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MONO- AND BINUCLEAR COORDINATION COMPOUNDS OF Ni(II) AND Mn(II) WITH DIOXIMIC AND DICARBOXYLIC LIGANDS

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Abstract. Two new compounds - a mononuclear nickel(II) compound with di-*p*-tolylglyoxime ($DpatH_2$) - $[Ni(DpatH_2)_3]SO_4\cdot 1,4\text{-}H_2bdc\cdot 2.5DMF\cdot H_2O$ (**1**) and a binuclear manganese(II) compound with dianilineglyoxime ($DAnH_2$) - $[Mn_2(DAnH_2)_2(1,3\text{-}bdc)_2(DMSO)_4]$ (**2**) (1,4- and 1,3-bdc are 1,4- and 1,3-benzenedicarboxylic acids, respectively) have been obtained. The IR spectra of the complexes were studied and molecular and crystal structures of the compounds were determined by single crystal X-ray diffraction method. Compound **1** has an ionic structure and contains a complex cation in which three neutral $DpatH_2$ ligands are coordinated to the nickel atom. Complex **2** is a molecular binuclear complex in which, in addition to the two neutral ligands $DAnH_2$ and four DMSO molecules, two 1,3-benzenedicarboxylic anions are coordinated to the metal atoms in a bridging manner.

Keywords: coordination compound, Ni(II), Mn(II), dioxime, X-ray study, hydrogen bond.

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Introduction

The systematic research of transition metal dioximates was initiated with their introduction into analytic and inorganic chemistry by the use of nitroso-naphthols for the quantitative determination of cobalt by Ilinsky, M. and Knorre, G.V. in 1882 [1] , followed by the application of dimethylglyoxime in the quantitative analysis of metals from the nickel triad by Chugaev, L. [2,3]. A change related to the substitution of CH_3 groups in dimethylglyoxime by various groups, including bulky ones or containing additional functional groups, led to the widening of the dioxime class as ligands for obtaining complex transition metal compounds. A *vic*-dioximes have gained increased application in important research fields, including supramolecular chemistry, analytic chemistry, biochemistry, and medicine [4-9].

It is known that dioximes exist in three isomeric forms, the *N*,*N*-chelate coordination mode favoured by the anti-(*E*,*E*) form is the most frequent in complexes [4,10,11], but there are known cases when these ligands also coordinate *via* oxygen atoms of the oxime groups [12,13]. In the last five years, our team has published results on complex compounds of transition metals with oxime ligands, in which the method of synthesis and the structure of mononuclear complexes of Co(III), Ni(II), Cu(II) [14-17] and binuclears of Zn(II) and Mn(II) [18,19], as well as a series of 1D and 2D coordination polymers of Ni(II), Zn(II), Mn(II) and Cd(II) [19,20], containing dianylglyoxime ($DAnH_2$), disulfanilamidoglyoxime ($DsamH_2$) and di-*m*-aminobenzoylglyoxime ($DmabaH_4$) are described. The structure of two newly synthesized coordination agents from the dioxime class was recently established: di-*p*-aminobenzoylglyoxime ($DpabaH_4$) and di-*p*-aminotolueneglyoxime ($DpatH_2$) [21], the latter exhibiting antimicrobial activity.

The aim of this study is the assembly of new coordination compounds $DpatH_2$, $DAnH_2$ by reaction with Ni(II) and Mn(II) salts and 1,4- and 1,3-benzenedicarboxylic acids (1,4-H_2bdc and 1,3-H_2bdc). As a result, two new compounds were obtained for which the crystal structure was determined: $[Ni(DpatH_2)_3]SO_4\cdot 1,4\text{-}H_2bdc\cdot 2.5DMF\cdot H_2O$ (**1**) and $[Mn_2(DAnH_2)_2(1,3\text{-}bdc)_2(DMSO)_4]$ (**2**).

Experimental

Materials

All reagents were purchased from commercial sources. The starting materials were: nickel(II) sulphate hexahydrate, mangan(II) acetate tetrahydrate, methanol, ethanol, dimethylformamide (DMF), dimethylsulfoxide (DMSO), 1,4- and 1,3-H_2bdc, all being purchased

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from Sigma Aldrich. DpatH_2 and DAnH_2 were synthetized by condensation of dichloroglyoxime with *p*-toluidine (pat) and aniline (An), as described in [17,18,21].

Synthesis of [Ni(DpatH_2)$_3$]SO_4·1,4-H_2bdc ·2.5DMF·H_2O (1).

