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HYDROGEN-BONDED METAL COMPLEXES CONTAINING DIPHENYLGLYOXIME LIGANDS

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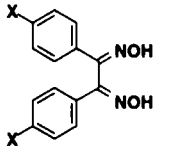
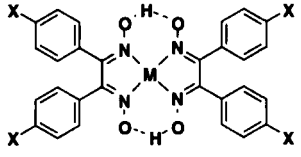
Abstract The crystal structures of the metal complexes containing bis(4-hydroxyphenyl)glyoxime (H_2bhpg) and bis(4-aminophenyl)glyoxime (H_2bapg) contain the intermolecular hydrogen-bonded (H-bonded) network and stacking interactions between benzene rings of the ligands.

INTRODUCTION

The molecular systems with cooperative interaction between hydrogen–bonding (H–binding) and charge–transfer (CT), the HBCT system, can be a good candidate for new molecular materials having interesting solid state properties.[1-3] The solid state properties of the HBCT system depend on the degree and cooperativity of H-bonding and CT. In order to develop such a chemistry, we need to explore new HBCT system. As the first step, we have intended to construct the H-bonding transition metal complexes having a direct intermolecular hydrogen-bonding. As a basic skeleton, we have utilized the diphenylglyoxime derivatives. The electrical and optical properties of one dimensional metal complexes with diphenylglyoxime ligand have been studied.[4,5] The metal complexes with diphenylglyoxime ligand are partially oxidized by electron acceptors such as halogen, so new mixed valence compounds are formed. We now report the crystal structures of the transition metal complexes containing bis(4-hydroxyphenyl)glyoxime (H_2bhpg) and bis(4-aminophenyl)glyoxime (H_2bapg) ligands which have the ability to form the intermolecular hydrogen-bonding.



X=OH H_2bhpg
X=NH_2 H_2bapg



X=OH $M(Hbhpg)_2$
X=NH_2 $M(Hbapg)_2$

EXPERIMENTAL

The bis(4-hydroxyphenyl)glyoxime (H_2bhpg) and bis(4-aminophenyl)glyoxime (H_2bapg) were synthesized by reaction of corresponding benzil derivatives with hydroxilamine hydrochloride in methanol or ethanol. The corresponding benzil derivatives were synthesized according to the procedure reported in the literatures.[6,7] Reaction of the ligands with $NiCl_2 \cdot 6H_2O$ in methanol gave [Ni(Hbhpg)$_2$] and [Ni(Hbapg)$_2$]. The single crystals of [Ni(Hbhpg)$_2$]·2EtOH (**1**) and [Ni(Hbapg)$_2$]·CH_3CN (**2**) were obtained by recrystallization from ethanol and acetonitrile–dimethylfolmamide, respectively.

CRYSTAL DATA

The Crystallographic data for **1** and **2** are summarized in Table 1.

TABLE 1 Crystallographic Data for **1** and **2**.

	1	**2**
Formula	$C_{32}H_{34}N_4NiO_{10}$	$C_{30}H_{29}N_9NiO_4$
Fw	693.34	638.32
space group	$P\bar{1}$	$P\bar{1}$
a, Å	11.042(2)	11.055(1)
b, Å	11.928(2)	11.384(1)
c, Å	6.4307(7)	6.169(1)
α, deg	93.76(1)	92.98(1)
β, deg	97.65(1)	100.30(1)
γ, deg	107.10(1)	110.133(9)
V, Å^3	801.0(2)	711.7(2)
Z	1	1
Dc, Mg·m^{-3}	1.437	1.489
T, K	296	296
λ, Å	0.71069	0.71069
R^a	0.067	0.039
$R_w{}^b$	0.075	0.041

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $R_w=\{(\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)\}^{1/2}$.

The atomic coordinates and thermal parameters of **1** and **2** are listed in Table 2 and 3, respectively.

