# Elevating the energetic capabilities of metal coordination compound by incorporating nitrate anions

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**Experimental Section**

Caution! All the compounds investigated are potentially explosive, energetic materials. Although we have experienced no difficulties in the syntheses and characterization of these compounds,

manipulations must be carried out by using appropriate standard safety precautions. Eye protection and leather gloves must be always worn.

**Materials and Methods:**

Reagents were purchased from Ak Scientifics, Acros Organics or Aldrich as analytical grade and were used as received. Melting and Decomposition temperatures (onset) were recorded using a dry nitrogen gas purge and at heating rate of 10 °C min$^{-1}$ on a differential scanning calorimeter (SDT650). IR spectra were recorded using Zn-Se pellets with ECO-ATR spectrometer (Bruker Alpha II). Density was determined at room temperature by employing Anton Par Ultra5000 gas pycnometer. Impact and friction sensitivity measurements were tested by employing a standard BAM Fall hammer and a BAM friction tester. The single-crystal X-ray data collection was carried out using Bruker APEX-II CCD diffractometer. The crystal was kept at 100 K during data collection Using Olex2[1]. The structure was solved with the olex2.solve[2] structure solution program using Charge Flipping and refined with the SHELXL[3] refinement package using Least Squares minimization. The non-covalent interactions and molecular drawings were studied using the Diamond program.[4]

**Synthesis of ECC1:**

Ni(NO$_3$)$_2$·6H$_2$O (58 mg, 0.2 mmol) was taken in 5 mL of water and added to the 5mL mixed solvent solution of NPAO (39 mg, 0.2 mmol) in water and methanol (1:1) and stirred the reaction mixture for 6 hrs at room temperature and observed the light green colored precipitate. The formed precipitate was filtered off, washed with water/methanol (10 mL each), and subsequently air-dried. Light green colored block-shaped single crystals of ECC1 were obtained in 10 days by slow evaporation of the solvent. Yield: 62%. Elemental Analysis Calculated for Ni$_2$N$_{16}$O$_{24}$C$_{10}$H$_{20}$: C,

13.87; H, 2.33; N, 25.89. Found: C, 13.41; H, 2.50; N, 26.04. $^1$H NMR (500 MHz, DMSO-d6): δ

(ppm) 14.50 (s, 1H), 9.04(s, 1H), 7.43 (s, 1H). $^{13}$C NMR (126 MHz, DMSO-d6): δ(ppm) 164.59,

149.98, 133.20, 131.84, 131.68. IR (ATR, ZnSe, cm$^{-1}$): 676, 773, 1052, 1180, 1437, 1515, 1705,

3020, 3340. IR (ATR ZnSe): 3437, 3336, 3097, 1664, 1507, 1392, 1338, 1260, 1051, 897, 816,