Compounds DpatH_2 (0.15 g, 0.2 mmol) and $NiSO_4·6H_2O$ (0.026 g, 0.1 mmol) were dissolved in a DMF–methanol mixture (12 mL) in a ratio of 1:3 (vol/vol). A solution of 1,4-H_2bdc (0.034 g, 0.2 mmol) in methanol (3 mL) 2 drops of H_2SO_4 was added to the obtained green-yellow solution at room temperature with permanent stirring. The reaction was stirred for 10–15 min. The solution was filtered off, and was left to stay at room temperature for crystallization. Prismatic brown crystals suitable for XRD were formed in 17 days. Yield: 47% (0.13 g).

Anal. calcd. for $C_{63.5}H_{79.5}N_{14.5}O_{17.5}SNi$ (%): C, 53.83; H, 5.66; N, 14.35, S, 2.26; Ni, 4.14. Found, %: C, 53.74; H, 5.71; N, 14.31; S, 2.24; Ni, 4.16. The IR spectra (ν, cm^{-1}): 3335 m, 3174 m, 3065 m, 2971 m, 2922 m, 2808 m, 2511 w, 1898 vw, 1654 m, 1602 vs, 1514 m, 1469 m, 1419 w, 1384 w, 1307 w, 1210 vw, 1179 w, 1083 s, 1047 s, 1012 vs, 971 w, 898 m, 811 m, 767 vw, 728 vw, 706 w, 690 w, 662 vw, 629 vw, 605 w, 590 w, 494 w, 458 w, 418 vw, 412 vw.

Synthesis of [Mn_2(DAnH_2)$_2$(1,3-bdc)$_2$(DMSO)$_4$] (2).

Compounds DAnH_2 (0.054 g, 0.2 mmol) and $Mn(CH_3COO)_2·4H_2O$ (0.024 g, 0.1 mmol) were dissolved in a DMSO-ethanol mixture (12 mL) in a ratio of 1:1 (vol/vol). A solution of 1,3-H_2bdc (0.034 g, 0.2 mmol) in ethanol (3 mL) was added to the obtained yellow solution at room temperature with permanent stirring. When the mixture was stirred for 10–15 min, a pink precipitate was formed. The precipitate was filtered off, and the filtrate was left to stay at room temperature for crystallization. Prismatic rose crystals suitable for XRD were formed in 31 days. Yield: 31% (0.06 g).

Anal. Calcd. for $C_{52}H_{60}N_8O_{16}S_4Mn_2$ (%): C, 48.37; H, 4.68; N, 8.68; S, 9.93; Mn, 8.51. Found, %: C, 48.40; H, 4.72; N, 8.63; S, 9.98; Mn, 8.52. The IR spectra (ν, cm^{-1}): 3201 vw, 3067 vw, 3038 vw, 3000 vw, 2919 vw, 2600 vw, 1867 vw, 1661 w, 1599 s, 1534 m, 1496 m, 1473 w, 1434 w, 1379 vs, 1312 w, 1292 w, 1279 w, 1178 w, 1156 w, 1075 w, 1011 vs, 950 s, 911 m, 896 vw, 835 vw, 807 w, 745 s, 705 s, 693 s, 656 w, 633 vw, 605 vw, 584 vw, 541 vw, 512 vw, 484 w, 442 w, 419 w.

Physical measurements

Elemental analysis of the complexes for C, H, S and N, was performed on a Vario EL (III) Elemental Analyzer and on an AAS-1N atomic absorption spectrometer (Carl Zeiss) for metals.

Infrared spectra (IR) were recorded on a FT-IR Spectrum-100 Perkin Elmer spectrometer using ATR technique (650–4000 cm^{-1}). Intensities are given as: vs - very strong, s - strong, m - medium, w - weak, vw - very weak.

Crystallographic studies. Single crystal X-ray diffraction measurements for **1** and **2** were carried out at room temperature (293 K) on a Xcalibur E CCD diffractometer equipped with a CCD area detector and a graphite monochromator, MoKα radiation (0.71073 Å). CrysAlis PRO software was used for data collection and reduction, unit cell determination [22]. The structures were solved and refined using the SHELXS97 and SHELXL2014 software packages [23,24]. The non-hydrogen atoms were treated anisotropically (full-matrix least squares method on F^2). The hydrogen atoms were placed in calculated positions and were treated using riding model approximations with Uiso(H)= 1.2Ueq(C), while the oxygen bounded H atoms were found from differential Fourier maps at an intermediate stage of the structure refinement. These hydrogen atoms were refined with the isotropic displacement parameter Uiso(H)= 1.5Ueq(O). The crystals obtained for **1** were not of the highest quality, so the diffraction was weaker (the ratio of observed/unique reflections is low, 38%), which affected the increase in the R-factor.

