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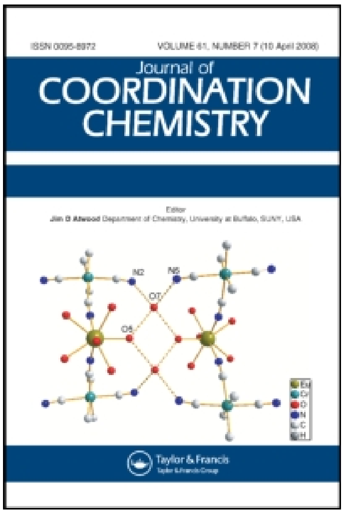

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# Synthesis and Crystal structure of an Iminodiacetatocobalt(Ii) complex with Benzimidazole

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# SYNTHESIS AND CRYSTAL STRUCTURE OF AN IMINODIACETATOCOBALT(II) COMPLEX WITH BENZIMIDAZOLE

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The title complex, $(C_7H_6N_2)_3(C_4H_5NO_4)Co \cdot 2H_2O$, has been prepared and its crystal structure determined by single-crystal X-ray diffraction methods. The cobalt atom is octahedrally coordinated by three benzimidazole molecules and an iminodiacetate anion. The anion coordinates facially as a tridentate. Extensive intermolecular hydrogen bonding and $C{-}H \cdots \pi$ interactions occur in the crystal. Thermal decomposition of the complex has been studied by thermogravimetry and differential scanning calorimetry. The IR spectral assignments were based on the molecular structure.

*Keywords:* Cobalt(II) complex; Crystal structure; Iminodiacetate; Benzimidazole; Hydrogen bond

## INTRODUCTION

Non-covalent chemistry is fundamental to interpreting and predicting relationships between chemical structure and function. For example, aromatic stacking interactions are correlated with electron transfer in some biological systems [1]. X-ray structural investigation of metal complexes with phenanthroline [2], quinoline [3] and benzimidazole [4–6] has shown that aromatic stacking commonly occurs in metal complexes with aromatic hetero-polycyclic ligands. As a part of an investigation of aromatic stacking, the title Co(II) compound containing benzimidazole has been prepared, but no such aromatic stacking was observed. Instead, weak $C{-}H \cdots \pi$ interactions [7] are present in the crystal.

## EXPERIMENTAL

### Synthesis

All reagents were commercially available and of analytical grade. Cobalt dichloride hexahydrate (1 mmol), iminodiacetic acid (IDA) (1 mmol), benzimidazole (BZIM)

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(2 mmol) and NaOH (2 mmol) were dissolved in a water (8 $cm^3$)/ethanol (2 $cm^3$) mixture. The solution was refluxed for 4 h until a small amount of precipitate appeared. The solution was cooled to room temperature and filtered. Red, single crystals were obtained from the filtrate after two days.

## Physical Measurements

Elemental analyses were performed on a Carlo-Erba 1160 instrument. Anal. Calcd. for $(C_7H_6N_2)_3(C_4H_5NO_4)Co \cdot 2H_2O$(%): C, 51.73; N, 16.89; H, 4.69. Found: C, 51.33; N, 17.49; H, 4.84. The IR spectrum of the title compound was measured in KBr pellets in the 4000–400 $cm^{-1}$ region using a Nicolet 5DX FT-IR spectrophotometer. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed with an automatically recording Netzsch STA 409 TG/PC analyzer. Some 4.2 mg of the compound was used for TG, and highly sintered $Al_2O_3$ was the reference material for the DSC measurement. TG and DSC curves were recorded up to 900 K at 5 K per min in static air.

X-Ray diffraction intensities were collected on a Rigaku RAXIS-RAPID diffractometer at room temperature. The structure was solved by direct methods followed by Fourier syntheses. Structure refinement was performed by full-matrix least-squares procedures using SHELX-97 on $F^2$ [8]. Crystal data and refinement conditions are summarized in Table I. Final fractional atomic coordinates and equivalent isotropic thermal parameters for the non-H atoms are listed in Table II. Full crystallographic data have been deposited at the CCDC, deposition number CCDC 224680.

