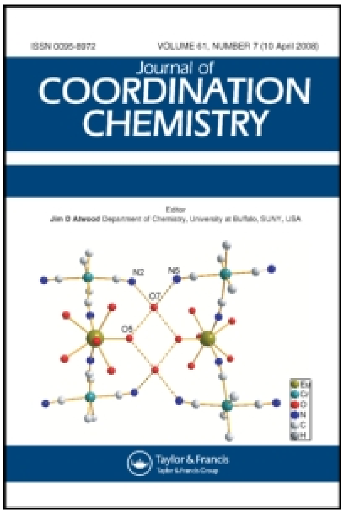

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Synthesis, characterization, and structure of a new cobalt(II) Schiff-base complex with quinoxaline- 2-carboxalidine-2-amino-5-methylphenol

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The mononuclear cobalt(II) complex $[CoL_2]\cdot H_2O$ (where HL is quinoxaline-2-carboxalidine-2-amino-5-methylphenol) has been prepared and characterized by elemental analysis, conductivity measurement, IR, UV-Vis spectroscopy, TG–DTA, and X-ray structure determination. The crystallographic study shows that cobalt(II) is distorted octahedral with each tridentate NNO Schiff base in a cis arrangement. The crystal exhibits a 2-D polymeric structure parallel to [010] plane, formed by $O-H\cdots N$ and $O-H\cdots O$ intermolecular hydrogen bonds and $\pi-\pi$ stacking interactions, as a racemic mixture of optical enantiomers. The ligand is a Schiff base derived from quinoxaline-2-carboxaldehyde.

Keywords: Quinoxaline-2-carboxaldehyde; 2-Amino-5–methylphenol; Crystal structure; Schiff base; Cobalt(II)

1. Introduction

Transition metal complexes with rigid ligands forming frameworks are good candidates for functional materials. Properties such as electronic switching, magnetic ordering, conductivity, and catalysis [1–5] have prompted chemists to design 1-, 2-, and 3-D frameworks spaced by rigid ligands forming wide channels or cavities. Oxygen and nitrogen donor Schiff bases are of particular interest because of their ability to form transition metal complexes with unusual configurations, structural lability, and sensitivity to molecular environments [6–8]. They have proven effective in constructing supramolecular architectures such as coordination polymers and helical assemblies [9–11], employed for modeling active sites in biological systems. Their metal complexes find wide applications as antibacterial, antiviral, and antimalarial agents [12–14], homogeneous and heterogeneous catalysts [15, 16], and magnetic materials [17]. Cobalt Schiff-base complexes have received attention because of their important biological

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applications [18] and there is continuing interest in the synthesis of new Schiff bases and their cobalt complexes.

A literature search reveals that the Schiff base derived from quinoxaline-2-carboxaldehyde and 2-amino-5-methylphenol has not been reported. The nitrogens in the quinoxaline unit can be an acceptor for hydrogen bonding [19] and may lead to polymeric structures. The electronic environment in the metal complexes of this Schiff base might be different from those derived from salicylaldehyde. In this article, we describe the synthesis and characterization of quinoxaline-2-carboxalidine-2-amino-5-methylphenol and its cobalt(II) complex. The crystal structure of the complex has been investigated by single crystal X-ray diffraction.

2. Experimental

2.1. *Materials and physical measurements*

Cobalt(II) acetate tetrahydrate (Merck) and 2-amino-5-methylphenol (Aldrich) were used as supplied. All other chemicals were of analytical grade purity and used without purification. Quinoxaline-2-carboxaldehyde was prepared using the reported procedure [20, 21]. Microanalyses of the compounds were done with an Elementar Vario EL III CHNS elemental analyzer; estimation of cobalt was carried out on a Thermo Electron Corporation, M series Atomic Absorption Spectrophotometer. The molar conductivity of the complex was measured using a Systronic conductivity bridge type 305 in dimethylformamide (DMF). FT-IR spectra were recorded in KBr pellets with a JASCO FTIR 4100 spectrophotometer from 4000 to 400 cm^{-1}. The electronic spectrum of the ligand was recorded on a Thermoelectron Nicolet evolution 300 UV-Vis spectrophotometer. The ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker 250 NMR spectrometer. TG-DTA analysis was carried out under nitrogen with a heating rate of 10°C min^{-1} using a Perkin Elmer Pyris Diamond TG/DTA analyzer.