744 cm$^{-1}$.
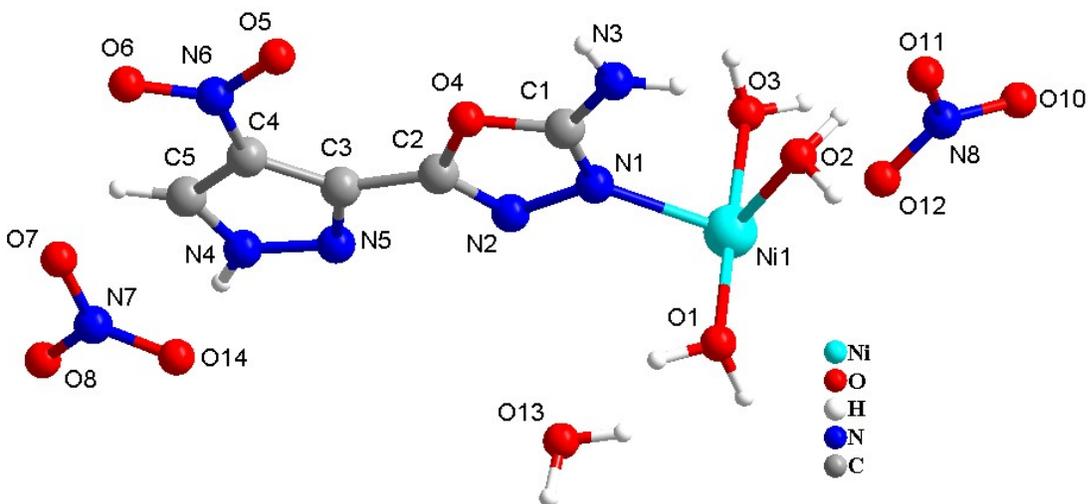




**Figure S1.** The asymmetric unit of ECC1.

**Table 1. Crystal data and structure refinement for ECC1.**

| CCDC NO. | **2325272** |
|---|---|

| | |
|---|---|
| Empirical formula | C10H22.6N16Ni2O25.3 |
| Formula weight | 889.26 |
| Temperature/K | 100.00 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 8.4655(8) |
| b/Å | 9.6141(9) |
| c/Å | 10.7999(10) |
| α/° | 91.342(3) |
| β/° | 104.194(3) |
| γ/° | 112.809(2) |
| Volume/Å3 | 778.58(13) |
| Z | 1 |
| ρcalcg/cm3 | 1.897 |
| μ/mm-1 | 1.336 |
| F(000) | 453.0 |
| Crystal size/mm3 | 0.12 × 0.11 × 0.1 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.528 to 50.094 |
| Index ranges | -10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -12 ≤ l ≤ 12 |
| Reflections collected | 8636 |
| Independent reflections | 2733 [Rint = 0.0549, Rsigma = 0.0548] |
| Data/restraints/parameters | 2733/0/256 |
| Goodness-of-fit on F2 | 1.067 |

Final R indexes [I>=2σ (I)]          R1 = 0.0439, wR2 = 0.1038

Final R indexes [all data]          R1 = 0.0524, wR2 = 0.1100

Largest diff. peak/hole / e Å-3          0.80/-0.65

**Table 2. Bond Lengths for ECC1.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| Ni1 | O3 | 2.056(3) | N2 | N1 | 1.399(4) |
| Ni1 | O2 | 2.039(3) | N2 | C2 | 1.287(5) |
| Ni1 | O6 | 2.021(3) | N5 | N4 | 1.339(4) |
| Ni1 | N2$^1$ | 2.122(3) | N5 | C3 | 1.333(5) |
| Ni1 | N5$^1$ | 2.099(3) | N1 | C1 | 1.321(5) |
| Ni1 | N1 | 2.060(3) | O7 | N7 | 1.246(4) |
| O4 | C2 | 1.349(4) | O12 | N8 | 1.243(4) |
| O4 | C1 | 1.366(4) | N6 | C4 | 1.427(5) |
| O13 | N6 | 1.232(4) | N4 | C5 | 1.337(5) |
| O14 | N7 | 1.255(4) | N3 | C1 | 1.308(5) |
| O10 | N8 | 1.260(4) | C2 | C3 | 1.451(5) |
| O8 | N7 | 1.256(4) | C3 | C4 | 1.403(5) |
| O11 | N8 | 1.273(4) | C4 | C5 | 1.378(5) |
| O5 | | N6 | 1.227(4) | | |

$^1$1-X,1-Y,1-Z

**Table 3. Bond Angles for ECC1.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O3 | Ni1 | N21 | 91.31(11) | C1 | N1 | N2 | 105.6(3) |
| O3 | Ni1 | N51 | 90.10(11) | O14 | N7 | O8 | 119.4(3) |
| O3 | Ni1 | N1 | 89.56(11) | O7 | N7 | O14 | 121.0(3) |
| O2 | Ni1 | O3 | 88.30(11) | O7 | N7 | O8 | 119.6(3) |
| O2 | Ni1 | N21 | 168.51(11) | O13 | N6 | C4 | 117.2(3) |
| O2 | Ni1 | N51 | 91.63(11) | O5 | N6 | O13 | 125.1(3) |
| O2 | Ni1 | N1 | 94.48(12) | O5 | N6 | C4 | 117.6(3) |
| O6 | Ni1 | O3 | 176.56(12) | O10 | N8 | O11 | 118.5(3) |
| O6 | Ni1 | O2 | 88.30(13) | O12 | N8 | O10 | 121.8(3) |
| O6 | Ni1 | N21 | 92.12(13) | O12 | N8 | O11 | 119.7(3) |
| O6 | Ni1 | N51 | 90.49(13) | C5 | N4 | N5 | 111.8(3) |
| O6 | Ni1 | N1 | 90.21(13) | O4 | C2 | C3 | 126.4(3) |
| N51 | Ni1 | N21 | 76.89(11) | N2 | C2 | O4 | 112.7(3) |
| N1 | Ni1 | N21 | 97.01(12) | N2 | C2 | C3 | 120.9(3) |
| N1 | Ni1 | N51 | 173.87(11) | N5 | C3 | C2 | 112.5(3) |
| C2 | O4 | C1 | 103.4(3) | N5 | C3 | C4 | 108.9(3) |
| N1 | N2 | Ni11 | 140.0(2) | C4 | C3 | C2 | 138.6(3) |
| C2 | N2 | Ni11 | 113.0(2) | C3 | C4 | N6 | 129.6(3) |
| C2 | N2 | N1 | 106.9(3) | C5 | C4 | N6 | 124.4(3) |
| N4 | N5 | Ni11 | 136.5(2) | C5 | C4 | C3 | 106.0(3) |
| C3 | N5 | Ni11 | 116.7(2) | N1 | C1 | O4 | 111.3(3) |
| C3 | N5 | N4 | 106.8(3) | N3 | C1 | O4 | 118.4(3) |
| N2 | N1 | Ni1 | 123.0(2) | N3 | C1 | N1 | 130.3(3) |
| C1 | N1 | Ni1 | 131.3(3) | N4 | C5 | C4 | 106.5(3) |