The X-ray data and the details of the refinement for **1** and **2** are summarized in Table 1, selected bond distances and bond angles - in Table 2 and geometric parameters of hydrogen bonds are listed in Table 3. The crystallographic data were deposited with the Cambridge Crystallographic Data Center, CCDC 2363771 and 2363772 for **1** and **2**, respectively. Copies of this information may be obtained free of charge from CCDC, 12 Union Road, Cambridge CHB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Results and discussion

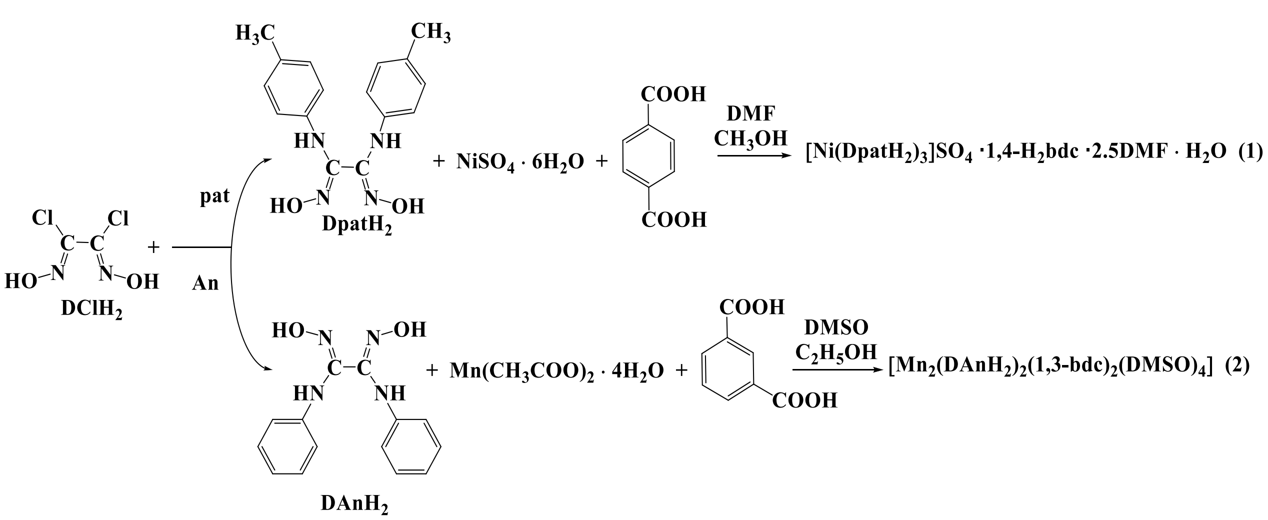
According to synthetic Scheme 1, two new compounds were obtained. It has been established that both ligands - oxime ligand and carboxylate - are involved in the formation of both compounds, but in **1** the latter is located in the outer sphere of the complex in a neutral form.

The IR spectra of compounds **1** and **2** are complex, but also have many common absorption bands. The bands at 3174 cm^{-1} (**1**) and 3201 cm^{-1} (**2**) are wide and can be attributed to the associated ν(NH) oscillations [25,26]. The set of bands in the 3065‒2808 cm^{-1} (**1**) and 3067-2919 cm^{-1} (**2**) spectral regions belong to aromatic and aliphatic ν(CH) oscillations [25]. Wide absorption bands at 2511 cm^{-1} (**1**) and equally wide 2600 cm^{-1} (**2**) are attributed to ν(OH) oscillations associated with the participation of carboxylic groups [25].

Table 1

Crystal data and details of data collection for 1 and 2.

Parameter	*Value*	
	1	***2***
Empirical formula	$C_{63.5}H_{79.5}N_{14.5}O_{17.5}SNi$	$C_{52}H_{60}N_8O_{16}S_4Mn_2$
M	1416.68	1291.20
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	$P\bar{1}$
a, Å	15.9434(8)	8.4949(3)
b, Å	16.5862(8)	14.8395(5)
c, Å	27.9012(13)	24.9128(9)
α, °	90	98.219(3)
β, °	90	93.329(3)
γ, °	90	90.076(3)
V, Å^3	7378.2(6)	3102.89(19)
Z	4	2
$\rho_{calcd.}$g/cm^3	1.275	1.382
μ, mm^{-1}	0.365	0.611
F(000)	2984	1340
Crystal size, mm	0.35x0.1x0.05	0.50x0.35x0.20
θ range, °	2.92 – 25.05	3.00 – 25.50
Index ranges	$-18 \le h \le 11$, $-18 \le k \le 19$, $-33 \le l \le 26$	$-10 \le h \le 10$, $-17 \le k \le 17$, $-30 \le l \le 17$
Reflections collected/independent reflections (R_{int})	17889/12432 (R_{int}= 0.0841)	20120/11533 (R_{int}= 0.0226)
Reflections with $I > 2\sigma(I)$	4712	8008
Completeness, %	99.6	99.7
Parameters	921	854
GOOF	1.006	1.005
Final R indices (I>2σ(I))	R_1= 0.0909, wR_2= 0.1328	R_1= 0.0653, wR_2= 0.1640
R indices (all data)	R_1= 0.2370, wR_2= 0.1888	R_1= 0.0965, $wR2$= 0.1831
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.586 – 0.264	0.985 – 0.860