Table 2. Atomic Coordinates and Isotropic Thermal Parameters (B_{eq}/Å^2)[a] of **1**.

atom	x	y	z	B_{eq}
Ni(1)	0	0	0	2.76(4)
O(1)	-0.1807(5)	-0.1313(5)	0.235(1)	4.1(1)
O(2)	0.2656(5)	0.0265(5)	0.0335(9)	4.0(1)
O(3)	-0.0770(8)	-0.4281(7)	0.963(1)	8.2(2)
O(4)	0.5993(6)	-0.1893(7)	0.613(1)	6.7(2)
N(1)	-0.0572(6)	-0.0970(6)	0.205(1)	3.1(1)
N(2)	0.1546(6)	-0.0269(6)	0.100(1)	3.2(2)
C(1)	0.0261(7)	-0.1380(7)	0.317(1)	2.8(2)
C(2)	0.1539(7)	-0.0947(7)	0.252(1)	3.0(2)
C(3)	-0.0042(7)	-0.2165(7)	0.483(1)	3.0(2)
C(4)	0.0586(8)	-0.3004(8)	0.519(1)	3.9(2)
C(5)	0.0345(9)	-0.3711(8)	0.680(2)	4.7(2)
C(6)	-0.053(1)	-0.3587(9)	0.808(1)	4.8(2)
C(7)	-0.1173(9)	-0.2785(8)	0.771(1)	4.4(2)
C(8)	-0.0938(8)	-0.2082(7)	0.610(1)	3.6(2)
C(9)	0.2707(7)	-0.1205(7)	0.347(1)	3.0(2)
C(10)	0.3337(8)	-0.1761(8)	0.225(1)	4.1(2)
C(11)	0.4446(8)	-0.2004(9)	0.317(2)	4.8(2)
C(12)	0.4890(8)	-0.1688(8)	0.528(2)	4.2(2)
C(13)	0.4269(8)	-0.1131(9)	0.652(1)	4.3(2)
C(14)	0.3172(8)	-0.0909(8)	0.561(1)	3.8(2)
H(01)	-0.2259	-0.0739	0.1314	4.8
H(03)	-0.0915	-0.4779	1.0757	9.8
H(04)	0.6763	-0.2051	0.6697	4.5
H(4)	0.1181	-0.3112	0.4223	4.6
H(5)	0.0794	-0.4290	0.7027	6.1
H(7)	-0.1811	-0.2701	0.8584	5.4
H(8)	-0.1419	-0.1518	0.5850	4.5
H(10)	0.3003	-0.1990	0.0728	5.1
H(11)	0.4909	-0.2403	0.2344	5.9
H(13)	0.4581	-0.0912	0.8033	5.0
H(14)	0.2721	-0.0511	0.6518	4.5

[a] $B_{eq}=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$

Table 3. Atomic Coordinates and Isotropic Thermal Parameters (B_{eq}/Å^2)[a] of **2**.

atom	x	y	z	B(eq)
Ni(1)	0	0	0	2.41(1)
O(1)	0.2462(2)	-0.0183(2)	-0.0220(4)	3.53(5)
O(2)	-0.0657(2)	0.1356(2)	0.3286(4)	4.13(5)
N(1)	0.1808(2)	0.0369(2)	0.0862(4)	2.70(5)
N(2)	0.0300(2)	0.1044(2)	0.2644(4)	2.81(5)
N(3)	0.7790(3)	0.2167(4)	0.6561(6)	4.62(8)
N(4)	0.3167(5)	0.5384(4)	1.1046(7)	6.4(1)
N(5)	0.977(2)	0.433(2)	0.243(3)	16.7(7)
C(1)	0.2418(3)	0.1110(3)	0.2715(5)	2.58(6)
C(2)	0.1519(3)	0.1564(3)	0.3739(5)	2.54(6)
C(3)	0.3820(3)	0.1411(3)	0.3715(5)	2.74(6)

Table 3. (continued)