[1]1-X,1-Y,1-Z
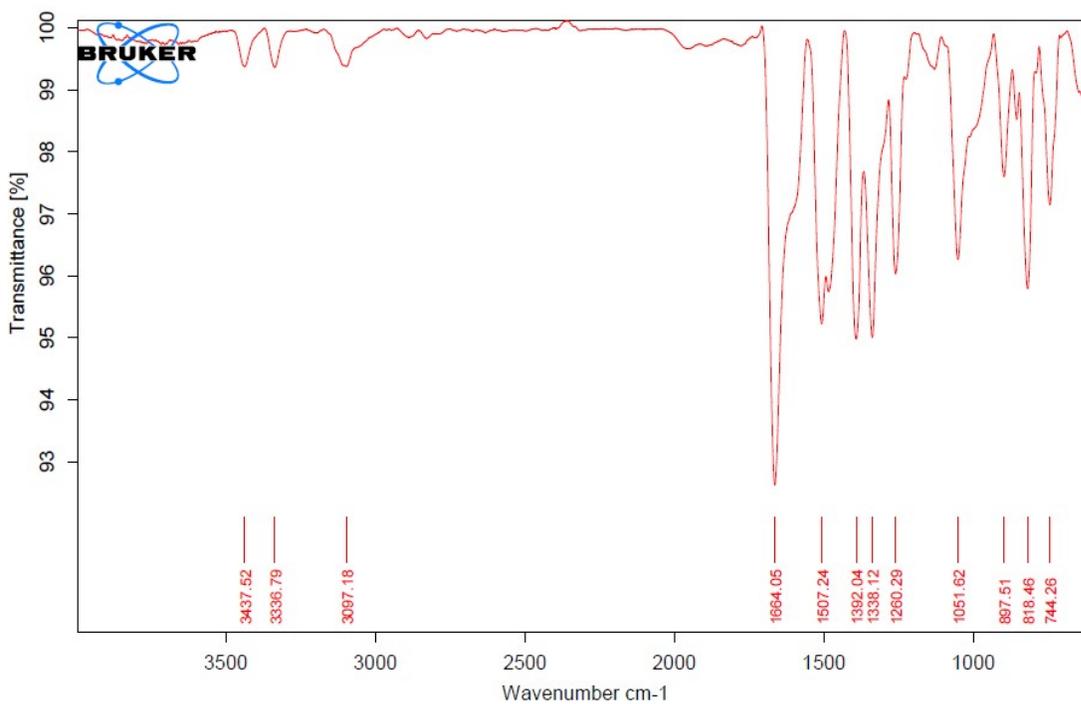


**Figure S2: IR Spectrum of ECC1.**
