

THERMAL DECOMPOSITION MECHANISM AND THERMODYNAMIC PROPERTIES OF $[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$

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Abstract

$[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$ was prepared by mixing the aqueous solution of 3-nitro-1,2,4-triazol-5-one and cadmium carbonate in excess. The single crystal structure was determined by a four-circle X-ray diffractometer. The crystal is monoclinic, space group $C2/c$ with crystal parameters of $a=2.1229(3)$ nm, $b=0.6261(8)$ nm, $c=2.1165(3)$ nm, $\beta=90.602(7)^\circ$, $V=2.977(6)$ nm³, $Z=4$, $D_c=2.055$ g·cm⁻³, $\mu=15.45$ cm⁻¹, $F(000)=1824$, $\lambda(\text{MoK}\alpha)=0.071073$ nm. The final R is 0.0282. Based on the results of thermal analysis, the thermal decomposition mechanism of $[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$ was derived. From measurements of the enthalpy of solution of $[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$ in water at 298.15 K, the standard enthalpy of formation, lattice energy, lattice enthalpy and standard enthalpy of dehydration have been determined as $-(1747.8\pm 4.8)$, -2394 , -2414 and 313.6 kJ mol⁻¹ respectively.

Keywords: cadmium coordination, crystal structure, enthalpy of solution, lattice energy, lattice enthalpy, NTO salt, preparation, standard enthalpy of dehydration, standard enthalpy of formation, thermal decomposition mechanism

Introduction

Much attention has been paid to 3-nitro-1,2,4-triazol-5-one (NTO) as a high energy and low sensitivity energetic material. Its metal salts also have some potential uses in ammunition. Therefore the authors prepared the single crystal of $[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$, determined its structure and studied its thermal decomposition mechanism and thermodynamic properties.

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Experimental

Materials

The $[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$ used in this work was prepared according to the following method: An appropriate amount of NTO was put into distilled water, then stirred and cadmium carbonate was added in excess at 60°C . When carbon dioxide evolution ceased, the resulting solution was stirred and heated at 60°C for 30 min, then filtered off while still hot. The precipitate was then dissolved in ethyl alcohol, and the undissolved CdCO_3 was separated. This solution was allowed to stand for 6 h until a yellow precipitate formed. The precipitate was recrystallized from distilled water in a Petri dish at 25°C to obtain the yellow single crystal for X-ray measurement. Its purity was better than 99.6%. The dimensions of the single crystal were $0.46\times 0.42\times 0.42\text{ mm}^3$. The conductivity of deionized water used in the experiment was $5.48\times 10^{-8}\text{ s cm}^{-1}$.

Experimental equipment and conditions

In the determination of the structure of the single crystal, X-ray intensities were recorded by a Siemens P_4 automatic diffractometer with graphite-monochromatized MoK_α radiation, $\lambda=0.071073\text{ nm}$. The 3287 independent reflections were obtained, among which 2523 with $F_0>4\sigma(F_0)$ were used for the determination and refinement of crystal structure. The coordinates of two Cd atoms were obtained by the Patterson method and those of the other atoms by difference Fourier synthesis.

The thermal decomposition process was studied using TG technique on a TGA-DTA instrument (TA Co., USA). The conditions of TG were as follows: sample mass about 1 mg; heating rate $10^\circ\text{C min}^{-1}$; atmosphere static air. The DSC experiments were carried out with a model CDR-1 differential scanning calorimeter with an aluminium cell (diameter $5\times 3\text{ mm}$), whose side was rolled up. The conditions of DSC measurement were as follows: sample mass about 1 mg; heating rate $10^\circ\text{C min}^{-1}$; atmosphere static air; reference sample $\alpha\text{-Al}_2\text{O}_3$; thermocouple plate, Ni/Cr-Ni/Si. The infrared spectra of the decomposition residues were recorded in KBr discs on a 60 SXR FT-IR spectrometer (Nicolet Co., USA) at 4 cm^{-1} resolution.