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TABLE I Crystal data and structure refinement conditions for the complex

| | |
|---|---|
| Empirical formula | $C_{25}H_{23}CoN_7O_4 \cdot 2H_2O$ |
| Formula weight | 580.47 |
| Crystal size (mm) | 0.24 × 0.19 × 0.05 |
| Temperature (K) | 293 |
| Wavelength (Å) | 0.71069 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions (Å,°) | $a = 13.5117(4)$<br>$b = 10.3263(5)$<br>$c = 19.3861(9)$<br>$\beta = 103.773(2)$ |
| Volume (Å$^3$) | 2627.09(19) |
| $Z$ | 4 |
| Density (calculated) (g $cm^{-3}$) | 1.468 |
| Absorption coefficient ($mm^{-1}$) | 0.707 |
| $F(000)$ | 1204 |
| $\theta$ Range for data collection (°) | 2.2 to 27.5 |
| Reflections collected | 21 734 |
| Independent reflections | 5742 |
| Parameters | 353 |
| Goodness-of-fit on $F^2$ | 1.075 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0576$, $wR_2 = 0.0905$ |
| $R$ indices (all data) | $R_1 = 0.0932$, $wR_2 = 0.0994$ |
| Extinction coefficient | 0.0014(2) |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.32 and −0.36 |

TABLE II Atomic coordinates [$\times 10^4$] for non-H atoms and equivalent isotropic displacement parameters [$\times 10^3$]

| *Atom* | *x/a* | *y/b* | *z/c* | *U(eq)* (Å$^2$) |
|---|---|---|---|---|
| Co | 2521(1) | 2425(1) | 2283(1) | 26(1) |
| O(1) | 2661(1) | 378(2) | 2064(1) | 35(1) |
| O(2) | 1842(2) | −1209(2) | 1391(1) | 54(1) |
| O(3) | 2213(1) | 1855(2) | 3242(1) | 36(1) |
| O(4) | 1016(2) | 1238(3) | 3783(1) | 50(1) |
| O(1W) | 79(2) | −1062(3) | 4082(1) | 60(1) |
| O(2W) | 547(3) | −2886(4) | 461(2) | 111(2) |
| N(11) | 4073(2) | 2690(2) | 2783(1) | 30(1) |
| N(13) | 5622(2) | 3552(3) | 3104(1) | 37(1) |
| N(21) | 2737(2) | 2679(2) | 1231(1) | 30(1) |
| N(23) | 2374(2) | 2985(3) | 60(1) | 35(1) |
| N(31) | 2202(2) | 4457(3) | 2450(1) | 34(1) |
| N(33) | 2186(2) | 6569(3) | 2209(2) | 45(1) |
| N(3) | 929(2) | 1846(2) | 1918(1) | 31(1) |
| C(1) | 1880(2) | −110(3) | 1668(2) | 33(1) |
| C(2) | 906(2) | 692(3) | 1474(2) | 38(1) |
| C(4) | 519(2) | 1659(4) | 2546(2) | 48(1) |
| C(5) | 1315(2) | 1556(3) | 3242(2) | 33(1) |
| C(12) | 4671(2) | 3651(3) | 2691(2) | 35(1) |
| C(14) | 6413(2) | 1897(4) | 4040(2) | 44(1) |
| C(15) | 6170(3) | 773(4) | 4334(2) | 49(1) |
| C(16) | 5217(3) | 180(3) | 4107(2) | 44(1) |
| C(17) | 4461(2) | 730(3) | 3581(2) | 37(1) |
| C(18) | 4691(2) | 1888(3) | 3287(1) | 30(1) |
| C(19) | 5657(2) | 2436(3) | 3500(2) | 33(1) |
| C(22) | 2073(2) | 3112(3) | 668(2) | 34(1) |
| C(24) | 4005(2) | 2102(3) | −181(2) | 38(1) |
| C(25) | 4913(3) | 1560(3) | 165(2) | 45(1) |
| C(26) | 5140(2) | 1332(3) | 897(2) | 42(1) |
| C(27) | 4469(2) | 1657(3) | 1304(2) | 34(1) |
| C(28) | 3550(2) | 2222(3) | 965(1) | 28(1) |
| C(29) | 3327(2) | 2417(3) | 232(1) | 31(1) |
| C(32) | 2205(3) | 5356(3) | 1971(2) | 42(1) |
| C(34) | 2141(3) | 7437(4) | 3414(2) | 57(1) |
| C(35) | 2107(3) | 7009(5) | 4080(2) | 68(1) |
| C(36) | 2105(3) | 5710(5) | 4242(2) | 64(1) |
| C(37) | 2133(2) | 4760(4) | 3741(2) | 46(1) |
| C(38) | 2170(2) | 5168(3) | 3067(2) | 34(1) |
| C(39) | 2168(2) | 6487(3) | 2912(2) | 39(1) |

*U*(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

# RESULTS AND DISCUSSION

## Crystal structure

The molecular structure of the title compound is illustrated in Fig. 1. Selected bond distances and angles are listed in Table III. Octahedral coordination geometry around Co(II) is formed by one IDA and three BZIM molecules. The tridentate IDA chelates the Co(II) atom in a *facial* manner, two five-membered chelating rings being nearly perpendicular to each other. The O(1)-ring [the chelating ring including atom O(1)] displays an envelope configuration, the N(3) atom at the flap position being 0.505 Å out of the mean plane formed by Co, O(1), C(1) and C(2) atoms.

