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Short communication

Structure analysis and the standard molar enthalpy of formation of a coordination polymer $[Co(TO)_2Cl_2]_n$ (TO = 1,2,4-triazole-5-one)

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Abstract

A coordination polymer was synthesized by the reaction of $CoCl_2$ with 1,2,4-triazole-5-one (TO) and charaterized by means of IR and TG–DTG. Single-crystal structure analysis showed that the complex crystallized in the monoclinic space group $C2/c$: $a = 23.105(9)$ Å, $b = 3.5683(2)$ Å, $c = 13.589(6)$ Å, $\alpha = 90°$, $\beta = 124.038(4)°$, $\gamma = 90°$, $V = 928.4(7)$ Å^3, $Z = 4$. The standard molar enthalpy of formation of the complex was determined to be $(-1034.28 \pm 0.95)\ \mathrm{kJ\,mol^{-1}}$.

Keywords: $[Co(TO)_2Cl_2]_n$; Coordination polymer; Standard molar enthalpy of formation

1. Introduction

Transition metal complexes with triazole derivatives have intrigued great interests in the past decades for their favorable application as functional materials, and most of the studies focus on the pharmaceutical application, photoluminescence properties, and magnetism of these metal coordination compounds [1–4]. Because the complexes of triazole derivatives and transition metal possess high enthalpies of formation and densities, they have been predicted the potential application as burning rate modifiers in the solid propellant. As a triazole derivative, the donor atoms (nitrogen and oxygen atoms) in the ring of 1,2,4-triazole-5-one make it coordinated with transition metals easily and form the insolvable precipitate, so it is difficult to raise the single crystals for these complexes in the solution [5]. The present work is one of our continuing studies on the synthesis, crystal structure and thermal properties of 1,2,4-triazole-5-one transition metal complex. In this communication, we have prepared the single crystal of the complex of TO with cobalt chloride in strong hydrochloride acid, and investigated thermal decomposition processes and the standard molar enthalpy of formation of $[Co(TO)_2Cl_2]_n$. We expect the contribution would benefit the potential application as burning rate modifiers in the solid propellant.

2. Experimental

2.1. Materials

$CoCl_2\cdot 6H_2O$(AR) was commercially available without further purification.

1,2,4-Triazole-5-one (TO) was synthesized using formic acid (88%, Xi'an Chemical Co.) and semicarbazide hydrochloride (99%, ACROS) according to the literature method, and the mp is 234.04 °C [6,7].

Benchmark benzoic acid was spectrum grade made by Shanghai No. 1 Reagent Company.

2.2. Preparation of complex

TO (1 mmol, 0.085 g) dissolved in water (5 mL) was mixed with ethanol solution (15 mL) of cobalt dichloride (0.5 mmol, 0.149 g) at 60 °C and a purple precipitate was obtained. Then, hydrochloric acid was added to the solution containing the precipitate until the solid dissolved. The clear solution was left at room temperature for 15 days to get the purple single crystals for X-ray investigation (48% yield based on cobalt dichloride). Anal. calcd for $CoC_4H_6N_6O_2Cl_2$,

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C, 16.02%; H, 2.02%; N, 28.02%; found: C, 16.45%; H, 2.38%; N, 27.79%. IR (KBr, cm^{-1}): υ (NH$^-$) 3428 cm^{-1}, υ (C–H) 2849 cm^{-1} (C=O) 1748 cm^{-1}, υ (C=N) 1567 cm^{-1}, υ (C–N) 1235 cm^{-1}, δ (framework of triazolone) 959, 779 and 529 cm^{-1}.

2.3. Instrumentation

C, H, N contents were determined on a Perkin-Elmer 2400 type elemental analyzer, IR spectra were measured using a Nicolet 60 SXR FT-IR (Nicolet, USA) spectrometer in the 4000–400 cm^{-1} region (KBr pellets). The TG–DTG experiments were performed with a Netzsch STA 449C instrument with heating rates 10 °C min^{-1}. The purge gas was N_2 (purity 99.999%) flowing of 30 mL min^{-1} and the sample mass is about 0.789 mg.