All measurements of the enthalpy of solution in deionized water were made using a Calvet microcalorimeter, type BT215 from Setaram, France and operated at $298.15\pm 0.01\text{ K}$.

The experimental precision and accuracy of enthalpies of solution were frequently checked by measurement of the enthalpies of solution $\Delta_{\text{sol}}H_\infty^\theta$ of crystalline KCl in deionized water at 298.15 K. The experimental value of $\Delta_{\text{sol}}H_\infty^\theta = 17.217\pm 0.053\text{ kJ mol}^{-1}$ is in excellent accord with that of $\Delta_{\text{sol}}H_\infty^\theta = 17.234\text{ kJ mol}^{-1}$ reported in the literature [1].

Table 1 Positional parameters and $U_{eq}/\text{nm}^2 \cdot 10^3$

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq} |
|-------|-------------|-------------|-------------|----------|
| Cd(1) | 0.0000 | 0.9423(1) | 0.2500 | 0.25(1) |
| Cd(2) | 0.2500 | 0.7500 | 0.0000 | 0.35(1) |
| O(1) | -0.1451(1) | 0.9193(4) | 0.1507(1) | 0.38(1) |
| O(2) | -0.0239(1) | 0.6247(5) | 0.3343(1) | 0.43(1) |
| O(3) | -0.1066(2) | 0.5030(5) | 0.3796(1) | 0.51(1) |
| O(4) | 0.0950(1) | 0.9774(4) | 0.1080(1) | 0.35(1) |
| O(5) | -0.0871(1) | 1.2674(4) | 0.2278(1) | 0.43(1) |
| O(6) | -0.1307(1) | 1.4044(5) | 0.1448(2) | 0.49(1) |
| O(7) | 0.2747(2) | 1.0736(5) | 0.0370(2) | 0.58(1) |
| O(8) | 0.3523(1) | 0.6740(6) | -0.0048(1) | 0.54(1) |
| O(9) | 0.2534(1) | 0.6127(6) | 0.0980(1) | 0.52(1) |
| O(10) | 0.5855(2) | 0.7798(5) | -0.0512(2) | 0.70(1) |
| O(11) | 0.2030(2) | 1.1707(7) | 0.1466(2) | 0.92(1) |
| N(1) | -0.1961(2) | 0.7428(5) | 0.2305(2) | 0.39(1) |
| N(2) | -0.1796(1) | 0.6431(5) | 0.2849(1) | 0.37(1) |
| N(3) | -0.0945(1) | 0.7909(5) | 0.2414(1) | 0.28(1) |
| N(4) | -0.0810(1) | 0.5968(4) | 0.3376(1) | 0.33(1) |
| N(5) | 0.0186(2) | 1.1757(5) | 0.0575(1) | 0.33(1) |
| N(6) | -0.0350(1) | 1.2729(4) | 0.0733(1) | 0.30(1) |
| N(7) | 0.0055(1) | 1.1066(4) | 0.1572(1) | 0.26(1) |
| N(8) | -0.0901(1) | 1.3036(5) | 0.1710(1) | 0.32(1) |
| C(1) | -0.1448(2) | 0.8274(6) | 0.2023(2) | 0.30(1) |
| C(2) | -0.1194(2) | 0.6809(5) | 0.2881(2) | 0.28(1) |
| C(3) | 0.0447(2) | 1.0766(5) | 0.1078(2) | 0.26(1) |
| C(4) | 0.0396(2) | 1.2243(5) | 0.1326(20) | 0.25(1) |
| H(1) | -0.2331(19) | 0.7258(50) | 0.2125(17) | 0.24(9) |
| H(5) | 0.0310(19) | 1.2059(63) | 0.0290(19) | 0.31(12) |
| H(7A) | 0.2440(27) | 1.0807(115) | 0.0629(32) | 1.28(32) |
| H(7B) | 0.3073(32) | 1.1614(130) | 0.0374(45) | 1.96(45) |
| H(8A) | 0.3696(25) | 0.6102(73) | -0.0402(20) | 0.80(17) |
| H(8B) | 0.3806(9) | 0.7736(68) | 0.0105(25) | 0.95 |
| H(9A) | 0.2874(15) | 0.5675(64) | 0.1100(20) | 0.45(13) |
| H(9B) | 0.2227(20) | 0.6644(93) | 0.1214(25) | 1.00(21) |

