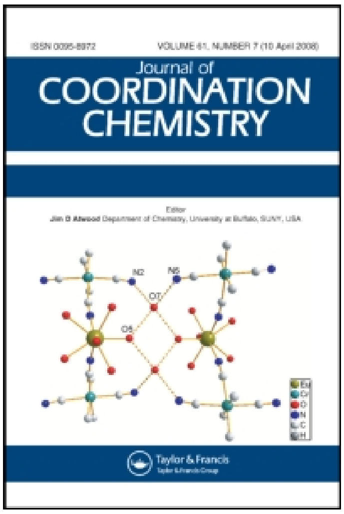

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A helical polymeric complex, tris(benzimidazole)nickel(II) (μ-maleato)

Yu-Hong Xue[a]; Jia-Geng Liu[a]; Duan-Jun Xu[a]
[a] Department of Chemistry, Zhejiang University, Hangzhou 310027, P.R. China

To cite this Article Xue, Yu-Hong , Liu, Jia-Geng and Xu, Duan-Jun(2005) 'A helical polymeric complex, tris(benzimidazole)nickel(II) (μ-maleato)', Journal of Coordination Chemistry, 58: 12, 1071 — 1076
To link to this Article: DOI: 10.1080/00958970500122581
URL: http://dx.doi.org/10.1080/00958970500122581

Journal of Coordination Chemistry
Vol. 58, No. 12, 15 August 2005, 1071–1076

Taylor & Francis
Taylor & Francis Group

A helical polymeric complex, tris(benzimidazole)nickel(II) (μ-maleato)

YU-HONG XUE, JIA-GENG LIU and DUAN-JUN XU*

Department of Chemistry, Zhejiang University, Hangzhou 310027, P.R. China

(*Received in final form 28 February 2005*)

The title polymeric complex $[Ni(C_7H_6N_2)_3(C_4H_2O_4)]_n$ has been prepared and its crystal structure determined by single-crystal X-ray diffraction methods. The complex is orthorhombic, space group $P2_12_12_1$ with $a = 9.320(1)$, $b = 12.015(1)$, $c = 20.964(2)$ Å. Three benzimidazole (bzim) and two maleate dianions coordinate to the Ni(II) atom with distorted octahedral geometry. Maleate dianions bridge neighbouring Ni(II) atoms through terminal carboxyl groups, one in monodentate and the other in chelate mode, to form polymeric molecular chains extending along the *a* axis. The structure is chiral, the Flack index of 0.002(10) suggesting that the helical polymeric chain is right-handed. Both intra-helical and inter-helical N–H···O hydrogen bonding occurs between bzim and carboxyl groups of maleate. The partially overlapped arrangement of nearly parallel bzim rings suggests the existence of π–π stacking in the crystal.

Keywords: Ni(II); Polymeric complex; Helical structure; Crystal structure; Maleate; Benzimidazole

1. Introduction

Helical polymeric metal complexes have attracted much attentions in the fields of coordination chemistry and materials science [1]. Much effort has been devoted to the preparation of helical polymeric complexes by careful design of bridging ligands [2, 3]. Dicarboxylates with a suitable length of carbon skeleton, such as succinate and maleate, have been shown to be potential helical bridging ligands if terminal carboxyl groups are twisted away from each other by an appropriate angle [4].

By using non-chiral components to construct a polymeric metal complex, both right- and left-handed helices are formed. We have reported a polymeric Co(II) complex bridged by the maleate dianion. An X-ray absolute structure analysis showed that it had a left-handed helical structure in the crystal selected [5]. Recently we prepared the corresponding Ni(II) complex for comparative purposes. Its structure, reported here, is that of a right-handed helix in the crystal selected.

---

*Corresponding author. Email: xudj@mail.hz.zj.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970500122581

2. Experimental

2.1. *Synthesis*

An aqueous solution ($5\,cm^3$) containing maleic acid (0.23 g, 2 mmol) and sodium carbonate (0.21 g, 2 mmol) was mixed with an aqueous solution ($5\,cm^3$) of $NiCl_2 \cdot 6H_2O$ (0.48 g, 2 mmol) and the mixture refluxed for 1 h. An ethanol solution ($5\,cm^3$) of benzimidazole (bzim; 0.47 g, 4 mmol) was then added. The mixture was refluxed for a further 3 h and filtered. Green single crystals were obtained from the filtrate after two weeks. C, N and H contents were analyzed using a Carlo-Erba 1106 instrument. Anal. Calcd for $C_{25}H_{20}NiN_6O_4$ (%): C, 57.32; H, 3.85; N, 16.05. Found: C, 57.84; H, 4.01; N, 15.65. IR spectra of the title complex were recorded (KBr discs) using a Nicolet 5DX FTIR spectrophotometer (4000–400 cm^{-1}).

