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# Synthesis and Crystal Structure of Complex: $[Ni(cdm)_2(H_2O)_4]\cdot 2H_2O$ (cdm = Carbamyldicyanomethanide Anion)

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Crystal engineering and the design of solid-state architectures have recently become areas of increasing interest [1–2]. Such crystal engineering may afford new materials with useful properties such as catalytic activity, microporosity, nonlinear optical activity, cooperative magnetic behavior and so on. Polynitrile-ligand is one of ideal multi-functional ligands and many complexes with polynitriles as ligands have displayed the special structures and distinguished physical properties [3–7]. Carbamyldicyanomethanide anion (cdm) as a polynitrile ligand of complexes of Zn(II), Co(II), Ni(II) and Cu(II) has been reported [8–9], however, there is no information of the crystal structure of these complexes. With the purpose of providing more useful information for crystal engineering we synthesized and characterized a series of the complexes with cdm as ligand and found that the literature did not provide the correct coordination information. Here we report the titled complex with the microporous structure characteristic.

A solution of sodium carbamyldicyanomethanide (0.3697 g, 2.82 mmol, in 20 $cm^3$ $H_2O$) was added to a solution of $Ni(ClO_4)_2\cdot 6H_2O$ (0.5154 g, 1.41 mmol, in 20 $cm^3$ $H_2O$) and then the mixed solution was stirred for a few minutes. The bluish single-crystal was obtained after the mixed solution rested at room temperature for a few of days. Found: C, 24.96; H, 4.49; N, 21.65; Ni, 15.04%. Calc. for $C_8H_{16}N_6NiO_8$: C, 25.09; H, 4.21; N, 21.95; Ni, 15.32%. Compared with the bands of sodium cdm, the characteristic bands of –CN have shifted from 2160 and 2200 $cm^{-1}$ to 2220 and 2260 $cm^{-1}$ and the sharp peaks at 3220, 3320 and 3455 $cm^{-1}$ for $-NH_2$ became a broad bands from 3220 to 3460 $cm^{-1}$. The intense bands at 1440, 1560 and 1660 $cm^{-1}$ for $-CONH_2$ have shifted to1443, 1510 and 1635 $cm^{-1}$, respectively, and at the same time the bands became broad and the absorption intensity decreased.

The determination of the crystal structure was carried out on an X-ray diffractometer, Model Bruker Smart-1000 CCD. Details of crystal parameters, data collection and structure refinement are given Table 1. All data reduction and structure refinement

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were performed using the SHELX97 program system. Fractional coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms and hydrogen atoms, selected bond lengths and angles, and hydrogen bond lengths and angles are listed in Tables 2, 3, 4 and 5, respectively.

**Table 1.** Crystallographic data and collection parameters for the complex.

| | |
|---|---|
| Formula | $C_8H_{16}N_6NiO_8$ |
| Formula weight | 382.98 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| $a$ (Å) | 9.319(3) |
| $b$ (Å) | 7.404(2) |
| $c$ (Å) | 11.963(4) |
| $\alpha = \gamma$ | 90° |
| $\beta$ | 108.477(4) ° |
| $V$ (Å$^3$) | 782.9(4) |
| $Z$ | 2 |
| $D_c$ (g/cm$^3$) | 1.625 |
| Crystal dimension (mm) | 0.25×0.20×0.15 |
| Temperature (K) | 293(2) |
| Radiation wavelength (Å) | MoK $\alpha$ 0.71073 |
| Absorption coefficient (mm$^{-1}$) | 1.290 |
| $F$ (000) | 396 |
| $\theta$ range for data collection | 2.43 to 25.02 |
| Limiting indices | $-11 \le h \le 8$, $-8 \le k \le 8$, $-8 \le l \le 14$ |
| Reflections collected/unique | 3814/1381 [R(int) = 0.0242] |
| Completeness to $\theta = 25.02°$ | 99.9% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 1381/0/106 |
| Goodness-of-fit on $F^2$ | 1.096 |
| Final R indices [$I > 2\sigma(I)$] | R1 = 0.0280, wR2 = 0.0662 |
| R indices (all data) | R1 = 0.0376, wR2 = 0.0695 |
| Largest diff. peak and hole | 0.277 and −0.258 e·Å$^{-3}$ |