Table 2 Bond distances/nm

| | | | |
|-------------|-----------|-------------|-----------|
| Cd(1)–N(3) | 0.2247(3) | Cd(1)–N(3A) | 0.2247(3) |
| Cd(1)–N(7) | 0.2250(3) | Cd(1)–N(7A) | 0.2250(3) |
| Cd(2)–O(8) | 0.2232(3) | Cd(2)–O(8A) | 0.2232(3) |
| Cd(2)–O(9A) | 0.2265(3) | Cd(2)–O(9) | 0.2265(3) |
| Cd(2)–O(7A) | 0.2340(3) | Cd(2)–O(7) | 0.2340(3) |
| O(1)–C(1) | 0.1252(4) | O(2)–N(4) | 0.1229(4) |
| O(3)–N(4) | 0.1218(4) | O(4)–C(3) | 0.1254(4) |
| O(5)–N(8) | 0.1227(4) | O(6)–N(8) | 0.1219(4) |
| N(1)–C(1) | 0.1367(4) | N(1)–N(2) | 0.1370(4) |
| N(2)–C(2) | 0.1303(4) | N(3)–C(2) | 0.1342(4) |
| N(3)–C(1) | 0.1366(4) | N(4)–C(2) | 0.1435(4) |
| N(5)–N(6) | 0.1351(4) | N(5)–C(3) | 0.1363(4) |
| N(6)–C(4) | 0.1302(4) | N(7)–C(4) | 0.1336(4) |
| N(7)–C(3) | 0.1358(4) | N(8)–C(4) | 0.1449(4) |

Table 3 Bond angles/^o

| | | | |
|-------------------|------------|-------------------|------------|
| N(3)–Cd(1)–N(3A) | 127.0(2) | N(3)–Cd(1)–N(7) | 101.49(10) |
| N(3A)–Cd(1)–N(7) | 103.45(10) | N(3)–Cd(1)–N(7A) | 103.45(10) |
| N(3A)–Cd(1)–N(7A) | 101.49(10) | N(7)–Cd(1)–N(7A) | 122.10(14) |
| O(8)–Cd(2)–O(8A) | 180.0 | O(8)–Cd(2)–O(9A) | 94.06(11) |
| O(8A)–Cd(2)–O(9A) | 85.94(11) | O(8)–Cd(2)–O(9) | 85.94(11) |
| O(8A)–Cd(2)–O(9) | 94.06(11) | O(9A)–Cd(2)–O(9) | 180.0 |
| O(8)–Cd(2)–O(7A) | 89.56(13) | O(8A)–Cd(2)–O(7A) | 90.44(13) |
| O(9A)–Cd(2)–O(7A) | 93.26(13) | O(9)–Cd(2)–O(7A) | 86.74(13) |
| O(8)–Cd(2)–O(7) | 90.44(13) | O(8A)–Cd(2)–O(7) | 89.56(13) |
| O(9A)–Cd(2)–O(7) | 86.74(13) | O(9)–Cd(2)–O(7) | 93.26(13) |
| O(7A)–Cd(2)–O(7) | 180.0 | C(1)–N(1)–N(2) | 111.5(3) |
| C(2)–N(2)–N(1) | 101.1(3) | C(2)–N(3)–C(1) | 103.2(3) |
| C(2)–N(3)–Cd(1) | 122.8(2) | C(1)–N(3)–Cd(1) | 131.5(2) |
| O(3)–N(4)–O(2) | 124.5(3) | O(3)–N(4)–C(2) | 118.4(3) |
| O(2)–N(4)–C(2) | 117.0(3) | N(6)–N(5)–C(3) | 112.0(3) |
| C(4)–N(6)–N(5) | 101.1(3) | C(4)–N(7)–C(3) | 103.2(3) |
| C(4)–N(7)–Cd(1) | 125.4(2) | C(3)–N(7)–Cd(1) | 129.7(2) |
| O(6)–N(8)–O(5) | 125.6(3) | O(6)–N(8)–C(4) | 117.9(3) |
| O(5)–N(8)–C(4) | 116.5(3) | O(1)–C(1)–N(3) | 127.7(3) |