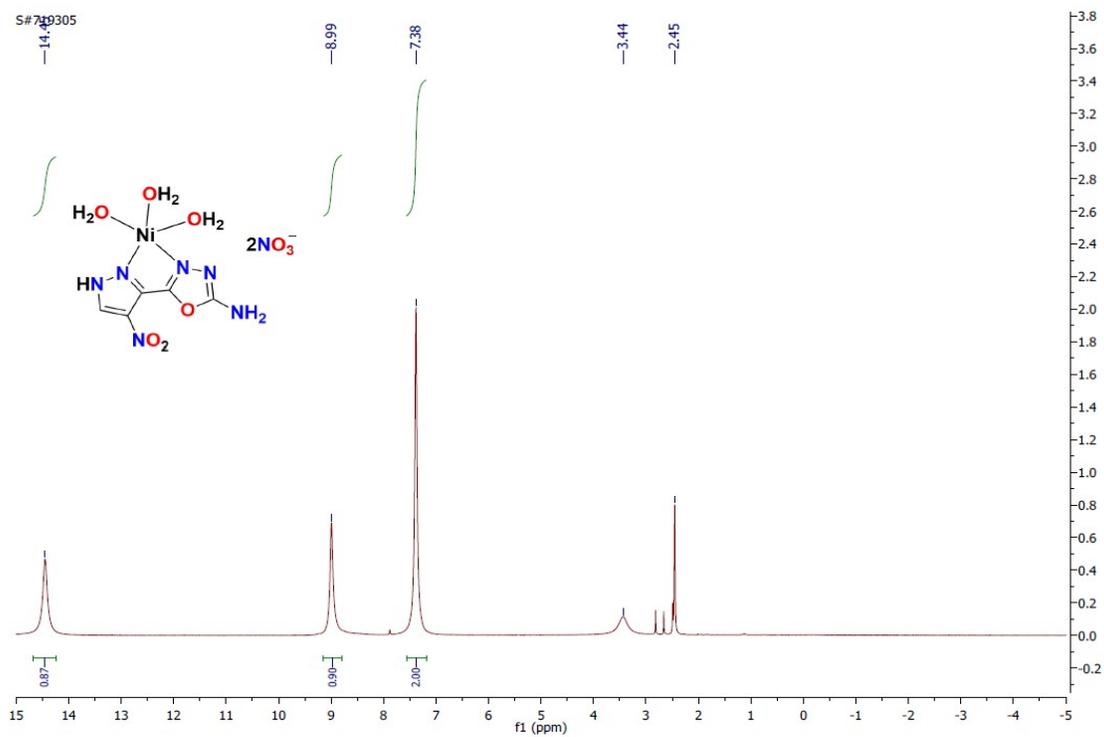
**Figure S3: ¹H NMR spectrum of ECC1.**
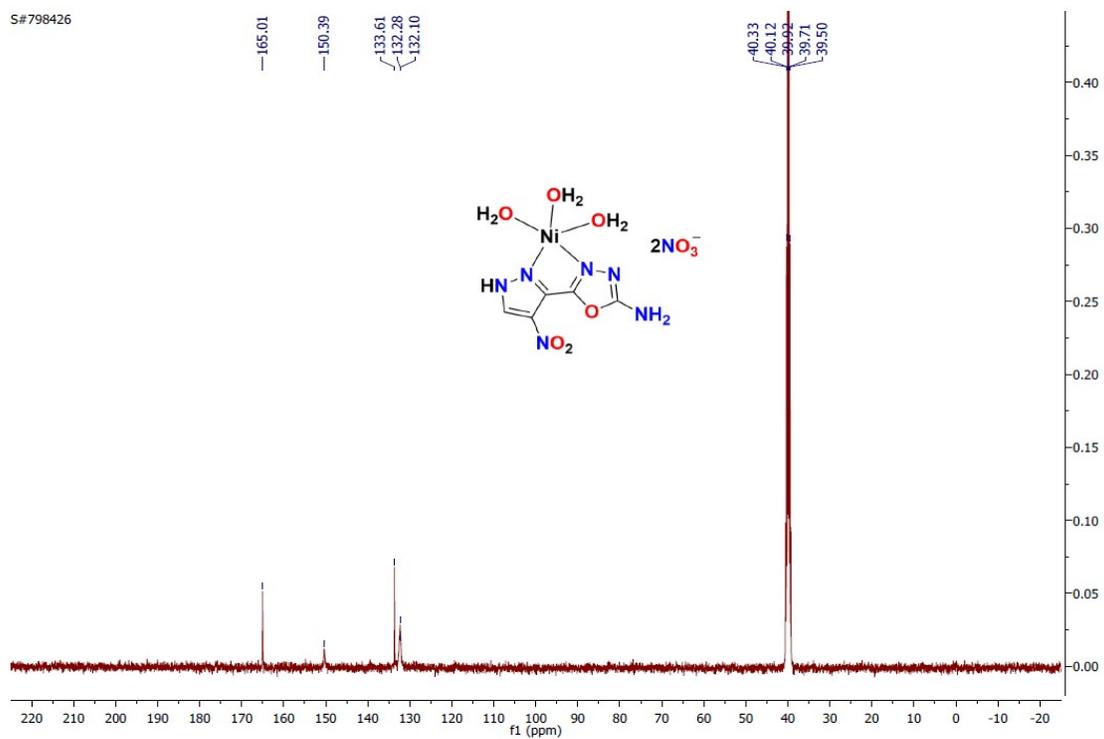


