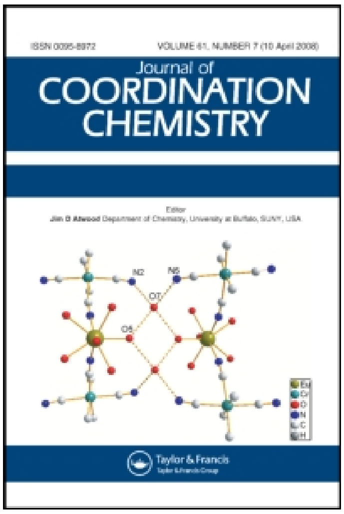

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Synthesis, characterization and density functional calculations on dichloro-<i>bis</i>(4-dimethylaminopyridine) cobalt(II) complex $[Co(II)(C_7H_{10}N_2)_2Cl_2]$

Fangfang Jian[a]; Jian Zheng[a]; Pusu Zhao[a]; YuFeng Li[a]
[a] New Materials & Function Coordination Chemistry Laboratory, Qingdao University of Science and Technology, Qingdao, P.R. China

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Synthesis, characterization and density functional calculations on dichloro-*bis*(4-dimethylaminopyridine) cobalt(II) complex [Co(II)$(C_7H_{10}N_2)_2Cl_2$]

FANGFANG JIAN, JIAN ZHENG, PUSU ZHAO* and YUFENG LI

New Materials & Function Coordination Chemistry Laboratory,
Qingdao University of Science and Technology, Qingdao 266042, P.R. China

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The title complex, [Co(II)$(C_7H_{10}N_2)_2Cl_2$], has been synthesized and characterized by elemental analysis, UV-vis spectra and X-ray single crystal diffraction. It crystallizes in the monoclinic system, space group *P*2/*c*, with lattice parameters $a = 8.1370(16)$ Å, $b = 6.4990(13)$ Å, $c = 16.416(5)$ Å, $\beta = 98.99(3)^\circ$ and $Z = 2$. The crystal structure of the title compound consists of monomeric molecules of [Co(II)$(C_7H_{10}N_2)_2Cl_2$] with C_2 symmetry and the two-fold axis through the Co(II) ion and the mid-point of two Cl^- anions. TG/DTG data indicate that thermal decomposition of the compound takes place in two steps and the residue is Co. Density functional theory (DFT) calculations of the structure, electronic spectra, natural population analysis and the thermodynamic properties at different temperatures have been performed. The calculated results show that electronic transitions are mainly derived from the contribution of an intraligand (IL) $\pi \rightarrow \pi^*$ transition, metal-to-ligand charge transfer (MLCT) and d–d transition. Bond strength of Co–Cl is stronger than that of Co–N, which agrees with the experimental data. The correlation equations of the thermodynamic properties of $C^0_{\mathrm{p,m}}$ and S^0_{m} with temperature are also obtained.

Keywords: Crystal structure; Electronic spectra; Thermal stability; Thermodynamic property; DFT calculations

1. Introduction

Cobalt(II) complexes CoL_2Cl_2 with L denoting pyridine (py), 2-picoline(pic), 3-pic, 4-pic, some lutidines and collidines, have been described in the literature [1–13]. Structural studies of these compounds have shown them to be capable of polymerization, whereby the cobalt atom assumes either an octahedral environment as highlighted by the violet $Co(py)_2Cl_2$ compound [1–3] or tetrahedral displayed by the blue $Co(py)_2Cl_2$ [1–3] and Co(4-pic)$_2$Cl$_2$ [4] compounds. These results have shown that the structure is dependent on the nature of the pyridine ring substituent [5]. Thermal behavior of these compounds has also been studied and their decomposition steps determined [5–13]. To the best of our knowledge, study on dichloro-*bis* (4-dimethylaminopyridine)cobalt(II) [Co(II)$(C_7H_{10}N_2)_2Cl_2$] is not available. The vast

