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Crystal structure and the standard molar enthalpy of formation of a coordination polymer $[Cu(nip)(phen)]_n$

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Abstract

A coordination polymer $[Cu(nip)(phen)]_n$ was hydrothermally synthesized by the reaction of $Cu(NO_3)_2$ with 5-nitroisophthalic acid and phen. Single-crystal structure analysis showed that the complex crystallized in the monoclinic space group $P2_1/c$; $a = 10.6566(13)$; $b = 12.5931(15)$; $c = 13.0514(16)$ Å; $\beta = 95.474(2)°$, $V = 1743.5(4)$ Å^3; $Z = 4$. The standard molar enthalpy of formation of the complex was determined to be -554 ± 11 kJ mol^{-1}.

Keywords: $[Cu(nip)(phen)]_n$; Coordination polymer; Standard molar enthalpy of formation

1. Introduction

In the last decade, rapid developments in the crystal engineering of metal-organic coordination polymers have produced many novel materials with various structural features and properties. One of the most effective and attractive approaches for the assembly of polymeric frameworks is the incorporation of appropriate metal ions and multifunctional bridging ligands. By a judicious choice of the bridging ligand and metal ions, novel coordination polymers may be obtained [1–7].

In this paper, 5-nitroisophthalic acid (nip) as a bridging ligand, phenanthroline (phen) as a second ligand, are used with copper(II) ions to assemble a novel coordination polymer $[Cu(nip)(phen)]_n$. The structure was determined by single-crystal X-ray crystallography. The constant-volume combustion energy of the complex was determined by a rotating bomb calorimeter, and the standard combustion enthalpy and the standard formation enthalpy were calculated.

2. Experimental

2.1. Materials

5-Nitroisophthalic acid was obtained from Acros. Copper nitrate ($Cu(NO_3)_2\cdot3H_2O$), NaOH, and 1,10-phenanthroline ($C_{12}H_8N_2$) were of reagent grade and used without further purification.

2.2. Preparation of complex

A mixture of $Cu(NO_3)_2\cdot3H_2O$ (1.0 mmol), nip (1 mmol), phen (1.0 mmol), NaOH (2.0 mmol), and water (6 mL) was stirred in air for 15 min, then transferred and sealed in a 12-mL Teflon-lined reactor, which was heated at 150 °C for 5 days and then cooled to room temperature at a rate of 5 °C h^{-1}. Sky-blue prisms were obtained, washed with deionized water (yield 85% based on Cu). $C_{20}H_{11}N_3O_6Cu$ (452.86): calcd. C 53.04, H 2.45, N 9.28; found C 53.21, H 2.68, N 9.35. IR (KBr, cm^{-1}): 3097 s, 1645 s, 1516 s, 1448 s, 1423 s, 1344 s, 1186 m, 1072 m, 917 w, 856 m, 781 m, and 723 m.

2.3. Instrumentation

C, H, N contents were determined on a Perkin-Elmer 2400 elemental analyzer. Infrared spectra were recorded in KBr discs

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for 4000–400 cm^{-1} on a Bruker EQ UINOX-550 spectrophotometer. TG–DTG tests were performed in a Perkin-Elmer thermobalance under dynamic atmosphere of high purity N_2 (mass fraction 0.99999) with flow rate of 60 $cm^3\,min^{-1}$. The initial temperature and a heating rate were of 333 K and 10 K min^{-1}, respectively. The phase structure of the solid compound was identified by a Rigua D/max-HIC X-ray diffractometer using Cu Kα radiation.

2.4. *X-ray data collection of the complex*

Data were collected for a 0.22 mm × 0.12 mm × 0.08 mm crystal on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 296 K. A complex of $M_r = 452.86$ crystallized in the monoclinic space group $P2_1/c$; $a = 10.6566(13)$; $b = 12.5931(15)$; $c = 13.0514(16)$ Å; $\beta = 95.474(2)°$, $V = 1743.5(4)$ Å^3; $Z = 4$; $D_{calc} = 1.725$ Mg m^{-3}; Mo Kα $\lambda = 0.71073$ Å; $\mu = 1.301$ mm^{-1}. The data were corrected for Lorentz and polarization effects. An absorption correction was applied using the SADABS program [8]. 10,783 reflections were collected for the 2θ range 4.50–58.04°, and 4283 independent reflections with $I > 2\sigma(I)$ were used in the refinement, $R_{int} = 0.0153$. The structures were solved with the direct methods of SHELXS-97 [9] and refined with full-matrix least-squares technique using SHELXL-97. Non-hydrogen atoms were refined anistropically. All calculations were performed on a microcomputer using Shelxl-97 [10]. The hydrogen atoms of the organic ligands were generated geometrically.

2.5. *Determination of constant-volume combustion energy*

The constant-volume combustion energy of the compound was measured by an RBC-type II precision rotary-bomb combustion calorimeter. The structure and principle of the calorimeter have been described in detail elsewhere [11,12]. The temperature of the water bath was maintained at 298.15 ± 0.001 K.