**Figure S4: ¹³C NMR spectrum of ECC1.**
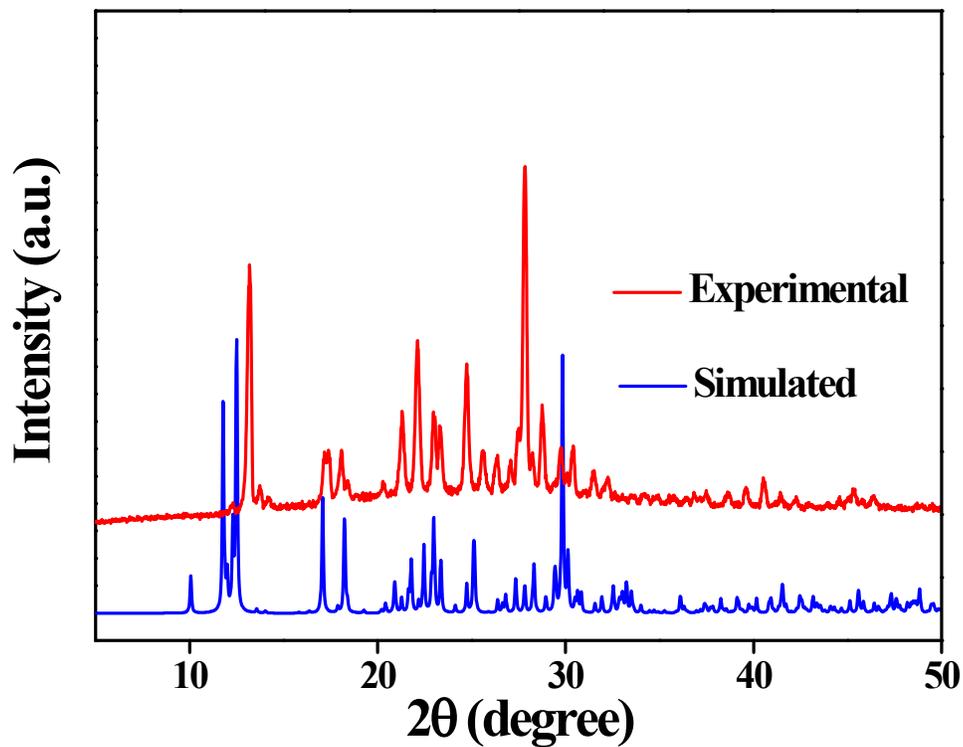
**Figure S5: PXRD Spectra of ECC1.**
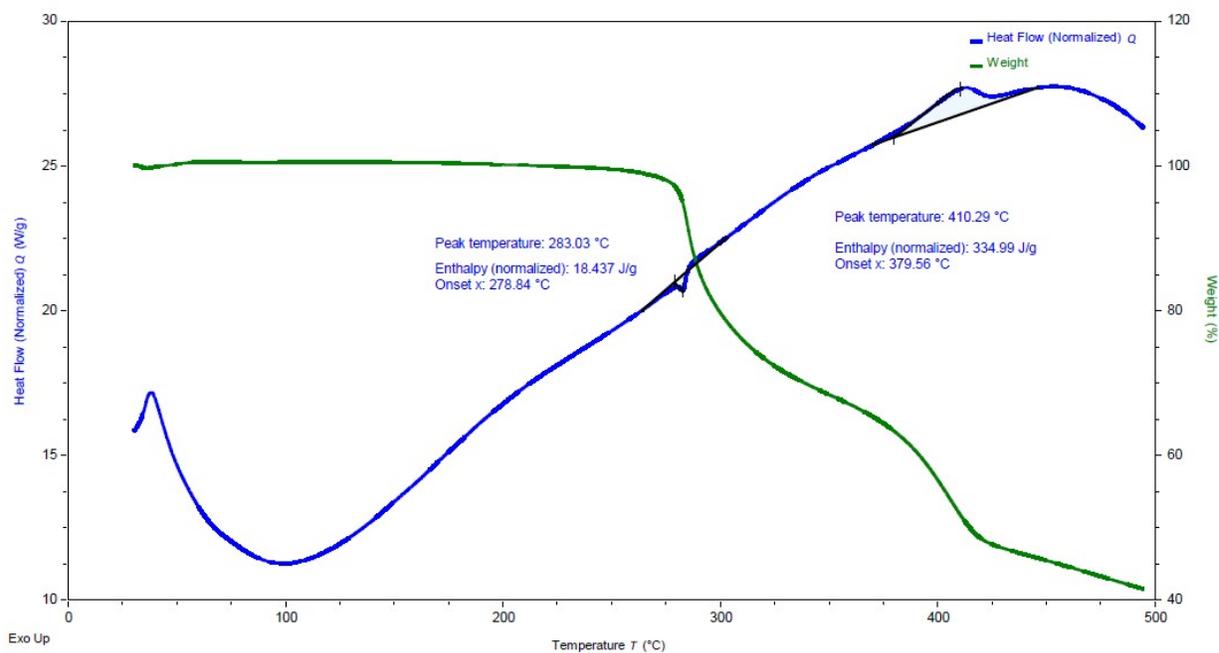