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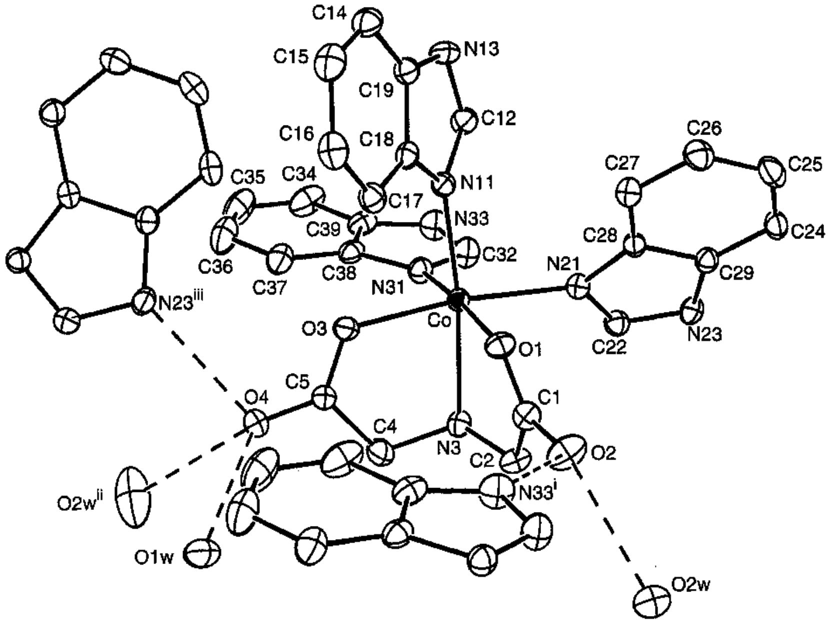

FIGURE 1 The molecular structure of the title complex with 30% probability thermal displacement ellipsoids, the dashed lines showing the hydrogen bonding. Symmetry codes: (i) $x$, $-1+y$, $z$; (ii) $-x$, $0.5+y$, $0.5-z$; (iii) $x$, $0.5-y$, $0.5+z$.

TABLE III Selected bond lengths (Å) and angles (°) for the complex

| | | | |
|---|---|---|---|
| Co–O(3) | 2.085(2) | Co–O(1) | 2.173(2) |
| Co–N(11) | 2.108(2) | Co–N(31) | 2.182(3) |
| Co–N(21) | 2.144(2) | Co–N(3) | 2.183(2) |
| O(1)–C(1) | 1.253(3) | O(3)–C(5) | 1.251(3) |
| O(2)–C(1) | 1.251(4) | O(4)–C(5) | 1.256(3) |
| O(3)–Co–N(11) | 90.86(8) | N(21)–Co–N(31) | 95.7(1) |
| O(3)–Co–N(21) | 169.85(9) | O(1)–Co–N(31) | 173.68(8) |
| N(11)–Co–N(21) | 94.36(8) | O(3)–Co–N(3) | 79.68(8) |
| O(3)–Co–O(1) | 86.85(9) | N(11)–Co–N(3) | 168.74(9) |
| N(11)–Co–O(1) | 95.35(9) | N(21)–Co–N(3) | 94.11(8) |
| N(21)–Co–O(1) | 84.01(9) | O(1)–Co–N(3) | 78.16(8) |
| O(3)–Co–N(31) | 92.88(9) | N(31)–Co–N(3) | 95.57(9) |
| N(11)–Co–N(31) | 90.96(9) | | |
| C(1)–O(1)–Co | 114.3(2) | C(5)–O(3)–Co | 117.9(2) |
| C(2)–N(3)–Co | 107.1(2) | C(4)–N(3)–Co | 107.8(2) |
| C(12)–N(11)–Co | 127.6(2) | C(18)–N(11)–Co | 127.4(2) |
| C(22)–N(21)–Co | 127.7(2) | C(28)–N(21)–Co | 127.2(2) |
| C(32)–N(31)–Co | 122.7(2) | C(38)–N(31)–Co | 132.3(2) |

The O(3)-ring is nearly coplanar, the maximum atomic deviation being 0.097(2) Å [C(4)]. Such a *facial* structure has been found in several IDA complexes [9]. Each carboxyl group of IDA coordinates to the Co(II) as a monodentate. Uncoordinated carboxyl oxygen atoms [O(2) and O(4)] are hydrogen bonded to lattice water molecules and BZIM from adjacent complex molecules, as shown in Fig. 1. Hydrogen bonding parameters are listed in Table IV.

