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Synthesis and Crystal Structures of Two Isostructural Cobalt(III) Complexes $[Co(C_{15}H_{21}N_2O)(C_8H_7O_2)(N_3)]$ and $[Co(C_{15}H_{21}N_2O)(C_8H_7O_2)(NCS)]$

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Synthesis and Crystal Structures of Two Isostructural Cobalt(III) Complexes [Co($C_{15}H_{21}N_2O$)($C_8H_7O_2$)(N_3)] and [Co($C_{15}H_{21}N_2O$)($C_8H_7O_2$)(NCS)]

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Two isostructural mononuclear cobalt(III) complexes, [Co($C_{15}H_{21}N_2O$)($C_8H_7O_2$)(N_3)] (1) and [Co($C_{15}H_{21}N_2O$)($C_8H_7O_2$)(NCS)] (2), were synthesized and characterized by elemental analysis, IR spectra, and X-ray single crystal structure determination. X-ray structural analysis indicates that both complexes crystallizing in the monoclinic space group $P2_1/c$, with $a = 13.190(2)$ Å, $b = 12.842(2)$ Å, $c = 18.428(2)$ Å, $\beta = 134.040(2)°$, $V = 2243.9(5)$ Å^3, $Z = 4$ for 1, and $a = 8.1284(8)$ Å, $b = 15.6112(15)$ Å, $c = 18.9260(17)$ Å, $\beta = 106.060(3)°$, $V = 2307.9(4)$ Å^3, $Z = 4$ for 2. The Co atom in each complex is coordinated by one Schiff base ligand, one 2-acetylphenolate ligand, and one pseudohalide ligand (N_3 for 1 and NCS for 2), forming an octahedral geometry.

Keywords cobalt, crystal structure, Schiff base, synthesis

INTRODUCTION

Schiff bases are considered as a very important class of organic compounds that have wide applications in coordination chemistry and biological aspects.[1–3] Mono- and multinuclear complexes of cobalt in its varied oxidation states have become a central theme of current research because of their potentially applications in many fields.[4–6] In the last few years, cobalt complexes with multi-dentate Schiff base ligands have been widely used to mimic cobalamine (B_{12}) coenzymes.[7–9] Among the N, O containing chelators, the tridentate mono-condensed Schiff base ligands have received much attention for the synthesis of mono- and polynuclear complexes. The copper, nickel, zinc, and manganese complexes with tridentate mono-condensed Schiff bases have widely been reported; however, the cobalt complexes with such ligands have been reported on relatively less. A literature search reveals that the Schiff base 2-[1-(2-piperidin-1-ylethylimino)ethyl]phenol derived from 1-(2-hydroxyphenyl)ethanone and 2-piperidin-1-ylethylamine has not been prepared. In this article, the author describes the synthesis and characterization of two new isostructural cobalt(III) complexes with the Schiff base and 2-acetylphenolate. The crystal structures of the complexes have been investigated by single crystal X-ray diffraction.

EXPERIMENTAL

Materials and Methods

All chemicals and solvents used for the syntheses were of analytical grade. 1-(2-Hydroxyphenyl)ethanone and 2-piperidin-1-ylethylamine were purchased from Aldrich Chemical Company, and other chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Perkin-Elmer 240C analytical instrument. The metal analysis was carried out by titration. IR spectra in the 4,000-400 cm^{-1} range were measured with a Thermo Nicolet 320 FT-IR spectrometer using KBr discs.

Synthesis of the Schiff Base 2-[1-(2-piperidin-1-ylethylimino)ethyl]phenol (HL^1)

To a vigorously stirred methanol solution (30 ml) of 1-(2-hydroxyphenyl)ethanone (0.136 g, 1 mmol), a methanol solution (20 ml) of 2-piperidin-1-ylethylamine (0.128 g, 1 mmol) was added. The mixture was stirred for about 30 min and then refluxed for 30 min. The resulting solution was evaporated under vacuum to remove the solvent to give a yellow gummy product. Anal. calc. for $C_{15}H_{22}N_2O$: C, 73.13; H, 9.00; N, 11.37%. Found: C, 73.32; H, 9.08; N, 11.23%.