2.2. *Synthesis of quinoxaline-2-carboxalidine-2-amino-5-methylphenol*

The monobasic tridentate Schiff base was prepared by mixing quinoxaline-2-carboxaldehyde (1.58 g, 0.01 mol) and 2-amino-5-methylphenol (1.23 g, 0.01 mol) in 1 : 1 molar ratio in methanol. The mixture was stirred at room temperature (27°C ± 1°C) for 1 h. The yellow flakes obtained were filtered, recrystallized from alcohol, and the purity was checked by TLC. Yield: 90%. Anal. Calcd for $C_{16}H_{13}N_3O$ (263.29) (%): C, 72.46; H, 4.21; N, 15.64. Found (%): C, 72.99; H, 4.98; N, 15.96. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): $\delta = 2.37$ (s, 3H, C–CH_3), 7.80–8.20 (8H, Ar–H), 8.98 (s, 1H, azomethine proton), 9.70 (s, 1H, Ar–OH).

2.3. *Synthesis of $[Co(L)_2] \cdot H_2O$*

Cobalt(II) acetate tetrahydrate (0.5 mmol, 1.25 g) was dissolved in a minimum of methanol and then added to 1 : 1 chloroform : methanol (100 mL) solution of HL (1.0 mmol, 2.63 g). During the addition, the color of the solution changed to dark violet.

Table 1. Crystal data summary for $[Co(L)_2]\cdot H_2O$.

Empirical formula	$C_{32}H_{26}CoN_6O_3$
Formula weight	601.52
Crystal size (mm^3)	$0.40 \times 0.36 \times 0.02$
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell and dimensions (Å, °)	
a	13.7959(15)
b	13.8622(15)
c	14.5161(16)
β	94.684(2)
Volume ($Å^3$), Z	2766.8(5), 4
Calculated density ($g\,cm^{-3}$)	1.444
Absorption coefficient (mm^{-1})	0.666
$F(000)$	1244
θ range for data collection (°)	1.96–26.03
Reflections collected	27217
Independent reflection	5445 [$R(\mathrm{int}) = 0.0841$]
Max. and min. transmission	0.987 and 0.766
Data/restraints/parameters	5416/2/391
Goodness-of-fit on F^2	1.205
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0980$, $wR_2 = 0.1840$
R indices (all data)	$R_1 = 0.1289$, $wR_2 = 0.1975$

$R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$, $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2/(F_o^2)^2\right]^{0.5}$.

It was then refluxed on a water bath for 3 h and left to cool at room temperature. Single crystals suitable for X-ray diffraction were obtained after 2 weeks by slow evaporation of the filtrate; the crystals obtained were thin. Yield: 85%. Anal. Calcd for $C_{32}H_{26}CoN_6O_3$ (601.52) (%): C, 63.73; H, 4.23; N, 14.24; Co, 9.80. Found (%): C, 63.90; H, 4.36; N, 13.97; Co, 9.75. Λ_M (DMF, Mho $cm^2\ mol^{-1}$): 3.9.

2.4. *X-ray crystallography*

X-ray crystal structure determination was performed with a Bruker SMART APEX CCD X-ray diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å, φ and ω scans). The data were reduced using SAINTPLUS [22] and a multiscan absorption correction using SADABS (Siemens area detector absorption) was performed [23]. The structure was solved using SHELXS−97 and full-matrix least-squares refinement against F^2 was carried out using SHELXL-97 in anisotropic approximation for nonhydrogen atoms [24]. All hydrogens were assigned on the basis of geometrical considerations and were allowed to ride upon the respective carbons. A summary of crystallographic data and refinement parameters is given in table 1.

3. Results and discussion

3.1. *Characterization of the ligand*

The Schiff base was obtained by the condensation of quinoxaline-2-carboxaldehyde and 2-amino-5-methyl phenol. This yellow compound is soluble in common organic solvents.