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*Corresponding author. Email: zhaopusu@163.com

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development of computational chemistry in the past decade allows theoretical modeling of transition metal chemistry. Many important chemical and physical properties can be predicted from first principles by various computational techniques [14]. Among numerous calculation methods, density functional theory (DFT) is recognized as a better tool in the study of transition metal chemical systems than traditional Hartree–Fock (HF) or Möller–Plesset perturbation theory at the second-order (MP2) methods [15, 16], due to the fact that it is computationally less demanding for inclusion of electron correlation and gives better and more reliable descriptions of the geometries, dipole moment and vibrational frequency. Herein, we report the synthesis and characterizations as well as the DFT calculational results on the title complex.

2. Experimental and calculational methods

2.1. *Physical measurements*

Elemental analyses for carbon, hydrogen and nitrogen were performed using a Perkin-Elmer 240C elemental instrument. Thermal gravimetric (TG) and differential analysis (DTA) were recorded on a SDT 2980 simultaneously for the samples of ca 10 mg under nitrogen (150 mL min^{-1}) at a heating rate of 20°C min^{-1}. Ultraviolet (UV) spectra were recorded in a GBC UV/vis spectrophotometer.

2.2. *Preparation of [Co(II)($C_7H_{10}N_2$)$_2$$Cl_2$]*

All chemicals were of analytical grade and used without further purification. To a warm solution of 4-dimethylaminopyridine (1.2 g, 10.0 mmol) in EtOH (50 mL) was added with stirring [$CoCl_2 \cdot 6H_2O$] (1.2 g, 5.0 mmol) and the mixture was refluxed for 40 min. The blue solution was filtered, and the filtrate was evaporated by heating. A blue solid appeared, which was separated by filtration. Yield 1.9 g (50%). Crystals suitable for an X-ray structure determination were obtained by slowly evaporating an acetonitrile solution of the compound in air. The C, H and N content were determined by elemental analysis: Anal. Calcd for [Co(II)($C_7H_{10}N_2$)$_2$$Cl_2$] (%): C, 44.94; H, 5.39; N, 14.98. Found: C, 44.79; H, 5.11; N, 14.72.

2.3. *Crystallographic data collection and solution of structure*

A summary of the key crystallographic information is given in table 1. The diffraction data were collected on a Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å, $T = 293$ K). The technique used was ω-scan with limits 2.51 to 26.19°. The structure of the title compound was solved by direct methods and refined by least squares on F^2 by using SHELXTL [17]. All non-hydrogen atoms were anisotropically refined. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final conventional $R = 0.0455$ and $R_w = 0.1232$ were obtained for 1324 reflections with $I > 2\sigma(I)$ using the weighting scheme, $w = 1/[\sigma^2(F_o^2) + (0.0883P)^2 + 0.2904P]$, where $P = (F_o^2 + 2F_c^2)/3$. The molecular graphics were plotted using SHELXTL.

Table 1. Summary of crystallographic results for the title compound.

Empirical formula	$C_{14}H_{20}Cl_2CoN_4$
Formula weight	374.17
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P2/c$
Unit cell dimensions (Å, °)	
a	8.1370(16)
b	6.4990(13)
c	16.416(5)
β	98.99(3)
Volume (Å^3)	857.5(4)
Z, Calculated density (Mg m^{-3})	2, 1.449
Absorption coefficient (mm^{-1})	1.310
$F(000)$	386
Crystal size (mm^3)	$0.25 \times 0.20 \times 0.18$
θ range for data collection (°)	2.51–26.19
Limiting indices	$-9 \leq h \leq 0$, $-7 \leq k \leq 0$, $-19 \leq l \leq 20$
Reflections collected/unique	1770/1650 [$R_{\text{int}} = 0.0394$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1650/0/97
Goodness-of-fit on F^2	1.048
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0455$, $wR_2 = 0.1232$
R indices (all data)	$R_1 = 0.0608$, $wR_2 = 0.1339$
Extinction coefficient	0.028(5)
Largest diff. peak and hole (e Å^{-3})	0.780 and −0.396

Atomic scattering factors and anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* [18].