TABLE IV Hydrogen bonding parameters (Å, °)

| *D*–*H*···*A* | *D*–*H* | *H*···*A* | *D*···*A* | *D*–*H*–*A* |
|---|---|---|---|---|
| O(1W)–H(1A)···O(4) | 0.965 | 1.853 | 2.816(3) | 176.3 |
| O(2W)–H(2A)···O(2) | 0.847 | 1.989 | 2.794(4) | 158.6 |
| C(27)–H(27)···N(11) | 0.930 | 2.540 | 3.220(4) | 130.3 |
| C(37)–H(37)···O(3) | 0.930 | 2.420 | 3.161(5) | 136.2 |
| O(1W)–H(1B)···O(2W)[i] | 0.891 | 2.048 | 2.815(4) | 143.6 |
| O(2W)–H(2B)···O(4)[ii] | 0.956 | 2.047 | 2.983(4) | 165.8 |
| N(3)–H(3)···O(1W)[iii] | 0.910 | 2.100 | 3.004(3) | 170.8 |
| N(13)–H(13)···O(1)[iv] | 0.860 | 2.220 | 3.067(3) | 169.1 |
| N(23)–H(23)···O(4)[v] | 0.860 | 1.980 | 2.824(3) | 167.7 |
| N(33)–H(33)···O(2)[vi] | 0.860 | 1.920 | 2.765(4) | 166.5 |
| C(14)–H(14)···O(2)[iv] | 0.930 | 2.600 | 3.320(4) | 134.7 |
| C(22)–H(22)···O(1W)[iii] | 0.930 | 2.270 | 3.176(4) | 165.9 |

Symmetry codes: [i] $x, -y-0.5, z+0.5$; [ii] $-x, y-0.5, -z+0.5$; [iii] $-x, y+0.5, -z+0.5$; [iv] $-x+1, y+0.5, -z+0.5$; [v] $x, -y+0.5, z-0.5$; [vi] $x, y+1, z$.

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The BZIM ligands display different spatial orientations. The N(11)-BZIM ring plane almost bisects the dihedral angle formed by the chelating rings of IDA. This may be due to van der Waals contacts between the N(11)-ring and IDA as the H(17)···O(1) (2.740 Å) and H(17)···O(3) (2.634 Å) separations are close to the sum of the van der Waals radii of O and H atoms. The N(31)-BZIM ligand coordinates to Co(II) atom with different Co–N–C angles, Co–N(31)–C(38) 132.3° and Co–N(31)–C(32) 122.7°. This difference in angles differs from the remaining Co–N–C angles, all nearing 127° (see Table II). This may be due to the weak intramolecular C(37)–H(37)··· O(3) hydrogen bond, as verified by the H(37)···O(3) separation of 2.420 Å and C(37)–H(37)···O(3) angle of 136.2° (Table IV).

Aromatic stacking between BZIM rings has been found in many other metal complexes, but no aromatic stacking occurs in the title compound. Instead of aromatic stacking, C–H···$\pi$ interactions occur in the crystal as shown in Fig. 2. The separation of 2.750 Å between H(16) and the centre of the C(24A)-ring and the C(16)–H(16)···centre [C(24A)-ring] angle of 139.8° suggests the existence of a weak C–H···$\pi$ interaction [7]. Likewise, the separation of 2.766 Å between H(26) and the centre of the C(34A)-ring and the C(26)–H(26)···centre [C(34A)-ring] angle of 147.5° suggests another C–H···$\pi$ interaction between neighbouring BZIM rings. The C–H···$\pi$ interactions seem to play a significant role in determining crystal packing [10–12]. The molecular packing is presented in Fig. 3, which shows hydrogen bonding involving water molecules.