**Figure S6: TGA-DSC Spectra of ECC1.**

**Heat of combustion**

The heat of combustion is a vital indicator for evaluating the energetic properties of the explosives. The constant-volume combustion energies of the compounds were determined by a precise oxygen bomb calorimetry (Parr 6200 calorimeter). Approximately, 200 mg of compound and benzoic acid were mixed with a mass ratio of 1:3. The sample was sealed in a bomb, which subsequently burned in the pure oxygen atmosphere.

The $\Delta_c U$ value for ECC (**1**) are determined to be $-10.97$ kJ·g$^{-1}$. The enthalpies of combustion ($\Delta_c H^o$) of **1** are calculated to be $-10.92$ kJ·g$^{-1}$, on the basis of $\Delta_c H = \Delta_c U + \Delta n R T$, where $\Delta n = n_g$ (products) $- n_g$ (reactants), $R = 8.314$ J·mol$^{-1}$·K$^{-1}$, $T = 298.15$ K ($n_g$ is the total molar amount of gases in the products or reactants). The combustion equations of the complexes are as follows-

$$NiC_5H_{10}N_8O_{12}(s) + 2O_2(g) = NiO(s) + 5CO_2(g) + 5H_2O(l) + 4N_2(g) \quad (1)$$
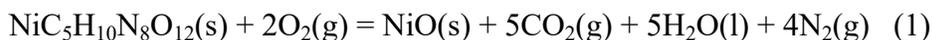
The $\Delta_f H^o$ values of ECCs **1** was calculated to be 2.53 kJ·g$^{-1}$, according to Hess's Law as shown in equation (2) with the known enthalpies of NiO (s, $-240.0$ kJ·mol$^{-1}$), H$_2$O (l, $-285.83$ kJ·mol$^{-1}$), and CO$_2$ (g, $-393.51$ kJ·mol$^{-1}$).

$$\Delta_f H^o[ECC1,s] = \Delta_f H^o[NiO,s] + 5\Delta_f H^o[CO_2,g] + 58\Delta_f H^o[H_2O,l] - \Delta_c H^o[ECC5,s] \quad (2)$$

**References**

1. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard J.A.K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339–341.

2. Bourhis, L. J.; Dolomanov, O.V.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment - Olex2 dissected. *Acta Cryst.* **2015**, *A71*, 59–75.

3. Sheldrick, G.M. Crystal Structure Refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3-8.

4. Bergerhoff, G.; Berndt, M.; Brandenburg, K. Evaluation of Crystallographic Data with the Program DIAMOND. *J. Res. Natl. Inst. Stand. Technol.* **1996**, *101*, 221–225.