2.2. *Crystal structure determination*

Diffraction intensity data for a single crystal of the complex, with approximate dimensions of $0.27 \times 0.16 \times 0.10$ mm, were collected on a Rigaku RAXIS-RAPID image plate diffractometer up to $\theta_{max} = 27.4°$ with Mo Kα radiation at room temperature. A total of 21793 reflections was collected (5353 independent; $R_{int} = 0.047$), among which 4675 were observed [$I > 2\sigma(I)$]. The structure was solved by direct methods and the absolute configuration of the crystal used was determined by the usual calculations [Flack index = 0.002(10)]. The crystal structure was anisotropically refined using SHELXL-97 [6]. H atoms were placed in calculated positions the C–H = 0.93 Å and N–H = 0.86 Å, and included in the final cycles of refinement in the riding model, with $U_{iso}(H) = 1.2\,U_{eq}$ of the carrier atoms. Final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are listed in table 1. Full crystallographic data have been deposited in the CCDC (deposition number CCDC 262896).

2.2.1. Crystal data. $Ni(C_7H_6N_2)_3(C_4H_2O_4)$, $M = 523.41$, Orthorhombic, space group $P2_12_12_1$, $a = 9.320(1)$, $b = 12.015(1)$, $c = 20.964(2)$ Å, $V = 2347.8(4)$ Å^3, $Z = 4$, $D_x = 1.491\,g\,cm^{-3}$, $\mu(Mo\text{-}K\alpha) = 0.872\,mm^{-1}$, $F(000) = 1088$, $S = 1.074$, $(\Delta/\sigma)_{max} = 0.002$, $(\Delta\rho)_{max} = 0.37$, $(\Delta\rho)_{min} = -0.31\,e\,Å^{-3}$. $R_1 = 0.035$ and $wR_2 = 0.063$ for observed reflections ($I > 2\sigma(I)$), $R_1 = 0.046$ and $wR_2 = 0.066$ for independent reflections, $w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 0.5P]$ where $P = (F_o^2 + 2F_c^2)/3$.

3. Results and discussion

3.1. *Crystal structure*

A segment of the structure of the polymeric complex is illustrated in figure 1. Selected bond distances and angles are listed in table 2. The Ni(II) atom is coordinated by three bzim molecules and two maleate dianions with distorted octahedron geometry. Bzim ligands coordinating to the same Ni(II) atom are nearly perpendicular to each other, dihedral angles between bzim mean planes being 73.15(8), 85.88(9) and 75.9(1)°, respectively. The carbon skeleton of the maleate dianion assumes a planar structure, the maximum displacement being 0.007(2) Å for C3. Maleate plays the role

Table 1. Final coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms.