2.4. *Theoretical methods*

The initial molecular geometry of dichloro-*bis*(4-dimethylaminopyridine) was obtained from its crystal structure. Then, DFT calculations with a hybrid functional B3LYP (Becke's three-parameter hybrid functional using the LYP correlation functional) at basis set LANL2DZ by the Berny method [19] were performed with the Gaussian 03 software package [20]. The vibrational frequencies calculated proved that the structure is stable (no imaginary frequencies). The thermodynamic properties of the title compound at different temperature have been obtained according to the vibrational analyses. Natural bond orbital (NBO) analyses and the time-dependent density functional theory (TD-DFT) [21–24] calculations of electronic absorption spectra were performed on the optimized structure.

All calculations were performed on a Pentium IV computer using the default convergence criteria.

3. Results and discussion

3.1. *Crystal structure and optimized geometry*

Figure 1 shows a perspective view of the title compound with atom numbering scheme and figure 2 shows a perspective view of the crystal packing in

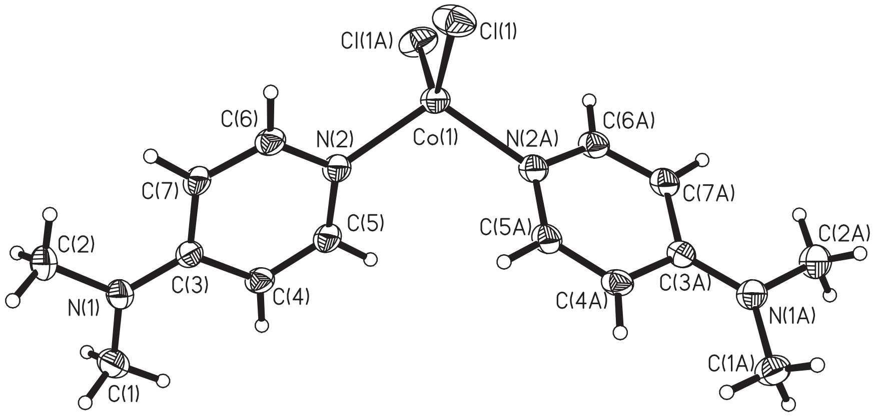


Figure 1. Molecular structure for the title compound with the atomic numbering scheme.

