DOI: 10.17344/acsi.2021.6721 *Acta Chim. Slov.* **2021,** *68,* 700–708

Scientific paper

Synthesis, Characterization and Crystal Structures of Zinc(II) and Cobalt(III) Complexes Derived from Tridentate NNO- and NON- Schiff Bases with Antibacterial Activities

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Received: 02-02-2021

Abstract

Two new polynuclear zinc complexes $[Zn_2Br_2(L^1)_2]$ (**1**) and $[Zn(\mu_{1,5}\text{-dca})L^2]_n$ (**2**), and two new mononuclear cobalt(III) complexes $[CoL^1N_3(Brsal)]$ (**3**) and $[CoL^2(HL^2)]$ (**4**), where L^1 = 5-bromo-2-(((2-dimethylamino)ethyl)imino)methyl) phenolate, L^2 = 5-bromo-2-(((2-hydroxyethyl)imino)methyl)phenolate, dca = dicyanoamide, Brsal = 5-bromo-2-formyl-phenolate, have been synthesized and characterized. The complexes were characterized by elemental analyses, IR, UV-Vis spectra, molar conductivity, and single crystal X-ray diffraction. X-ray analysis indicates that the Zn atoms in complex **1** are in distorted square pyramidal coordination, the Zn atoms in complex **2** are in distorted trigonal bipyramidal coordination, and the Co atoms in complexes **3** and **4** are in octahedral coordination. The molecules of the complexes are stacked through π···π interactions and hydrogen bonds. The complexes were assayed for antibacterial activities against three Gram-positive bacterial strains (*B. subtilis*, *S. aureus*, and *St. faecalis*) and three Gram-negative bacterial strains (*E. coli*, *P. aeruginosa*, and *E. cloacae*) by MTT method.

Keywords: Schiff base; zinc complex; cobalt complex; X-ray diffraction; antibacterial activity

1. Introduction

Schiff bases are an important class of organic compounds and a great number of Schiff base compounds have been prepared due to their facile synthesis. These compounds have received considerable attention in pharmaceutical fields because of their excellent biological activities.[1] Moreover, Schiff bases are a kind of significant ligands in coordination chemistry, which can form versatile structures with interesting biological, magnetic, catalytic and photoluminescent properties.[2] In recent years, much efforts have been paid on zinc and cobalt complexes with Schiff base ligands due to their indispensable application in biological area such as antimicrobial agents.[3] We have reported some manganese and zinc complexes with antibacterial activities.[4] In continuation of our work on the exploration of new antibacterial agents, we report herein the synthesis, characterization including single crystal X-ray structures of two new zinc(II) and two new cobalt(III) complexes, $[Zn_2Br_2(L^1)_2]$ (**1**), $[Zn(\mu_{1,5}\text{-dca})L^2]_n$ (**2**), $[CoL^1N_3(Brsal)]$ (**3**) and $[CoL^2(HL^2)]$ (**4**), where L^1 = 5-bromo-2-(((2-dimethylamino)ethyl)imino)methyl)phenolate, L^2 = 5-bromo-2-(((2-hydroxyethyl)imino)methyl)phenolate, dca = dicyanoamide, Brsal = 5-bromo-2-formylphenolate. The antibacterial activity against three Gram-positive bacterial strains (*B. subtilis*, *S. aureus*, and *St. faecalis*) and three Gram-negative bacterial strains (*E. coli*, *P. aeruginosa*, and *E. cloacae*) by MTT method was studied.

2. Experimental

2. 1. Materials and Physical Methods

4-Bromosalicylaldehyde, *N,N*-dimethylethane-1,2-diamine and 2-aminoethanol were purchased from Sigma-Aldrich. All other reagents and solvents were purchased from commercial sources and used as received. FT-IR spectra were recorded as KBr pellets on Bruker Tensor-27. Elemental (C, H, and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. Electronic

spectra were obtained with Lambda 35 spectrophotometer. Single crystal X-ray diffraction was carried out with a Bruker Apex II CCD diffractometer. Molar conductivity of the complexes in methanol was measured with a DDS-11A molar conductivity meter.