Table 3 Continued

| | | | |
|----------------|----------|----------------|----------|
| O(1)–C(1)–N(1) | 125.8(3) | N(3)–C(1)–N(1) | 106.6(3) |
| N(2)–C(2)–N(3) | 117.5(3) | N(2)–C(2)–N(4) | 120.9(3) |
| N(3)–C(2)–N(4) | 121.5(3) | O(4)–C(3)–N(7) | 127.1(3) |
| O(4)–C(3)–N(5) | 126.5(3) | N(7)–C(3)–N(5) | 106.4(3) |
| N(6)–C(4)–N(7) | 117.3(3) | N(6)–C(4)–N(8) | 121.0(3) |
| N(7)–C(4)–N(8) | 121.6(3) | | |

Results and discussion

Crystal structure

The crystal structure was found to be monoclinic, which belongs to space group $C2/c$ with crystallographic parameters of $a=2.1229(3)$ nm, $b=0.6261(8)$ nm, $c=2.1165(3)$ nm, $\beta=90.602(7)^\circ$, $V=2.977(6)$ nm³, $Z=4$, $D_c=2.055$ g cm⁻³, $\mu=15.45$ cm⁻¹, $F(000)=1824$. The final $R=0.0282$.

The atomic coordinates, thermal parameters, bond lengths and bond angles are summarized in Tables 1, 2 and 3. The molecular structure and atom labelling are shown in Fig. 1 and the packing of the molecule in the crystal lattice is illustrated in Fig. 2.

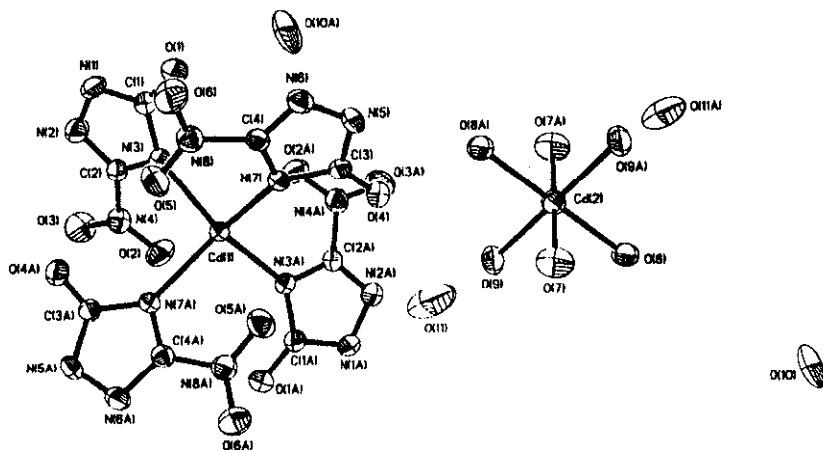


Fig. 1 Molecular structure of $[Cd(NTO)_4Cd(H_2O)_6] \cdot 4H_2O$

The analytical results indicate that Cd(1) and Cd(2) atoms are at quadric axis and symcentre. Four N atoms in four NTO^- and Cd (1) form $[Cd(NTO)_4]^{2-}$, Cd (2) and six water molecules form $[Cd(H_2O)_6]^{2+}$. Through electrostatic action $[Cd(NTO)_4]^{2-}$ is combined with $[Cd(H_2O)_6]^{2+}$.