The temperature rise was corrected for heat exchange with the surroundings [13].

The analyses of the combustion gas of reaction were done as descried in [14]. The amount of CO_2 (g) was determined from the weight increase in a tube containing alkali asbestos.

The total amount of nitric acid was obtained by titration with a standard solution of NaOH. The identity of the final solid product was checked by chemical analysis and XRD. The analyses of the combustion products indicated that the compound was combusted to CO_2 (g), H_2O (l), and CuO(s). NO_x and CO in the final gas phase were not formed.

NBS benzoic acid (sample 39i) was used for calibration of the calorimeter. The specific energy of combustion is $-26{,}434 \pm 3$ J g^{-1} under certificate conditions. The energy equivalent of the RBC-type II calorimeter, ε_{calor}, obtained from six calibration measurements was 17775.09 ± 7.43 J K^{-1}.

The combustion energy of the sample was calculated by the formula:

$$\Delta_c E(s) = \frac{W\,\Delta T - aG - 5.983b}{m} \qquad (1)$$

where $\Delta_c E$ (s) denotes the constant-volume combustion energy of the samples, W the energy equivalent of the calorimeter (J K^{-1}), ΔT the corrected temperature rise, a the length of Ni–Cr wire consumed (cm), G the combustion enthalpy of Ni–Cr wire for ignition (0.9 J cm^{-1}), 5.983 the formation enthalpy and solution enthalpy of nitric acid corresponding to 1 cm^{-3} of 0.1000 mol dm^{-3} NaOH (J cm^{-3}) and b the volume (cm^{-3}) of consumed 0.1000 mol dm^{-3} solution of NaOH and m the mass (g) of the sample.

3. Results and discussion

The IR spectra of the complex shows characteristic bands of the dicarboxylate groups in the usual region at 1645 and 1516 cm^{-1} for the asymmetric stretching and at 1448(s), 1344(s) for symmetric stretching. The separations (Δ) between $\nu_{as}(CO_2)$ and $\nu_{sym}(CO_2)$ are 197–172 cm^{-1}, which are attributed to the monodentate binding of the carboxylate groups [15].

Single-crystal analysis shows the complex crystallizes in monoclinic space group $P2_1/c$ and exists as a one-dimensional infinite chain. As shown in Fig. 1a, there is one Cu(II) atom, one bis(monodentate) nip ligand and one phen ligand in each independent crystallographic unit. Each Cu(II) is coordinated by two N atoms from the phen ligands (Cu1–N1 2.022(3), Cu1–N2 2.020(4) Å) and two O atoms from bis(monodentate) nip ligands (Cu1–O1 1.962(4), Cu1–O3A 1.930(5) Å) in a distorted square-planar geometry. Additionally, each pair of Cu(II) atoms are bridged by V-shaped nip ligands with bis(monodentate) coordination mode to give rise to an infinite single-stranded helical chain (shown in Fig. 1b). Furthermore, each Cu(1) center interacts weakly with O(1) (Cu1–O1 2.526(2) Å) from an adjacent chain positioned perpendicular to the $[CuN_2O_2]$ square plane, creating a pseudo-square-pyramid geometry. As a result, the single helical chains are further linked by Cu–O interaction to afford a two-dimensional network. In contrast to $[Cu_2(ipa)_2(phen)_2(H_2O)]_n$ [7], the phen ligands in $[Cu_2(ipa)_2(phen)_2(H_2O)]_n$ are alternately attached to both sides of a single-stranded helical chain, and are orientated either approximately parallel or perpendicular to the chain, while the phen ligands are located alternately at the same side of the helical chain parallel or perpendicularly in $[Cu(nip)(phen)]_n$ due to the nip ligand having more steric hindrance.

The TG–DTG curves of the complex are shown in Fig. 2. Thermal decomposition begins at 333 K and complete at 609 K with the mass loss of 82%. The complex is transformed to CuO via one-step; 82.13% is the calculated value of the mass loss.

The constant-volume combustion energy is 19,970 ± 11 J g^{-1} (S.D., $n = 6$).

