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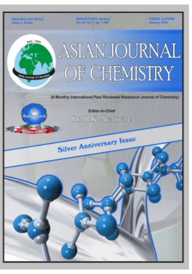

Synthesis and Crystallographic Study of Cobalt Complex Derived from 5-Chloro-salicylaldehyde and Cyclohexanamine

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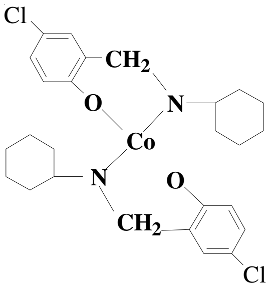
The coblat complex with molecular formula [$C_{26}H_{30}Cl_2CoN_2O_2$, Mr = 532.35] has been synthesized and characterized by elemental analysis and X-ray diffraction. As expected, the molecular structure adopts a *trans* configuration about the C=N double bond. It crystallizes in monoclinic system, space group Pbca with a = 14.875(3) Å, b = 13.569(2) Å, c = 24.957(5) Å, β = 90º, V = 5037.6(14) $Å^3$, Z = 8, Dc = 1.404 Mg/m^3, $F_{(000)}$ =2216, $\mu(MoK_\alpha)$ = 0.919 m m^{-1}, R = 0.0415 and wR = 0.0492 of the 5667 collection, 4690 were unique. The title compound, [$C_{26}H_{30}Cl_2N_2O_2$] is a mononuclear cobalt(II) complex. The Co atom is four-coordinated by two N atoms and two O atoms from two Schiff base ligands in a slightly distorted tetrahedral geometry.

Key Words: *Bis*[4-chloro-2-(cyclohexyliminomethyl)phenolato]cobalt(II), Crystal structure, Cobalt compound.

INTRODUCTION

Cobalt complexes are of great interest in coordination chemistry in relation to catalysis, enzymatic reactions, magnetism and molecular architectures[1-3]. As an extension of work on the structural characterization of cobalt compound, the crystal structure of a newly synthesized compound(**I**) is reported here.



Compared the new synthesized compound with two cobalt(II) compounds reported previously[4].

EXPERIMENTAL

Cyclohexanamine used in the experiment is of analytical purity and 5-chlorosalicylaldehyde is a biochemical reagent.

Preparation of the crystal: 5-Chlorosalicylaldehyde (0.1 mmol, 15.7 mg), $CoCl_2·6H_2O$ (0.1 mmol, 24.2 mg) and cyclohexanamine (0.1 mmol, 9.3 mg) were dissolved in methanol (10 mL). The mixture was stirred for 0.5 h at room temperature to give a clear brown solution. After keeping the resulting solution in air for 11 d, brown block-shaped crystals of (**I**) were formed on slow evaporation of the solvent. The crystals were collected, washed with methanol and dried in a vacuum desiccator using anhydrous $CaCl_2$ (yield 54 %). The reaction mechanism is shown in Fig. 1. Analysis found: C 58.64, H 5.63 %; calculated for: [$C_{26}H_{30}Cl_2CoN_2O_2$] C 58.64, H 5.64 %.

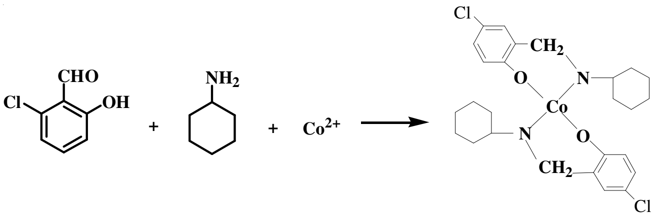


Fig. 1. Scheme of the chemical reaction

Crystal structure determination and refinement: Solvent loss technique has been employed for the growth of yellow rod-shaped crystals of the title compound. A crystal having good morphology (0.48 mm × 0.48 mm × 0.12 mm) was chosen for three-dimensional intensity data collection using a SMART diffractometer. MoK_α radiation (λ = 0.71073 Å) was used for the data collection. A total of 5667 reflections were recorded and out of this number 4690 reflections ($0 \le h \le 18$, $0 \le k \le 16$, $-30 \le l \le 1$) were treated as observed. The structure has been solved with SHELXS-97 and full-matrix least-squares refinement has been carried out using SHELXTL-97 software. The final refinement cycle converged R = 0.0415 and wR = 0.0492. The maximum shift to esd. ratio for all atoms in the final cycle is 0.001. Final cycle of refinement results the residual electron density in the range from -0.252 to 0.353 e/Å^3. The crystallographic data are summarized in Table-1.