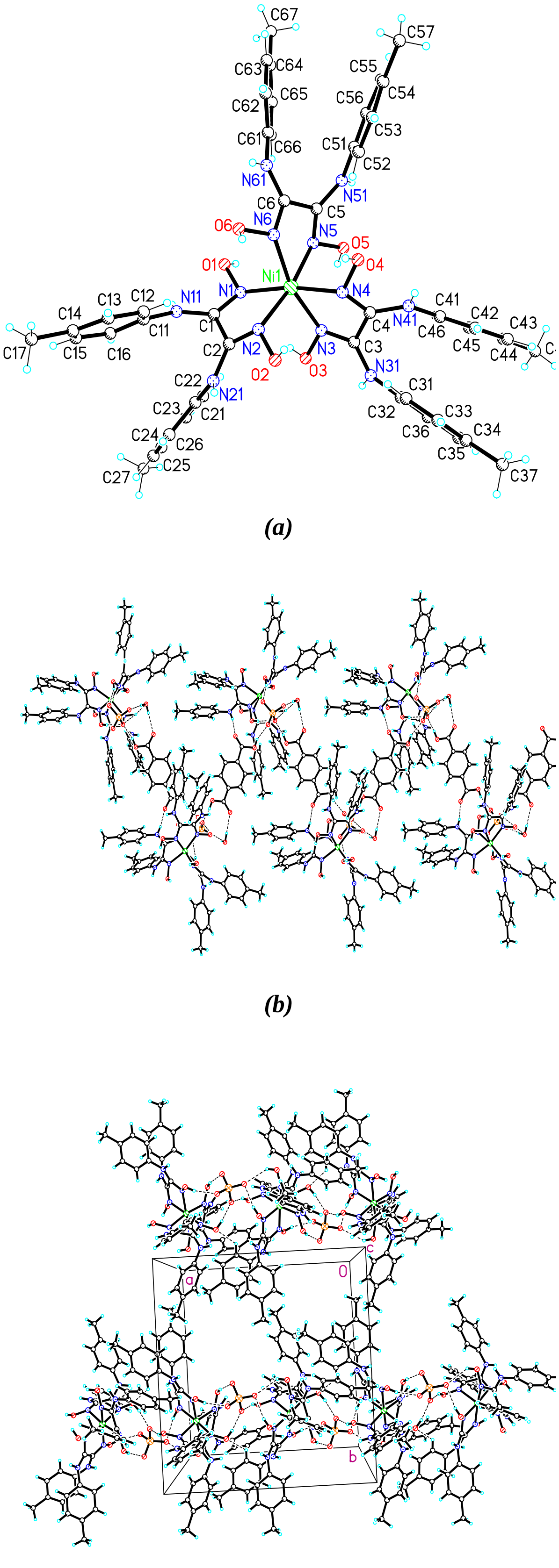


Scheme 1. Synthetic pathways to dioxime ligands and complexes 1 and 2.

At the coordination of the carboxylate group (COO^{-}) inclusive and in the bridge-bidentate mode (**2**) the spectrum shows the $\nu_{as}(COO^{-})$ oscillations at 1599 cm^{-1} and the $\nu_{s}(COO^{-})$ oscillations at 1379 cm^{-1} [27,28]. In the spectrum of compound **1**, the frequencies of $\nu(C{=}O)_{DMF}$ coordinated at 1654 cm^{-1} and of the SO_4^{2-} anion are observed: 1180, 1097, 1050, 973, 629, 605, 590 and 494 cm^{-1} [25,28]. The 1,4-substitution type in the aromatic rings of the ligand in complex **1** is confirmed by the intensive band at 813 cm^{-1} [25]. The high intensity band at 1012 cm^{-1} in spectrum of **1** is attributed to $\nu(S{=}O)$ oscillations in coordinated DMSO [25,26]. The 1,3- substitution type in the benzene ring is confirmed by the bands of high intensity at 745 and 693 cm^{-1}, and monosubstituted (5 adjacent hydrogen atoms) - bands 746 and 705 cm^{-1} [25,27].