Atom	x/a	y/b	z/c	U_{eq}/Å^2
Ni	0.53256(3)	0.72844(2)	0.88752(1)	0.0249(1)
O1	0.4467(2)	0.6186(1)	0.95373(7)	0.0314(5)
O2	0.2482(2)	0.5664(2)	0.90177(7)	0.0410(6)
O3	0.1442(2)	0.6158(1)	1.13249(7)	0.0309(5)
O4	0.1156(2)	0.6685(1)	1.03296(7)	0.0305(5)
N11	0.1476(2)	0.8840(2)	0.93807(9)	0.0383(7)
N13	0.3432(2)	0.8182(2)	0.89017(9)	0.0300(6)
N21	0.4396(2)	0.5578(2)	0.71510(9)	0.0395(7)
N23	0.5059(2)	0.6651(2)	0.79596(8)	0.0309(6)
N31	0.9559(2)	0.6050(2)	0.90556(9)	0.0361(6)
N33	0.7236(2)	0.6376(2)	0.8926(1)	0.0295(6)
C1	0.3317(2)	0.5637(2)	0.9478(1)	0.0289(7)
C2	0.3019(3)	0.4802(2)	0.9995(1)	0.0323(8)
C3	0.2269(3)	0.4931(2)	1.0527(1)	0.0313(7)
C4	0.1585(2)	0.5985(2)	1.0728(1)	0.0265(7)
C12	0.2747(3)	0.8339(2)	0.9445(1)	0.0337(8)
C14	0.2674(3)	0.8698(3)	0.7781(1)	0.0475(9)
C15	0.1585(4)	0.9193(3)	0.7449(1)	0.069(1)
C16	0.0381(4)	0.9624(3)	0.7745(2)	0.070(1)
C17	0.0202(3)	0.9557(3)	0.8395(1)	0.054(1)
C18	0.1294(3)	0.9042(2)	0.8738(1)	0.0340(8)
C19	0.2521(3)	0.8626(2)	0.8443(1)	0.0306(8)
C22	0.4197(3)	0.5864(2)	0.7768(1)	0.0369(8)
C24	0.7024(3)	0.7661(3)	0.7353(1)	0.0484(9)
C25	0.7662(4)	0.7714(3)	0.6760(1)	0.063(1)
C26	0.7222(3)	0.7038(3)	0.6254(1)	0.059(1)
C27	0.6146(3)	0.6285(3)	0.6324(1)	0.045(1)
C28	0.5493(3)	0.6230(2)	0.6921(1)	0.0343(8)
C29	0.5911(3)	0.6910(2)	0.7429(1)	0.0330(7)
C32	0.8542(2)	0.6794(2)	0.8925(1)	0.0344(7)
C34	0.6467(3)	0.4358(2)	0.9080(1)	0.0455(9)
C35	0.7006(4)	0.3321(3)	0.9210(2)	0.062(1)
C36	0.8471(4)	0.3147(3)	0.9329(2)	0.064(1)
C37	0.9445(3)	0.3998(2)	0.9299(1)	0.047(1)
C38	0.8899(3)	0.5055(2)	0.9158(1)	0.0323(8)
C39	0.7440(3)	0.5244(2)	0.9061(1)	0.0308(7)

$U_{eq} = 1/3$ of the trace of the orthogonalized U tensor.

of the bridging ligand in the crystal, terminal carboxyl groups binding to Ni(II) atoms symmetrically related by a screw axis in different coordination modes; the C1–carboxyl acts as a monodentate and the C4–carboxyl as a chelate. The chelating carboxyl group is inclined to the carbon skeleton (dihedral angle 28.4(2)°), while the monodentate carboxyl group is nearly perpendicular to the carbon skeleton (dihedral angle 89.0(8)°). This results in a large deviation (2.46(1) Å) for the O1 atom from the chelating C4–carboxyl plane, and so the carboxyl groups bind to neighbouring Ni(II) atoms to form a helical chain along the *a* axis, as shown in figure 2. The helix has a pitch height of 9.320(1) Å and the repeat unit of the helical backbone includes two Ni(II) atoms and two maleate anions.

The polymeric chain shown in figure 2 is right-handed. The Flack index of 0.002(10) calculated in the structure refinement suggests that this is the correct absolute configuration for the crystal selected for the structure determination [7], and differs from the left-handed helical structure for the corresponding Co(II) complex structure determination [5]. Specific optical rotations of samples were not determined because