The proton NMR spectrum of the Schiff base was recorded in $CDCl_3$ solution using tetramethylsilane as internal standard. The signal at 9.70 ppm corresponds to phenolic –OH proton. The azomethine proton appears as a singlet at 8.98 ppm, and all eight aromatic protons appear as a multiplet at 7.80–8.20 ppm [25]. The methyl group attached to the phenolic ring is at 2.37 ppm as a singlet. The IR spectrum of the ligand exhibits a broad band in the range 3300–3500 cm^{-1} due to phenolic (O–H) stretching. A strong band at 1262 cm^{-1} is due to νC–O (phenolic). Weak bands in the region 2800–3060 cm^{-1} are related to C–H stretches. The ν(C=N) of azomethine and that of quinoxaline appear as a group of bands in the region 1570–1630 cm^{-1}. The peaks at 1626 and 1579 cm^{-1} have been assigned to the azomethine –C=N stretch and quinoxaline (C=N) stretch, respectively [25, 26].

The electronic spectrum of the Schiff base was taken in methanol (10^{-4} M). The wavelength maxima are observed at 46,511, 42,553, 34,013, and 25,974 cm^{-1}. The strong bands at 46,511 and 42,553 cm^{-1} are attributed to quinoxaline $\pi-\pi^*$ and phenyl π–π^* transitions, respectively. The band at 25,974 cm^{-1} is due to n–π^* transition of azomethine and ring (C=N) [27, 28]. The analytical data and spectral properties are consistent with the expected structure of the Schiff base.

3.2. *Characterization of the complex*

The cobalt complex was obtained as shining violet crystals, stable in air and soluble in polar organic solvents such as ethanol, methanol, DMF, and dimethylsulfoxide (DMSO). The molar conductivity of the complex in DMF confirms the nonelectrolytic nature [29]. Microanalytical data of the complex is in agreement with calculated values for $[Co(L)_2] \cdot H_2O$.

3.2.1. Infrared spectra. FTIR spectra of the ligand and complex are given in Supplementary material. Comparison of the IR spectra of the complex with those of the uncomplexed ligand gives information regarding bonding sites of the ligand. Peaks in the region 3500–3300 cm^{-1} for the complex are due to (O–H) stretching vibrations of lattice water and indicate hydrogen bonding [16]. The band observed at 935 cm^{-1} for the complex is attributed to bending vibration of H_2O [30]. The complex displays a medium peak at 1667 cm^{-1} due to azomethine (C=N) stretching. The azomethine ν(C=N) band in the complex is shifted by about 41 cm^{-1} to higher energy compared to the free ligand. This increase in azomethine stretching frequency on coordination might be due to the extensive delocalization of the π-electrons in fully conjugated Schiff-base ligand [16]. The (C=N) stretch of quinoxaline ring in the complex appears as a strong band at 1575 cm^{-1} for coordination of metal to ring nitrogen with a small shift for this band ($\sim$5 cm^{-1}) on complexation, which might be due to involvement of the quinoxaline ring nitrogen in coordination. Such small shifts have been observed for benzimidazole complexes [31]. The C–O (phenolic) stretching band is observed at 1251 cm^{-1} in the complex. These spectral assignments show that the Schiff base is coordinated to cobalt through azomethine nitrogen, phenolic oxygen, and quinoxaline nitrogen [32]. Conclusive evidence of the bonding is also shown by the presence of new bands in the spectrum of the complex at 567 and 468 cm^{-1}, which can be attributed to (Co–O) and (Co–N) stretching vibrations, respectively [16].

3.2.2. Electronic spectra. Solution electronic spectra of the complexes were recorded in methanol in the UV-Vis region (200–900 nm) (Supplementary material). The band at 25,974 cm^{-1} of the ligand shifts to 27,027 cm^{-1} on complexation suggesting coordination of azomethine nitrogen with cobalt. The band at 18,553 cm^{-1} is due to the $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ [33, 34]. The intensity of this d–d band is considerably increased possibly due to the influence of nearby intense charge-transfer transitions ($\log \varepsilon = 4.6$). The other d−d transitions are masked by the strong charge transfer band, as observed in similar Schiff-base complexes [35, 36].

3.2.3. Thermal analysis. TG-DTA curves (Supplementary material) show the mass loss corresponding to one water molecule at 50−120°C, due to loss of lattice water [16]. The organic part of the complex decomposes into two steps, the first lies in the range 300–393°C with a DTG peak at 343°C. DTA shows an endotherm at 348°C corresponding to this step. The mass loss (39%) corresponds to loss of two 2-amino-5-methylphenol parts of the two Schiff bases. The next stage of decomposition starts at 412°C and is continuous. Since the TG curve of the complex showed continuous degradation at this stage, we were not able to isolate the intermediates. The steady mass loss observed at this stage may be due to the removal of the quinoxaline of the ligand. The decomposition was not complete even at 800°C.

