

Note

Preparation and Molecular Structure of Binuclear Nickel (II) Complex Bridged by 1, 2, 4, 5-Benzenetetracarboxylato Tetra-valent Anion

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The title complex $[(\text{H}_2\text{O})_2(\text{IMI})_3\text{Ni}(\text{TCB})\text{Ni}(\text{IMI})_3(\text{H}_2\text{O})_2]\text{H}_2\text{O}$ (TCB = 1, 2, 4, 5-benzenetetracarboxylato tetra-valent anion; IMI = imidazole) has been prepared by the reaction of $\text{Ni}(\text{IMI})_3(\text{Ac})_2$ and TCB in aqueous solution. The crystal structure has been determined by single-crystal X-ray diffraction method. It crystallizes in the monoclinic system, space group $P2_1/c$ (# 14), $a = 1.2714(4)$ nm, $b = 0.9411(3)$ nm, $c = 1.5869(4)$ nm, $\beta = 108.54(2)^\circ$, $V = 1.8001(9)$ nm³, $Z = 2$. The main feature of the crystal structure is a symmetric binuclear unit made up of two slightly distorted coordination octahedrons, which are bridged by TCB in monodentate fashion to each metal ion. Moreover three nitrogen atoms from three imidazoles, three oxygen atoms from two water molecules and one carboxylate group of TCB coordinated to a nickel(II) ion are found on a face of the octahedron respectively, so the octahedron is a facial isomer.

Keywords Binuclear, nickel(II), crystal structure, octahedron geometry, 1,2,4,5-benzenetetracarboxylato tetra-valent anion bridged

Introduction

The increasing interest in coordination chemistry of multi-carboxylic acids has been fueled by the knowledge that multi-dentate complexing agents like TCB are capable of forming one-, two-, or three-dimensionally infinite connections between cations and anions.¹ Furthermore, up to date, five kinds of coordination fashions of carboxylate group have been found.² Especially to our great

interest, a TCB molecule has four carboxylate groups, and some carboxylate groups of TCB may participate in coordination in five possible fashions while the others may be free, so that the complexes bridged by TCB possess a bulky variety of structural features. With different coordination modes of carboxylate groups of TCB, a series of interesting complexes bridged by TCB have been synthesized. Some polymeric complexes with linear or three dimensional network structures have been reported.^{3,4}

In our group, we have studied some transition metal complexes bridged by TCB, such as Co(II) complex.⁵ As a part of this series of research, we report here a new binuclear nickel(II) complex, of which structural feature is different from that of the Co(II) complex mentioned above.

Experimental

Preparation

Imidazole (6 mmol) was dissolved in 10 mL of water, and $\text{Ni}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ (2 mmol) was also dissolved in 10 mL of water. The two solutions were mixed to give green solution. Pyromellitic acid (1 mmol) was added to the aqueous solution containing NaOH (4 mmol) with stirring at room temperature, then the green solution was added into above solution with stirring. The solution

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changed its colour from green to light green, and the reaction mixture was filtered. The filtrate stood for five

days until the green single crystals were obtained.

Table 1 Crystallographic data for $\text{Ni}_2\text{C}_{28}\text{H}_{36}\text{N}_{12}\text{O}_{13}$

Chemical Formula	$\text{Ni}_2\text{C}_{28}\text{H}_{36}\text{N}_{12}\text{O}_{13}$
Crystal system	Monoclinic
Space group	$P2_1/c$ (# 14)
a (nm)	1.2714(4)
b (nm)	0.9411(3)
c (nm)	1.5869(4)
β ($^\circ$)	108.54(2)
V (nm^3)	1.8001(9)
D_c ($\text{g}\cdot\text{cm}^{-3}$)	1.601
Z	2
θ range ($^\circ$)	1 to 25
T (K)	293
Total reflections	3384
Unique reflections	3324
Reflections with $I > 2.50\sigma(I)$	2293
R values	$R = 0.043$, $R_w = 0.053$
Maximum shift (Δ/σ) _{max}	0.00
Goodness-of-fit	1.81
Residual max in final difference map ($e \times 10^3 \text{ nm}^{-3}$)	0.45 to -0.52

Elemental analysis

C, H and N were analyzed using a Carlo-Erba 1106 Elemental Analyzer and Ni was analyzed by complexometric titration with EDTA. Anal. Calcd for $\text{Ni}_2\text{C}_{28}\text{H}_{36}\text{N}_{12}\text{O}_{13}$: C 38.83, H 4.16, N 19.41, Ni 13.56; Found; C 38.54, H 4.23, N 19.13, Ni 13.18.