Synthesis of [Co($C_{15}H_{21}N_2O$)($C_8H_7O_2$)(N_3)] (1)

To a methanol solution (10 ml) of cobalt nitrate hexahydrate (29.1 mg, 0.1 mmol), a methanol solution (10 ml) of HL^1 (24.6 mg, 0.1 mmol) and 1-(2-hydroxyphenyl)ethanone (13.6 mg, 0.1 mmol) was added dropwise and the mixture was stirred for 10 min. Then to the mixture was added a minimum volume of aqueous solution of sodium azide (6.5 mg, 0.1 mmol) under stir-

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ring. The resulting mixture was further stirred for 1 h at ambient temperature to give a deep brown solution. The solution, on slow evaporation, gave brown single crystals of the complex. The crystals were filtered off and dried in air. Yield 27.3 mg (57% based on Co). Anal. calc. for $C_{23}H_{28}CoN_5O_3$: C, 57.38; H, 5.86; N, 14.55; Co, 12.24%. Found: C, 57.10; H, 5.97; N, 14.70; Co, 12.45%.

Synthesis of $[Co(C_{15}H_{21}N_2O)(C_8H_7O_2)(NCS)]$ (2)

Complex **2** was obtained using the same procedure as described for complex **1** taking sodium azide in place of ammonium thiocyanate (7.6 mg, 0.1 mmol). The brown crystals of **2** were filtered off and dried in air. Yield 33.0 mg (66% based on Co). Anal. calc. for $C_{24}H_{28}CoN_3O_3S$: C, 57.94; H, 5.67; N, 8.45; Co, 11.85%. Found: C, 57.73; H, 5.75; N, 8.31; Co, 12.03%.

X-Ray Crystallography

Diffraction intensities for both complexes were collected on a Bruker SMART 1000 CCD area diffractometer equipped with graphite monochromated Mo Kα radiation with a radiation wavelength of 0.71073 Å using the ω-scan technique at 298(2) K. Absorption corrections were performed using the SADABS program.[10] The structures were solved by direct method and refined by full-matrix least-squares against F^2 using SHELXTL.[11] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom isotropic displacement parameters were all treated as riding on the parent atoms (1.2 or 1.5 U_{eq} for the carbon H atoms). All hydrogen atoms were generated geometrically and were included in the refinement in the riding model approximation. Selected crystallographic data are summarized in Table 1. Coordinate bond lengths and angles are listed in Table 2.

TABLE 1
Crystallographic parameters of **1** and **2**

	1	**2**
Empirical formula	$C_{23}H_{28}CoN_5O_3$	$C_{24}H_{28}CoN_3O_3S$
Formula weight	481.43	497.48
Temperature (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a (Å)	13.190(2)	8.1284(8)
b (Å)	12.842(2)	15.6112(15)
c (Å)	18.428(2)	18.9260(17)
β (°)	134.040(2)	106.060(3)
V (Å^3)	2243.9(5)	2307.9(4)
Z	4	4
ρ_{calc} (g cm^{-3})	1.425	1.432
μ (mm^{-1})	0.800	0.865
F(000)	1008	1040
Crystal size (mm)	0.20 × 0.20 × 0.18	0.30 × 0.30 × 0.28
θ Range for data collection (∞)	2.21–26.99	2.24–27.00
Max. and min. transmission	0.8564, 0.8694	0.7813, 0.7937
Reflections collected	17886	18570
Unique (R_{int})	4885	5028
Observed reflections [$I > 2\sigma(I)$]	3032	3665
Restraints	0	0
Parameters	291	291
Goodness-of-fit on F^2	1.021	1.021
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0445$, $wR_2 = 0.1033$	$R_1 = 0.0364$, $wR_2 = 0.0834$
R indices (all data)	$R_1 = 0.0885$, $wR_2 = 0.1221$	$R_1 = 0.0610$, $wR_2 = 0.0982$
Largest diffraction peak and hole (eÅ^{-3})	0.343 and –0.298	0.430 and –0.266