C(4)	0.4782(3)	0.1835(3)	0.2463(5)	3.15(7)
C(5)	0.6096(3)	0.2091(3)	0.3395(6)	3.38(7)
C(6)	0.6478(3)	0.1902(3)	0.5593(5)	3.17(6)
C(7)	0.5506(3)	0.1467(3)	0.6822(5)	2.99(7)
C(8)	0.4202(3)	0.1235(3)	0.5909(5)	2.80(6)
C(9)	0.1965(3)	0.2532(3)	0.5672(5)	2.73(6)
C(10)	0.3124(3)	0.3577(3)	0.5885(6)	3.47(7)
C(11)	0.3525(4)	0.4524(3)	0.7646(6)	3.89(8)
C(12)	0.2780(4)	0.4455(3)	0.9275(6)	3.89(8)
C(13)	0.1645(4)	0.3407(3)	0.9086(6)	3.65(8)
C(14)	0.1230(3)	0.2465(3)	0.7322(5)	3.03(7)
C(15)	1.001(4)	0.473(3)	0.398(6)	12(1)
C(16)	1.002(4)	0.526(3)	0.602(6)	11(1)
H(01)	0.166	-0.079	-0.189	9
H(4)	0.454	0.201	0.094	3.0
H(5)	0.676	0.243	0.257	3.2
H(7)	0.573	0.130	0.820	2.4
H(8)	0.352	0.091	0.684	4.4
H(10)	0.363	0.371	0.477	4.0
H(11)	0.428	0.525	0.762	4.4
H(13)	0.118	0.325	1.008	2.7
H(14)	0.041	0.170	0.720	3.8
H(31)	0.790	0.186	0.792	8
H(32)	0.823	0.220	0.582	5
H(41)	0.376	0.592	1.120	5
H(42)	0.256	0.542	1.177	8

[a] $B_{eq}=(8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$

(1) [Ni(Hbhpg)$_2$]·2EtOH (1)

Figure 1 shows the centrosymmetric Ni(Hbhpg)$_2$ molecule. The Ni–N distances of 1.866(6) and 1.868(6) Å are normal, being close value of ca. 1.85 Å observed in several four-coordinate Ni(II) complexes.[8] The N–C distances of 1.318(9) and 1.313(9) Å and the N–O distances of 1.347(7) and 1.344(8) Å in coordinated glyoxime ligand are comparable with those in bis(dimethylglyoximato) nickel(II) complex (Ni(Hdmg)$_2$).[9] The distances of C(1)–C(2) (1.48(1) Å) and O(1)–O(2*) (2.447(5) Å) are also comparable with the analogous Ni(Hdmg)$_2$ parameters of 1.54(3) and 2.40(2) Å, respectively. The benzene rings tipped 34.4° (ring A) and 60.6° (ring B) from the chelate plane. Packing diagrams of **1** is presented in Figure 2. The ethanol molecules are disordered.which have been omitted. The Ni(Hbhpg)$_2$ molecule are linked by double H-bonding interactions between Hbhpg ligands (O(4)···O(2*)) in the [101] direction and the stacking of benzene rings. The H-bonded distance (R(O···O)) is 2.83(1) Å. The interplanar distance between the benzene rings is 3.34 Å (Fig. 3a). A further H-bonds exist between the hydroxy groups of the neighboring metal complexes and form the network toward [0, 1, –2] direction (Fig. 3b). The H-bonded distance (R(O···O)) is 2.77(2) Å.

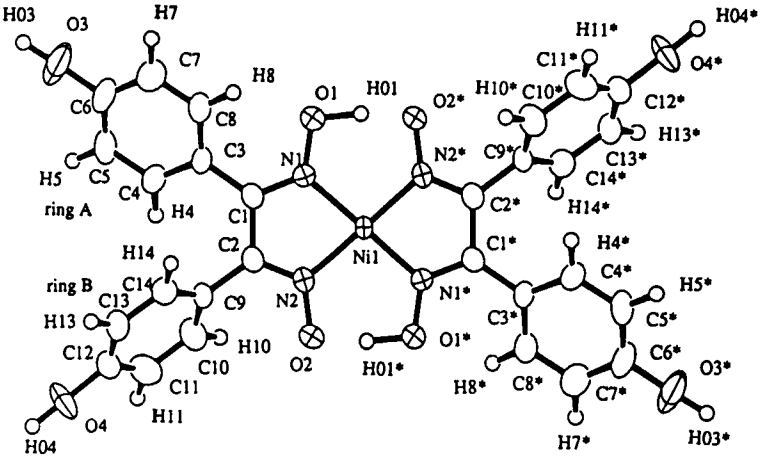


FIGURE 1 ORTEP diagram for **1** with atomic numbering scheme and 50 % thermal ellipsoids. Selected bond lengths (Å) are as follows: Ni(1)–N(1), 1.866(6); Ni(1)–N(2), 1.868(6); N(1)–C(1), 1.318(9); N(2)–C(2), 1.313(9); N(1)–O(1), 1.347(7); N(2)–O(2), 1.344(8); C(1)–C(2), 1.48(1); O(1)–O(2*), 2.445(7).