Infrared spectrum

Infrared spectrum of the title complex was recorded with a Nicolet AVATAAR FT-IR Model 360 spectrophotometer ($4000\text{--}400 \text{ cm}^{-1}$) in KBr pellets.

Crystal structure determination

A green single crystal (approximately $0.20 \times 0.20 \times 0.30 \text{ mm}$) of the title complex was mounted on a Rigaku AFC7R diffractometer. X-ray diffraction intensity data were collected up to 2θ value of 50.0° with graphite monochromated MoK_α radiation ($\lambda = 0.071069 \text{ nm}$) by the ω - 2θ scan technique. A total of 3384 reflections was

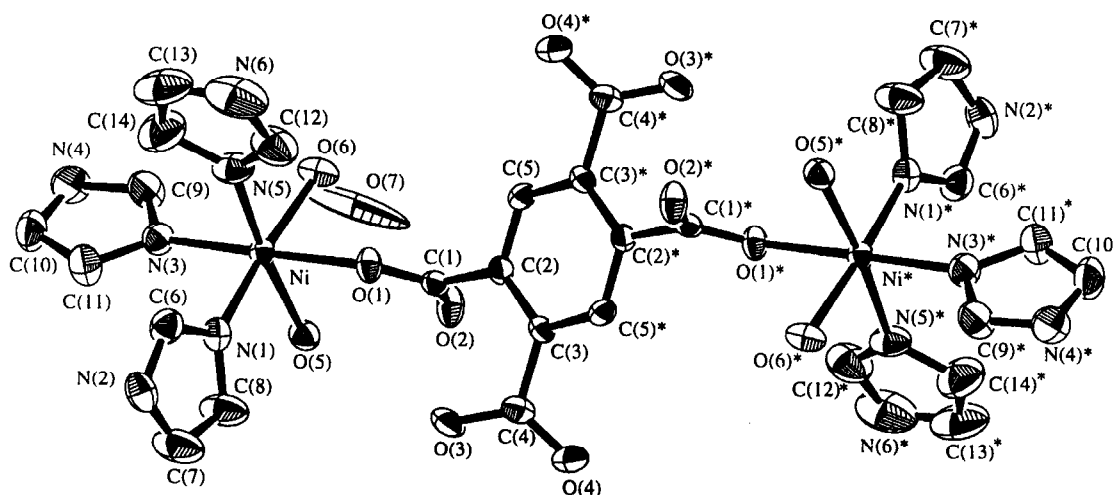
collected, of which 2293 reflections with [$I > 2.50\sigma(I)$] were considered as observed and used for the structure refinement. Usual L_p and empirical absorption corrections were applied. The structure was solved by Patterson method followed by Fourier syntheses. Structure refinement was carried out by full-matrix least-squares procedures using the TEXSAN program package.⁶ H atoms were located in a difference Fourier map, and their coordinates and thermal parameters were fixed during structure refinement. Anisotropic refinement including all the non-H atoms converged at agreement factors $R = 0.043$ and $R_w = 0.053$, where $w = 1/\sigma^2(F_0)$. Atomic scattering factors were taken from International Tables for X-ray Crystallography.⁷ Crystal parameters and refinement results are summarized in Table 1.

Results and discussion

Selected bond distances and angles are listed in Table 2. The molecular structure of the title complex with the atom numbering scheme is illustrated in Fig. 1.