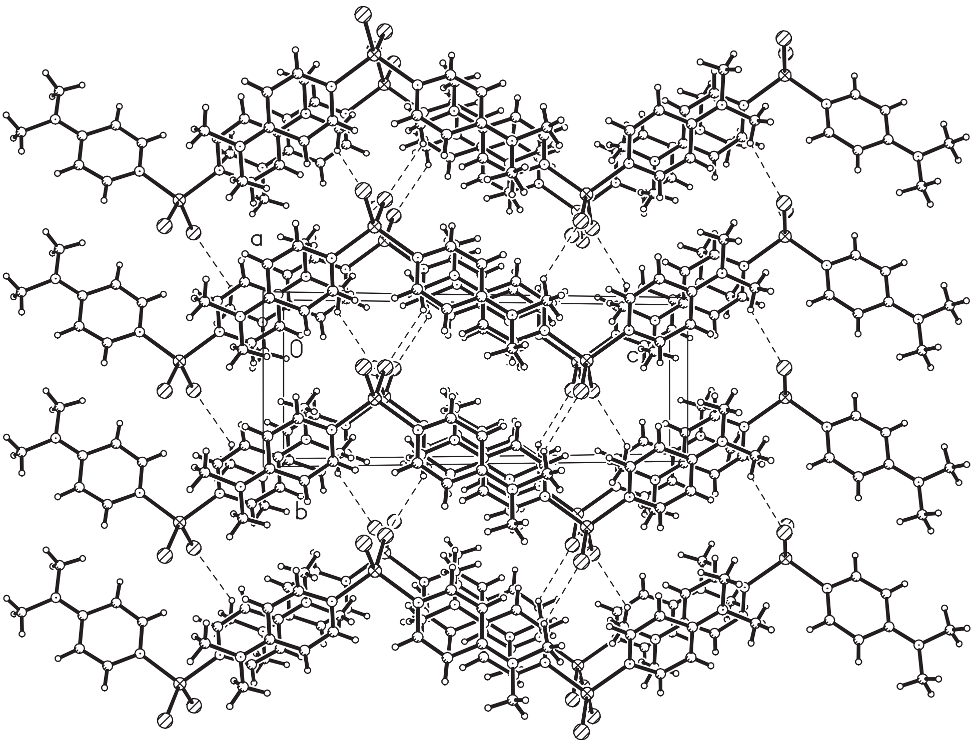


Figure 2. A view of the crystal packing down the *a* axis for the title compound.

the unit cell. Selected bond lengths and angles are presented in table 2 along with the optimized geometric parameters.

The crystal structure of the title complex is built of discrete monomer molecules. The central cobalt(II) ion is coordinated by two Cl^{-} anions and two

Table 2. Selected bond lengths (Å) and angles (°) of the title compound.

	Exp.	Calcd
Co(1)–N(2)	2.079(3)	2.0570
Co(1)–Cl(1)	2.2075(11)	2.3321
N(1)–C(1)	1.455(4)	1.4710
N(1)–C(2)	1.433(4)	1.4711
C(3)–C(7)	1.420(4)	1.4289
N(1)–C(3)	1.402(4)	1.3800
N(2)–C(5)	1.360(4)	1.3651
N(2)–C(6)	1.315(4)	1.3653
C(3)–C(4)	1.383(4)	1.4291
N(2)–Co(1)–N(2A)	110.40(14)	116.360
N(2A)–Co(1)–Cl(1)	102.53(8)	102.385
N(2A)–Co(1)–Cl(1A)	113.18(7)	102.285
C(3)–N(1)–C(1)	125.90(3)	120.197
C(1)–N(1)–C(2)	112.10(3)	119.590
C(7)–C(3)–C(4)	111.20(3)	116.248
N(2)–C(6)–C(7)	124.80(3)	122.940
N(2)–Co(1)–Cl(1)	113.18(7)	102.286
N(2)–Co(1)–Cl(1A)	102.53(8)	102.384
Cl(1)–Co(1)–Cl(1A)	115.34(6)	132.196
C(3)–N(1)–C(2)	121.60(3)	120.180
C(5)–N(2)–C(6)	111.40(3)	117.758
C(5)–C(4)–C(3)	120.80(3)	120.012
C(6)–C(7)–C(3)	123.90(2)	120.050

Table 3. Intermolecular interactions and C–H $\cdots\pi$ supramolecular interaction.

D–H $\cdots$ A	Symmetry	D $\cdots$ A (Å)	∠D–H $\cdots$ A (°)
C(1)–H(1C) $\cdots$ Cl(1)	$2-x,\ -y,\ -z$	3.6990	158.60
C(2)–H(2A) $\cdots$ Cl(1)	$2-x,\ -1-y,\ -z$	3.5661	145.37
C(5)–H(5A) $\cdots$ Cl(1)	$2-x,\ 1+y,\ 1/2-z$	3.5781	138.77
C(1)–H(1B) $\cdots$ Cl(1)	$1-x,\ -y,\ -z$	3.660(3)	149.13

