

Study on self-assembly of Cobalt(II) complexes using diaminodiamide ligands

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Abstract

The self-assembly of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with four diaminodiamide ligands that are 4,7-diazadecanediamide, 4,8-diazaundecanediamide, 4,7-dimethyl-4,7-diazadecanediamide and N,N'-Bis(β -carbamoyl ethyl)1,2-diaminocyclohexane gave compounds $[(\text{C}_8\text{H}_{18}\text{N}_4\text{O}_2)\text{Co}(\text{OH})_2\text{Co}(\text{C}_8\text{H}_{18}\text{N}_4\text{O}_2)] \cdot 2\text{Cl}$ (**1**), $[\text{Co}(\text{C}_9\text{H}_{20}\text{N}_4\text{O}_2)(\text{Cl})(\text{H}_2\text{O})]\text{Cl} \cdot 2\text{H}_2\text{O}$ (**2**), $[\text{Co}(\text{C}_{10}\text{H}_{22}\text{N}_4\text{O}_2)(\text{H}_2\text{O})]2\text{Cl} \cdot 2\text{H}_2\text{O}$ (**3**) and $[\text{Co}(\text{C}_{12}\text{H}_{24}\text{N}_4\text{O}_2)(2\text{H}_2\text{O})] \cdot 2\text{Cl}$ (**4**), respectively. Structures of **1**, **2**, **3** and **4** were characterized by single-crystal X-ray diffraction analysis. Structural data for **1** indicate that the cobalt atom presents in a novel type of binuclear complex with distorted octahedral coordination geometry around the cobalt atoms through hydroxo bridges, where one N- and one O-donor set of ligand and two OH located at equatorial positions and one N- and one O-donor set of ligand occupied at axial positions. Structural data for **2** indicate that the cobalt atom presents in a six-coordinated distorted octahedral geometry of $\text{CoN}_2\text{O}_3\text{Cl}$ core, where two N- and two O-donor sets of ligand located at equatorial positions and a chlorine, a water molecule occupy the axial positions. Structural data for **3** indicate that the cobalt atom presents in a six-coordinated distorted octahedral geometry of CoN_2O_4 core, where two N-donor set of ligand and two water molecules sets located at equatorial positions and two O-donor set of ligand occupy the axial positions. Structural data for **4** indicate that the cobalt atom presents in a six-coordinated distorted octahedral geometry of CoN_2O_4 core, where two N- and two O-donor set of ligand located at equatorial positions and two water molecules occupy the axial positions. Co(II) complexes using diaminodiamide ligands generate special supramolecular architecture through intermolecular hydrogen-bonding interactions.

Keywords: Self-Assembly; Complex; Diaminodiamide; Co(II); Supramolecular

1. Introduction

The crystal-engineering of supramolecular architectures is a growing field that has attracted much attention in the past decades¹⁻⁷ Inorganic-organic hybrid materials have been studied for potential application in gas storage, catalysis, separations, and molecular recognition.⁸⁻¹⁰ Organic components containing N- or O-donors in the framework offer a great potential for chemical and structural diversity.¹¹⁻¹³ With the recent development of self-assembly strategies, it is possible to rationally design and synthesize supramolecular architectures based on covalent or supramolecular contacts and dispersion forces.¹⁴ Among weak noncovalent forces, hydrogen bonds are commonly used as structure directing entities and hence allow their application on crystal design.

Organic amides have long proved to be

very useful in self-assembly through hydrogen bonding, and the assembled products have relevance to biological systems. The amide–amide hydrogen bonding did increase the supramolecular complexity in the solid states.¹⁵⁻¹⁸ We report herein on the self-assembly and structure of Co(II) with these two diaminodiamide ligands. Although the four ligands should have a similar coordination capacity, different geometries are observed in the solid state. The four complexes have been characterized by single-crystal structural analysis.

2. Experimental Section

2.1. Chemicals and Instruments

$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, $\text{HNCH}_3\text{CH}_2\text{CH}_2\text{CH}_3\text{NH}_2$, $\text{CH}_2\text{CHCONH}_2$, $\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 1,2-diaminocyclohexane and ethanol were purchased commercially and were used as received

without further purification. The IR spectra were recorded using an AVATAR FTIR-320 spectrophotometer in KBr pellets. Elemental analyses were performed using an Heraeus CHN-OS-RAPID elemental analyzer.

