Electronic Structure Calculation and Crystal Structure of Trimethylpyridine Cobalt Chloride Complex

Tao Deng[*]
School of Mathematics and Computer Science,
Northwest University for Nationalities, Lanzhou 730030, P. R. China.

Abstract. The new complex of 2, 4, 6-trimethylpyridine (TMPy) cobalt chloride consists of $CoCl_4$ anions and trimethylpyridine cations by ionic electrostatic force. This complex belongs in space group of $P2_1/c$, having crystalline parameters of a = 8.915, b = 17.339, c = 13.945 Å, β = 102.54°, Z = 4 and $D_m = 1.37$ Mg·m^{-3}. Electronic structure calculation results indicated stronger covalence of $(CoCl_4)^{2-}$ and demonstrated that the coordination compound of $CoCl_4{\cdot}(HTMPy)_2$ is very stable. There are positive charges on C_2, C_4 and C_6 positions, and negative charges on C_3 and C_5 positions in pyridine ring. Mulliken bond grade and atom net charge were derived.

Keywords: cobalt complex, trimethylpyridine, crystal structure, electronic structure calculation, Mulliken bond grade

Introduction

Structure of complexes of Lewis base containing nitrogen with main group elements and transition metals had been widely reported (MacDonald et al., 2000; Chandrasekhar et al., 2011; Xie et al., 2012). In above coordination compounds some ligands did not coordinate to metal atom. It is remarkable that coordination compounds of the cobalt or the nitrogen heterocyclic ring have special structure and extensive application (Ma et al., 2008; Seo et al., 2000; Horcajada et al., 2006; Kaye et al., 2005; Deng, 2016; Zhang, 2005; Song et al., 2006). In this paper, the new complex of cobalt chloride and 2, 4, 6-trimethylpyridine (TMPy, Fig. 1) had been synthesized.

---

*Author for correspondence; E-mail: dttom@lzu.edu.cn

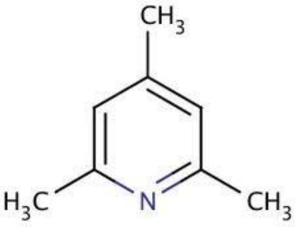

Fig. 1. The structure of 2, 4, 6-trimethylpyridine (TMPy, $C_8H_{11}N$).

The $CoCl_4 \cdot (HTMPy)_2$ derived at acidic condition was characterized by crystal structure and structural calculation. In this complex, the nitrogen of pyridine ring did not coordinate to cobalt atom. There is 0.00104 positive charge on cobalt atom which bonded to chlorine atoms in strong covalence. Some bond angles of H—C—H groups have been distorted seriously in electrostatic field. In view of the calculation, the complex is very stable.

Materials and Methods

Preparation. The complex was prepared by reaction of TMPy and $CoCl_2$ in 2:1 molar ratio in 5 mL water at acidic condition (pH = 2 – 3), adjusted with HCl (0.2 M). Good shaped blue needle crystal suited to X-ray diffractometer was derived from this solution evaporating at room temperature about 20 ℃ for a week. The density of this crystal was measured by flotation in CH_3I/CCl_4. Element analysis: found, Co 13.28, C 43.27, H 5.45, N 6.29; calculation for $C_{16}H_{24}Cl_4CoN_2$: Co 13.24, C 43.17, H 5.44, N 6.29 %.

Data collection. A blue needle single crystal (0.30×0.25×0.20 mm) was chosen for data collection using an Enraf-Nonius CAD-4 diffractometer. 25 hkl reflections were used to refine the lattice parameters. Details of data collections are reported. Lorentz and polarization correction were applied. Empirical absorption corrections were performed.

Structural analysis and refinement. The structure was determined using direct methods leading to the location of all non-hydrogen atoms. All hydrogen atoms were then evidenced from the difference Fourier map and they were added to the structure factor calculations as fixed at 0.97 Å from their relative attached atoms. Scattering factors for neutral atoms and anomalous dispersion correction for scattering factors were taken from the data, respectively (Cromer and Waber, 1974; Cromer, 1974). Both calculations with PDP-Plus structure Determination Package and illustrations with ORTEP software were performed on PDP-11 computer (Frenz, 1980).