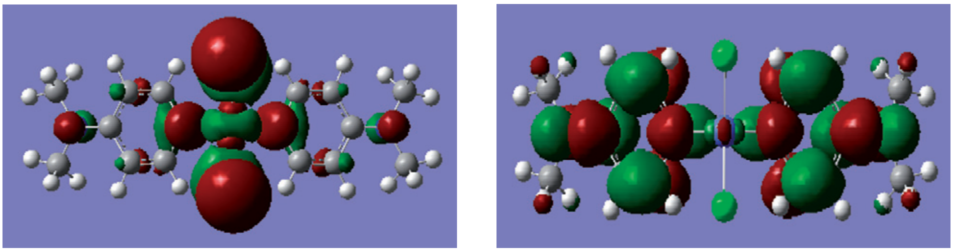
4-dimethylaminopyridine ligands in C_2 symmetry, with the two-fold axis passing through the Co(II) ion and the mid-point of two Cl^- anions. The cobalt(II) ion is a distorted tetrahedron CoN_2Cl_2 and all angles around Co(II) ion range from 102.53(8) to 115.34(6)°. The Co–Cl bond length of 2.2075(11) Å is comparable to the corresponding values in reported tetrahedral cobalt(II) complexes [25–27]. The Co–N bond length is 2.079(3) Å, consistent with those in Co(2-mopy)$_2$Cl$_2$ [2.059(3) and 2.082(3) Å; 2-mopy = 2-methoxypyridine] [28] and slightly longer than those found in similar tetrahedral cobalt(II) complexes [29–31]. All the bond lengths and angles in 4-dimethylaminopyridine ligand are in the normal range.

The pyridine rings with the dimethylamino group are fairly planar, the largest deviation from the least squares plane of the ring atoms is 0.039 Å for C(2). In the crystal lattice, there are some potential weak intermolecular interactions (C–H $\cdots$ Y, Y = Cl) [32, 33] and C–H $\cdots\pi$ supermolecule interaction [34] (see table 3), which stabilize the crystal structure.

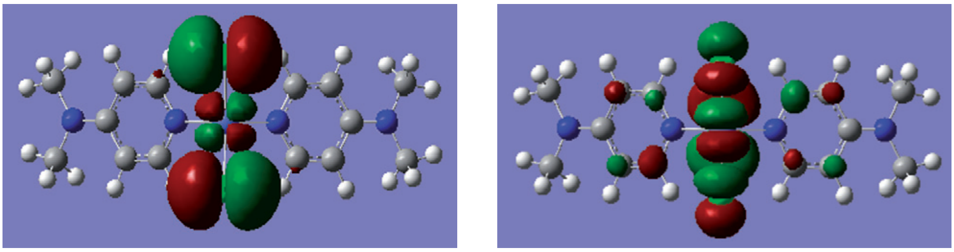
The optimized geometry also has C_2 symmetry. Comparison of the theoretical and experimental values in table 2 shows that most of the optimized bond lengths are slightly longer than those in the crystal structure and bigger differences are for Co(II). The biggest difference of bond length is 0.1246 Å for Co(1)–Cl(1) and the biggest difference of bond angle is 16.856° for Cl(1)–Co(1)–Cl(1A). The reason may be that the theoretical calculations belong to isolated molecules in gaseous phase at 0 K and the experimental results belong to molecules in solid phase. In the crystal state, the close packing of all the molecules and weak intermolecular interactions of C–H ··· Cl in the crystal lattice may lead to some differences of Co(1)–Cl(1) and Cl(1)–Co(1)–Cl(1A) between the experimental and predicted values. In spite of these differences, the Co(II) ion in the optimized geometry still adopts a distorted tetrahedron and 4-dimethylaminopyridine groups of the molecule represent a good approximation with the crystal structure. Based on the optimized geometry, the natural population analysis (NPA), electronic spectra and thermodynamic property of the title compound are calculated.