Table 2 Selected interatomic distances (nm) and interbond angles ($^{\circ}$) for $\text{Ni}_2\text{C}_{28}\text{H}_{36}\text{N}_{12}\text{O}_{13}$

Bonds distances (nm)			
Ni—O(1)	0.2093(3)	Ni—O(5)	0.2121(3)
Ni—O(6)	0.2116(3)	Ni—N(1)	0.2063(4)
Ni—N(3)	0.2070(4)	Ni—N(5)	0.2065(4)
O(1)—C(1)	0.1267(5)	O(2)—C(1)	0.1250(5)
O(3)—C(4)	0.1245(5)	O(4)—C(4)	0.1264(5)
C(1)—C(2)	0.1505(5)	C(3)—C(4)	0.1498(6)
Bond angle ($^{\circ}$)			
O(1)-Ni-O(5)	86.2(1)	O(1)-Ni-O(6)	87.1(1)
O(1)-Ni-N(1)	88.6(1)	O(1)-Ni-N(3)	178.6(1)
O(1)-Ni-N(5)	89.8(1)	O(5)-Ni-O(6)	86.6(1)
O(5)-Ni-N(1)	92.3(1)	O(5)-Ni-N(3)	93.4(1)
O(5)-Ni-N(5)	174.3(1)	O(6)-Ni-N(1)	175.6(1)
O(6)-Ni-N(3)	91.6(1)	O(6)-Ni-N(5)	89.1(1)
N(1)-Ni-N(3)	92.7(1)	N(1)-Ni-N(5)	91.7(2)
N(3)-Ni-N(5)	90.5(2)	Ni-O(1)-C(1)	131.2(3)
O(1)-C(1)-O(2)	125.9(4)	O(1)-C(1)-C(2)	115.3(2)
O(2)-C(1)-C(2)	118.8(4)	O(3)-C(4)-O(4)	124.3(4)
O(2)-C(1)-C(2)	116.7(2)	O(3)-C(5)-O(4)	124.2(2)
O(3)-C(4)-C(3)	117.4(4)	O(4)-C(4)-C(3)	118.3(4)

**Fig. 1** Molecular structure of the title complex.

The main feature of the molecular structure is the symmetric binuclear unit made up of two slightly distorted coordination octahedrons. One oxygen atom from the carboxylate group of TCB, two oxygen atoms from two coordinated water molecules and three nitrogen atoms from three imidazole molecules coordinate to a $\text{Ni}(\text{II})$ ion to complete the coordination geometry of a six-coordinated octahedron around the $\text{Ni}(\text{II})$ ion. It is worthy to

take a look at the distances and angles around $\text{Ni}(\text{II})$ ion in this complex. The bond angles of $\text{N}(1)\text{-Ni-N}(3)$, $\text{N}(3)\text{-Ni-N}(5)$, $\text{N}(1)\text{-Ni-N}(5)$, are $92.7(1)^{\circ}$, $90.5(2)^{\circ}$, $91.7(2)^{\circ}$ respectively, which are all bigger than 90° . On the contrary, the bond angles of all the O-Ni-O are smaller than 90° : $\text{O}(1)\text{-Ni-O}(5)$ [$86.2(1)^{\circ}$], $\text{O}(1)\text{-Ni-O}(6)$ [$87.1(1)^{\circ}$], $\text{O}(5)\text{-Ni-O}(6)$ [$86.6(1)^{\circ}$]. Therefore, the coordination geometry

formed by three nitrogen atoms and three oxygen atoms is a distorted octahedron. However it is surprising that three nitrogen atoms from three imidazoles and three oxygen atoms from two water molecules and one carboxylate group of TCB coordinated to a nickel(II) ion are found on a face of the octahedron respectively, so the octahedron is a facial isomer.⁸ In the facial isomer, each pair of the nitrogen atom and the oxygen atom is in the opposite sides of nickel(II) ion position, and the distances of the three pairs are approximately equal to each other: O(1)—N(3)[4.163], O(5)—N(5)[4.186], O(6)—N(1)[4.179].

The two slightly distorted octahedrons mentioned above are bridged by two *para*-carboxylate groups of TCB to form a symmetric binuclear structure, and the other two *para*-carboxylate groups of TCB are free. Moreover, the angle of O(1)-C(1)-O(2), 125.9(4)°, is bigger than that of O(3)-C(4)-O(4), 124.3(4)°, which illustrates that the former is in monodentate fashion and the latter is in free state.⁹ The stretching vibrations of the carboxylate group observed at 1561.95 cm⁻¹ and 1328.82 cm⁻¹ are attributed to $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ stretching vibration of the coordinated carboxylate groups. The $\Delta\nu$ value [$\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$] of 233.13 cm⁻¹ suggests the monodentate coordination of the

carboxylate groups,¹⁰ it is also in agreement with the crystal structure as mentioned above.

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