**Table 2.** Atomic coordinates (×10$^4$) and equivalent isotropic displacement parameters (Å$^2$×10$^3$). U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| Ni(1) | 5000 | 0 | 10000 | 25(1) |
| N(1) | 9028(3) | 3996(3) | 8771(2) | 39(1) |
| N(2) | 6773(2) | 410(3) | 9366(2) | 33(1) |
| N(3) | 10196(3) | −2052(3) | 8055(2) | 53(1) |
| O(1) | 10784(2) | 2642(2) | 8142(1) | 33(1) |
| O(2) | 3544(2) | 966(3) | 8453(2) | 37(1) |
| O(3) | 5269(2) | 2550(2) | 10765(2) | 32(1) |
| O(4) | 7089(3) | 5079(3) | 201(2) | 41(1) |
| C(1) | 9646(2) | 2505(3) | 8491(2) | 26(1) |
| C(2) | 9003(2) | 787(3) | 8588(2) | 27(1) |
| C(3) | 7766(3) | 574(3) | 9007(2) | 27(1) |
| C(4) | 9661(3) | −783(4) | 8287(2) | 33(1) |

**Table 3.** Hydrogen coordinates (×10$^4$) and isotropic displacement parameters (Å$^2$ ×10$^3$).

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H(1) | 9400(30) | 5040(40) | 8610(20) | 47(8) |
| H(2) | 8290(30) | 3940(40) | 9070(20) | 49(8) |
| H(3) | 2720(30) | 1300(40) | 8390(30) | 52(9) |
| H(4) | 3890(40) | 1510(50) | 8080(30) | 70(13) |
| H(5) | 5430(30) | 2490(40) | 11390(30) | 41(10) |
| H(6) | 6020(60) | 3250(80) | 10700(50) | 170(20) |
| H(7) | 7540(30) | 5440(40) | 610(20) | 18(10) |
| H(8) | 6290(70) | 5930(90) | –240(50) | 200(30) |

**Table 4.** Selected bond lengths (Å) and bond angles (°).

| | | | |
|---|---|---|---|
| Ni(1)–N(2) | 2.048(2) | Ni(1)–N(2A) | 2.048(2) |
| Ni(1)–O(2) | 2.0458(19) | Ni(1)–O(2A) | 2.0458(19) |
| Ni(1)–O(3) | 2.0784(18) | Ni(1)–O(3A) | 2.0784(18) |
| N(2)–Ni(1)–N(2A) | 180.0 | N(2)–Ni(1)–O(2A) | 90.31(9) |
| N(2)–Ni(1)–O(2) | 89.69(9) | N(2)–Ni(1)–O(3A) | 88.29(8) |
| N(2)–Ni(1)–O(3) | 91.71(8) | O(2A)–Ni(1)–O(3A) | 91.92(8) |
| O(2)–Ni(1)–O(3A) | 88.08(8) | | |

**Table 5.** Hydrogen bond lengths (Å) and bond angles (°) (D: donor atom; A: acceptor atom; l: length; ST: symmetry transformation for acceptor atom).

| D–H | l(D–H) | l(H···A) | ∠DHA | l(D···A) | A | ST |
|---|---|---|---|---|---|---|
| N(1)–H(1) | 0.890 | 2.440 | 174.70 | 3.327 | N(3) | [x, y + 1, z] |
| N(1)–H(2) | 0.874 | 2.179 | 149.65 | 2.966 | O(4) | [x, y, z + 1 ] |
| O(3)–H(5) | 0.711 | 2.023 | 177.21 | 2.733 | O(1) | [x – 1/2, –y + 1/2, z + 1/2] |
| O(2)–H(3) | 0.791 | 1.994 | 167.69 | 2.772 | O(1) | [x – 1, y, z ] |
| O(4)–H(7) | 0.594 | 2.284 | 166.95 | 2.866 | O(1) | [–x + 2, –y + 1, –z + 1] |
| O(2)–H(4) | 0.741 | 2.110 | 176.72 | 2.851 | N(3) | [–x + 3/2, y + 1/2, –z + 3/2] |
| O(4)–H(8) | 0.992 | 1.785 | 167.84 | 2.763 | O(3) | [–x + 1, –y + 1, –z + 1] |
| O(3)–H(6) | 0.895 | 1.886 | 161.59 | 2.750 | O(4) | [x, y, z + 1] |

Fig. 1 shows the ORTEP diagram of the title complex with the atom numbering scheme and the connecting pattern between the complexes through hydrogen bonds is given in Fig. 2. Fig. 3 displays the arrangement of the one-dimensional chains and the microporosity of the crystal. Fig. 1 indicates that Ni(II) is coordinated by two N atoms of the –CN radical and four O atoms of $H_2O$ to form a slightly distorted octahedron. The coordination state of the complex is utterly different from the reported coordinated pattern that claims that the $H_2O$ molecules are in the outer sphere [8]. The neutral complexes connect to each other through the hydrogen bonds to form a one-dimensional chain as shown in Fig. 2 and 3. Fig. 3 also shows that the 1D chains connect through the hydrogen bonds to form the countless microporosities in *a* direction of the cell. In addition, there exist four non-coordinated $H_2O$ molecules in each cell and the same free $H_2O$ molecules seem to be absorption in the microporous structure.