2.2. Synthesis of 4,7-Diazadecanediamide

The 4,7-diazadecanediamide was prepared as previously reported from an ethanol solution of ethylenediamine (13.2 ml, 0.20 mol) and acrylamide (28.4 g, 0.40 mol) in ethanol (100 cm³) by heating under reflux for 2 h. The solution was cooled and the product filtered off, washed with cold ethanol, recrystallized from ethanol, and dried in vacuo. The compound was 99.8% pure as determined by titration with standard base. Anal. Calcd. for C₈H₁₈N₄O₂: C, 47.52; H, 8.91; N, 27.27. Found: C, 47.49; H, 8.61; N, 26.75. IR (KBr cm⁻¹): 3267(s), 3081(s), 2962(m), 2891(w), 2839(m), 1696(vs), 1650(vs), 1481(m), 1451(m), 1403(s), 1242(m), 1171(m), 1115(m), 917(m), 888(m), 735(m).

2.3. Synthesis of 4,8-Diazadecanediamide

The 4,8-diazadecanediamide was prepared as previously reported from an acetonitrile solution of 1,3-diaminopropane (16.6 ml, 0.20 mol) and acrylamide (28.4 g, 0.40 mol) in acetonitrile (100 cm³) by heating under reflux for 3 h. The solution was cooled and the product filtered off, washed with cold ethanol, recrystallized from chloroform, and dried in vacuo. The compound was 80% pure as determined by titration with standard base. Anal. Calcd. for C₈H₁₈N₄O₂: C, 50.0; H, 9.30; N, 25.9. Found: C, 49.55; H, 9.20; N, 25.85. IR (KBr cm⁻¹): 3267(s), 3081(s), 2962(m), 2891(w), 2839(m), 1685(vs), 1663(vs), 1410(m), 1314(m), 1114(m), 917(m), 886(m), 732(m).

2.4. Synthesis of

4,7-dimethyl-4,7-diazadecanediamide

The 4,7-dimethyl-4,7-diazadecanediamide was prepared as previously reported from an acetonitrile solution of N,N'-dimethylethylenediamine (13.4 ml, 0.20 mol) and acrylamide (28.4 g, 0.40 mol) in acetonitrile (100 cm³) by heating under reflux for 4 h. The solution was cooled and the product filtered off, washed with cold ethanol, recrystallized from chloroform, and dried in vacuo. The compound was 76% pure as determined by titration with standard base. IR (KBr cm⁻¹): 3259(s), 3190(s), 2991(m), 2911(w), 2836(m), 1690(vs), 1663(w), 1415(m), 1314(m), 1319(w), 1272(w), 1196(m), 1112(m),

1067(w), 1022(w), 988(w), 933(w), 844(w), 766(w), 742(w), 571(w), 531(w).

2.5. Synthesis of N,N'-Bis(β-carbamoyl ethyl)1,2-diaminocyclohexane

The N,N'-Bis(β-carbamoyl ethyl)1,2-diaminocyclohexane was prepared as previously reported from an acetonitrile solution of 1,2-diaminocyclohexane (18.39 ml, 0.15 mol) and acrylamide (21.32 g, 0.30 mol) in acetonitrile (170 cm³) by heating under reflux for 3 h. The solution was cooled and the product filtered off, washed with cold ethanol, recrystallized from methanol, and dried in vacuo. The compound was 82% pure as determined by titration with standard base. Anal. Calcd. for C₈H₁₈N₄O₂: C, 56.25; H, 7.81; N, 21.88. Found: C, 56.25; H, 8.04; N, 22.46. IR (KBr cm⁻¹): 3388(s), 3288(s), 3189(s), 2928(s), 2852(s), 1655(s), 1497(m), 1450(m), 1405(m), 1366(m), 1304(m), 1242(m), 1198(m), 1129(m), 1048(w), 895(m), 882(m), 840(m).