2.4. X-ray data collection of the complex

All single crystal X-ray experiments were performed on a Bruker Smart-1000CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using ω and φ scan modes within a range of $2.13 < \theta < 25.15$ at 273 K. The crystal size was 0.35 mm × 0.28 mm × 0.16 mm. Of 2064 measured reflections, 828 observes reflections with $I > 2\sigma(I)$ were used in the refinement. The single crystal structure of complex was solved by direct methods using SHELXS-97 [8] and all non-hydrogen atoms were located using subsequent difference Fourier maps. Non-hydrogen atoms were refined anistropically. All hydrogen atoms were placed in ideal geometry and were refined using a riding model. The crystal data and structure refinement details for the complex are given in Table 1.

Table 1
Crystallographic data for the complex

Empirical formula	$CoC_4H_6N_6O_2Cl_2$
Formula weight	299.98
Space group	*C2/c*
a (Å)	23.105(9)
b (Å)	3.5683(2)
c (Å)	13.589(6)
α (°)	90
β (°)	124.038(4)
γ (°)	90
V (Å^3)	928.4(7)
Z	4
D_c (mg m^{-3})	2.146
F (0 0 0)	596
Absorption coefficient (mm^{-1})	2.412
Limiting indices	$-24 \le h \le 26$, $-4 \le k \le 4$, $-15 \le l \le 16$
Goodness-of-fit on F^2	1.085
R (int)	0.0216
R_1, $wR_2(I > 2\sigma(I))$	0.0348, 0.0943
R_1, wR_2(all data)	0.0394, 0.0967
$\Delta\rho_{\max}$ and $\Delta\rho_{\min}$ (e Å^{-3})	0.796, 0.523

2.5. Determination of the constant-volume combustion energy

The constant-volume combustion energy of the complex was determined by a precise rotating bomb calorimeter (RBC-type II). The main experimental procedures were described previously [9]. The initial temperature was regulated to (25.0000 ± 0.001) °C, and the initial oxygen pressure was 2.5 MPa. The correct value of the heat exchange was calculated according to the Linio–Pyfengdelel–Wsava formula [10]. The calorimeter was calibrated with benzoic acid of 99.999% purity. It had an isothermal heat of combustion at 25 °C of (−26434 ± 3) J g^{-1}. The energy equivalent of the calorimeter was determined to be (17936.01 ± 9.08) kJ K^{-1}. The analytical methods to analyze final products (gas, liquid and solid) were the same as reported in Ref. [9]. The analytical results indicate that the combustion reactions were complete. As a result, either carbon deposits or carbon monoxide formed during the combustion reactions and the amounts of NO_x in the final gas phase were negligible.

The constant-volume combustion energy of the complex was measured by six experiments and the method used was the same as that for calibration of the calorimeter with benzoic acid. The combustion energies of the complex were calculated according to Ref. [9].

$$\Delta_c U = \frac{W\Delta T - aG - 5.983b}{m} \tag{1}$$

where $\Delta_c U$ is the constant-volume combustion energy of the complex, W the energy equivalent of the RBC-type II calorimeter (in J K^{-1}), ΔT the correct value of the temperature rising, a the length of actual Ni–Cr wire consumed (in 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 mL of 0.1000 mol L^{-1} solution of NaOH (in J ml^{-1}), b the volume in mL of consumed 0.1000 mol L^{-1} solution of NaOH and m is the mass in g of the sample.

3. Results and discussion

As shown in Fig. 1, the Co(II) atom is coordinated by four Cl$^-$ ions (Co(1)–Cl(1)$^{\text{ii}}$ 2.4835 Å, Co(1)–Cl(1)$^{\text{iii}}$ 2.4835 Å, Co(1)–Cl(1) 2.4898 Å, Co(1)–Cl(1)$^{\text{i}}$ 2.4898 Å) in the equatorial plane and two axial (N_2) atoms from two TO lignads (Co(1)–N(2)$^{\text{i}}$ 2.1563 Å, Co(1)–N(2) 2.1563 Å) which leads to a typical octahedral environment. Selected bond lengths and angles are shown in Table 2. Each pair of Co(II) atoms is bridged by two Cl$^-$ ions to form a one-dimensional chain (Fig. 2). The hydrogen bonds of the title complex have been examined by PLATON 98, and all interatomic distances and corresponding angles are in the normal range (see Table 3). The hydrogen bonds formed between the donor atoms (N(1), N(3), C(1) atoms of the TO ligands), the acceptor O(1) of the TO ligand and the coordinated Cl$^-$ ion leads to the formation of a two-dimensional layer in the (0 1 0) plane. These layers together with the chains running along [0 1 0] form the three-dimensional structure of the title compound (Fig. 3).