TABLE-1
CRYSTAL DATA AND OTHER EXPERIMENTAL DETAILS

No.	y2041
Crystal description	Yellow rod
Chemical formula	$C_{26}H_{30}Cl_2CoN_2O_2$
Molecular weight	532.35
Cell parameters	a = 14.875(3) Å b = 13.569(2) Å c =24.957 (5) Å β =90º
Unit cell volume	5037.6(14) Å 3
Crystal system	Orthorhombic
Space group	Pbca
Density (calculated)	1.404 mg/m^3
No. of molecules per unit cell Z	8
Absorption coefficient (?)	0.9195 m m^{-1}
Absorption correction	psi-scan
Max. and min. transmission	0.9997 and 0.8955
$F_{(000)}$	2216
Crystal size	0.48 mm × 0.48 mm × 0.12 mm
Completeness to theta= 25.02	99.5 %
θ range for entire data collection	1.63 < θ <25.50º
Reflections collected	5667
Independent reflections	4690[$R_{(int)}$ = 0.0245]
Observed reflections	2154
Refinement method	Full-matrix least-squares on F_2
Data/restraints/parameters	4690/0/299
Limiting indices	0⇐h⇐18, 0⇐k⇐16, -30⇐l⇐1
Final R-factor	0.0415
WR	0.0492
Weight	$w = 1/[\sigma^2(Fo)^2 + (0.0100P)^2 + 0.0000P]$ where $P = (Fo^2 + 2Fc^2)/3$
Goodness-of-fit on F_2	0.837
Final residual electron density	-0.252< ρ <0.353 e Å -3
(Δ/σ)max in the final cycle	0.001

RESULTS AND DISCUSSION

Selected bond distances and bond angles are listed in Table-2. Selected torsion angles are given in Table-3. An ORTEP view of the molecule with the atomic numbering scheme (the structure of (**I**), showing 30 % probability displacement ellipsoids and the atom-numbering) is shown in Fig. 2. The geometry of the molecule has been calculated using the software. From the results, it is known that all the bond lengths and angles are in normal ranges comparable to those observed in a similar antipyrine Schiff base (Table-4).

Compared the newly synthesized cobalt(II) compounds with the other two (the structures are shown in Figs. 4 and 5), it was found that compound structures obtained are different in the three cobalt systems. When $Co(NO_3)_2·6H_2O$ or $CoCl_2·6H_2O$ was used, the structures of the synthesized cobalt(II) compounds are almost the same.

$Co(CH_3COOH)_2·4H_2O$ system: 5-Chlorosalicylaldehyde (0.1 mmol, 15.7 mg) and cobalt(II) acetate tetrahydrate (0.1 mmol, 24.9 mg) and cyclohexanamine (0.1 mmol, 9.3 mg) were dissolved in methanol (10 mL). The mixture was stirred for 0.5 h at room temperature to give a clear brown solution. After allowing the resulting solution to stand in air for 11 d, brown block-shaped crystals were formed at the bottom of the vessel by slow evaporation of the solvent. The crystals were isolated by filtration, washed with methanol and dried in a vacuum desiccator using anhydrous $CaCl_2$ (yield 54 %).

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (º)

Bond	Dist (Å)	Angle	(º)
Co-O(2)	1.912(2)	O(2)-Co-O(1)	121.06(9)
Co-O(1)	1.916(2)	O(2)-Co-N(2)	94.93(10)
Co-N(2)	1.994(2)	O(1)-Co-N(2)	112.86(10)
Co-N(1)	1.998(2)	O(2)-Co-N(1)	112.82(10)
N(2)-C(7)	1.283(3)	O(1)-Co-N(1)	94.45(10)
N(1)-C(20)	1.281(3)	N(2)-Co-N(1)	122.94(10)
N(2)-C(8)	1.486(3)	C(14)-O(1)-Co	123.4(2)
O(1)-C(14)	1.315(3)	C(1)-O(2)-Co	125.6(2)
O(2)-C(1)	1.298(3)	C(20)-N(1)-C(21)	117.4(3)
C(1)-C(2)	1.415(4)	C(20)-N(1)-Co	122.0(2)
C(2)-C(3)	1.363(4)	C(21)-N(1)-Co	120.6(2)
C(3)-C(4)	1.387(4)	C(7)-N(2)-C(8)	116.5(3)
C(2)-H(2)	0.9300	C(7)-N(2)-Co	122.0(2)
C(3)-H(3)	0.9300	C(8)-N(2)-Co	121.5(2)
C(12)-H(12A)	0.9700	O(2)-C(1)-C(2)	119.3(3)