2.6. Preparation of

[(C₈H₁₈N₄O₂)Co(OH)₂Co(C₈H₁₈N₄O₂)]Cl₂ (1)

A solution of CoCl₂ · 6H₂O (0.30 mmol) and 4,7-diazadecanediamide (0.30 mmol) in water (5 ml) was stirred for 10 min. It was then allowed to stand at room temperature for several days, whereupon red block crystals. The solid product was washed with deionized water and ethanol, and dried in vacuo. IR bands (KBr cm⁻¹): 3332(s), 3215(s), 2925(m), 2868(m), 1648(s), 1597(s), 1453(m), 1423(w), 1325(m), 1267(w), 683(m).

2.7. Preparation of

[Co(C₉H₂₀N₄O₂)(Cl)(H₂O)]Cl · 2H₂O (2)

A solution of CoCl₂ · 6H₂O (0.10 mmol) and 4,8-diazadecanediamide (0.10 mmol) in water (10 ml) was stirred for 10 min. It was then allowed to stand at room temperature for several days, whereupon pale red block crystals. The solid product was washed with deionized water and ethanol, and dried in vacuo. IR bands (KBr cm⁻¹): 3333(s), 3187(s), 2874(m), 1655(m), 1596(s), 1459(s), 1410(m), 1335(w), 1302(m), 1087(w), 1031(m), 741(w), 643(m), 548(m).

2.8. Preparation of

[Co(C₁₀H₂₂N₄O₂)(H₂O)]₂Cl₂ · 2H₂O (3)

A solution of CoCl₂ · 6H₂O (0.10 mmol) and 4,7-dimethyl-4,7-diazadecanediamide (0.10 mmol) in methanol (10 ml) was stirred for 10 min. It was then allowed to stand at room temperature for several days, whereupon red block crystals. The

solid product was washed with deionized water and ethanol, and dried in vacuo. IR bands (KBr cm^{-1}): 3287(s), 2876(m), 1665(s), 1596(s), 1462(s), 1415(m), 1324(w), 1300(m), 1268(w), 1219(w), 1181(w), 1135(w), 1059(w), 966(w), 898(w), 825(m), 725(s).

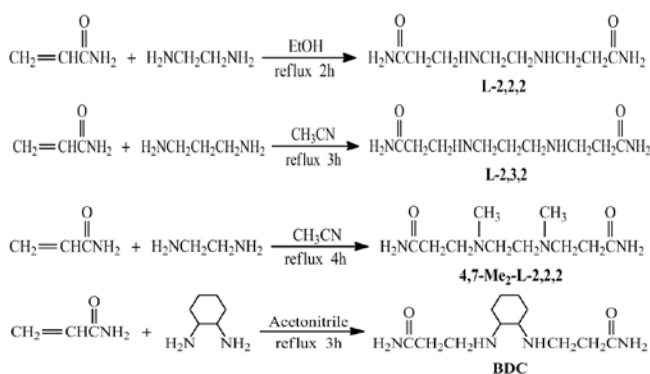
2.9. Preparation of

$[\text{Co}(\text{C}_{12}\text{H}_{24}\text{N}_4\text{O}_2)(2\text{H}_2\text{O})] \cdot 2\text{Cl}$ (**4**)

A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.10 mmol) and N,N' -Bis(β -carbamoyl ethyl)1,2-diaminocyclohexane (0.10 mmol) in water (10 ml) was stirred for 10 min. It was then allowed to stand at room temperature for several days, whereupon red block crystals. The solid product was washed with deionized water and ethanol, and dried in vacuo. IR bands (KBr cm^{-1}): 3168(s), 2950(m), 2879(m), 1685(m), 1646(s), 1594(s), 1455(m), 1405(m), 1362(w), 1327(w), 1268(w), 1128(w), 1082(w), 1012(w), 942(w), 872(w), 588(m), 448(w).

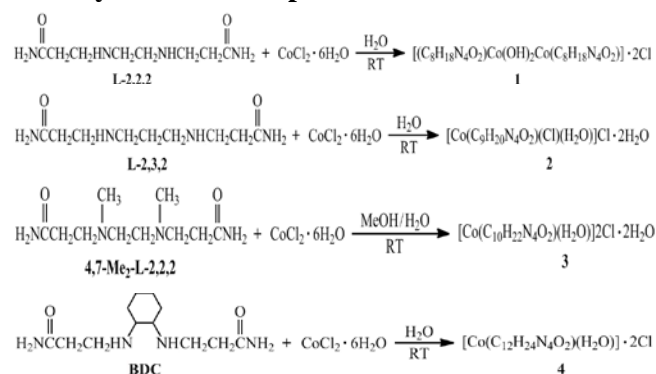
3. Results and Discussion

3.1. Synthesis of ligands



Scheme 1. Preparation of ligands.