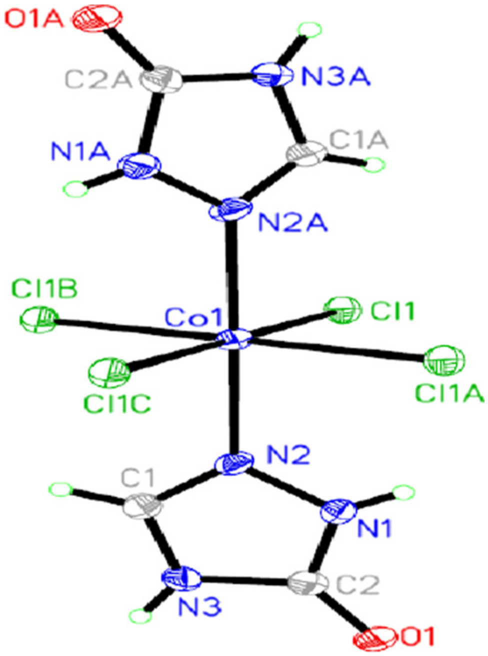

Fig. 1. The coordination environment of cobalt atoms with 50% thermal ellipsoid probability.

Table 2
Selected bond lengths (Å) and bond angles (°)

Co(1)–N(2)^{i}	2.156(3)	Co(1)–N(2)	2.156(3)
Co(1)–Cl(1)^{ii}	2.4835(1)	Co(1)–Cl(1)^{iii}	2.4835(1)
Co(1)–Cl(1)	2.4898(1)	Co(1)–Cl(1)^{i}	2.4898(1)
N(1)–C(2)	1.365(5)	N(1)–N(2)	1.388(5)
O(1)–C(2)	1.244(5)	N(2)–C(1)	1.298(5)
N(3)–C(1)	1.379(5)	N(3)–C(2)	1.386(6)
N(2)^{i}–Co(1)–N(2)	177.07(2)	N(2)^{i}–Co(1)–Cl(1)^{ii}	91.87(1)
N(2)–Co(1)–Cl(1)^{ii}	90.23(1)	N(2)^{i}–Co(1)–Cl(1)^{ii}	90.23(1)
N(2)–Co(1)–Cl(1)^{iii}	91.87(1)	Cl(1)^{ii}–Co(1)–Cl(1)^{iii}	88.45(6)
N(2)^{i}–Co(1)–Cl(1)	89.76(1)	N(2)–Co(1)–Cl(1)	88.13(1)
Cl(1)^{ii}–Co(1)–Cl(1)	91.70(4)	Cl(1)^{iii}–Co(1)–Cl(1)	179.86(4)
N(2)^{i}–Co(1)–Cl(1)^{i}	88.13(1)	N(2)–Co(1)–Cl(1)^{i}	89.76(1)
Cl(1)^{ii}–Co(1)–Cl(1)^{i}	179.86(4)	Cl(1)^{iii}–Co(1)–Cl(1)^{i}	91.70(4)
Cl(1)–Co(1)–Cl(1)^{i}	88.16(6)		

Symmetry codes: (i) $-x+1, y, -z+3/2$; (ii) $x, y+1, z$; (iii) $-x+1, y+1, -z+3/2$.

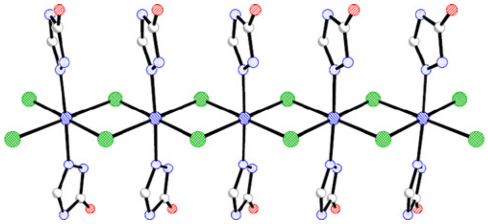

Fig. 2. The one-dimensional chain bridged by Cl^- ions.