## Thermal Analysis

TG and DSC curves indicate that the title complex decomposes via various steps. The first step beginning at 60°C shows a broad endothermic peak and 4.9% weight loss corresponding to lattice water. The second and third steps overlap and begin at 230°C. This endothermic process is due to the loss of an IDA molecule (calcd. 22.6%, found 22.7%). The next begins at 280°C with a broad endothermic peak and the weight loss corresponds to one BZIM molecule (calcd. 20.3%, found 20.5%). Above 320°C, decomposition suddenly becomes exothermic. Here two sharp exothermic peaks appear at 330°C and 340°C, respectively. These are ascribed to the loss of

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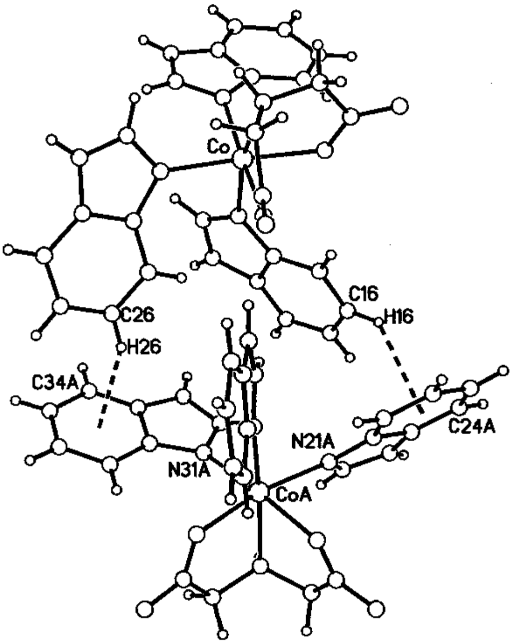

FIGURE 2 Diagram showing the intermolecular C—H···π interaction. Symmetry code: (A) $1-x$, $-0.5+y$, $0.5-z$.

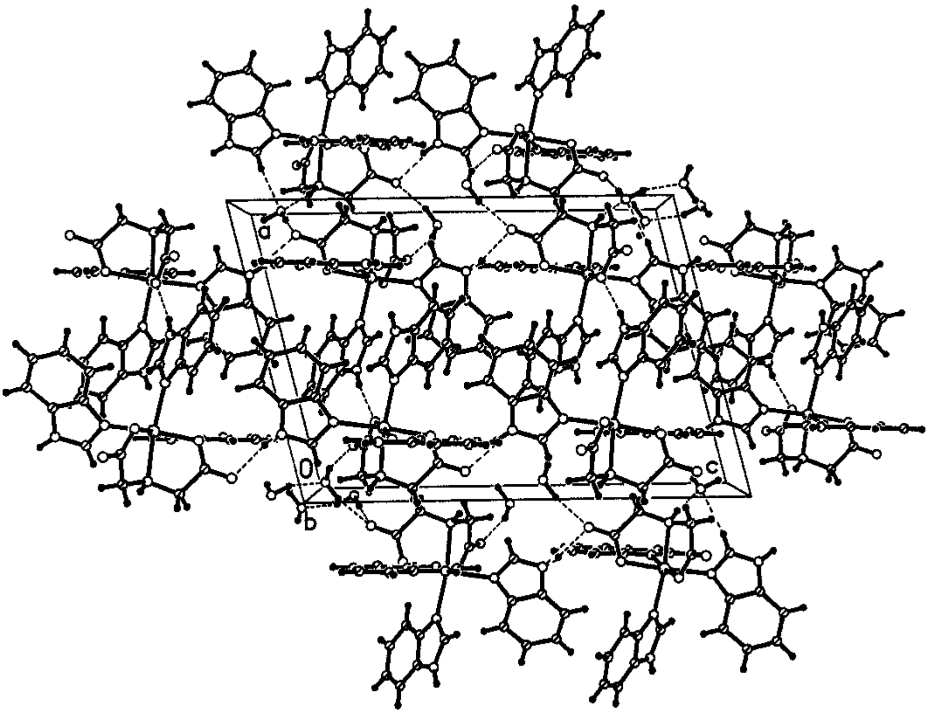

FIGURE 3 The molecular packing diagram, dashed lines showing hydrogen bonding.

two benzimidazole molecules. The final residue was CoO (calcd. 12.91%, found 12.39%).

## IR Spectra

IR spectra of the complex were assigned based on the crystal structure. Stretching of the carboxyl group was observed at 1600 [$\nu_{as}$(coo)] and 1407 cm$^{-1}$ [$\nu_s$(coo)]. The $\Delta\nu$ value of 193 cm$^{-1}$ agrees with monodentate coordination of the carboxyl group [13]. Stretching vibrations of water appear in the range 3430–3500 cm$^{-1}$. Compared to 3580–3650 cm$^{-1}$ found for the free hydroxyl group, $\nu(H_2O)$ is an indication of hydrogen-bonded water molecules. Likewise, the N–H stretch in the chelating IDA moiety (3248 cm$^{-1}$) is also significantly lower in frequency than 3400–3330 cm$^{-1}$ for the free imino group.

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