3.2. Synthesis of complexes



Scheme 2. Preparation of complexes.

3.3. Crystal Structure of **1**

Compound **1** was crystallized in a Monoclinic space group $P21/a$. An ORTEP diagram with a labeling scheme is shown in Figure 1 and pertinent crystallographic data are provided in Tables 1. In

compound **1**, the cobalt atom adopts a six-coordinated $\text{N}_2\text{O}_2(\text{OH})_2$ environment, giving an octahedral geometry, where one N- and one O-donor set of ligand and two OH located at equatorial positions and one N- and one O-donor set of ligand occupied at axial positions. The bond lengths, $\text{Co-N} = 1.942(3)\text{-}1.945(3)$ Å and $\text{Co-O} = 1.896(2)\text{-}1.958(2)$ Å around the cobalt center are typical. The distance between two cobalt atoms is 7.28 Å. The neutral ligand offers N_2O_2 -donor sets to chelate the cobalt center, forming fused metalocyclic (6,5,6)-membered rings with the two terminal O,N bite angles of $91.06(12)^\circ$, $93.35(11)^\circ$, and the central N,N bite angle of $85.32(12)^\circ$.

In compound **1**, through $\text{NH}\cdots\text{N}$ hydrogen bonds ($\text{N}\cdots\text{N}$ 2.74 Å), a 1D chainlike structure is formed (Figure 2), which is further linked to neighboring ones via weak $\text{NH}\cdots\text{Cl}_{\text{free}}$ contacts ($\text{N}\cdots\text{Cl}_{\text{free}}$ 3.19-3.20 Å) extending to a charged hydrogen-bonded 2D supramolecular layer (Figure 3).

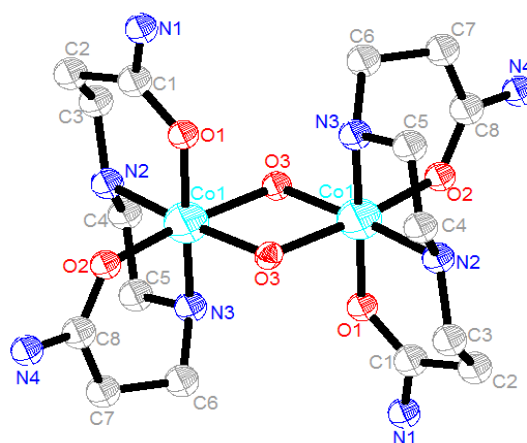


Figure 1. ORTEP diagram of compound **1** represented by thermal ellipsoids drawn at the 50% probability level.

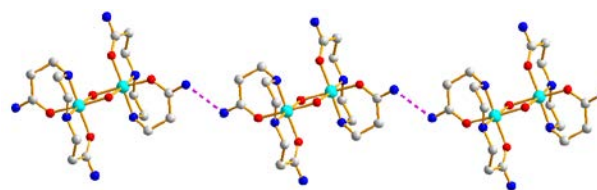


Figure 2. 1D chainlike structure of compound **1**. Color scheme: Co, turquoise; N, blue; O, red; C, gray. H bonds, purple and yellow dashed lines.

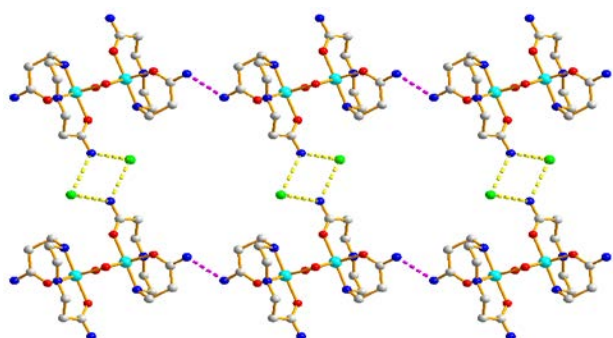


Figure 3. 2D supramolecular architecture of compound **1**. Color scheme: Co, turquoise; N, blue; O, red; C, gray, Cl, green. H bonds, purple and yellow dashed lines.