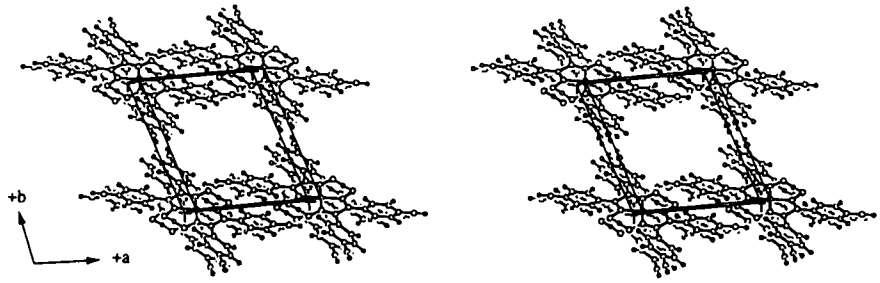
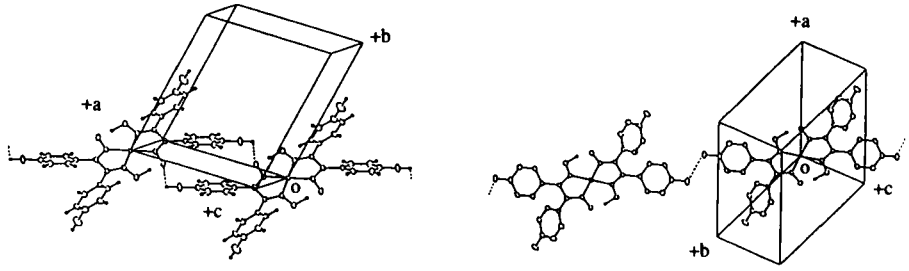


FIGURE 2 Stereoview of the crystal packing for **1**.



(a) (b)

FIGURE 3 Hydrogen bonding scheme of **1**. The dotted lines represent intermolecular hydrogen bondings.

(2) $[Ni(Hbapg)_2]\cdot CH_3CN$ (**2**)

Figure 4 shows the centrosymmetric $Ni(Hbapg)_2$ molecule. The bond length of the chelate moiety is normal, similarly to **1**. The benzene rings tipped 51.5° (ring A) and 42.5° (ring B) from the chelate plane. Packing diagrams of **2** is presented in Figure 5. In analogy with **1**, the $Ni(Hbapg)_2$ molecule are linked by double H-bonding interactions between Hbapg ligands (O(1)···N(3*)) in the [101] direction and the stacking of benzene