The mononuclear compound $[Ni(DpatH_2)_3]SO_4\cdot 1,4\text{-}H_2bdc\cdot 2.5DMF\cdot H_2O$ (**1**) crystallizes in orthorhombic space group $P2_12_12_1$ (Table 1). This is an ionic compound and co-crystallization compound at the same time which consisted of the complex cation $[Ni(DpatH_2)_3]^{2+}$, SO_4^{2-} anion, one 1,4-H_2bdc molecule, DMF molecules and one water molecule in the outer sphere. The octahedral coordination polyhedron of the nickel atom is formed by donor N_6 atoms belonging to three oxime ligands $DpatH_2$, which are coordinated to the metal atom in a chelate-bidentate manner in a neutral form through the nitrogen atoms of the oxime groups. (Figure 1*(a)*). In the complex cation, three identical metallocycles of five atoms form angles of 91.7, 86.1 and 78.6° between them, which does not allow the oxime groups to participate in the formation of intramolecular hydrogen bonds, distinguishing them very much from nickel(II) *trans*-dioximates, in which the metal is square-planar and these two similar ligands are linked by strong O–H···O bonds [29].

The Ni–N interatomic distances in the coordination polyhedron of the metal atom in the complex cation are in the range 2.034(10)–2.134(11) Å (Table 2) and correspond to those of known Ni(II) *tris*-dioximates [15,30], where the Ni–N bond length varies from 2.039(2) to 2.110(3) Å. The core fragment of the oxime ligand is flexible, which favours the bidentate-chelate coordination mode of the ligand: the NCCN torsion angles in the $DpatH_2$ coordinated ligands in **1** are equal to 34.4, 31.3, and 36.2° and differ from those determined for this non-coordinated $DpatH_2$ molecules equal to 61.9 and 62.4° [21].



(a)

(b)

(c)

Figure 1. Structure of the complex cation $[Ni(DpatH_2)_3]^{2+}$ of 1 *(a)*, chain formation and a fragment of the crystal structure *(b,c)*.

In the crystals of **1**, the complex cations and outer-sphere crystallization molecules of dicarboxylic acid, DMF and water molecules are linked *via* an intricate system of hydrogen bonds in a three-dimensional supramolecular network (Table 3). $[Ni(DpatH_2)_3]^{2+}$ cations join each other only through fine C-H···O bonds, these form chains with the SO_4^{2-} anions through intermolecular hydrogen bonds in which all the −OH groups of the oxime fragments are involved as proton donors, the oxygen atoms O7, O8, O9, O10 of the inorganic anions acting as acceptors (Figure 1*(b)*). The donor-acceptor distances in these hydrogen bonds are within the range of 2.562(13)–3.115(13) Å. These chains in the crystal are arranged in such a way that cavities occupy 38.7% of the volume of the elementary cell. The anilinic =NH groups from the cation ligands are especially attracted to the formation of hydrogen bonds with the DMF molecules (O11, O12) and with the carbonyl atoms of the 1,4-H_2bdc (O14C) molecules, favouring the retention of these molecules in the crystal. The latter form hydrogen bonds with the inorganic anions through the −OH hydroxyl groups, thus joining the chains together. As a result, double chains can be seen in the crystal, during the formation of which the 1,4-H_2bdc crystallization molecules are attracted (Figure 1*(c)*), which results in layer formation. Water molecules form intermolecular hydrogen bonds of the O–H···O and C–H···O types both with the complex cations acting as acceptors, as well as inorganic anions and these uncoordinated 1,4-H_2bdc molecules acting as proton donors and stabilizing the supramolecular network.

The binuclear complex $[Mn_2(DAnH_2)_2(1,3\text{-}bdc)_2(DMSO)_4]$ (**2**) crystallizes in the triclinic space group $P\bar{1}$ (Table 1). The asymmetric part of the unit cell of the crystal contains two crystallographically independent Mn^{2+} cations, two neutral $DAnH_2$ ligands, two diprotonated dicarboxylate anions $(1,3\text{-}bdc)^{2-}$ and four DMSO molecules, the latter being located in two positions each with an occupancy coefficient of 0.5. As a result, two crystallographically independent centrosymmetric binuclear molecular complexes (A and B) are formed in the crystal, in which the two metal atoms are linked to each other *via* two *exo*-bidentate dicarboxylate ligands (Figure 2*(a)*,*(b)*). The octahedral coordination polyhedron of each metal atom is formed by the N_2O_4 donor atoms, in which one $DAnH_2$ ligand coordinates as bidentate-chelate *via* two nitrogen atoms, *via* an oxygen atom monodentate - two $(1,3\text{-}bdc)^{2-}$ ligands and two ligands DMSO.