Table 1. Selected Bond Lengths [Å] and Angles [°] for Compound **1**

Co(1)-Co(1)#1	2.9390(8)	Co(1)-N(3)	1.942(3)
Co(1)-O(2)	1.896(2)	Co(1)-N(2)	1.945(3)
Co(1)-O(3)	1.907(2)	Co(1)-O(1)	1.958(2)
Co(1)-O(3)#1	1.930(2)	O(3)-Co(1)#1	1.930(2)
O(2)-Co(1)-O(3)	172.41(10)	O(2)-Co(1)-O(3)#1	92.42(10)
O(3)-Co(1)-O(3)#1	80.01(10)	O(2)-Co(1)-N(3)	93.67(11)
O(3)-Co(1)-N(3)	86.70(10)	O(3)#1-Co(1)-N(3)	96.33(10)
O(2)-Co(1)-N(2)	91.06(12)	O(3)-Co(1)-N(2)	96.53(11)
O(3)#1-Co(1)-N(2)	176.05(10)	N(3)-Co(1)-N(2)	85.32(12)
O(2)-Co(1)-O(1)	88.54(10)	O(3)-Co(1)-O(1)	91.28(9)
O(3)#1-Co(1)-O(1)	84.87(9)	N(3)-Co(1)-O(1)	177.44(10)
N(2)-Co(1)-O(1)	93.35(11)	O(2)-Co(1)-Co(1)#1	132.14(8)
O(3)-Co(1)-Co(1)#1	40.29(6)	O(3)#1-Co(1)-Co(1)#1	39.72(6)
N(3)-Co(1)-Co(1)#1	92.01(8)	N(2)-Co(1)-Co(1)#1	136.78(9)
O(1)-Co(1)-Co(1)#1	87.47(7)	Co(1)-O(3)-Co(1)#1	99.99(10)

3.4. Crystal Structure of **2**

Compound **2** was crystallized in a monoclinic space group $P2_1nb$. An ORTEP diagram with a labeling scheme is shown in Figure 1 and pertinent crystallographic data are provided in Tables 2. In compound **2**, the cobalt atom adopts a six-coordinated N_2O_3Cl environment, giving an distorted octahedral geometry, where two N- and two O-donor sets of ligand located at equatorial positions and one Cl-donor and one water molecules occupy the axial positions. The bond lengths, Cu-N = 2.122(5)-2.124(5) Å, Cu-O = 2.068(4)-2.093(4) Å and Cu-Cl = 2.4918(17) Å around the copper center are typical. The neutral ligand offers N_2O_2 -donor sets to chelate the cobalt center, forming fused metallocyclic (6,6,6)-membered rings with the two terminal O,N bite angles of 90.02(18)° and 91.30(16)°, and the central N,N bite angle of 97.30(19)°.

In compound **2**, through $OH\cdots Cl-Co$ hydrogen bonds (O \cdots Cl, 3.08 Å), a 1D chainlike structure is formed (Figure 5), which is further linked to neighboring ones via weak $NH\cdots Cl-Co$ contacts (H \cdots Cl 3.24 Å), extending to a charged

hydrogen-bonded 2D supramolecular layer (Figure 6).

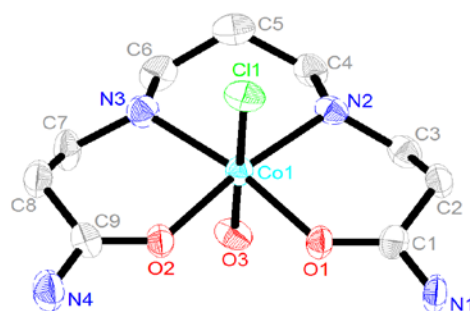


Figure 4. ORTEP diagram of compound **2** represented by thermal ellipsoids drawn at the 50% probability level.

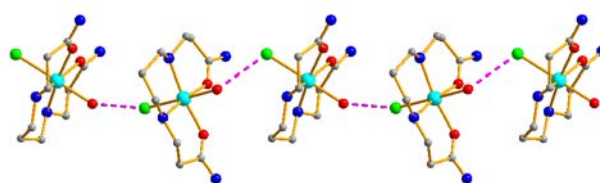


Figure 5. 1D chainlike structure of compound **2**. Color scheme: Ni, turquoise; N, blue; O, red; C, gray. H bonds, purple and yellow dashed lines.

