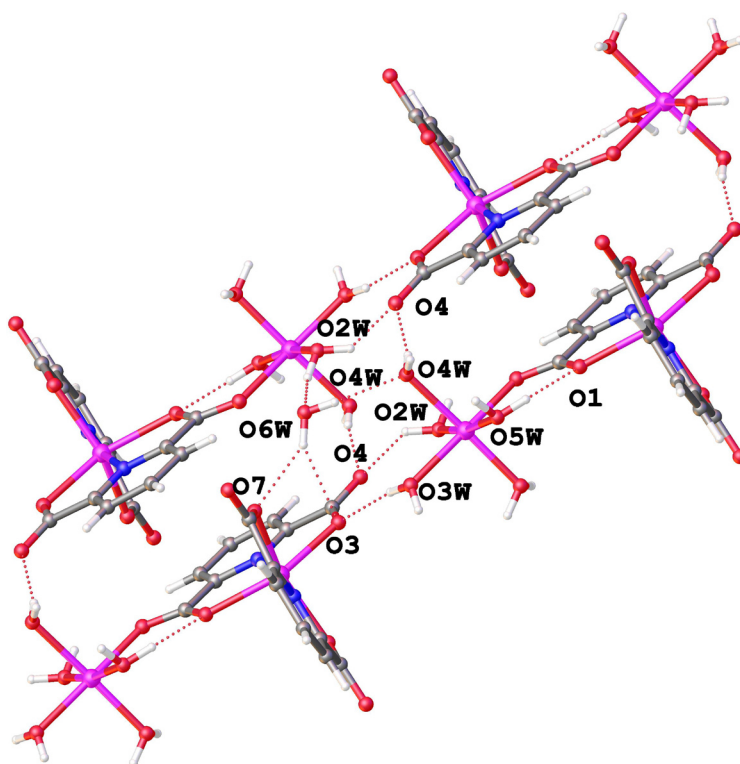


Fig. 4. Hydrogen bonds in the crystal structure of **1**.

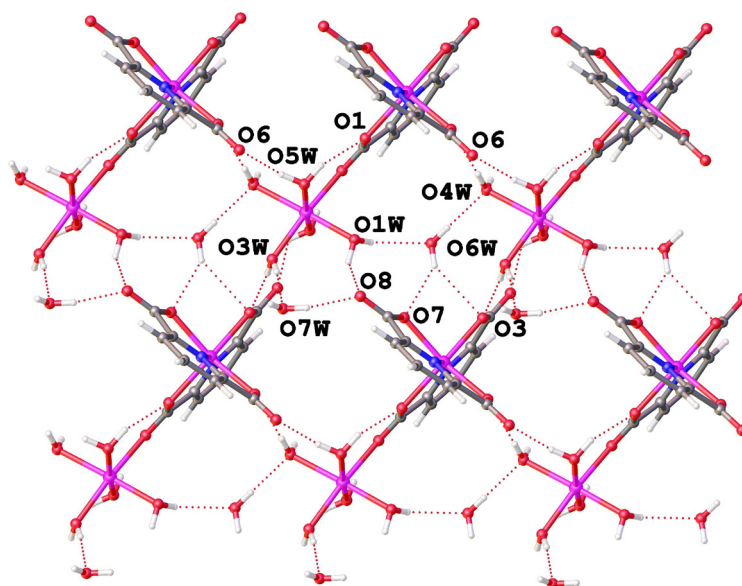


Fig. 5. 3-D supramolecular H-bonds network in the crystal structure of **1**.

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Tab. 3. Hydrogen bonds parameters for 1.

D—H...A	$d(\text{H}\cdots\text{A})/\text{\AA}$	$d(\text{D}\cdots\text{A})/\text{\AA}$	$\langle(\text{D}-\text{H}-\text{A})/\text{\AA}^\circ$
O1W—H1WA...O6W	2.14	2.806(3)	134
O1W—H1WB...O8 ¹	2.00	2.710(2)	140
O2W—H2WA...O6W ²	2.21	2.938(2)	143
O2W—H2WB...O4 ³	1.99	2.633(2)	131
O3W—H3WA...O3 ³	1.91	2.757(2)	162
O3W—H3WB...O7W	1.86	2.651(3)	169
O4W—H4WA...O5 ⁴	1.96	2.786(2)	155
O4W—H4WB...O4 ⁷	1.95	2.674(2)	167
O5W—H5WA...O6 ⁴	1.84	2.700(2)	168
O5W—H5WB...O1	2.04	2.815(2)	146
O6W—H6WA...O3 ¹	2.51	3.197(3)	139
O6W—H6WA...O7 ¹	2.28	3.003(2)	144
O6W—H6WA...O4W ⁵	2.05	2.896(2)	174
O7W—H7WA...O6 ⁶	1.92	2.766(2)	177
O7W—H7WA...O8 ¹	1.94	2.765(3)	162

Symmetry codes: ¹+x, +y, -1 + z; ²1 - x, 1 - y, -z; ³-1 + x, +y, -1 + z; ⁴-1 + x, +y, +z; ⁵1 + x, +y, +z; ⁶-1 + x, 1/2 - y, -1/2 + z; ⁷1 - x, 1 - y, 1 - z.

Tab. 4. Hydrogen bonds parameters for 2.