Caution! Azide complexes of metal ions are potentially explosive. Only a small amount of material should be prepared, and they should be handled with caution.

2. 2. Synthesis of Complex 1

4-Bromosalicylaldehyde (0.20 g, 1.0 mmol) and *N,N*-dimethylethane-1,2-diamine (0.088 g, 1.0 mmol) were dissolved in methanol (30 mL), to the mixture was added zinc bromide (0.23 g, 1.0 mmol). A colorless solution was formed immediately. After 20 min stirring, the solution was filtered and the filtrate was kept for slow evaporation. The diffraction quality colorless single crystals that deposited over a period of a few days were collected by filtration and washed with methanol. The yield was 0.25 g (60%). Anal. Calcd. for $C_{22}H_{28}Br_4N_4O_2Zn_2$ (%): C, 31.80; H, 3.40; N, 6.74. Found (%): C, 31.95; H, 3.51; N, 6.68. IR data (KBr, cm^{-1}): 1647, 1585, 1523, 1512, 1478, 1427, 1388, 1323, 1289, 1178, 1131, 1081, 1062, 951, 920, 863, 850, 823, 811, 778, 726, 692, 667, 612, 565, 518, 490, 461. UV-Vis data in methanol [λ_{max} (nm), ε ($L{\cdot}mol^{-1}{\cdot}cm^{-1}$)]: 225, 7250; 270, 6350; 330, 2610.

2. 3. Synthesis of Complex 2

4-Bromosalicylaldehyde (0.20 g, 1.0 mmol) and 2-aminoethanol (0.061 g, 1.0 mmol) were dissolved in methanol (30 mL), to the mixture was added zinc nitrate hexahydrate (0.30 g, 1.0 mmol) and sodium dicyanoamide (0.089 g, 1.0 mmol). A colorless solution was formed immediately. After 20 min stirring, the solution was filtered and the filtrate was kept for slow evaporation. The diffraction quality colorless single crystals that deposited over a period of a few days were collected by filtration and washed with methanol. The yield was 0.12 g (32%). Anal. Calcd. for $C_{11}H_9BrN_4O_2Zn$ (%): C, 35.28; H, 2.42; N, 14.96. Found (%): C, 35.09; H, 2.53; N, 15.11. IR data (KBr, cm^{-1}): 3635, 2341, 2275, 2195, 1643, 1584, 1529, 1466, 1428, 1402, 1377, 1343, 1292, 1250, 1195, 1131, 1067, 941, 906, 851, 779, 673, 610, 528, 504, 457. UV-Vis data in methanol [λ_{max} (nm), ε ($L{\cdot}mol^{-1}{\cdot}cm^{-1}$)]: 245, 6830; 275, 4260; 360, 1572.

2. 4. Synthesis of Complex 3

4-Bromosalicylaldehyde (0.20 g, 1.0 mmol) and *N,N*-dimethylethane-1,2-diamine (0.088 g, 1.0 mmol) were dissolved in methanol (30 mL), to the mixture was added cobalt chloride hexahydrate (0.24 g, 1.0 mmol), sodium azide (0.065 g, 1.0 mmol) and additional 4-bromosalicylaldehyde (0.20 g, 1.0 mmol). A brown solution was formed immediately. After 20 min stirring, the solution was filtered and the filtrate was kept for slow evaporation. The diffraction quality colorless single crystals that deposited over a period of a few days were collected by filtration and washed with methanol. The yield was 0.23 g (40%). Anal. Calcd. for $C_{18}H_{18}Br_2CoN_5O_3$ (%): C, 37.85; H, 3.18; N, 12.26. Found (%): C, 37.72; H, 3.25; N, 12.33. IR data (KBr, cm^{-1}): 2027, 1647, 1618, 1589, 1521, 1497, 1454, 1430, 1387, 1295, 1185, 1133, 1059, 1022, 995, 922, 854, 778, 729, 692, 613, 570, 515, 493, 466. UV-Vis data in methanol [λ_{max} (nm), ε ($L{\cdot}mol^{-1}{\cdot}cm^{-1}$)]: 225, 7030; 260, 9150; 325, 3120.