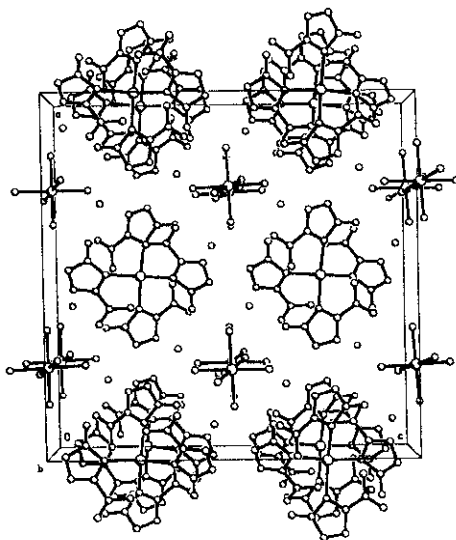


Fig. 2 Packing of the molecule $[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$ in the crystal lattice

There are four water molecules of crystallization in the crystal, denoted as $[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$.

As shown in Table 2, the distances between Cd(1) and the N atoms of four NTO cycles are 0.2247~0.2250 nm, the distances between Cd(2) and six coordination water molecules are 0.2232~0.2340.

According to calculations the plane equations of four NTO^- are as follows:

$$-2.980x + 5.608y + 10.907z = 7.273 \quad (\text{I})$$

$$11.215x + 5.457y + 4.255z = 6.8389 \quad (\text{II})$$

$$2.980x + 5.608y - 10.907z = 1.819 \quad (\text{III})$$

$$-11.215x + 5.457y - 4.255z = 4.711 \quad (\text{IV})$$

The dihedral angles between planes (I) and (II), (I) and (III), (II) and (III), (I) and (IV), (II) and (IV), (III) and (IV) are 43.2° , 64.4° , 48.3° , 48.3° , 69.1° and 43.2° , respectively.

The plane equations of Cd(2) and coordination water molecules are as follows:

$$-0.722x - 2.222y + 19.932z = -1.847 \quad (\text{V})$$

$$20.695x - 1.289y - 2.521z = 4.207 \quad (\text{VI})$$

$$4.783x + 5.925y + 8.135z = 5.639 \quad (\text{VII})$$

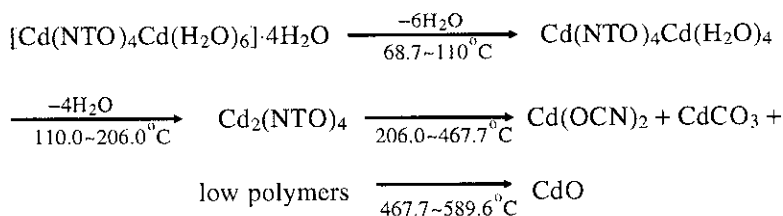
The dihedral angles between planes (V) and (VI), (V) and (VII), (VI) and (VII) are 94.0° , 86.8° and 89.8° , respectively.

Mechanism of thermal decomposition of $[Cd(NTO)_4Cd(H_2O)_6] \cdot 4H_2O$

The DSC curve shows that there are two endothermic and two exothermic processes at temperatures higher than 68.7°C . The first endothermic process is at $68.7\text{--}110.0^\circ\text{C}$. The TG curve shows that the mass loss corresponding to this temperature range is 12.26% which coincides with the value of 11.73%, calculated for the loss of six water molecules from the complex.