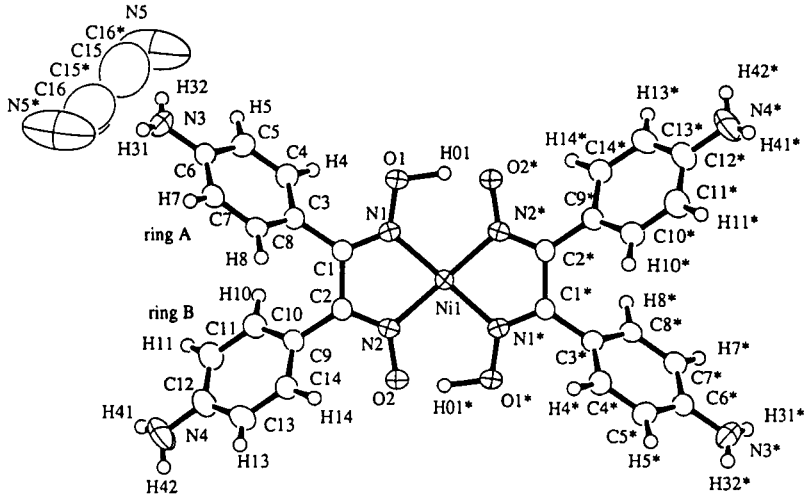


FIGURE 4 ORTEP diagram for **2** with atomic numbering scheme and 50 % thermal ellipsoids. Selected bond lengths (Å) are as follows: Ni(1)–N(1), 1.864(2); Ni(1)–N(2), 1.875(2); N(1)–C(1), 1.306(3); N(2)–C(2), 1.307(4); N(1)–O(1), 1.343(3); N(2)–O(2), 1.340(3); C(1)–C(2), 1.482(4); O(1)–O(2*), 2.428(3).

rings. The H-bonded distance (R(N···O)) is 3.255(5) Å. The interplanar distance between the benzene rings is 3.40 Å. The molecule are further linked to each other via double H-bonds between Hbapg ligands (O(2)···N(3)) along the a axis direction (Fig. 6). The H-bonded distance (R(N···O)) is 3.166(4) Å.

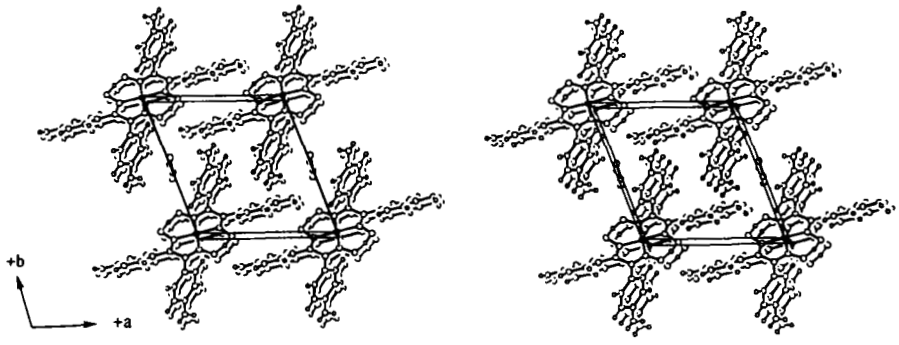


FIGURE 5 Stereoview of the crystal packing for **2**.

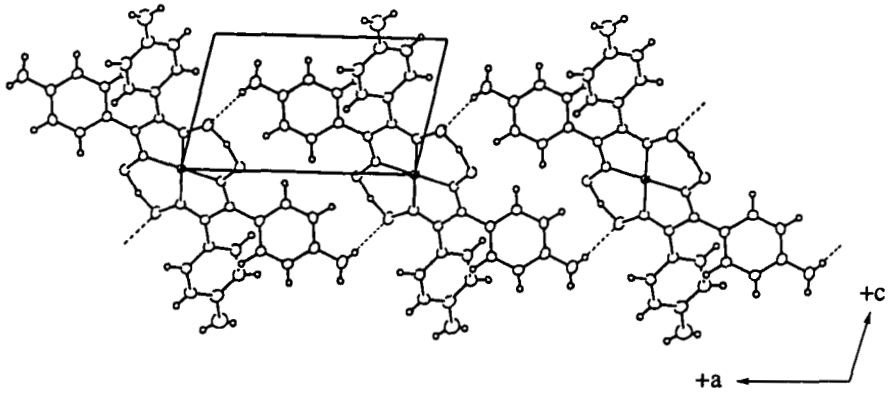


FIGURE 6 Hydrogen bonding scheme of **2**. The dotted lines represent intermolecular hydrogen bondings.

The monotonic correlations between O–H and N–H stretching frequencies and the corresponding interatomic distances of O···O, O···N, and N···N for the H-bonded compounds have been well established.[10] We applied the observed absorption bands in the region of 3600–2600 cm^{-1} of the complex **2** to the correlation for NH···O type H-

bonded systems. The estimated bond distances of 3.08 and 3.12 Å are relativery in good agreement with the observed bond distances of 3.166(4) and 3.255(5) Å. Therefore, the correlations are convenient experimental tool to estimate H-bonding distances of structurally unknown compound.

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