Electronic structure calculation. Electronic structure of the complex is calculated using the INDO program package on M-340S computer and the data for structure calculation come from the result of X-ray diffraction. The base parameters come from the articles (Ren et al., 1982; Ren et al., 1982).

Results and Discussion

The bond lengths and the bond angles presented in Tables 1 – 2, which showed that the crystal is built up by unit of $(CoCl_4)^{2-}$ anion and 2, 4, 6-trimethylpyridine cation $(HTMPy)^+$ (Figs. 2 – 3). The data collections are collected in Tables 3 – 4. The different positions of atoms and bonds are numbered in Fig. 4. The atom net charges and Mulliken bond grade of coordination compound derived from calculation are tabulated in Tables 5 – 6. The cobalt atom is in the middle of a “square” constituted with the four chlorine atoms [Co-Cl from shorter of 2.237(1) Å to longer of 2.290(1) Å]. The interaction distances in the trimethylpyridine are not constituted with bond lengths in a conjugated ring ($1.389 \geqq d \geqq 1.352$ Å) (Busnot et al., 1983). The electrons are divided into two types: α and β, according to their different spinning directions. The results indicated electron energy limits to -0.42607 – 0.19920 Hartree for α-electron and -0.43547 – 0.19883 for β-electron, and electron energy limits of calculation to -2.23361 – 0.4842 Hartree for α-electron and -2.26333 – 0.49103 Hartree for β-electron. In view of calculation result, the atom net charges are -0.2066 – -0.2741, av. -0.2484 for chlorine atoms and +0.00104 for cobalt, although the cobalt atom is +2 of valence, therefore, the anion of $(CoCl_4)^{2-}$ is bound through strong covalence. There are negative charges on nitrogen atoms, C_2 and C_4, and positive charges on C_1, C_3 and C_5, showing no difference with which have been known that electrophilic substitution reaction (e.g. acylation) often occurs on o-position, and nucleophilic substitution reaction (e.g. alkanisation) often occurs on p- and m-positions in aromatic ring. The substituted methyl groups of trimethylpyridine ring being in electrostatic field are seriously distorted, compared with that in coordination field. All eighteen H—C—H bond angles have been changed obviously except that on C_7 (av. 108.6˚) and C_{14} (av. 107.3˚) being similar to classical tetrahedral angle. Considering the energy in this system of complex, the electronic energy (EE) is -1379.6929 Hartree, and the nuclear energy is +1167.7988 Hartree, so that the total energy (TE) is -211.8941 Hartree, which indicated that the ionic complex is very stable.

Table 1. Selected bond distances (Å)

Co-Cl_1	2.290(1)	Co-Cl_2	2.293(1)
Co-Cl_3	2.237(1)	Co-Cl_4	2.245(1)
N_1-C_1	1.442(6)	N_1-C_5	1.381(6)
N_2-C_9	1.373(5)	N_2-C_{13}	1.407(5)
C_1-C_2	1.363(7)	C_1-C_8	1.475(6)
C_2-C_3	1.391(6)	C_3-C_4	1.339(5)
C_3-C_7	1.478(6)	C_5-C_6	1.480(6)
C_9-C_{10}	1.345(5)	C_9-C_{16}	1.482(6)
C_{10}-C_{11}	1.313(5)	C_{11}-C_{12}	1.383(6)
C_{11}-C_{15}	1.488(6)	C_{12}-C_{13}	1.377(6)
C_{13}-C_{14}	1.481(6)	N_1-H_{N1}	1.054(8)

Table 2. Selected bond angles (˚)