Table 3
Hydrogen bond distance (Å) and angles (°) of the complex

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(3)–H(3)···O(1)^{v}	0.84(5)	2.02(5)	2.823(5)	161(5)
N(1)–H(2A)···O(1)^{vi}	0.77(5)	2.16(5)	2.878(5)	155(5)
C(1)–H(1)···Cl(1)	0.93	2.78(4)	3.487(4)	133(2)

Symmetry codes: (v) $-x+3/2, y-1/2, -z+5/2$; (vi) $-x+3/2, -y+3/2, -z+2$.

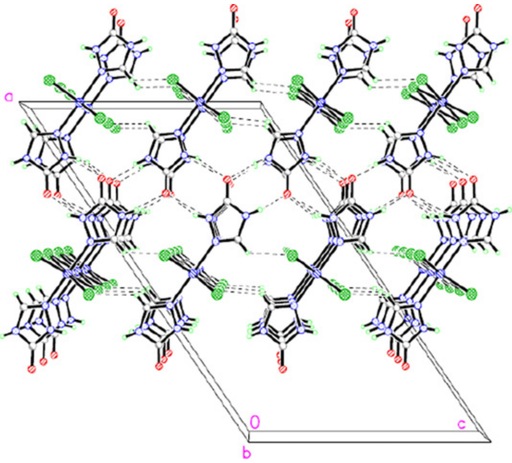

Fig. 3. Packing arrangement of the title complex views along the *b* direction.

The TG–DTG curves of the complex are shown in Fig. 4. The thermal decomposition processes start at 363.5 K and are completed at 496.4 K being accompanied by a mass loss of 58.6%. The mass loss of 58.6% is in agreement with the emission of the TO molecule (calc. 56.7%) [11,12], which should be considered as the break of the triazole ring. The residues are further decomposed as cobaltous oxide at 741 K with the residue amount 25.4% (cal. 25.0%). The final decomposition residue cobaltous oxide is identified by XPRD and IR spectrum. The decomposition temperature of the title complex is higher than that prepared with the same ligand, indicating the thermal stability of the title complex [11,12].

The constant-volume combustion energy of the complex was measured by six experiments. The method used was the same as that for calibration of the calorimeter with benzoic acid and the constant-volume combustion energy was determined as $(-1545.13 \pm 0.79)\ \mathrm{kJ\,mol^{-1}}$ (see Table 4).

The standard combustion enthalpy of the complex, $\Delta_c H_m^\theta$ ($[Co(TO)_2Cl_2]_n$, s, 298.15 K), was referred to the combustion enthalpy change of the following ideal combustion reaction at 298.15 K and 100 kPa.

$$[\mathrm{Co(TO)_2Cl_2}]_n(\mathrm{s}) + \tfrac{9}{2}n\mathrm{O_2(g)} = n\mathrm{CoO(s)} + 4n\mathrm{CO_2(g)} + 2n\mathrm{H_2O(l)} + 2n\mathrm{HCl(g)} + 3n\mathrm{N_2(g)} \quad (2)$$

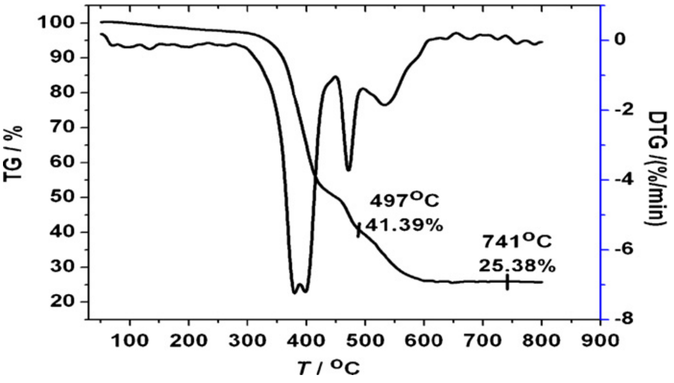

Fig. 4. TG–DTG curves of the complex $[Co(TO)_2Cl_2]_n$ with the heating rate $10\,^{\circ}\mathrm{C\,min^{-1}}$.