RESULTS AND DISCUSSION

A 1:1 molar ratio of 1-(2-hydroxyphenyl)ethanone and 2-piperidin-1-ylethylamine in methanol was reacted to prepare the unsymmetrical tridentate Schiff base ligand. The Co atom readily adopts octahedral coordination in the complexes. The reaction of the tridentate Schiff bases (L) bearing NNO donors with cobalt salts usually gives $[CoL_2]$ complexes,[12–15] which made the pseudohalides difficult to coordinate to the Co atom. In the present work, the bidentate 1-(2-hydroxyphenyl)ethanone was used as a secondary ligand. A tridentate Schiff base ligand and a bidentate 1-(2-hydroxyphenyl)ethanone supplied five donors, which made the small ligands such as azide and thiocyanate easily furnish the octahedral coordination of the Co atoms. The air-stable, moisture-insensitive complexes were obtained as deep brown crystals, which are soluble in a range of common organic solvents such as methanol, ethanol, dichloromethane, acetonitrile, dimethylformamide, and dimethylsulphoxide, but are insoluble in water. The molar conductance values of the complexes measured in methanol at the concentration of 10^{-3} M are in the range 20–30 Ω^{-1} cm^2 mol^{-1}, indicating they are non-electrolytes.[16] Microanalytical analyses of the complexes are in agreement with the formulae proposed by the single crystal X-ray determination.

Infrared Spectra

Comparison of the IR spectra of the complexes with that of the free ligands gives information regarding bonding sites of the ligands. The complexes display intense peaks at 1605 and 1577 cm^{-1} due to the carbonyl (C = O) and azomethine (C = N) stretching, respectively, which are shifted by about 20–30 cm^{-1} to lower frequencies compared to the free ligands. The shift of these bands towards lower frequencies compared to those of the free ligands indicates the coordination of the carbonyl O and imine N atoms to the metal center. For the complexes, the phenolic C—O stretching is observed at about

TABLE 2
Selected bond distances (Å) and bond angles (°) for **1** and **2**

1			
Co1-O1	1.863(2)	Co1-O2	1.927(2)
Co1-O3	1.9113(19)	Co1-N1	1.903(2)
Co1-N2	2.046(2)	Co1-N3	1.941(3)
O1-Co1-N1	94.86(10)	O1-Co1-O3	86.16(8)
N1-Co1-O3	177.77(9)	O1-Co1-O2	89.04(9)
N1-Co1-O2	86.23(9)	O3-Co1-O2	91.80(8)
O1-Co1-N3	91.36(10)	N1-Co1-N3	91.04(10)
O3-Co1-N3	90.92(9)	O2-Co1-N3	177.27(9)
O1-Co1-N2	176.67(9)	N1-Co1-N2	88.12(9)
O3-Co1-N2	90.91(8)	O2-Co1-N2	92.63(9)
N3-Co1-N2	87.11(10)		
2			
Co1-O1	1.8654(16)	Co1-O2	1.9058(16)
Co1-O3	1.8583(16)	Co1-N1	1.8927(18)
Co1-N2	2.0537(19)	Co1-N3	1.910(2)
O3-Co1-O1	88.51(8)	O3-Co1-N1	84.26(8)
O1-Co1-N1	95.08(8)	O3-Co1-O2	93.50(7)
O1-Co1-O2	86.71(7)	N1-Co1-O2	177.09(8)
O3-Co1-N3	174.10(8)	O1-Co1-N3	89.57(9)
N1-Co1-N3	90.36(9)	O2-Co1-N3	91.96(8)
O3-Co1-N2	91.87(8)	O1-Co1-N2	176.80(7)
N1-Co1-N2	88.12(8)	O2-Co1-N2	90.10(7)
N3-Co1-N2	90.35(8)		

1250 cm^{-1}. The presence of new bands in the spectra of the complexes in the range 420–580 cm^{-1} can be attributed to the Co-O and Co-N stretching vibrations. The intense absorption band of the azide ligand in **1** is observed at 2022 cm^{-1}, and that of the thiocyanate ligand in **2** is observed at 2071 cm^{-1}.