Cl_1-Co-Cl_2	108.97(5)	Cl_1-Co-Cl_3	107.97(5)
Cl_1-Co-Cl_4	109.03(5)	Cl_2-Co-Cl_3	111.16(5)
Cl_2-Co-Cl_4	108.02(5)	C_1-N_1-C_5	119.3(4)
C_9-N_2-C_{13}	120.5(4)	N_1-C_1-C_8	119.2(4)
N_1-C_1-C_2	118.8(5)	C_1-C_2-C_3	120.3(4)
C_2-C_1-C_8	122.0(4)	C_2-C_3-C_4	118.5(4)
C_2-C_3-C_7	122.9(4)	C_3-C_4-C_5	124.3(4)
N_1-C_5-C_4	119.0(4)	N_1-C_5-C_6	122.9(4)
C_4-C_5-C_6	118.1(5)		
$H_{6'}$-C_6-H_6	104.1(8)	H_{14}-C_{14}-$H_{14''}$	94.3(7)
$H_{6'}$-C_6-$H_{6''}$	90.4(7)	H_{14}-C_{14}-$H_{14'}$	126.3(7)
H_6-C_6-$H_{6''}$	84.4(6)	$H_{14''}$-C_{14}-$H_{14'}$	101.3(7)
$H_{7'}$-C_7-$H_{7''}$	119.7(9)	H_{15}-C_{15}-$H_{15'}$	106.7(6)
$H_{7'}$-C_7-H_7	94.3(7)	H_{15}-C_{15}-$H_{15''}$	64.1(5)
$H_{7''}$-C_7-H_7	112(1)	$H_{15'}$-C_{15}-$H_{15''}$	128.3(7)
$H_{8'}$-C_8-H_8	67.1(7)	H_{16}-C_{16}-$H_{16'}$	97.8(9)
$H_{8''}$-C_8-H_8	100.1(6)	H_{16}-C_{16}-$H_{16''}$	88.0(8)
$H_{8'}$-C_8-$H_{8''}$	103(2)	$H_{16''}$-C_{16}-H_{16}	99.3(8)

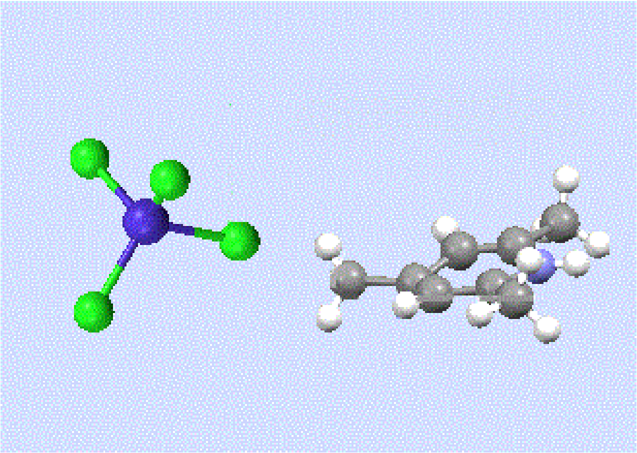

Fig. 2. The anion of $(CoCl_4)^{2-}$and the cation of $(HTMPy)^+$.