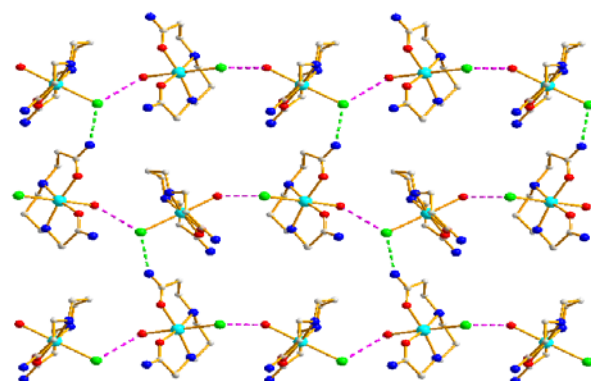


Figure 6. 2D supramolecular architecture of compound **2**. Color scheme: Ni, turquoise; N, blue; O, red; C, gray. H bonds, purple, yellow and green dashed lines.

Table 2. Selected Bond Lengths [Å] and Angles [°] for Compound **2**

Co(1)-O(1)	2.068(4)	Co(1)-N(2)	2.122(5)
Co(1)-O(2)	2.093(4)	Co(1)-N(3)	2.124(5)
Co(1)-O(3)	2.132(4)	Co(1)-Cl(1)	2.4918(17)
O(1)-Co(1)-O(2)	80.67(15)	O(1)-Co(1)-N(2)	91.93(16)
O(2)-Co(1)-N(2)	172.45(17)	O(1)-Co(1)-N(3)	170.27(18)
O(2)-Co(1)-N(3)	90.02(18)	N(2)-Co(1)-N(3)	97.30(19)
O(1)-Co(1)-O(3)	88.22(17)	O(2)-Co(1)-O(3)	88.05(18)
N(2)-Co(1)-O(3)	90.27(18)	N(3)-Co(1)-O(3)	88.7(2)
O(1)-Co(1)-Cl(1)	92.40(13)	O(2)-Co(1)-Cl(1)	91.70(14)
N(2)-Co(1)-Cl(1)	90.06(15)	N(3)-Co(1)-Cl(1)	90.67(16)
O(3)-Co(1)-Cl(1)	179.29(13)		

3.5. Crystal Structure of **3**

Compound **3** was crystallized in a orthorhombic space group $P2_1/c$. An ORTEP diagram with a labeling scheme is shown in Figure 7 and pertinent crystallographic data are provided in Tables 3. In compound **3**, the cobalt atom adopts a six-coordinated N_2O_4 environment, giving an octahedral geometry, where two N- and two water molecules sets located at equatorial positions and two O-donor occupy the axial positions. The bond lengths, Co-N = 2.172(7)-2.196(9) Å and Co-O = 2.065(9)-2.110(5) Å around the cobalt center are typical. The neutral ligand offers N_2O_2 -donor sets to chelate the cobalt center, forming fused metallocyclic (6,5,6)-membered rings with the two terminal O,N bite angles of 88.15(7)° and 88.72(6)°, and the central N,N bite angle of 84.63(7)°.

In compound **3**, through $OH\cdots O_{free}$, $OH_{free}\cdots Cl_{free}$ and $CH\cdots Cl_{free}$ hydrogen bonds ($O\cdots O_{free}$ 2.67 Å, $O_{free}\cdots Cl_{free}$ 3.13 Å and $C\cdots Cl_{free}$ 3.85 Å), a 1D chainlike structure is formed (Figure 8), which is further linked to neighboring ones via weak $OH\cdots N$ contacts ($O\cdots N$ 3.051 Å) extending to a charged hydrogen-bonded 2D supramolecular layer (Figure 9).

