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CRYSTAL STRUCTURE OF A NICKEL(II) COMPLEX WITH THE MACROCYCLIC LIGAND 4-METHYL-1,3,5,8,11,14-HEXAAZATRICYCLOOCTADECANE**X. Jiang, H. Xia, G. Yan, B. Tao, Y.-F. Zhu, X. Wang**

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The crystal structure of the macrocyclic complex $[\text{Ni}(\text{PCHA})](\text{ClO}_4)_2$ (II) (PCHA = 4-methyl-1,3,5,8,11,14-hexaazatricyclooctadecane) is described. In the presence of succinate acid, $[\text{Ni}(\text{PCHA})](\text{ClO}_4)_2$ (II) is obtained by recrystallization of orange crystals of $[\text{Ni}(\text{PCHA})] \times (\text{ClO}_4)_2$ (I), whose structure has previously been identified. The $[\text{Ni}(\text{PCHA})](\text{ClO}_4)_2$ (II) crystal belongs to the monoclinic $P2(1)/c$ space group with $a = 15.8561(3) \text{ \AA}$, $b = 9.4409(2) \text{ \AA}$, $c = 13.9297(2) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 94.8840(10)^\circ$, $\gamma = 90^\circ$, $M_r = 526.02$, $Z = 4$, $V = 2077.65(7) \text{ \AA}^3$. The structure is ionic with $[\text{Ni}(\text{L})]^{2+}$ and two perchlorate anions with a supermolecular interaction.

Keywords: Ni(II), macrocyclic complex, crystal structure, PCHA, supermolecular interaction.

Macrocyclic complexes attract chemists' interest due to their application in the fields of bioinorganic chemistry [1], magnetism [2], porous materials [3], and other fields. More coordination complexes have recently been reported based on the macrocyclic complexes [4—6]. Metal template syntheses often provide selective routes to the products that are not obtainable in the absence of a metal ion. Especially, the template reactions involving formaldehyde and amines facilitate the preparation of macrocyclic and macropolycyclic complexes. The advantage of those macrocyclic complexes are that the axial sites on the metal are not sterically protected and are commonly accessible to additional ligands [7—9]. A new complex could be obtained by the reaction of a macrocyclic complex with a bridging ligand. In this work, we attempted the synthesis of a new macrocyclic complex with a bridging ligand by the reaction of the macrocyclic complex with succinate acid, but only $[\text{Ni}(\text{PCHA})] \times (\text{ClO}_4)_2$ (II) was obtained, which is the isomeric of $[\text{Ni}(\text{PCHA})](\text{ClO}_4)_2$ (I) whose structure has previously been identified [10].

MATERIALS AND PHYSICAL MEASUREMENTS

All chemicals and solvents were of reagent grade and used as received. Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Vario EL III CHNS/O elemental analyzer. IR spectra were measured from KBr pellets on a Nicolet Avatar 370 Fourier Transform Infrared spectrometer.

Preparation of $[\text{Ni}(\text{PCHA})](\text{ClO}_4)_2$ (II). The precursor macrocyclic complex $[\text{Ni}(\text{PCHA})](\text{ClO}_4)_2$ (I) was prepared according to the literature procedure [10]. A mixture of succinate acid (60 mg, 0.5 mmol), $[\text{Ni}(\text{PCHA})](\text{ClO}_4)_2$ (I) (265 mg, 0.5 mmol), methanol (5.0 ml), and H_2O (10.0 ml) was stirred for 15 min in air until a yellow solution resulted. Orange-red block single crystals suitable for the X-ray analysis were obtained after one month. Yield: 100 mg, 38 %. Anal. Calc. for

Table 1

Crystal data and structure refinements of complex II

| | |
|--|--|
| Empirical formula | $C_{13}H_{28}Cl_2N_6NiO_8$ |
| Formula weight | 526.02 |
| Temperature, K | 296(2) |
| Wavelength, Å | 0.71073 |
| Crystal system | Monoclinic |
| Space group | $P2(1)/c$ |
| Unit cell dimensions $a, b, c, \text{Å}; \beta$, deg. | 15.8561(3), 9.4409(2), 13.9297(2); 94.8840(10) |
| Volume, Å ³ | 2077.65(7) |
| Z , Calculated density, Mg/m ³ | 4, 1.682 |
| Absorption coefficient, mm ⁻¹ | 1.246 |
| $F(000)$ | 1096 |
| Theta range for data collection, deg. | 1.29—24.99 |
| Index ranges | $-18 \leq h \leq 18, -11 \leq k \leq 10, -16 \leq l \leq 16$ |
| Reflections collected/unique | 15342/3652 [$R(\text{int}) = 0.0212$] |
| Completeness to $\theta = 24.99\%$, deg. | 99.9 |
| Absorption correction | None |
| Max. and min. transmission | 0.7626 and 0.7459 |
| Refinement method | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3652 / 0 / 284 |
| Goodness-of-fit on F^2 | 1.039 |
| Final R indices [$I > 2\sigma(I)$] | $R1 = 0.0490, wR2 = 0.1386$ |
| R indices (all data) | $R1 = 0.0521, wR2 = 0.1427$ |
| Largest diff. peak and hole, e/Å ⁻³ | 1.292 and -0.613 |