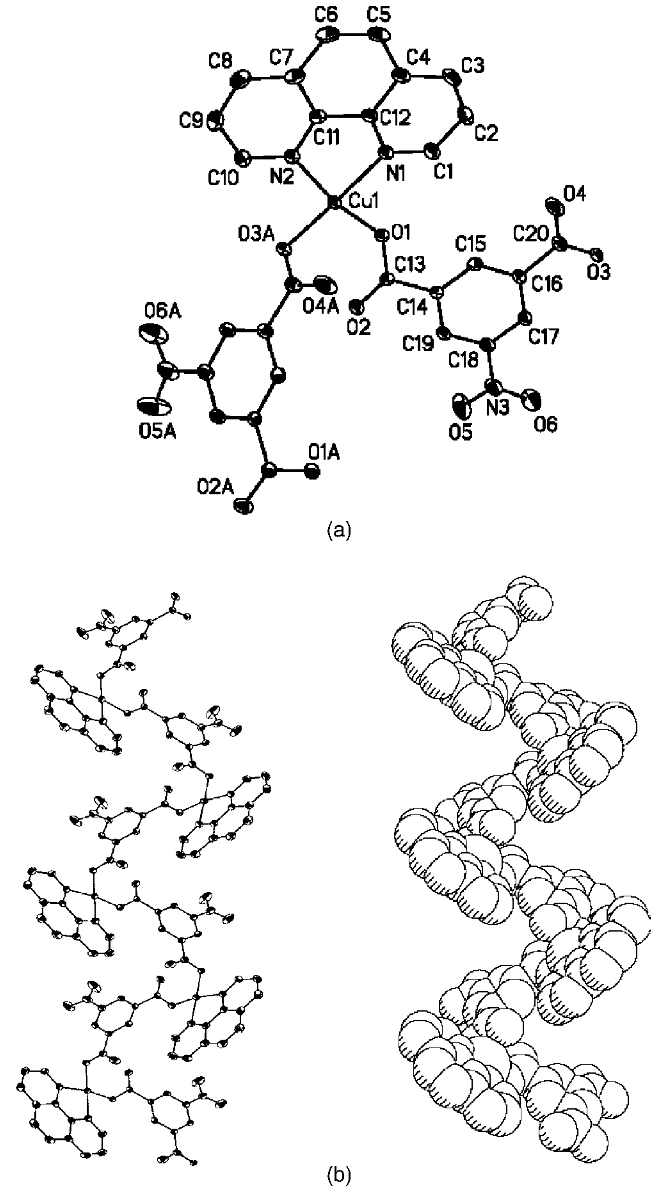

Fig. 1. The coordination environments of copper atoms (a) and single-stranded helical chain (b) in $[Cu(nip)(phen)]_n$.

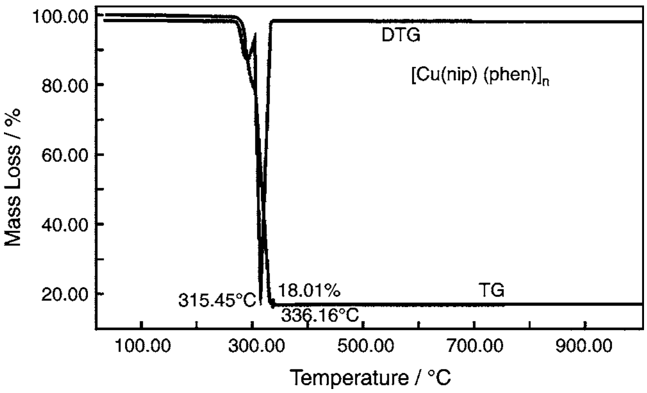

Fig. 2. The TG–DTG curves of the complex.

The standard combustion enthalpy of the compound, $\Delta_c H_m$, is represented:

$$[\mathrm{Cu(nip)(phen)}]_n(\mathrm{s}) + \tfrac{81}{4} n\mathrm{O_2}\,(\mathrm{g}) = n\mathrm{CuO}\,(\mathrm{s}) + 20n\mathrm{CO_2}\,(\mathrm{g}) + \tfrac{11}{2} n\mathrm{H_2O}\,(\mathrm{l}) + \tfrac{3}{2} n\mathrm{N_2}\,(\mathrm{g}) \quad (2)$$

$\Delta_c H_m$ at 298.15 K and 101.325 kPa was calculated by Eqs. (3) and (4):

$$\Delta_c H_m = \Delta_c E + \Delta n RT \quad (3)$$

$$\Delta n = n_g(\text{products}) - n_g(\text{reactants}) \quad (4)$$

where n_g is the total amount in mole of gases present as products or reactants and $k = 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$, to be $-9044 \pm 11\,\mathrm{kJ\,mol^{-1}}$.

The standard enthalpy of formation of the sample, $\Delta_c H_m^\theta$, was calculated by Hess's law according to the following thermochemical equation:

$$\Delta_{\mathrm{f,[Cu(nip)(phen)]}_n\,(\mathrm{s})} H_m^\theta = [n\Delta_{\mathrm{f,CuO\,(s)}} H_m^\theta + 20n\Delta_{\mathrm{f,CO_2\,(g)}} H_m^\theta + \tfrac{11}{2} n\Delta_{\mathrm{f,H_2O\,(l)}} H_m^\theta] - \Delta_{\mathrm{c,[Cu(nip)(phen)]}_n\,(\mathrm{s})} H_m^\theta \quad (5)$$

where $\Delta_{\mathrm{f,CuO\,(s)}} H_m^\theta = -155.23\,\mathrm{kJ\,mol^{-1}}$, $\Delta_{\mathrm{f,CO_2\,(g)}} H_m^\theta = -393.51 \pm 0.13\,\mathrm{kJ\,mol^{-1}}$, $\Delta_{\mathrm{f,H_2O\,(l)}} H_m^\theta = -285.83 \pm 0.042\,\mathrm{kJ\,mol^{-1}}$, to be $-554 \pm 11\,\mathrm{kJ\,mol^{-1}}$.

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