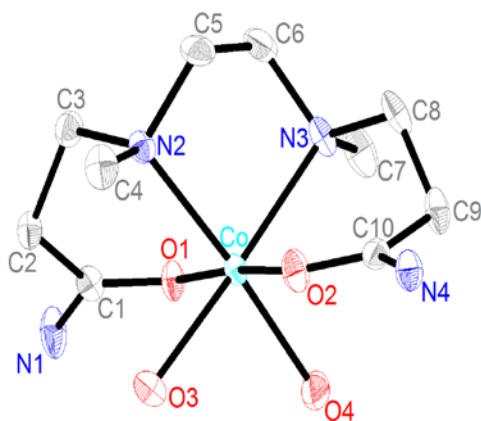


Figure 7. ORTEP diagram of compound **3** represented by thermal ellipsoids drawn at the 50% probability level.

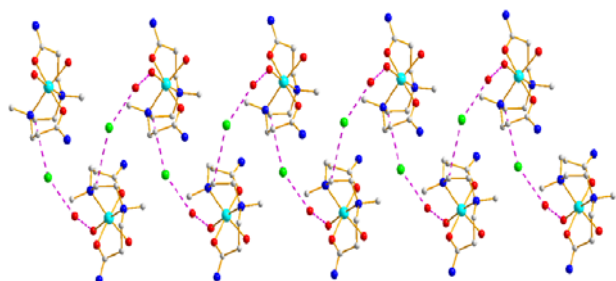


Figure 8. 1D chainlike structure of compound **3**. Color scheme: Co, turquoise; N, blue; O, red; C, gray. H bonds, purple dashed lines.

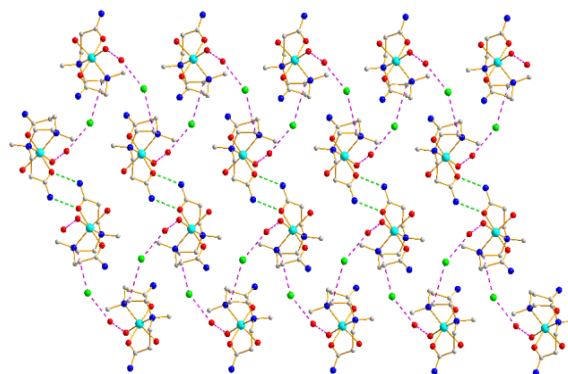


Figure 9. 2D supramolecular architecture of compound **3**. Color scheme: Co, turquoise; N, blue; O, red; C, gray. H bonds, green dashed lines.

Table 3. Selected Bond Lengths [Å] and Angles [°] for Compound **3**

Co-O(2)	2.0659(15)	Co-O(1)	2.0898(14)
Co-O(4)	2.0936(17)	Co-O(3)	2.1105(17)
Co-N(2)	2.1727(18)	Co-N(3)	2.1969(19)
O(2)-Co-O(1)	175.38(6)	O(2)-Co-O(4)	94.55(7)
O(1)-Co-O(4)	83.06(6)	O(2)-Co-O(3)	87.52(7)
O(1)-Co-O(3)	88.44(7)	O(4)-Co-O(3)	87.72(8)
O(2)-Co-N(2)	93.59(6)	O(1)-Co-N(2)	88.72(6)
O(4)-Co-N(2)	171.73(7)	O(3)-Co-N(2)	91.17(7)
O(2)-Co-N(3)	88.15(7)	O(1)-Co-N(3)	96.05(6)
O(4)-Co-N(3)	97.09(8)	O(3)-Co-N(3)	173.77(7)
N(2)-Co-N(3)	84.63(7)		

3.6. Crystal Structure of **4**

Compound **4** was crystallized in a monoclinic space group $P-1$. An ORTEP diagram with a labeling scheme is shown in Figure 10 and pertinent crystallographic data are provided in Tables 4. In compound **4**, the cobalt atom adopts a six-coordinated N_2O_4 environment, giving a distorted octahedral geometry, where two N- and two O-donor sets located at equatorial positions and two water molecules occupy the axial positions. The bond lengths, Co-N = 2.125(6)-2.126(7) Å, Co-O = 2.055(2)-2.164(0) Å around the cobalt center are typical. The neutral ligand offers N_2O_2 -donor sets to chelate the cobalt center, forming fused metallocyclic (6,5,6)-membered rings with the two terminal O,N bite angles of 91.19(7)° and 91.97(7)°, and the central N,N bite angle of 81.72(7)°.