$C_{13}H_{28}Cl_2N_6NiO_8$: C, 29.69; H, 5.37; N, 15.98 %. Found: C, 29.88; H, 5.65; N, 16.25 %. IR spectra (KBr, cm⁻¹): 3179 (m), 1468 (s), 1081 (s), 822 (m), 705 (m), 625 (s).

Single crystal X-ray diffraction analysis. Suitable single crystals with the dimensions of 0.25×0.25×0.23 mm³ of the complex were selected for the single crystal X-ray diffraction analysis. Data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) in the ω scanning mode at 293(2) K. For the complex, a total of 15342 (3652 unique, $R_{\text{int}} = 0.0212$) reflections were measured. The structures were solved by a direct method and refined by the full-matrix least-squares procedure on F^2 by the SHELXL-97 program [11]. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were located geometrically and refined isotropically and using a riding model. The CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 806556, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif. The crystal structure data are listed in Table 1.

RESULTS AND DISCUSSION

The IR spectra of $[\text{Ni}(\text{PCHA})](\text{ClO}_4)_2$ (II) show $\nu(\text{NH})$ bands for secondary amines of the ligands in the 3179 cm⁻¹ region and $\nu(\text{ClO}_4^-)$ at 1081 cm⁻¹ and 625 cm⁻¹. The ORTEP view of $[\text{Ni}(\text{PCHA})](\text{ClO}_4)_2$ (II) with the atomic numbering scheme is presented in Fig. 1. The selected bond lengths and angles are listed in Table 2.

Single crystal X-ray diffraction reveals that the structure of $[\text{Ni}(\text{PCHA})](\text{ClO}_4)_2$ (II) consists of a discrete mononuclear $[\text{Ni}(\text{PCHA})]^{2+}$ cation and two perchlorate anions. There are four tertiary nitrogen atoms (N(1), N(2), N(5), and N(6)) and two secondary nitrogen atoms (N(3) and N(4)) in the ligand.

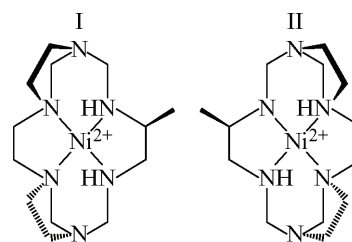
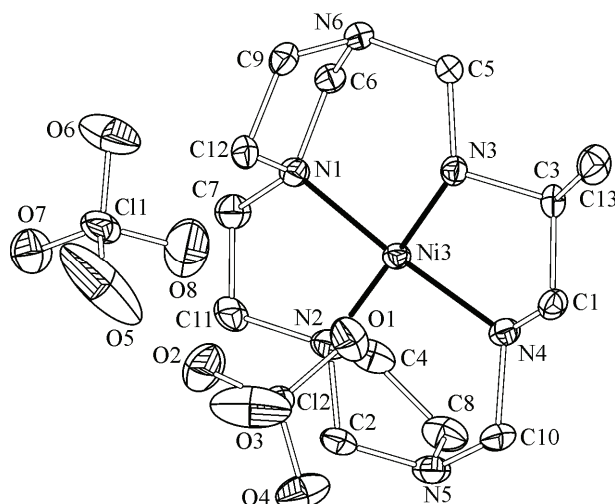


Fig. 1 (left). ORTEP diagram of $[\text{Ni}(\text{PCHA})] \times (\text{ClO}_4)_2$ (II) with the atom numbering scheme (perchlorate anions are omitted for clarity)

Fig. 2 (right). Enantiomers of complexes II and I

The nickel ion is coordinated by two tertiary and two secondary nitrogen atoms; N—Ni bonds are 1.927(3) Å, 1.935(3) Å, 1.944(3) Å, 1.928(3) Å respectively and the N—Ni—N angles range from 86.91(12)° to 94.31(14)° (Table 2). The crystal structure of the complex cation was described best by a slightly distorted square-planar geometry. The Ni—N(3) distance (1.944(3) Å) is longer than the Ni—N(1) distance (1.927(3) Å), i.e., Ni—N distances involving tertiary nitrogen atoms are significantly longer than those involving secondary nitrogen atoms. It has been observed that N-methylation of the secondary nitrogen donors of the macrocyclic complexes results in a decrease in the ligand field strength, and this has been explained by an increase in the Ni—N distances in the N-methylated complexes [12–14]. The Ni—N(3) distance (1.944(3)) is longer than the Ni—N(2) distance (1.935(3)) because of the methylation of C(13).