2. 5. Synthesis of Complex 4

4-Bromosalicylaldehyde (0.20 g, 1.0 mmol) and 2-aminoethanol (0.061 g, 1.0 mmol) were dissolved in methanol (30 mL), to the mixture was added cobalt nitrate hexahydrate (0.29 g, 1.0 mmol). A brown solution was formed immediately. After 20 min stirring, the solution was filtered and the filtrate was kept for slow evaporation. The diffraction quality colorless single crystals that deposited over a period of a few days were collected by filtration and washed with methanol. The yield was 0.15 g (28%). Anal. Calcd. for $C_{18}H_{17}Br_2CoN_2O_4$ (%): C, 39.74; H, 3.15; N, 5.15. Found (%): C, 39.83; H, 3.10; N, 5.24. IR data (KBr, cm^{-1}): 3427, 1647, 1586, 1523, 1464, 1425, 1383, 1328, 1289, 1246, 1200, 1131, 1103, 1058, 938, 907, 847, 783, 730, 675, 657, 606, 576, 550, 499, 470, 443. UV-Vis data in methanol [λ_{max} (nm), ε ($L{\cdot}mol^{-1}{\cdot}cm^{-1}$)]: 245, 8160; 275, 3920; 360, 2335.

2. 6. X-Ray Structure Determination

Intensity data of the complexes were collected at 298(2) K on a Bruker Apex II CCD diffractometer using graphite-monochromated MoK_a radiation (λ = 0.71073 Å). For data processing and absorption correction the packages SAINT and SADABS were used.[5] Structures of the complexes were solved by direct and Fourier methods and refined by full-matrix least-squares based on F^2 using SHELXL.[6] The non-hydrogen atoms were refined anisotropically. The H atoms of the hydroxyl groups of complexes **2** and **4** were located from difference Fourier maps and refined with O–H distances restrained to 0.85(1) Å. The remaining hydrogen atoms have been placed at geometrical positions with fixed thermal parameters. Crystallographic data of the complexes are summarized in Tables 1a and 1b. Selected bond lengths and angles are listed in Table 2.

2. 7. Antibacterial Activity

Antibacterial activity of the complexes was tested against *B. subtilis*, *S. aureus*, *S. faecalis*, *P. aeruginosa*, *E. coli*, and *E. cloacae* using MTT medium. The minimum inhibitory concentrations (MICs) of the compounds were determined by a colorimetric method using MTT dye.[7] A stock solution of the compounds (50 μg mL^{-1}) in DMSO was prepared and quantities of the compounds were incorporated in specified quantity of sterilized liquid medium.

Table 1a. Crystallographic data and refinement details for the zinc complexes

	1	2
Molecular formula	$C_{22}H_{28}Br_4N_4O_2Zn_2$	$C_{11}H_9BrN_4O_2Zn$
Molecular weight	830.86	374.50
Crystal color, habit	Colorless, block	Colorless, block
Crystal size, mm	0.26 × 0.23 × 0.23	0.27 × 0.26 × 0.23
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	$P2_1/c$
Unit cell dimensions:		
a, Å	7.3961(12)	7.5248(13)
b, Å	11.4754(13)	15.8344(10)
c, Å	17.3227(15)	11.5157(12)
α, °	82.449(1)	90
β, °	82.053(1)	97.377(1)
γ, °	88.895(1)	90
V, Å^3	1443.5(3)	1360.7(3)
Z	2	4
ρ_{calcd}, g cm^{-3}	1.912	1.828
μ, mm^{-1}	7.223	4.743
θ Range collected, °	1.20–25.50	2.20–25.49
T_{min} and T_{max}	0.2553 and 0.2874	0.3608 and 0.4084
Reflections collected/ unique	6833/5179	7112/2519
Observed reflections ($I \geq 2s(I)$)	3685	2032
Data/restraints/ parameters	5179/0/311	2519/1/176
GOOF on F^2	1.018	1.205
R_1, wR_2 ($I \geq 2s(I)$)	0.0417, 0.0888	0.0613, 0.1727
R_1, wR_2 (all data)	0.0722, 0.1013	0.0741, 0.1788