TABLE-3
SELECTED TORSION ANGLES (º)
FOR NON-HYDROGEN ATOMS

$O_2CoO_1C_{14}$ 144.7(2)	$N_2CoO_1C_{14}$ -104.0(2)
$N_1CoO_1C_{14}$ 24.6(2)	$O_1CoO_2C_1$ 136.3(2)
$N_2CoO_2C_1$ 15.8(3)	$N_1CoO_2C_1$ -113.2(3)
$O_2CoN_1C_{20}$ -141.8(2)	$O_1CoN_1C_{20}$ -15.4(2)
$N_2CoN_1C_{20}$ 105.6(2)	$O_2CoN_1C_{21}$ 36.2(2)
$O_1CoN_1C_{21}$ 162.7(2)	$N_2CoN_1C_{21}$ -76.3(2)
$O_2CoN_2C_7$ -8.7(3)	$O_1CoN_2C_7$ -135.4(2)
$N_1CoN_2C_7$ 112.6(2)	$O_2CoN_2C_8$ 168.5(2)
$O_1CoN_2C_8$ 41.8(2)	$N_1CoN_2C_8$ -70.1(2)
$CoO_2C_1C_2$ 166.4(2)	$CoO_2C_1C_6$ -14.0(5)

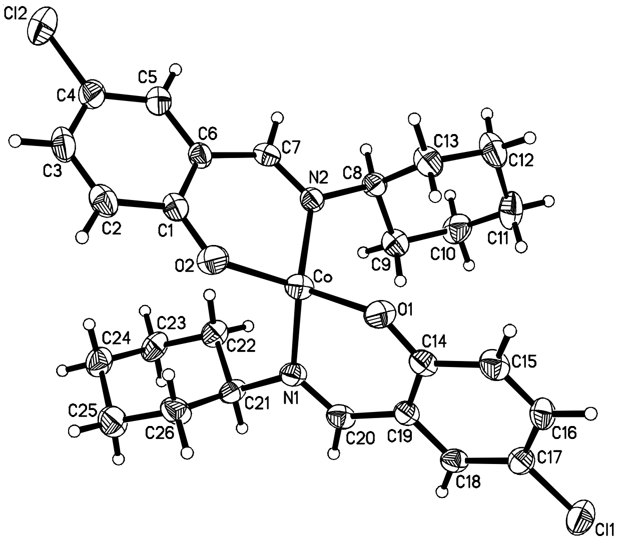


Fig. 2. The structure of (**I**), showing 30 % probability displacement ellipsoids and the atom-numbering

$Co(NO_3)_2·6H_2O$ system: 5-Chlorosalicylaldehyde (0.1 mmol, 15.7 mg), Co $(NO_3)_2·6H_2O$ (0.1 mmol, 29.1 mg) and cyclohexanamine (0.1 mmol, 9.3 mg) were dissolved in methanol (10 mL). The mixture was stirred for 0.5 h at room