Table 2

Bond lengths [Å] and angles [°] for 1 and 2.

Ni(II)	***(1)***	*Mn(II)*	***(2, A)***	***(2, B)***
Bond	*Bond length, Å*	*Bond*	*Bond length, Å*	*Bond length, Å*
Ni(1)-N(1)	2.041(11)	Mn(1)-N(1)	2.364(3)	2.353(3)
Ni(1)-N(2)	2.134(11)	Mn(1)-N(2)	2.260(3)	2.268(3)
Ni(1)-N(3)	2.088(11)	Mn(1)-O(3)	2.087(3)	2.111(3)
Ni(1)-N(4)	2.034(10)	Mn(1)-O(5)$^{\#1/\#2}$	2.120(3)	2.103(3)
Ni(1)-N(5)	2.074(11)	Mn(1)-O(1S)/(3S)	2.136(4)	2.167(3)
Ni(1)-N(6)	2.056(11)	Mn(1)-O(2S)/(4S)	2.188(4)	2.125(4)
Bond angle	*Bond angle value, °*	*Bond angle*	*Bond angle value, °*	*Bond angle value, °*
N(1)–Ni(1)-N(2)	77.4(4)	N(1)–Mn(1)–N(2)	69.47(11)	69.23(11)
N(1)–Ni(1)-N(3)	98.3(4)	N(1)–Mn(1)–O(3)	95.54(11)	97.77(11)
N(1)–Ni(1)-N(4)	170.6(5)	N(1)–Mn(1)–O(5)$^{\#1/\#2}$	168.83(11)	168.19(12)
N(1)–Ni(1)-N(5)	96.4(5)	N(1)–Mn(1)–O(1S)/(3S)	90.36(14)	84.41(15)
N(1)–Ni(1)-N(6)	92.9(4)	N(1)–Mn(1)–O(2S)/(4S)	87.81(16)	89.93(16)
N(2)–Ni(1)-N(3)	95.2(4)	N(2)–Mn(1)–O(3)	164.07(12)	166.85(12)
N(2)–Ni(1)-N(4)	95.2(4)	N(2)–Mn(1)–O(5)$^{\#1/\#2}$	99.84(11)	99.18(12)
N(2)–Ni(1)-N(5)	170.8(4)	N(2)–Mn(1)–O(1S)/(3S)	89.70(16)	85.24(13)
N(2)–Ni(1)-N(6)	97.3(4)	N(2)–Mn(1)–O(2S)/(4S)	81.37(15)	89.47(15)
N(3)–Ni(1)-N(4)	76.4(4)	O(3)–Mn(1)–O(5)$^{\#1/\#2}$	94.75(12)	93.72(12)
N(3)–Ni(1)-N(5)	92.5(4)	O(3)–Mn(1)–O(1S)/(3S)	95.96(17)	91.65(15)
N(3)–Ni(1)-N(6)	164.8(4)	O(3)–Mn(1)–O(2S)/(4S)	93.02(17)	92.60(16)
N(4)–Ni(1)-N(5)	91.6(4)	O(5)$^{\#1/\#2}$–Mn(1)–O(1S)/(3S)	92.86(16)	92.55(18)
N(4)–Ni(1)-N(6)	93.8(4)	O(5)$^{\#1/\#2}$–Mn(1)–O(2S)/(4S)	87.35(18)	92.29(18)
N(5)–Ni(1)-N(6)	76.0(4)	O(1S)/(3S)–Mn(1)–O(2S)/(4S)	170.96(18)	173.34(17)

Symmetry transformations used to generate equivalent atoms $^{\#1}$ $-x+1, -y+2, -z$; $^{\#2}$ $-x, -y+1, -z+1$