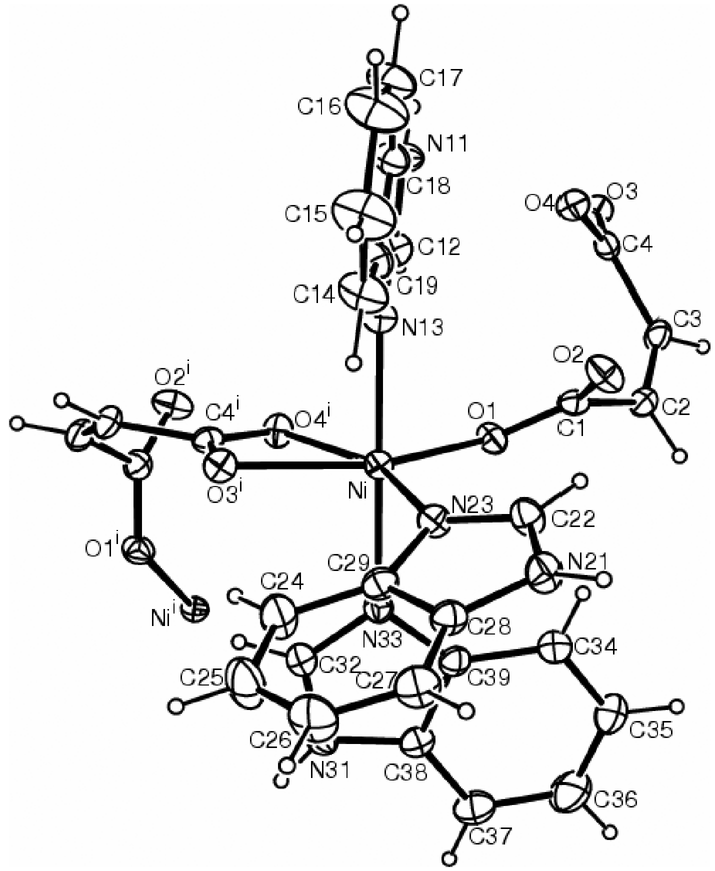

Figure 1. A segment of the structure of the polymeric complex; symmetry code i: $x+1/2$, $-y+3/2$, $-z+2$.

of insufficient material, and thus it is not presently known whether or not the Ni(II) complex is a conglomerate, even though this is most likely. Nevertheless, both cases represent instances of spontaneous resolution.

Intra-helical N–H$\cdots$O hydrogen bonding occurs between bzim and a carboxyl group of the maleate ion, as shown in table 3 and figure 2, which stabilizes the helical structure. Neighbouring helices are held together by N–H$\cdots$O hydrogen bonding, as shown in figure 2. Pronounced π–π stacking between bzim rings is usually found in its metal complexes [8, 9]. A partially overlapped arrangement between nearly parallel N13–bzim and neighbouring N23^{ii}–bzim rings is observed in the crystal (figure 3). Distances of 3.448(3) Å for the C27^{ii} atom and 3.534(3) Å for the C28^{ii} atom to the mean plane of the C18–benzene ring suggest the existence of π–π stacking between neighbouring bzim rings.

3.2. *Infrared spectra*

Stretching vibrations at 1435 cm^{-1} [ν_s(COO)] and 1530 cm^{-1} [ν_{as}(COO)] are assigned to the C4–carboxyl group. The $\Delta\nu$ value of 95 cm^{-1} is in agreement with those found

Table 2. Selected bond distances (Å) and angles (°) for the complex.

Ni–N13	2.069(2)	Ni–N23	2.080(2)
Ni–N33	2.092(2)	Ni–O1	2.076(2)
Ni–O3^{i}	2.182(2)	Ni–O4^{i}	2.216(2)
O1–C1	1.264(3)	O2–C1	1.240(3)
O3–C4	1.276(3)	O4–C4	1.250(3)
C1–C2	1.504(3)	C2–C3	1.325(3)
C3–C4	1.479(3)		
O1–Ni–N13	89.10(7)	O1–Ni–N23	109.77(7)
O1–Ni–N33	87.84(7)	O1–Ni–O3^{i}	149.07(6)
O1–Ni–O4^{i}	89.26(6)	N13–Ni–N23	96.52(7)
N13–Ni–N33	175.52(8)	N13–Ni–O3^{i}	88.01(7)
N13–Ni–O4^{i}	89.22(7)	N23–Ni–N33	87.59(8)
N23–Ni–O3^{i}	101.16(7)	N23–Ni–O4^{i}	160.13(7)
N33–Ni–O3^{i}	92.94(7)	N33–Ni–O4^{i}	87.48(7)
O3^{i}–Ni–O4^{i}	59.92(6)	O1–C1–O2	126.5(2)
O1–C1–C2	115.7(2)	O2–C1–C2	117.6(2)
O3–C4–O4	120.8(2)	O3–C4–C3	117.6(2)
O4–C4–C3	121.6(2)	C1–C2–C3	128.8(2)
C2–C3–C4	124.5(2)		

Symmetry code used is i: $x+1/2, -y+3/2, -z+2$.