Two coordination water and four crystallization waters are released together, because the coordination bond lengths of $Cd(2)\text{--}O(7)$ and $Cd(2)\text{--}O(7A)$ [0.2340 nm] are longer than the other the bond lengths of $Cd(2)$ and water molecules [0.2232~0.2265 nm]. The second endothermic process is at $110.0\text{--}206.0^\circ\text{C}$, the mass loss is 7.78%, which coincides with the calculated value of 7.82%, corresponding to the loss of four water molecules. In this step the remaining coordination waters are released. Further decomposition of the dehydrated complex occurs at $206.0\text{--}467.7^\circ\text{C}$, the characteristic absorption peaks of $Cd(OCN)_2$, $CdCO_3$ and polymers containing the --CO--NH -group formed after the first exothermic peak appear at 2169 and 1187, 1483 and 774, 3383, 1632, 1557 and 1332 cm^{-1} , respectively. These observations show that the decomposition residue for this stage is a mixture. The amount of each component can not be determined from the present experiments and it is impossible to determine the stoichiometry of decomposition. The characteristic absorption peak of the residue formed after the second exothermic process ($467.7\text{--}589.6^\circ\text{C}$) at 588 cm^{-1} is assigned to CdO . At the end of this stage, the residue amounted to 26.58%. This value is in good agreement with the calculated amount of 27.88%.

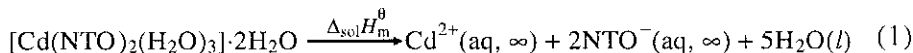
On the basis of experimental and calculated results, the thermal decomposition mechanism of $[Cd(NTO)_4Cd(H_2O)_6] \cdot 4H_2O$ is postulated to be as follows:



Enthalpy of solution in water of $[Cd(NTO)_4Cd(H_2O)_6] \cdot 4H_2O$

The mean of the enthalpy of solution of $[Cd(NTO)_4Cd(H_2O)_6] \cdot 4H_2O$ in deionized water at 298.15 K is $54.17 \pm 0.55\text{ kJ mol}^{-1}$. The molar ratios $n(H_2O)/n\{[Cd(NTO)_4Cd(H_2O)_6] \cdot 4H_2O\}$ are 35130~51872. Therefore, the mean of $\Delta_{\text{sol}}H_m^\theta$ can be considered at infinite dilution.

Because $[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$ is completely ionized in aqueous solution, its ionization process can be represented as*



Standard enthalpy of formation of $[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$ (cr)
 $\Delta_{\text{f}}H_{\text{m}}^{\ominus}\{[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}\}$

By substituting the mean of $\Delta_{\text{sol}}H_{\text{m}}^{\ominus}$ and the reported values

$$\begin{aligned} \Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{Cd}^{2+}, \text{aq}, \infty) &= -75.9 \text{ kJ mol}^{-1} [2], \\ \Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{NTO}^{-}, \text{aq}, \infty) &= -(94.3 \pm 2.1) \text{ kJ mol}^{-1} [3], \\ \text{and } \Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{H}_2\text{O}, l) &= -285.83 \text{ kJ mol}^{-1} [2], \text{ into Eq. (2),} \\ \Delta_{\text{f}}H_{\text{m}}^{\ominus}\{[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}\} &= \Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{Cd}^{2+}, \text{aq}, \infty) + \\ & 2\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{NTO}^{-}, \text{aq}, \infty) + 5\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{H}_2\text{O}, l) - \Delta_{\text{sol}}H_{\text{m}}^{\ominus} \end{aligned} \quad (2)$$

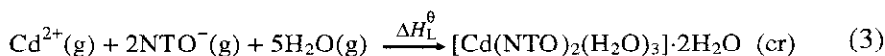
the following value was obtained:

$$\Delta_{\text{f}}H_{\text{m}}^{\ominus} = -1747.8 \pm 4.8 \text{ kJ mol}^{-1}$$

Lattice enthalpy and energy of $[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$

$$\begin{aligned} \Delta H_{\text{L}}^{\ominus}\{[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}, \text{cr}\}, \\ \Delta U_{\text{L}}^{\ominus}\{[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}, \text{cr}\} \end{aligned}$$