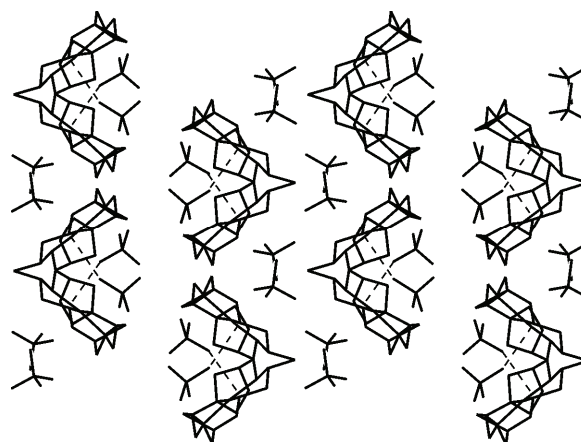
Both $[\text{Ni}(\text{PCHA})](\text{ClO}_4)_2$ (II) and $[\text{Ni}(\text{PCHA})](\text{ClO}_4)_2$ (I) consist of $[\text{Ni}(\text{PCHA})]^{2+}$ cations and outer-sphere perchlorate anions, but they have the most different crystal structure. $[\text{Ni}(\text{PCHA})] \times (\text{ClO}_4)_2$ (II) belongs to the monoclinic $P2(1)/c$ space group with $a = 15.8561(3)$ Å, $b = 9.4409(2)$ Å, $c = 13.9297(2)$ Å, $\alpha = 90^\circ$, $\beta = 94.8840(10)^\circ$, $\gamma = 90^\circ$, $V = 2077.65(7)$ Å³; and $[\text{Ni}(\text{PCHA})](\text{ClO}_4)_2$ (I) belongs to the orthorhombic, $P212121$ space group with $a = 11.2531(4)$ Å, $b = 12.7903(4)$ Å, $c = 14.2098(4)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 2045.22(11)$ Å³. The different crystal structures are explained by the enantiomers of $[\text{Ni}(\text{PCHA})]^{2+}$ cations that are of mirror symmetry (Fig. 2). The sites of the perchlorate anion were located in difference syntheses. In complex I, perchlorate anions interact via the hydrogen bond with secondary amine of the macrocycle [10]; in complex II, one of the perchlorate anions forms a hydrogen bond with secondary amine of the macrocycle (Fig. 3); another exists independently in the crystal. The axial sites on nickel are not sterically protected and are accessible to additional ligands.

Table 2

Selected bond lengths (Å) and angles (deg.) for complex II

| | | | | | |
|-----------------|------------|-----------------|-----------|-----------------|------------|
| N(1)—Ni(3) | 1.927(3) | C(5)—N(6) | 1.453(5) | C(8)—N(5) | 1.481(6) |
| N(3)—Ni(3) | 1.944(3) | C(5)—N(3) | 1.499(4) | C(9)—N(6) | 1.469(5) |
| C(1)—N(4) | 1.478(5) | C(6)—N(6) | 1.432(5) | C(10)—N(5) | 1.435(6) |
| C(2)—N(5) | 1.431(5) | N(2)—Ni(3) | 1.935(3) | C(10)—N(4) | 1.503(5) |
| C(2)—N(2) | 1.499(5) | N(4)—Ni(3) | 1.928(3) | C(11)—N(2) | 1.495(6) |
| C(3)—N(3) | 1.513(4) | C(6)—N(1) | 1.496(5) | C(12)—N(1) | 1.506(6) |
| C(4)—N(2) | 1.491(6) | C(7)—N(1) | 1.495(5) | | |
| N(1)—Ni(3)—N(4) | 174.96(14) | N(4)—Ni(3)—N(2) | 94.31(14) | N(4)—Ni(3)—N(3) | 86.91(12) |
| N(1)—Ni(3)—N(2) | 87.56(14) | N(1)—Ni(3)—N(3) | 91.74(13) | N(2)—Ni(3)—N(3) | 173.74(13) |

Fig. 3. Crystal packing of complex II; dotted lines represent the hydrogen bonds (*c* axis)



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