3.2.4. Description of the crystal structure. The molecular structure of the complex was solved at 298 K. The complex crystallizes in monoclinic crystal system with the space group *P2₁/n* and the unit cell contains four molecules of $C_{32}H_{26}CoN_6O_3$. Figure 1 gives the ORTEP diagram with atomic labeling scheme. The important interatomic distances and angles are listed in table 2. Two of the monoanionic

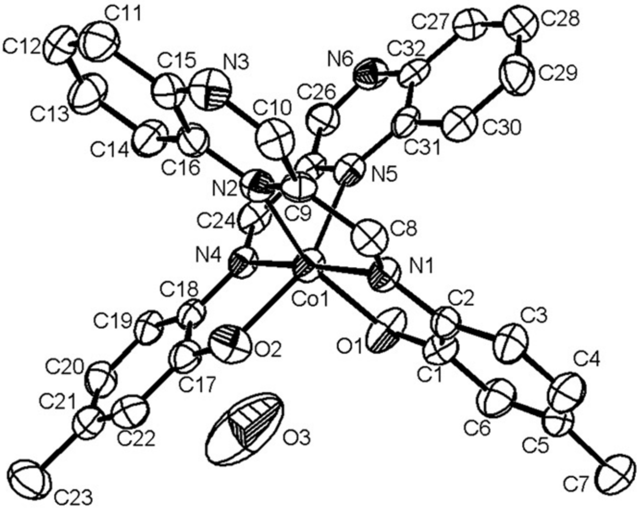

Figure 1. ORTEP diagram of $[Co(C_{16}H_{13}N_3O)_2] \cdot H_2O$ showing the atom labeling scheme with 50% probability ellipsoids.

Table 2. Selected bond lengths (Å) and angles (°) for $[Co(L)_2]\cdot H_2O$.

Co(1)–O(1)	2.031(4)	Co(1)–N(2)	2.256(4)
Co(1)–O(2)	2.045(4)	Co(1)–N(5)	2.310(4)
Co(1)–N(4)	2.049(4)	N(1)–C(8)	1.288(6)
Co(1)–N(1)	2.052(4)	N(4)–C(24)	1.278(6)
O(1)–Co(1)–O(2)	100.55(18)	O(2)–Co(1)–N(5)	153.46(15)
O(1)–Co(1)–N(4)	96.58(15)	N(4)–Co(1)–N(5)	74.89(16)
O(2)–Co(1)–N(4)	79.73(15)	N(1)–Co(1)–N(5)	106.11(15)
O(1)–Co(1)–N(1)	79.98(16)	N(2)–Co(1)–N(5)	92.47(14)
O(2)–Co(1)–N(1)	99.71(15)	C(1)–O(1)–Co(1)	112.90(3)
N(4)–Co(1)–N(1)	176.38(17)	C(17)–O(2)–Co(1)	112.90(3)
O(1)–Co(1)–N(2)	155.61(15)	C(8)–N(1)–Co(1)	118.70(4)
O(2)–Co(1)–N(2)	87.80(15)	C(2)–N(1)–Co(1)	113.30(3)
N(4)–Co(1)–N(2)	107.50(16)	C(24)–N(4)–C(18)	126.30(4)
N(1)–Co(1)–N(2)	76.01(16)	C(24)–N(4)–Co(1)	120.30(4)
O(1)–Co(1)–N(5)	90.03(16)	C(18)–N(4)–Co(1)	113.40(3)

Table 3. Selected hydrogen bond interactions in the complex.