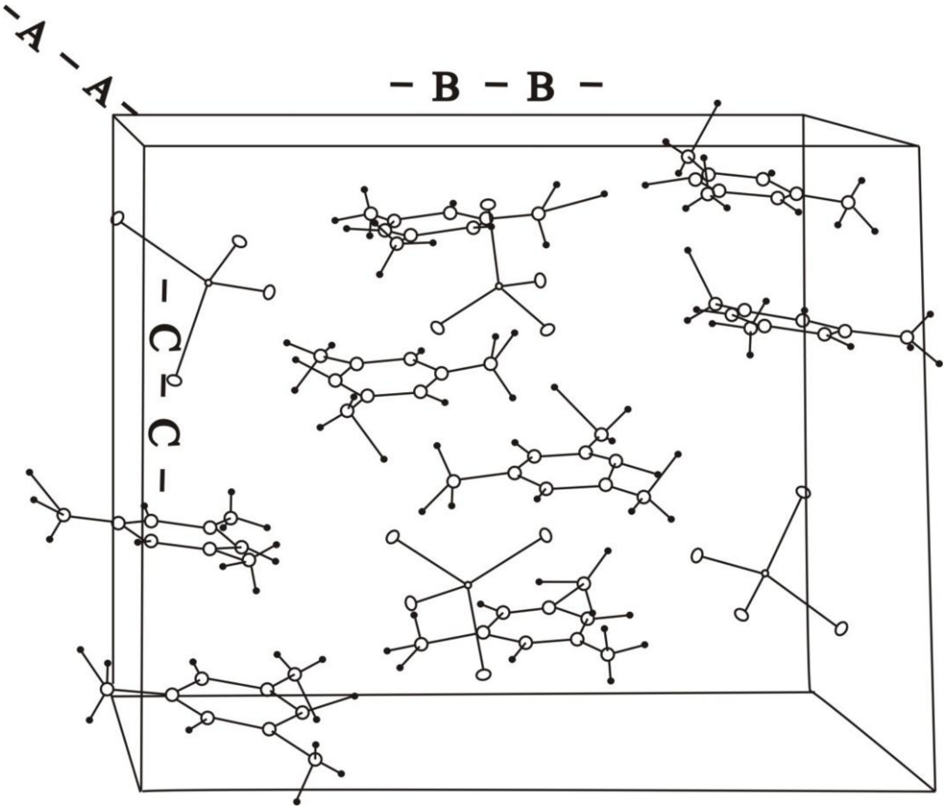

Fig. 3. The crystal structure of complex $[CoCl_4{\cdot}(HTMPy)_2]$.

Table 3. Physical properties and parameters for data collection and refinement

Formula	$C_{16}H_{24}Cl_4CoN_2$
Mol. Wt.	445.1
Space group	$P2_1/c$
a (Å)	8.915
b (Å)	17.339
c (Å)	13.945
β (deg)	102.54
V ($Å^3$)	2104.1
Z	4
Dx	1.386 $Mg{\cdot}m^{-3}$
Dm	1.37 $Mg{\cdot}m^{-3}$
F(000)	456.03
μ (Cu Kα) (cm^{-1})	115.08
λ	1.54184 Å
Scan type	θ/2θ
Scan width	$0.5 + 0.35 \tan\theta$
No. of reflection measured	3380
No. of observed refection	2505
No. of variable, NV	208
R	0.067
Rw	0.101

Table 4. Fractional atomic coordinates and equivalent isotropic thermal parameter (Å^2)

Atom	x	y	z	Ueq
Co	0.24324(1)	0.08741(6)	0.23538(7)	2.54(2)
Cl_1	0.33706(2)	0.05079(1)	0.39489(1)	3.96(4)
Cl_2	0.17724(2)	-0.02073(1)	0.14096(1)	3.83(4)
Cl_3	0.03584(2)	0.16215(1)	0.23289(2)	4.86(5)
Cl_4	0.42873(2)	0.14923(1)	0.17994(2)	4.81(2)
N_1	0.30086(7)	0.29179(5)	0.42654(5)	5.4(2)
N_2	0.22353(8)	0.35656(4)	0.15402(5)	4.9(2)
C_1	0.43141(8)	0.33373(4)	0.41228(5)	3.4(1)
C_2	0.42065(8)	0.41189(4)	0.40244(5)	3.5(2)
C_3	0.28320(8)	0.44923(4)	0.40411(4)	2.7(1)
C_4	0.16425(6)	0.40704(3)	0.41845(4)	1.6(1)
C_5	0.16700(7)	0.33109(4)	0.42894(5)	3.3(2)
C_6	0.02739(9)	0.29255(5)	0.44658(6)	4.8(2)
C_7	0.26450(1)	0.53377(4)	0.39469(5)	4.4(2)
C_8	0.57601(9)	0.29207(6)	0.41316(8)	6.7(3)
H_{N1}	0.27734	0.23242	0.41602	4*
H_{N2}	0.22070	0.29883	0.16602	4*