3.2. *Electronic absorption spectra*

Electronic absorption spectra of the title compound in EtOH exhibit three bands. The sharp peak at 205 nm is ascribed to the intra-ligand transition between Cl^- ion and 4-dimethylaminopyridine groups, while the shoulder from 320 to 370 nm is assigned to charge transfer transitions from the d orbitals of cobalt(II) to the low-energy π^* orbital of the ligand (MLCT) [35]. The third broad band in the range 550–700 nm are d–d transitions of Co(II), which may be taken as evidence for tetrahedral geometry [36]. The DT-DFT electronic spectra calculations show that there are four electronic transition bands which correspond to the experimental data. The first shoulder band in the range 258.06 to 265.90 nm has some red shifts compared with the experimental value (205 nm) with the bigger oscillator strengths being 0.1495 at 263.30 nm and 0.1344 at 262.08 nm, respectively. The second broad band falls in the range 282.94 to 342 nm with the biggest oscillator strengths being 0.0136 at 287.78 nm, blue shifted compared with the experimental values of 320 ~ 370 nm. The third peak at 571.74 nm and the fourth peak at 686.34 nm are very weak with oscillator strengths being 0.0054 at 571.74 nm and 0.0035 at 686.34 nm. These two peaks in the visible range correspond to experimental data 550–700 nm. The reasons for the discrepancy between the experimental values and theoretical predictions may be that the TD-DFT approach is based on the random-phase approximation (RPA) method [37, 38], which provides an alternative to computationally demanding multireference configuration interaction methods in the study of excited states. TD-DFT calculations do not evaluate the spin-orbit splitting; the values are averaged. Here the objective is to evaluate the electronic structure by direct electronic excitations. Only singlet–singlet transitions are considered in these quasi-relativistic calculations. In addition, the role of the solvent is not included in the theoretical calculations. Natural population analyses indicate that the frontier molecular orbitals are mainly composed of d and p atomic orbitals, so the electronic transitions are mainly derived from intraligand (IL) $\pi \rightarrow \pi^*$, metal-to-ligand charge transfer (MLCT) and d–d transitions. Figure 3 shows the HOMO and LUMO surfaces of the alpha and beta orbitals for the title compound, supporting the conclusions.



HOMO of alpha LUMO of alpha



HOMO of beta LUMO of beta

Figure 3. Some frontier molecular orbital stereographs for the title compound.

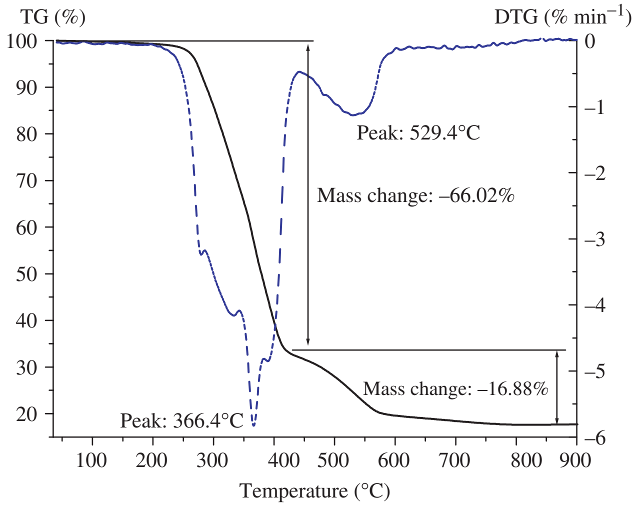


Figure 4. The thermal analysis curve of the title compound.

3.3. *Thermal property analysis and the bond order*

The thermal analysis curve of the title compound is given in figure 4. Decomposition has two weight-loss processes, the first from 250 to 420°C and the second from 420 to 850°C. During the first weight loss, there is a strong exothermal peak at 366.4°C and the weight loss is 66.02%, assigned to breaking the Co–N bond and decomposition of

Table 4. The thermodynamic properties of the title compound at different temperatures at B3LYP/LANL2DZ level.