TABLE-4
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°) OF THREE SYSTEM

System	Bond	Dist (Å)	Angle	(°)
$Co(NO_3)_2·6H_2O$	Co-O(2)	1.9092(18)	O(2)-Co-O(1)	121.42(8)
	Co-O(1)	1.9149(16)	O(2)-Co-N(2)	95.18(8)
	Co-N(2)	1.997(2)	O(1)-Co-N(2)	112.63(8)
	Co-N(1)	2.0055(19)	O(2)-Co-N(1)	112.57(8)
	O(1)-C(1)	1.314(3)	O(1)-Co-N(1)	94.41(8)
	O(2)-C(14)	1.300(3)	N(2)-Co-N(1)	122.87(8)
$Co(OAc)_2·4H_2O$	Co–O(1)	2.0251(18)	O(1)-Co–O(2)	91.16(8)
	Co-O(2)	2.072(3)	O(1)-Co-O(3)	176.36(6)
	Co-O(3)	2.0265(18)	O(1)–Co-O(4)	89.13(9)
	Co-O(4)	2.072(3)	O(1)–Co-O(5)	89.21(8)
	Co-O(5)	2.114(2)	O(1)–Co-O(6)	90.67(8)
	Co-O(6)	2.057(2)	O(2)–Co-O(3)	88.87(8)
$CoCl_2·6H_2O$	Co-O(2)	1.912(2)	O(2)-Co-O(1)	121.06(9)
	Co-O(1)	1.916(2)	O(2)-Co-N(2)	94.93(10)
	Co-N(2)	1.994(2)	O(1)-Co-N(2)	112.86(10)
	Co-N(1)	1.998(2)	O(2)-Co-N(1)	112.82(10)
	O(1)-C(14)	1.315(3)	O(1)-Co-N(1)	94.45(10)
	O(2)-C(1)	1.298(3)	N(2)-Co-N(1)	122.94(10)

temperature to give a clear brown solution. After keeping the resulting solution in air for 11 d, brown block-shaped crystals of (**I**) were formed on slow evaporation of the solvent. The crystals were collected, washed with methanol and dried in a vacuum desiccator using anhydrous $CaCl_2$ (yield 54 %).

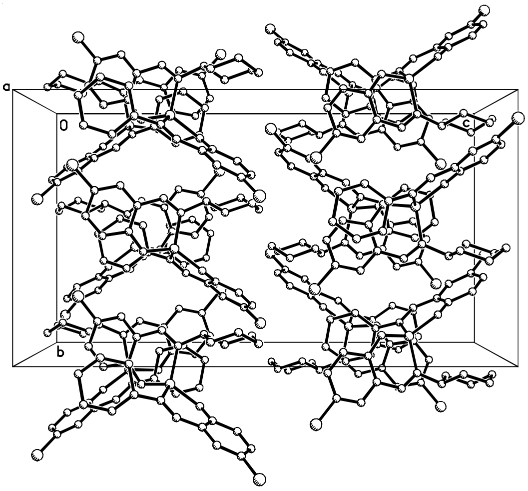


Fig. 3. Packing diagram viewed down the b-axis

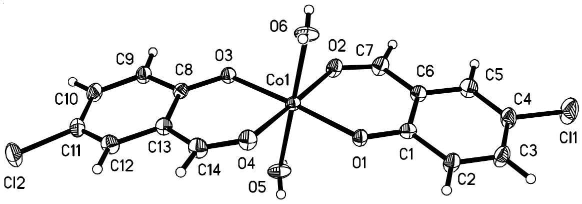


Fig. 4. Crystal structure of $Co(CH_3COOH)_2·4H_2O$ system

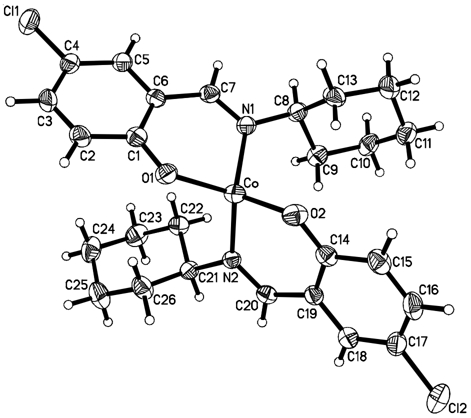


Fig. 5. Crystal structure of $Co(NO_3)_2·6H_2O$ system

Conclusion

As shown in Fig. 4, at the horizontal positions, the three *trans* angles at Co1 are all close to 180°. The other angles are close to 90°, varying from 84.79(8)-95.96(8)°, which indicates a slightly distorted octahedral geometry of the Co1 atom. The bond lengths around the Co1 atom are ranging from 2.025(2)-2.112(2) Å. The dihedral angle between the two benzene rings is 20.4(3)°.

Compound (**I**) is a mononuclear Co(II) complex. The Co(II) ion coordinated by two O and two N atoms from two Schiff base ligands. This CoN_2O_2 coordination forms a distorted tetrahedral geometry, with angles subtended at the Co(II) atom in the range 94.41(8)-122.87(8) %. The bond lengths of Co-O range from 1.9092(18)-2.0055(19) % A. The results were identical in both Figs. 3 and 5.

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