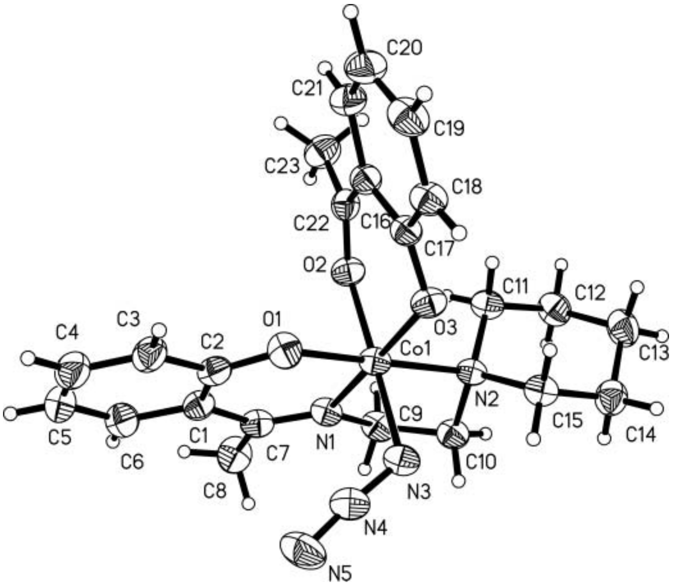

FIG. 1. Molecular structure of **1** drawn with 30% probability ellipsoids for non-hydrogen atoms.

Crystal Structures

The molecular structures of the complexes **1** and **2** are shown in Figures 1 and 2, respectively. The Co atom in each complex is hexacoordinated with a N_3O_3 coordination mode arising from one Schiff base ligand, one 1-(2-hydroxyphenyl)ethanone, and one pseudohalide (azide for **1** and thiocyanate for **2**). The coordination is best described as a slightly distorted octahedral, with the three *trans* angles lying in the ranges 176.7(1)–177.8(1)° for **1** and 174.1(1)–177.1(1)° for **2**. The *cis* angles around the Co atoms are also close to the ideal values for octahedral geometry, ranging from 86.2(1) to 94.9(1)° for **1**, and from 84.3(1) to 95.1(1)° for **2**. The corresponding bond distances in both complexes are comparable to each other. The distances of Co1-N2 in both complexes are longer than those of the Co1-N1, and both comparable to the Co-N distances observed in other cobalt(III) complexes with Schiff bases.[14,15] The two benzene rings in each complex are approximately perpendicular to each other, with the dihedral angles of 70.3(3)° for **1** and 84.5(3)° for **2**, respectively. The phenolic hydroxyls are deprotonated on complexation. The azide and thiocyanate groups are nearly linear and show bent coordination modes with the Co atoms. In **1**, N3-N4-N5/Co1-N3-N4 = 175.0(3)/120.2(2)°; In **2**, N3-C24-S1/Co1-N3-C24 = 179.0(2)/175.4(2)°.

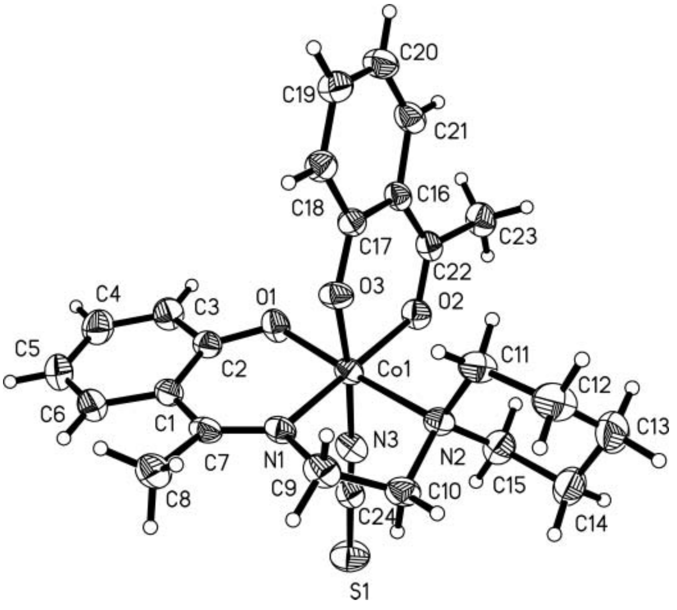

FIG. 2. Molecular structure of **2** drawn with 30% probability ellipsoids for non-hydrogen atoms.

CONCLUSION

Two new cobalt(III) complexes have been synthesized and characterized by various physicochemical studies. Conductivity measurements show that both complexes have non-electrolytic nature. The crystallographic study shows that the Co coordination spheres are distorted octahedrally. To the best of the author's knowledge, this is the first report of the crystal structures of complexes with the Schiff base 2-[1-(2-piperidin-1-ylethylimino)ethyl]phenol.

SUPPLEMENTARY MATERIALS

CCDC 787914 and 787915 contain the supplementary crystallographic data for complexes **1** and **2**, respectively. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033 or email: deposit@ccdc.cam.ac.uk.

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