D—H...A	$d(\text{H}\cdots\text{A})/\text{\AA}$	$d(\text{D}\cdots\text{A})/\text{\AA}$	$\langle(\text{D}-\text{H}-\text{A})/\text{\AA}^\circ$
O1W—H1WA...O6W	2.13	2.823(3)	138
O1W—H1WB...O8 ¹	2.00	2.711(2)	140
O2W—H2WA...O6W ²	2.20	2.930(2)	144
O2W—H2WB...O4 ³	1.88	2.631(2)	146
O3W—H3WA...O3 ³	1.93	2.770(2)	159
O3W—H3WB...O7W	1.79	2.641(2)	162
O4W—H4WA...O5 ⁴	1.98	2.806(2)	155
O4W—H4WB...O4 ⁷	1.87	2.682(2)	177
O5W—H5WA...O6 ⁴	1.82	2.682(2)	169
O5W—H5WB...O1	2.06	2.838(2)	147
O6W—H6WA...O3 ¹	2.54	3.182(2)	134
O6W—H6WA...O7 ¹	2.25	3.020(2)	151
O6W—H6WA...O4W ⁵	2.09	2.920(2)	165
O7W—H7WA...O6 ⁶	1.93	2.771(2)	179
O7W—H7WA...O8 ¹	1.94	2.762(2)	164

Symmetry codes: ¹+x, +y, -1 + z; ²1 - x, 1 - y, -z; ³-1 + x, +y, -1 + z; ⁴-1 + x, +y, +z; ⁵1 + x, +y, +z; ⁶-1 + x, 1/2 - y, -1/2 + z; ⁷1 - x, 1 - y, 1 - z.

References

- Bourhis LJ, Dolomanov OV, Gildea RJ, Howard JAK, Puschmann H (2015) *Acta Crystallogr.* A71: 59–75.
- Brayshaw PA, Hall AK, Harrison WTA, Harrowfield JM, Pearce D, Shand TM, Skelton BW, Whitaker CR, White AH (2005) *Eur. J. Inorg. Chem.* 1127–1141.
- Das B, Baruah JB, (2012) *Polyhedron.* 31: 361–367.
- Das B, Baruah JB, (2013) *J. Mol. Struct.* 1034: 144–151.
- Dolomanov OV, Bourhis LJ, Gildea RJ, Howard JAK, Puschmann H (2009) *J. Appl. Crystallogr.* 42: 339–341.
- Gao HL, Yi L, Zhao B, Zhao XQ, Cheng P, Liao DZ, Yan SP (2006) *Inorg. Chem.* 45: 5980–5988.
- Ghosh SK, Bharadwaj PK (2004) *Inorg. Chem.* 43: 2293–2298.
- Janiak C (2000) *J. Chem. Soc., Dalton Trans.* 21: 3885–3896.
- Kirillova MV, Guedes da Silva MFC, Kirillov AM, Fraústo da Silva JJR, Pombeiro AJL (2007) *Inorg. Chim. Acta.* 360: 506–512.
- Kirillova MV, Kirillov AM, Guedes da Silva MFC, Kopylovich MN, Fraústo da Silva JJR, Pombeiro AJL (2008) *Inorg. Chim. Acta.* 361: 1728–1737.

- Laine P, Gourdon A, Launay JP (1995) *Inorg. Chem.* 34: 5138–5149.
- Mirzaei M, Eshtiagh-Hosseini H, Bauzá A, Zarghami S, Ballester P, Maguee JT, Frontera A (2014) *Cryst. Eng. Comm.* 16: 6149–6158.
- Mooibroek TJ, Gamez P, Pevec A, Kasunič M, Kozlevčar B, Fu WT, Reedijk J (2010) *J. Chem. Soc., Dalton Trans.* 39: 6483–6487.
- Palatinus L, Chapuis G (2007) *J. Appl. Crystallogr.* 40: 786–790.
- Parent AR, Vedachalam S, Landee CP, Turnbull MM (2008) *J. Coord. Chem.* 61: 93–108.
- Pramanik A, Das G (2009) *J. Chem. Crystallogr.* 39: 416–422.
- Qi Y, Wang Y, Fan H, Cao M, Mao L, Hu Ch, Wang E, Hu N, Jia H (2004) *J. Mol. Struct.* 694: 73–78.
- Reinhard C, Güdel HU (2002) *Inorg. Chem.* 41: 1048–1055.
- Sharif S, Khan IU, Sahin O, Ahmad S, Büyükgüngör O, Ali S (2012) *J. Inorg. Organomet. Polym.* 22: 1165–1173.
- Sheldrick GM (2015a) *Acta Crystallogr. A* 71: 3–8.
- Sheldrick GM (2015b) *Acta Crystallogr. C* 71: 3–8.
- Ucar I, Bulut A, Karadag A, Kazak C (2007) *J. Mol. Struct.* 837: 38–42.
- Wang L, Duan L, Xiao D, Wang E, Hu C (2004) *J. Coord. Chem.* 57: 1079–1087.
- Wen YH, Li ZJ, Qin YY, Kang Y, Chen YB, Cheng JK, Yao YG (2002) *Acta Crystallogr. E* 58: m762–m764.
- Yang L, Crans DC, Miller SM, la Cour A, Anderson OP, Kaszynski PM, Godzala ME, Austin LD, Willsky GR (2002) *Inorg. Chem.* 41: 4859–4871.