Table 1b. Crystallographic data and refinement details for the cobalt complexes

	3	4
Molecular formula	$C_{18}H_{18}Br_2CoN_5O_3$	$C_{18}H_{17}Br_2CoN_2O_4$
Molecular weight	571.12	544.09
Crystal color, habit	Brown, block	Brown, block
Crystal size, mm	0.17 × 0.15 × 0.15	0.15 × 0.08 × 0.08
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions:		
a, Å	6.5842(17)	16.2848(13)
b, Å	13.6064(13)	25.8585(13)
c, Å	23.301(2)	21.4256(13)
α, °	90	90
β, °	92.048(2)	94.958(2)
γ, °	90	90
V, Å^3	2086.1(6)	8988.6(10)
Z	4	16
ρ_{calcd}, g cm^{-3}	1.818	1.608
μ, mm^{-1}	4.683	4.343
θ Range collected, °	1.73–25.50	1.84–25.50
T_{min} and T_{max}	0.5032 and 0.5401	0.5620 and 0.7226
Reflections collected/ unique	10831/3868	47610/16621
Observed reflections ($I \geq 2s(I)$)	2344	7217
Data/restraints/ parameters	3868/0/264	16621/11/973
GOOF on F^2	1.050	0.979
R_1, wR_2 ($I \geq 2s(I)$)	0.0540, 0.1252	0.0795, 0.2014
R_1, wR_2 (all data)	0.1069, 0.1481	0.1878, 0.2636

A specified quantity of the medium containing the compounds was poured into micro-titration plates. Suspension of the microorganism was prepared to contain approximately 10^5 cfu mL^{-1} and applied to micro-titration plates with serially diluted compounds in DMSO to be tested, and incubated at 37°C for 24 h for bacteria. After the MICs were visually determined on each micro-titration plate, 50 μL of phosphate buffered saline (PBS 0.01 mol L^{-1}, pH 7.4: $Na_2HPO_4 \cdot 12H_2O$ 2.9 g, KH_2PO_4 0.2 g, NaCl 8.0 g, KCl 0.2 g, distilled water 1000 mL) containing 2 mg mL^{-1} of MTT was added to each well. Incubation was continued at room temperature for 4–5 h. The content of each well was removed, and 100 μL of isopropanol containing 5% 1 mol L^{-1} HCl was added to extract the dye. After 12 h of incubation at room temperature, the optical density (OD) was measured with a microplate reader at 570 nm.

3. Results and Discussion

3. 1. Chemistry

Reaction of the newly formed Schiff base HL[1] with zinc bromide affords the dinuclear zinc complex **1**, with cobalt chloride and sodium azide affords the mononuclear cobalt complex **3**. Similarly, reaction of the newly formed Schiff base HL[2] with zinc nitrate and sodium dicyanoamide affords the polynuclear zinc complex **2**, with cobalt nitrate affords the mononuclear cobalt complex **4**. The poor conductivity of the complexes (20–45 Ω^{-1} cm^2 mol^{-1}) indicated that the ligands are coordinated to the metal centers and are not dissociated in solution.[8]

3. 2. Infrared and Electronic Spectra

In the infrared spectra, the weak absorptions at 3635 cm^{-1} for **2** and 3427 cm^{-1} for **4** are assigned to the hydroxyl groups of the Schiff base ligands. The characteristic imine stretching of the complexes is observed at 1643–1647 cm^{-1} as strong signal.[9] In the spectrum of **2**, appearance of intense bands at 2341, 2275 and 2195 cm^{-1} indicates the presence of dicyanoamide ligand.[10] In the spectrum of **3**, appearance of intense band at 2027 cm^{-1} indicates the presence of azide ligand.[11] The Schiff base ligands coordination is substantiated by the phenolic C–O stretching bands at 1170–1200 cm^{-1} in the four complexes.[12] Coordination of the Schiff bases is further confirmed by the appearance of weak bands in the low wave numbers 400–600 cm^{-1}, corresponding to ν(M–N) and ν(M–O).[13]