Setting $\Delta H_{\text{L}}^{\ominus}\{[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}\}, \text{cr}$ as the lattice enthalpy in forming the crystal $[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$ from $\text{Cd}^{2+}(\text{g})$, $\text{NTO}^{-}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ at 298.15 K, and $\Delta U_{\text{L}}^{\ominus}\{[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}, \text{cr}\}$ as the crystal lattice energy



we have

$$\Delta H_{\text{L}}^{\ominus} = \Delta_{\text{f}}H_{\text{m}}^{\ominus} - \Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{Cd}^{2+}, \text{g}) - 2\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{NTO}^{-}, \text{g}) - 5\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{H}_2\text{O}, \text{g}) \quad (4)$$

and

$$\Delta U_{\text{L}}^{\ominus} = \Delta H_{\text{L}}^{\ominus} - \Delta nRT \quad (5)$$

where $\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{Cd}^{2+}, \text{g}) = 2623.5 \text{ kJ mol}^{-1}$ [2]; $\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{NTO}^{-}, \text{g}) = -374.3 \text{ kJ mol}^{-1}$ [4]; $\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{H}_2\text{O}, \text{g}) = 241.82 \text{ kJ mol}^{-1}$ [2]; $\Delta n = -8$; $RT = 2.5 \text{ kJ mol}^{-1}$.

* This is the simplest formula of $[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$

By substituting the above-mentioned data into Eqs (4) and (5), the following values are obtained

$$\begin{aligned}\Delta H_{\text{L}}^{\ominus}[\{\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6\}\cdot 4\text{H}_2\text{O}] &= -2414 \text{ kJ mol}^{-1} \\ \Delta U_{\text{L}}^{\ominus}[\{\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6\}\cdot 4\text{H}_2\text{O}] &= -2394 \text{ kJ mol}^{-1}\end{aligned}$$

*Lattice energy and enthalpy of Cd(NTO)₂ (cr), $\Delta U_{\text{L}}^{\ominus}[\text{Cd}(\text{NTO})_2, \text{cr}]$
 $\Delta H_{\text{L}}^{\ominus}[\text{Cd}(\text{NTO})_2, \text{cr}]$*

Values of $\Delta U_{\text{L}}^{\ominus}[\text{Cd}(\text{NTO})_2, \text{cr}]$ are calculated using Kapustinskii's equation [5]:

$$\Delta U_{\text{L}}^{\ominus} = 1201.6 \frac{\eta_1 \eta_2 \sum n'}{\gamma_1 + \gamma_2} \left(1 - \frac{0.345}{\gamma_1 + \gamma_2} \right) \text{ kJ mol}^{-1} \quad (6)$$

where η_1 and η_2 are the moduli of the anion and cation charges; n' is the number of ions in the molecule; γ_1 and γ_2 are the radii of anion and cation in Å. For $\text{Cd}(\text{NTO})_2(\text{cr})$, $\eta_1 = \eta_{\text{NTO}^-} = 1$; $\eta_2 = \eta_{\text{Cd}^{2+}} = 2$; $n' = 3$; $\gamma_1 = \gamma(\text{NTO}^-, \text{g}) = 2.5 \text{ \AA}$ [6]; $\gamma_2 = \gamma(\text{Cd}^{2+}, \text{g}) = 0.97 \text{ \AA}$ [7].

The result of the calculation is:

$$\Delta U_{\text{L}}^{\ominus}[\text{Cd}(\text{NTO})_2, \text{cr}] = -1872 \text{ kJ mol}^{-1}$$

$\Delta H_{\text{L}}^{\ominus}[\text{Cd}(\text{NTO})_2, \text{cr}]$ is calculated according to Eq. (7):

$$\Delta H_{\text{L}}^{\ominus}[\text{Cd}(\text{NTO})_2, \text{cr}] = \Delta U_{\text{L}}^{\ominus}[\text{Cd}(\text{NTO})_2, \text{cr}] + \Delta nRT \quad (7)$$

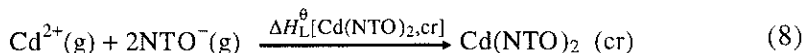
where $\Delta n = -3$; $RT = 2.5 \text{ kJ mol}^{-1}$.