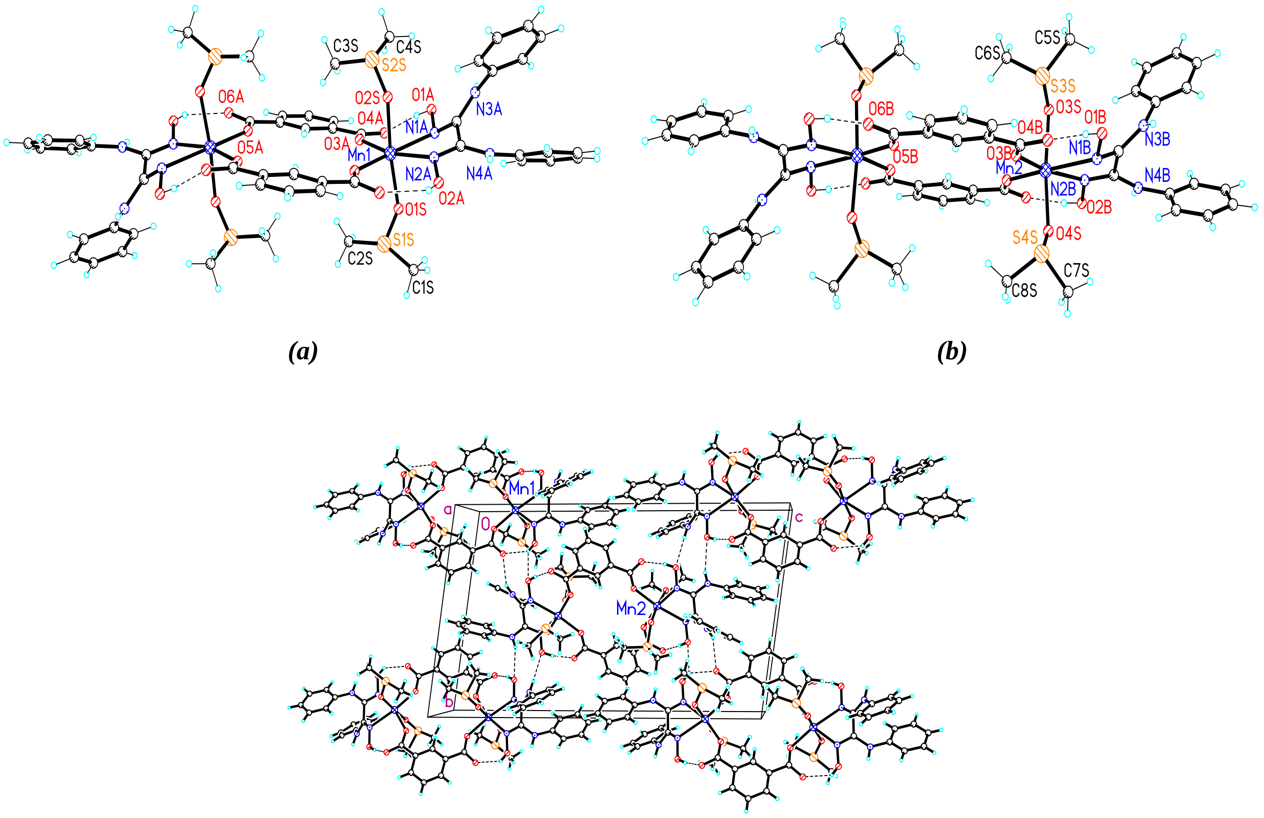
The Mn-N$_{(oxime)}$ interatomic distances in the equatorial plane of the coordination polyhedra of the Mn(1) and Mn(2) atoms fall within the range of 2.260(3)–2.364(3) Å, Mn-O$_{(bdc)}$ - 2.087(3)–2.120(3) Å, and the bond lengths with atoms located in axial positions Mn-O$_{(DMSO)}$ 2.125(4)–2.188(4) Å (Table 2). These distance values in the coordination polyhedra of Mn(1) and Mn(2) atoms are consistent with those established for similar Mn(II) complexes, which differ by the DMF molecules coordinated in axial positions [18]. The NCCN torsion angles in the basic fragment of the DAnH$_2$ ligands in **2** are equal to 3.8 and 37.3° and differ from those established for these non-coordinated molecules which are in the range of 47.6–58.2° [18]. The complex compounds of **2** are stabilized by the two intramolecular hydrogen bonds O(1)/(O(2)–H···O(4)/O(6), which are formed by each DAnH$_2$ ligand with the two (1,3-bdc)$^{2-}$ ligands, the O···O donor–acceptor distances varying in the range of 2.520(4)–2.567(4) Å (Table 3).

In the crystal of **2**, the binuclear complexes are connected to each other by intermolecular hydrogen bonds, in which the =NH functional groups act as proton donors, and the oxygen atoms of the oxime and carboxylic ligands in both ligands - as acceptors (Table 3). The A and B complexes individually connected to each other only through fine C–H···O and C–H···S hydrogen bonds, and A and B unite with each other in layers arranged along the *x*-axis, where each A complex is surrounded by four B complexes and vice versa through the N(3)–H···O(2)/O(6), N(4)–H···O(1) and O(2)–H···O(1) hydrogen bonds, the donor-acceptor distances being in the range 2.875(4)–3.184(4) Å (Figure 2*(c)*). These layers are joined in the crystal only by fine C–H···O bonds.

Table 3

Hydrogen bond distances (Å) and angles (°) for 1 and 2.