In compound **4**, through $OH\cdots O_{free}$ hydrogen bonds ($O\cdots O$, 2.92-3.59 Å), a 1D chainlike structure is formed (Figure 5), which is further linked to neighboring ones via weak $NH\cdots O_{free}$, $OH_{free}\cdots Cl_{free}$ and $OH\cdots Cl_{free}$ contacts ($N\cdots O$ 3.61 Å, $O_{free}\cdots Cl_{free}$ 3.06 Å and $O\cdots Cl_{free}$ 3.03 Å), extending to a charged hydrogen-bonded 2D supramolecular layer (Figure 6).

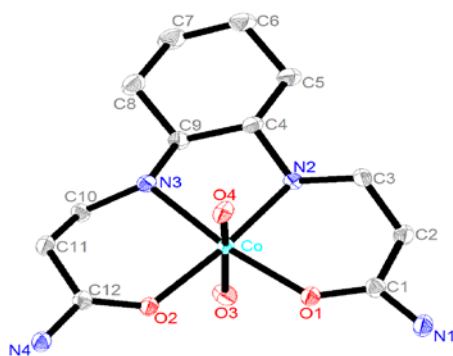


Figure 10. ORTEP diagram of compound **4** represented by thermal ellipsoids drawn at the 50% probability level.

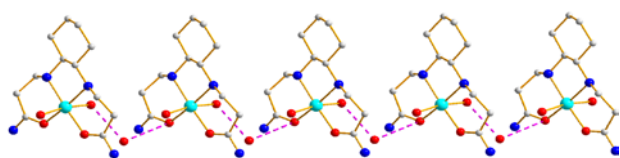


Figure 11. 1D chainlike structure of compound **4**. Color scheme: Co, turquoise; N, blue; O, red; C, gray. H bonds, purple dashed lines.

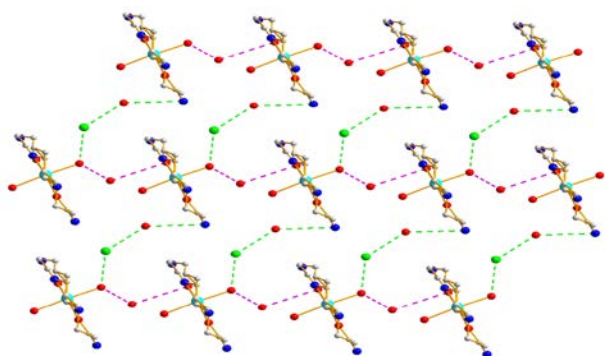


Figure 12. 2D supramolecular architecture of compound **4**. Color scheme: Co, turquoise; N, blue; O, red; C, gray, Cl, green. H bonds, green dashed lines.

Table 4. Selected Bond Lengths [Å] and Angles [°] for Compound **4**

Co-O(1)	2.0552(16)	Co-O(2)	2.0708(16)
Co-N(2)	2.1256(19)	Co-N(3)	2.1267(19)
Co-O(3)	2.1640(18)	Co-O(4)	2.1593(18)
O(1)-Co-O(2)	95.62(6)	O(1)-Co-N(2)	91.97(7)
O(2)-Co-N(2)	171.18(7)	O(1)-Co-N(3)	171.10(7)
O(2)-Co-N(3)	91.19(7)	N(2)-Co-N(3)	81.72(7)
O(1)-Co-O(3)	89.56(7)	O(2)-Co-O(3)	85.33(7)
N(2)-Co-O(3)	90.28(8)	N(3)-Co-O(3)	96.71(7)
O(1)-Co-O(4)	85.64(7)	O(2)-Co-O(4)	87.07(7)
N(2)-Co-O(4)	97.99(7)	N(3)-Co-O(4)	89.02(8)
O(3)-Co-O(4)	170.57(8)		

4. Conclusion

Four interesting Co(II) complexes containing

the diaminodiamide ligands are synthesized and characterized by an X-ray diffraction study. This study provides an opportunity to explore the different ligands on the coordination mode of the metal atom. Comparing compounds **1**, **2**, **3** and **4** shows a variety of coordination possibilities. For compound **1**, the structure of binuclear coblate(II) complex shows distorted octahedral coordination geometry. For compound **2**, **3** and **4**, the structure of mononuclear coblate(II) complex shows distorted octahedral coordination geometry.

5. References

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