		Distances (Å)		Angles (°)
D−H···A	Symmetry	D···A	H···A	D−H···A
O(3)−H(31)···O(2)	$1-x$, $1-y$, $1-z$	2.895(9)	2.01(8)	169(6)
O(3)−H(32)···N(3)	$1/2+x$, $3/2-y$, $-1/2+z$	3.035(10)	2.51(8)	124(6)
C(3)−H(3)···N(6)	$1/2+x$, $3/2-y$, $1/2+z$	3.467(7)	2.62	152
C(8)−H(8)···N(6)	$1/2+x$, $3/2-y$, $1/2+z$	3.388(7)	2.53(5)	157.1(12)
C(14)−H(14)···N(4)	$1/2+x$, $3/2-y$, $1/2+z$	3.426(7)	2.57	153
C(24)−H(24)···O(1)	$-x$, $1-y$, $1-z$	3.041(7)	2.35(3)	139(3)

tridentate Schiff-base ligands wrap the cobalt(II) center in the *cis* mode with coordination of two oxygens and four nitrogens (N_4O_2) in a distorted octahedral geometry. The molecule has no symmetry elements other than a C2 symmetry axis and is expected to exhibit optical isomerism. However, both enantiomers coexist in the unit cell, making the space group centrosymmetric. The two phenolic hydroxyls are deprotonated on complexation. The azomethine (C=N) bond lengths (1.288(6) and 1.279(6) Å) are within the range of theoretical value (1.285 Å) [37]. The complex geometry can be explained by a rigid structure resulting in O(2)–Co(1)–N(5) and O(1)–Co(1)–N(2) bond angles that deviate significantly from linearity, i.e. 153.46(15) and 155.61(15)°. In the coordination sphere, the Co−O bond lengths are 2.031(4) and 2.045(4) Å; Co−N bond lengths are 2.049(4), 2.052(4), 2.256(4), and 2.310(4) Å. The Co–N (quinoxaline) bonds are elongated compared to Co–N (azomethine) bonds probably due to rigidity of the Schiff base. The benzene rings of the symmetry related quinoxalines are stacked *via* $\pi-\pi$ interactions, having a centroid to centroid distance of 3.532 Å. Molecules are held together by O(3)−H(2)···N(3) and O(3)−H(31)···O(2) intermolecular hydrogen bonding and weak inter and intramolecular hydrogen bonding (table 3) forming a 2-D polymeric structure parallel to the [010] plane. Figure 2 illustrates the unit cell packing and polymeric structure of the molecules in the complex.

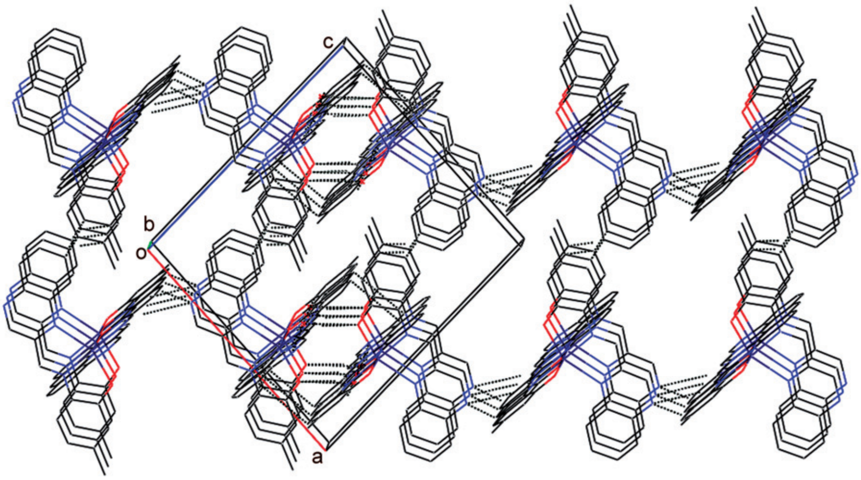

Figure 2. Packing diagram showing the 2-D polymeric chain along crystallographic *b*-axis (hydrogen atoms are omitted for clarity).

4. Conclusion

Cobalt(II) complex of a new Schiff base has been synthesized and characterized. The crystallographic study shows that the cobalt(II) coordination sphere is distorted octahedrally with a *cis* arrangement of N_4O_2 donor set of two tridentate NNO Schiff bases. The molecules exhibit a 2-D polymeric structure parallel to the [010] plane, formed by $O-H\cdots N$ and $O-H\cdots O$ intermolecular hydrogen bonds and $\pi-\pi$ stacking. The crystal is a racemic mixture of two crystallographically independent enantiomers of the complex. To the best of our knowledge, this is the first report of the crystal structure of a mononuclear metal complex of a Schiff base derived from quinoxaline-2-carboxaldehyde.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 729051. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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