The result of the calculation is:

$$\Delta H_{\text{L}}^{\ominus}[\text{Cd}(\text{NTO})_2, \text{cr}] = -1880 \text{ kJ mol}^{-1}$$

*Standard enthalpy of formation of Cd(NTO)₂ (cr), $\Delta_{\text{f}}H_{\text{m}}^{\ominus}[\text{Cd}(\text{NTO})_2, \text{cr}$
298.15 K]*

The values of $\Delta_{\text{f}}H_{\text{m}}^{\ominus}[\text{Cd}(\text{NTO})_2, \text{cr}, 298.15 \text{ K}]$ is calculated according to the process (8) and Eq. (9):



and

$$\begin{aligned}\Delta_{\text{f}}H_{\text{m}}^{\ominus}[\text{Cd}(\text{NTO})_2, \text{cr}, 298.15 \text{ K}] &= \Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{Cd}^{2+}, \text{g}) \\ &+ 2\Delta_{\text{f}}H_{\text{m}}^{\ominus}(\text{NTO}^{-}, \text{g}) + \Delta H_{\text{L}}^{\ominus}[\text{Cd}(\text{NTO})_2, \text{cr}]\end{aligned} \quad (9)$$

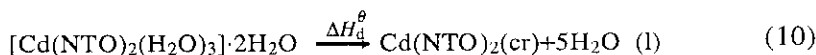
where $\Delta_f H_m^\theta(\text{Cd}^{2+}, \text{g}) = 2623.5 \text{ kJ mol}^{-1}$; $\Delta_f H_m^\theta(\text{NTO}^-, \text{g}) = -374.3 \text{ kJ mol}^{-1}$;
 $\Delta_f H_m^\theta[\text{Cd}(\text{NTO})_2, \text{cr}] = -1880 \text{ kJ mol}^{-1}$.

By substituting the above data into Eq. (9), the following value is obtained:

$$\Delta_f H_m^\theta[\text{Cd}(\text{NTO})_2, \text{cr}] = -5.1 \text{ kJ mol}^{-1}$$

*Standard enthalpy of dehydration of $[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6] \cdot 4\text{H}_2\text{O}(\text{cr})$,
 $\Delta_f H_d^\theta\{[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6] \cdot 4\text{H}_2\text{O}, \text{cr}\}$*

According to process (10) and Eq. (11)



$$\begin{aligned} \Delta_f H_d^\theta &= \Delta_f H_m^\theta[\text{Cd}(\text{NTO})_2, \text{cr}] + 5\Delta_f H_m^\theta(\text{H}_2\text{O}, \text{l}) \\ &- \Delta_f H_m^\theta\{[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6] \cdot 4\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}\} \end{aligned} \quad (11)$$

the value of $\Delta_f H_d^\theta\{[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6] \cdot 4\text{H}_2\text{O}, \text{cr}\}$ of $313.6 \text{ kJ mol}^{-1}$ may be obtained from the values of $\Delta_f H_m^\theta\{[\text{Cd}(\text{NTO})_4\text{Cd}(\text{H}_2\text{O})_6] \cdot 4\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}\} = -1747.8 \text{ kJ mol}^{-1}$ and $\Delta_f H_m^\theta[\text{Cd}(\text{NTO})_2, \text{cr}] = -5.1 \text{ kJ mol}^{-1}$, obtained in this work, and the reported values $\Delta_f H_m^\theta[\text{H}_2\text{O}, \text{l}] = -285.83 \text{ kJ mol}^{-1}$ [2].

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