Table 4
the six experimental result of constant-volume combustion energy ΔcU ($J\,g^{-1}$)

No.	Mass of sample, m (g)	Calibrated heat of combustion wire Q_c (J)	Calibrated heat of acid Q_N (J)	Calibrated ΔT (K)	Combustion energy of sample $-\Delta_C U$ ($J\,g^{-1}$)
1	1.15690	12.60	350.00	0.3561	5157.84
2	1.20362	12.60	363.01	0.3699	5150.63
3	1.21538	12.60	367.55	0.3732	5145.32
4	1.20041	12.60	361.52	0.3695	5159.72
5	1.19875	12.60	361.14	0.3682	5147.90
6	1.18960	11.70	358.38	0.3651	5144.25
Mean					5150.78 ± 2.65

The standard combustion enthalpy of the complex was calculated by the following equations:

$$\Delta_c H_m^\theta = \Delta_c U + \Delta n RT \quad (3)$$

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

where n_g is the total amount in mole of gases present as products or as reactants, $R = 8.314\,J\,K^{-1}\,mol^{-1}$, $T = 298.15\,K$. The result is (-1533.98 ± 0.79) $kJ\,mol^{-1}$.

The Standard enthalpies of formation of the complex, $\Delta_f H_m^\theta$ was calculated by Hess's law according to the above thermochemical equations:

$$\begin{aligned}\Delta_f H_m^\theta([Co(TO)_2Cl_2]_n, s, 298.15\,K) &= n\Delta_f H_m^\theta(CoO, s)+4n\Delta_f H_m^\theta(CO_2, g)+2n\Delta_f H_m^\theta(H_2O, l)\\ &\quad +2n\Delta_f H_m^\theta(HCl, g) - \Delta_c H_m^\theta([Co(TO)_2Cl_2]_n, s) \quad (5)\end{aligned}$$

When $\Delta_f H_m^\theta(CO_2, g, 298.15\,K) = (-393.51 \pm 0.13)\,kJ\,mol^{-1}$, $\Delta_f H_m^\theta(H_2O, l, 298.15\,K) = (-285.83 \pm 0.042)\,kJ\,mol^{-1}$ [13], the results obtained is (-1034.28 ± 0.95) $kJ\,mol^{-1}$.

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References

[1] J.P. Zhang, Y.Y. Lin, X.C. Huang, X.M. Chen, J. Am. Chem. Soc. 127 (2004) 5495.

[2] R.W. Clark, P.J. Squattrito, A.K. Sen, S.N. Dubey, Inorg. Chim. Acta 293 (1999) 61.

[3] G. Vos, R.A. le Fêbre, R.A.G. de Graaff, J.G. Haasnoot, J. Reedijk, J. Am. Chem. Soc. 105 (1983) 1682.

[4] J.R. Song, R.Z. Hu, B. Kang, F.P. Li, Thermochim. Acta 331 (1999) 49.

[5] J.G. Haasnoot, Coordin. Chem. Rev. 200–202 (2000) 131.

[6] M.M. Boudakian, D.A Fidler, US Patent 4,927,940, May 22, 1990.

[7] J.R. Li, B.R. Chen, Y.X. Ou, Energ. Mater. 6 (3) (1998) 107 (in Chinese).

[8] G.M. Sheldrick, SHELX-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.

[9] X.W. Yang, S.P. Chen, S.L. Gao, H.Y. Li, Q.Z. Shi, Instrum. Sci. Technol. 30 (3) (2002) 311.

[10] M.M. Popov, Thermometry and Calorimetry, Moscow University Publishing House, Moscow, 1954, p. 382.

[11] N. Li, S.P. Chen, S.L. Gao. J. Therm. Anal. Cal. doi:10.1007/s10973-006-7600-8, On Line, Feb. 13, 2007.

[12] G.X. Ma, T.L. Zhang, J.G. Zhang, K.B. Yu, Z. Anorg, Allg. Chem. 630 (2004) 423.

[13] J.D. Cox, J. Chem. Thermodyn. 10 (1978) 903.