D–H···A	*d(H···A)*	*d(D···A)*	*∠(DHA)*	*Symmetry transformation for acceptor*
		1		
N(11)–H···O(14C)	2.10	2.945(16)	166	*–x+1/2, –y+1, z–1/2*
N(21)–H···O(12)	2.24	3.066(18)	161	*x, y, z*
N(31)–H···O(11)	2.23	3.05(2)	159	*x–1/2, –y+3/2, –z+1*
N(41)–H···O(14C)	2.25	3.087(17)	165	*–x+1, y+1/2, –z+3/2*
N(51)–H···O(12)	2.17	3.006(17)	165	*x–1/2, –y+3/2, –z+1*
O(1)–H···O(10)	1.77	2.562(13)	162	*x–1/2, –y+3/2, –z+1*
O(2)–H···O(10)	1.86	2.635(13)	158	*x, y, z*
O(3)–H···O(9)	1.96	2.760(13)	166	*x–1/2, –y+3/2, –z+1*
O(4)–H···O(7)	1.99	2.798(14)	166	*x, y, z*
O(5)–H···O(8)	2.07	2.978(15)	167	*x–1/2, –y+3/2, –z+1*
O(6)–H···O(7)	2.47	3.115(13)	137	*x, y, z*
O(6)–H···O(1W)	2.13	2.791(15)	138	*x, y, z*
O(11C)–H···O(7)	1.90	2.630(15)	148	*x, y, z*
O(13C)–H···O(9)	1.95	2.739(14)	160	*–x+1, y–1/2, –z+3/2*
C(8)–H(3)···O(8)	2.65	3.49(3)	146	*x, y, z*
C(12)–H···O(1W)	2.66	3.48(2)	148	*x, y, z*
C(32)–H···O(1)	2.53	3.186(17)	128	*x+1/2, –y+3/2, –z+1*
C(66)–H···O(2)	2.59	3.353(18)	140	*x–1/2, –y+3/2, –z+1*
O(1W)–H(1)···O(8)	2.07	2.898(16)	176	*x, y, z*
O(1W)–H(2)···O(12)	2.06	2.921(18)	179	*x, y, z*
		2		
N(3A)–H···O(2B)	2.15	2.983(4)	162	*–x+1, –y+1, –z+1*
O(1A)–H···O(4A)	1.75	2.562(4)	170	*x, y, z*
O(2A)–H···O(6A)	2.01	2.567(4)	131	*–x+1, –y+2, –z*
O(2A)–H···O(1B)	2.28	2.875(4)	137	*–x+1, –y+2, –z+1*
N(3B)–H···O(6A)	2.27	2.995(4)	141	*x, y, z+1*
N(4B)–H···O(1A)	2.39	3.184(4)	153	*–x+1, –y+1, –z+1*
O(1B)–H···O(4B)	1.75	2.561(5)	173	*x, y, z*
O(2B)–H···O(6B)	1.71	2.520(4)	169	*–x, –y+1, –z+1*
C(1SA)–H(1)···O(2A)	2.48	3.22(1)	135	*x–1, y, z*
C(1SA)–H(2)···O(4B)	2.62	3.32(2)	130	*–x, –y+2, –z+1*
C(8SA)–H(8)···S(3SA)	2.64	3.66(7)	163	*x–, y, z*



(a) ***(b)***

(c)

Figure 2. Structure of molecular complexes [$Mn_2(DAnH_2)_2(1,3\text{-bdc})_2(DMSO)_4$] of 2 (*a*,*b*), layer formation (c).

Conclusions

Depending on the nature of the metal, dioxime and dicarboxylate used, coordination compounds with different structures are formed: nickel(II) with di-*p*-aminotolueneglyoxime ($DpatH_2$) forms a mononuclear ionic compound, having the carboxylate in the outer sphere of complex - [$Ni(DpatH_2)_3$]$SO_4\cdot 1,4\text{-}H_2bdc$; manganese(II) with dianylinglyoxime ($DAnH_2$) forms a binuclear molecular complex, in whose formation the carboxylate is involved as a bridging ligand - [$Mn_2(DAnH_2)_2(1,3\text{-bdc})_2(DMSO)_4$].

The coordination polyhedron of the nickel atom in **1** represents an octahedron and is formed by six nitrogen atoms belonging to three $DpatH_2$ ligands, the metallic rings whose angles equal around 85.47°, an arrangement that makes impossible the formation of intramolecular hydrogen bonds between the oxime groups. In **2**, the manganese atoms are coordinated in a bidentate-chelate manner through two nitrogen atoms to the neutral ligands $DAnH_2$, and the octahedral coordination polyhedron is completed by two oxygen atoms belonging to two bideprotonated *exo*-bidentate ligands $(1,3\text{-bdc})^{2-}$ and two oxygens of two DMSO ligands.

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