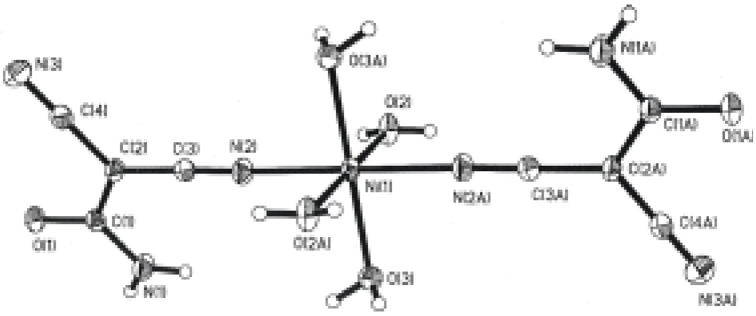

**Figure 1.** The ORTEP drawing of the title complex with atom numbering scheme.

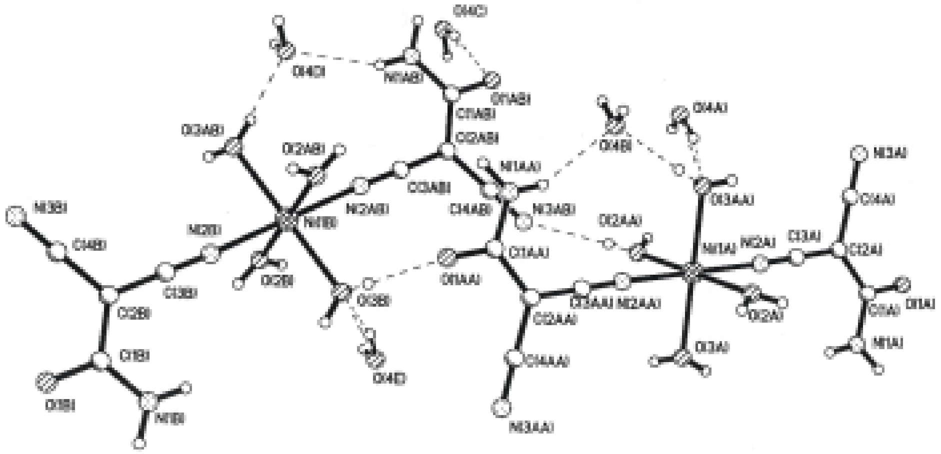

**Figure 2.** The connecting pattern between the complexes.

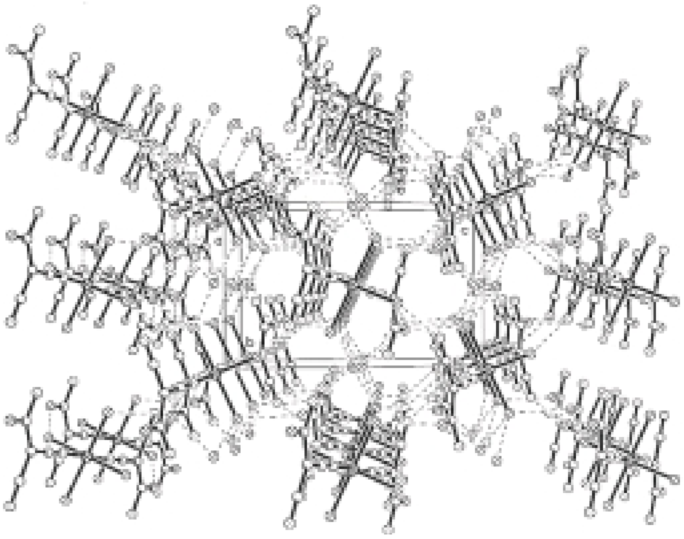

**Figure 3.** The unit cell, the arrangement of 1D chains and the microporosity.

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