T (K)	$C^0_{\mathrm{p,m}}$ (J mol^{-1} K^{-1})	S^0_{m} (J mol^{-1} K^{-1})	H^0_{m} (kJ mol^{-1})
100	191.25	462.32	11.84
200	284.99	624.96	35.84
300	374.38	757.28	68.77
400	462.55	877.22	110.68
500	539.96	9890.00	160.91
600	604.32	1093.32	218.23
700	657.43	1190.59	281.40

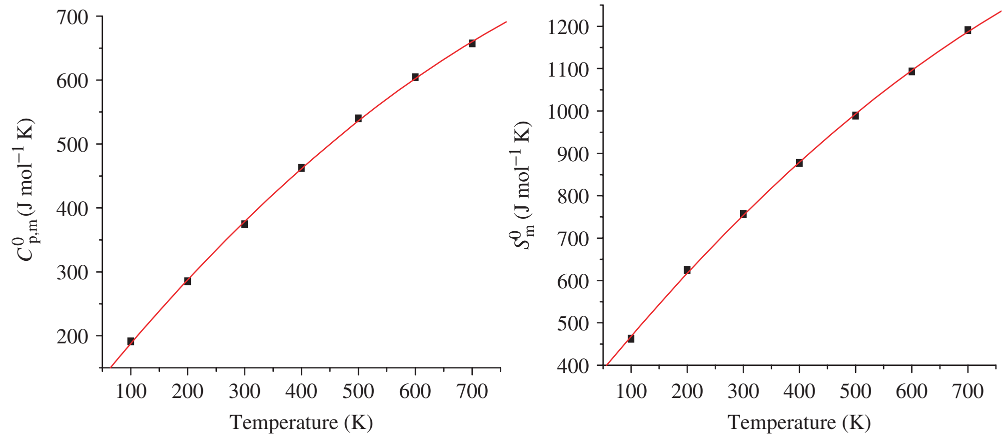


Figure 5. Correlation graphics of thermodynamic properties and temperatures.

4-dimethylaminopyridine groups (Calcd 65.28%). After 420°C, the title compound has a second loss corresponding to another strong exothermal peak at 529.4°C; the weight loss, 16.88%, is assigned to breaking the Co–Cl bond with loss of two $\mathrm{Cl^-}$ ions (Calcd 18.97%). The residue of the decomposition (15.75%) is Co (Calcd 17.1%). Experimentally the strength of Co–Cl is stronger than the Co–N bond; theoretical calculations at B3LYP/LANL2DZ level of theory show that the bond orders of Co–Cl bond and Co–N bonds are 0.304671 and 0.155970, respectively. The theoretical prediction is correct by the thermal analysis of the title compound.

3.4. *Thermodynamic properties*

On the basis of vibrational analysis at B3LYP/LANL2DZ level and statistical thermodynamic, the standard thermodynamic functions, heat capacities ($C^0_{\mathrm{p,m}}$), entropies (S^0_{m}) and enthalpies (H^0_{m}) were obtained and listed in table 4. The scale factor for frequencies is 0.96, which is a typical value for B3LYP method.

From table 4, it can be observed that standard heat capacities, entropies and enthalpies increase at any temperature ranging from 100.00 to 700.00 K, due to the intensities of molecular vibration increasing with temperature.

Correlations between these thermodynamic properties and temperatures T are shown in figure 5. The linear equations are:

$$C^0_{\mathrm{p,m}} = 80(2) + 1.120(9) \times T - 4.16(1) \times 10^{-4} T^2, \ \sum d^2 = 63, \ R^2 = 0.9996$$

$$S^0_{\mathrm{m}} = 308(2) + 1.658(9) \times T - 5.8(1) \times 10^{-4} \times T^2, \ \sum d^2 = 158, \ R^2 = 0.9996$$

which will be helpful for further studies of the title compound.

Supplementary data

CCDC-602549 for the title compound contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0) 1223-336033; Email: deposit@ccdc.cam.ac.uk.

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