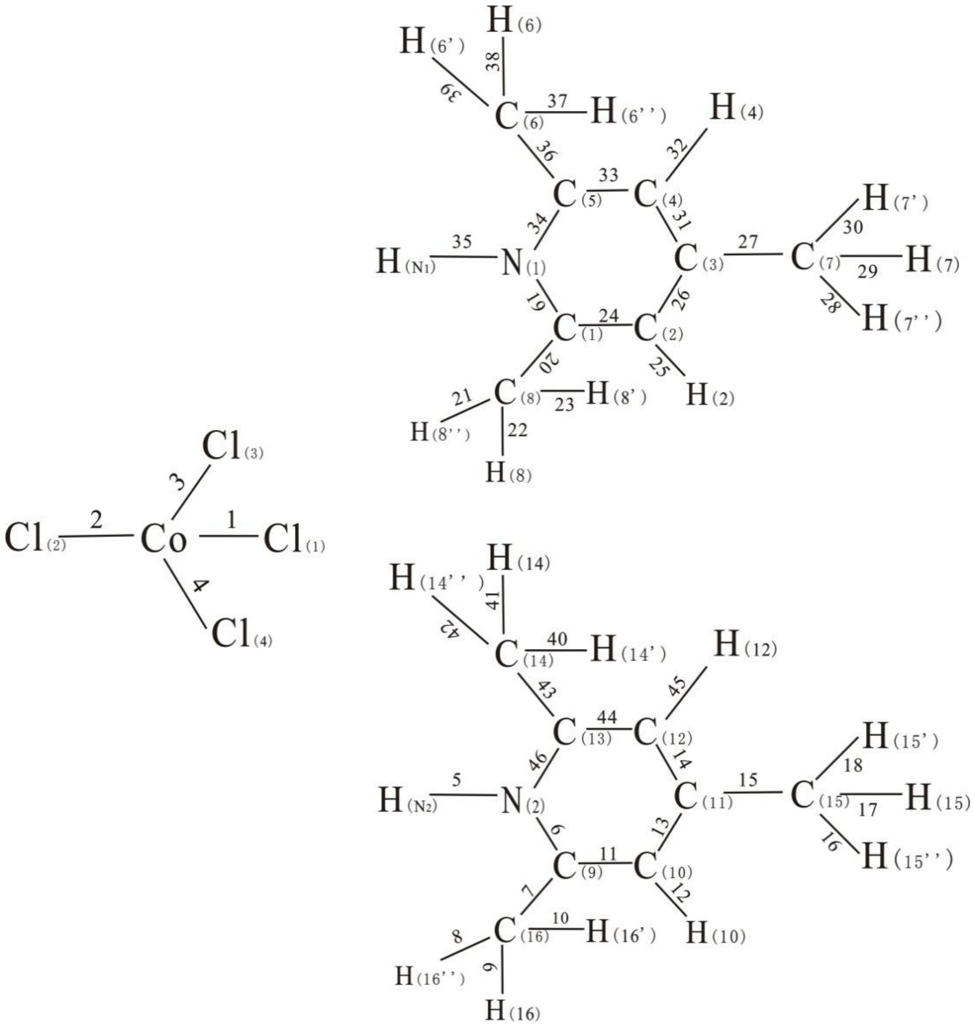

Fig. 4. The numerical atoms and bonds of complex

Table 5. Some atom net charges of coordination compound

Co	0.00104	C_1	0.2494	C_8	-0.1351	C_{15}	-0.0884
Cl_1	-0.2564	C_2	-0.1111	C_9	0.2489	C_{16}	-0.1214
Cl_2	-0.2066	C_3	0.1826	C_{10}	-0.1496	H_{N1}	0.1802
Cl_3	-0.2741	C_4	-0.1205	C_{11}	0.2067	H_{N2}	0.1563
Cl_4	-0.2585	C_5	0.2509	C_{12}	-0.1111	H_2	0.0443
N_1	-0.05846	C_6	-0.0489	C_{13}	0.2189	H_4	0.0561
N_2	-0.05724	C_7	-0.0800	C_{14}	-0.0890		

Table 6. The Mulliken bond grades of coordination compound

1	0.6375	13	1.0780	25	0.7273	37	0.7546
2	0.6477	14	1.0070	26	1.0016	38	0.8142
3	0.6615	15	0.8550	27	0.8018	39	0.5028
4	0.6609	16	0.6668	28	0.8735	40	0.7448
5	0.6529	17	0.6196	29	0.8215	41	0.7953
6	0.8451	18	0.5878	30	0.7004	42	0.7034
7	1.0612	19	0.8218	31	1.0617	43	0.8320
8	0.8054	20	0.8751	32	0.8300	44	1.0023
9	0.8007	21	0.5640	33	1.1007	45	0.8168
10	0.7225	22	0.7506	34	0.8689	46	0.8022
11	1.1061	23	0.8116	35	0.6246		
12	0.8852	24	1.0826	36	0.8546		

References

MacDonald J. C., Dorrestein P. C., Pilley M. M., Foote M. M., Lundberg J. L., Henning R. W. 2000. Design of layered crystalline materials using coordination chemistry and hydrogen bonds. *Journal of the American Chemical Society*, **122:** 11692-11702.