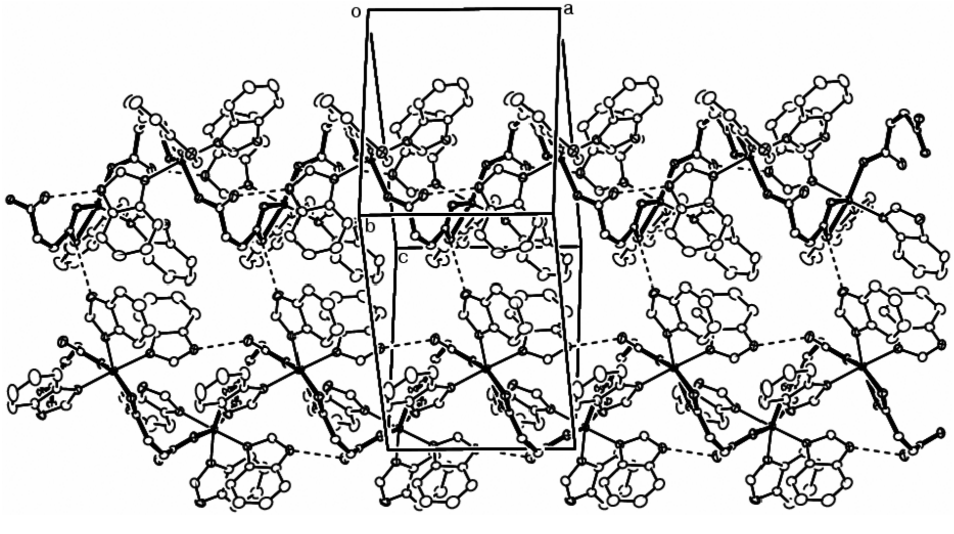

Figure 2. Unit cell packing diagram showing the helical structure of the polymeric complex. Dashed lines indicate hydrogen bonding.

Table 3. Hydrogen bonding parameters (Å,°) for the complex.

Donor–H···Acceptor	D–H	H···A	D···A	D–H–A
N11–H11···O1^{iii}	0.86	2.12	2.942(2)	160
N21–H21···O3^{iv}	0.86	2.00	2.822(3)	159
N31–H31···O2^{v}	0.86	1.98	2.764(3)	151

Symmetry codes used are iii: $x-1/2, -y+3/2, -z+2$; iv $-x+1/2, -y+1, z-1/2$; v: $x+1, y, z$.

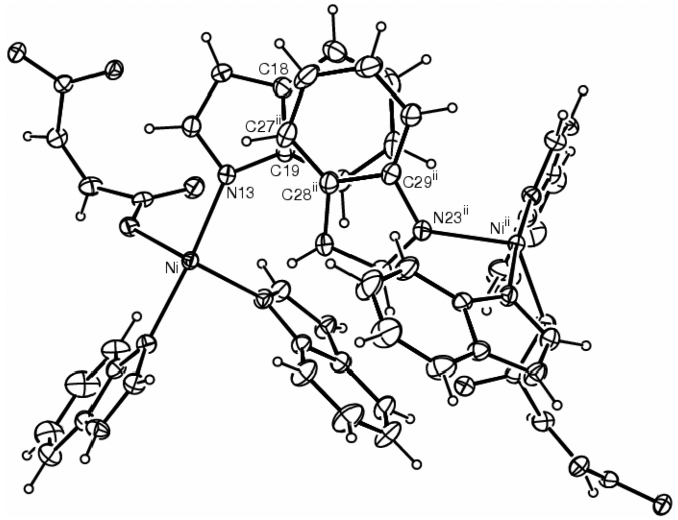

Figure 3. Partially overlapped arrangement of neighbouring benzimidazole rings; symmetry code ii: $-x+1$, $y+1/2$, $-z+3/2$.

in complexes with a chelating carboxyl group [10]. The stretches at 1380 cm^{-1} and 1572 cm^{-1} are assigned to the C1–carboxyl group, the $\Delta\nu$ value of 192 cm^{-1} being consistent with a carboxyl group with a monodentate coordination mode [10].

Acknowledgements

The project was supported by the National Natural Science Foundation of China (20443003).

References

[1] M. Munakata, L.-P. Wu, T. Kuroda-Sowa. *Adv. Inorg. Chem.*, **46**, 173 (1999).
[2] A. Erxleben. *Inorg. Chem.*, **40**, 2928 (2001).
[3] T. Ezuhara, K. Endo, Y. Aoyama. *J. Am. Chem. Soc.*, **121**, 3279 (1999).
[4] Z. Chen, D.-J. Xu, Z.-Y. Li, J.-Y. Wu, M.-Y. Chiang. *J. Coord. Chem.*, **56**, 253 (2003).
[5] Y.-H. Xue, D.-J. Up, J.-M. Gu. *Acta Cryst.*, **C59**, m387 (2003).
[6] G.M. Sheldrick. *SHELXL-97*, University of Göttingen, Germany (1997).
[7] H.D. Flack. *Acta Cryst.*, **A39**, 876 (1983).
[8] B.-X. Liu, J.-R. Su, D.-J. Xu. *Acta Cryst.*, **C60**, m183 (2004).
[9] H. Li, K.-L. Yin, D.-J. Xu. *Acta Cryst.*, **C61**, m19 (2005).
[10] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, p. 235, John Wiley and Sons, New York (1978).