Chandrasekhar V., Thirumoorthi R., Metre R. K., Mahanti B. 2011. *Journal of Organometallic Chemistry*, **696:** 600-606.

Xie Z. L., Xie Y. R., Xu G. H., Du Z. Y., Zhou Z. G., Lai W. L. 2012. Four novel alkaline-earth metal coordination polymers with networks controlled by the diverse coordination modes of amino-sulfonated ligand: Synthesis, crystal structures and luminescent properties. *Inorganica Chimica Acta*, **384:** 117-124.

Ma S., Sun D., Simmons J. M., Collier C. D., Yuan D., Zhou H. C. 2008. Metal-organic framework from an anthracene derivative containing nanoscopic cages exhibiting high methane uptake. *Journal of the American Chemical Society*, **130:** 1012-1016.

Seo J. S., Whang D., Lee H., Jun S. I., Oh J., Jeon Y. J., Kim K. 2000. A homochiral metal-organic porous materials for enantioselective separation and catalysis. *Nature*, **404:** 982-986.

Horcajada P., Serre C., Vallet-Regi M., Sebban M., Taulelle F., Férey G. 2006. Met-organic framework as efficient materials for drug delivery. *Angewandte Chemie International Edition*, **45:** 5974-5978.

Kaye S. S., Long J. R. 2005. Hydrogen storage in the dehydrated Prussian blue analogues $M_3[Co(CN)_6]_2$ (M=Mn, Fe, Co, Ni, Cu, Zu). *Journal of the American Chemical Society*, **127:** 6506-6507.

Deng, T. 2016. Study on Schiff bases derived from sulfathiazole and sulfamethoxypyridazine. *Journal of the Chemical Society of Pakistan*, **18:** 133-138.

Zhang X. M. 2005. Hydro(solvo)thermal in situ ligand syntheses. *Coordination Chemistry Reviews*, **249:** 1201-1219.

Song, Y. M., Yao, X. Q., Deng, T., Wu J. X., Wu, Q. 2006. Structure of tetrakis(pyridinioacetate) neodymium(Ⅲ) tetrahydrate perchlorate. *Chemical Papers*, **60:** 302-305.

Cromer D. T., Waber J. T. 1974. International Tables for X-ray Crystallograph, Vol. Ⅳ, Table 2.2.B. Kynoch Press, Birmingham, UK.

Cromer D. T. 1974. International Tables for X-ray Crystallograph, Kynoch Press, Birmingham, Vol. Ⅳ, Table 2.3.1. Kynoch Press, Birmingham, UK.

Frenz B. A. & Associates, Inc. 1980. SDP-Plus, Version 1.0, Enraf-Nonius, Deft, The Netherlands.

Ren J. Q., Li L. M., Wang X. Z., Hsu K. S. 1982. The INDO method applicable to the electronic structure calculation of lanthanide compounds. Ⅰ. The formulas required for computer programming. *Acta Scientiarum Naturalium Universitatis Pekinensis*, **28(3):** 30-48.

Ren J. Q., Li L. M., Wang X. Z., Hsu K. S. 1982. The INDO method applicable to the electronic structure calculation of lanthanide compounds. Ⅱ. The selection of parameters and the computer program. *Acta Scientiarum Naturalium Universitatis Pekinensis*, **28(3):** 49-62.

Busnot, A., Busnot, F., Leclaire, A., Bernard, M. 1983. Structure of diacetatiobis (2, 4, 6-trimethyl pyridine) copper(Ⅱ). *Zeitschrift für Anorganische und Allgemeine Chemie* **503:** 207-212.