Table 2. Selected bond distances (Å) and angles (°) for the complexes

1			
Zn1–Br3	2.3869(10)	Zn2–Br4	2.3923(9)
Zn1–O1	1.995(3)	Zn1–O2	2.121(4)
Zn1–N3	2.089(5)	Zn1–N4	2.198(5)
Zn2–N1	2.089(4)	Zn2–N2	2.189(5)
Zn2–O1	2.106(3)	Zn2–O2	2.016(3)
O1–Zn1–N3	135.37(18)	O1–Zn1–O2	75.09(13)
N3–Zn1–O2	82.28(17)	O1–Zn1–N4	100.58(17)
N3–Zn1–N4	80.5(2)	O2–Zn1–N4	149.77(19)
O1–Zn1–Br3	111.83(12)	N3–Zn1–Br3	111.38(14)
O2–Zn1–Br3	107.00(11)	N4–Zn1–Br3	102.37(15)
O2–Zn2–N1	132.01(16)	O2–Zn2–O1	75.01(13)
N1–Zn2–O1	82.47(15)	O2–Zn2–N2	99.64(17)
N1–Zn2–N2	81.05(17)	O1–Zn2–N2	151.69(17)
O2–Zn2–Br4	116.62(11)	N1–Zn2–Br4	110.05(12)
O1–Zn2–Br4	105.80(11)	N2–Zn2–Br4	101.41(14)
2			
Zn1–O1	2.000(6)	Zn1–O2	2.231(7)
Zn1–N1	2.007(6)	Zn1–N2	1.988(8)
Zn1–N4A	2.017(7)		
N2–Zn1–O1	98.7(3)	N2–Zn1–N1	128.6(3)
O1–Zn1–N1	91.1(2)	N2–Zn1–N4A	108.2(3)
O1–Zn1–N4A	97.6(3)	N1–Zn1–N4A	120.3(3)
N2–Zn1–O2	86.7(3)	O1–Zn1–O2	167.5(2)
N1–Zn1–O2	76.8(3)	N4A–Zn1–O2	91.3(3)
3			
Co1–O1	1.890(4)	Co1–O2	1.926(4)
Co1–O3	1.943(5)	Co1–N1	1.871(5)
Co1–N2	2.036(5)	Co1–N3	1.973(5)
N1–Co1–O1	95.0(2)	N1–Co1–O2	86.99(19)
O1–Co1–O2	87.43(18)	N1–Co1–O3	178.2(2)
O1–Co1–O3	86.52(19)	O2–Co1–O3	94.05(18)
N1–Co1–N3	89.6(2)	O1–Co1–N3	90.0(2)
O2–Co1–N3	175.5(2)	O3–Co1–N3	89.5(2)
N1–Co1–N2	86.3(2)	O1–Co1–N2	178.2(2)
O2–Co1–N2	91.4(2)	O3–Co1–N2	92.3(2)
N3–Co1–N2	91.3(2)		

4			
Co1–O1	1.880(7)	Co1–O2	1.912(7)
Co1–O3	1.893(7)	Co1–O4	1.908(7)
Co1–N1	1.888(9)	Co1–N2	1.910(8)
Co2–O5	1.892(7)	Co2–O6	1.912(7)
Co2–O7	1.891(6)	Co2–O8	1.926(6)
Co2–N3	1.909(8)	Co2–N4	1.872(8)
Co3–O9	1.881(7)	Co3–O10	1.912(7)
Co3–O11	1.861(7)	Co3–O12	1.941(6)
Co3–N5	1.920(8)	Co3–N6	1.909(7)
Co4–O13	1.884(7)	Co4–O14	1.912(8)
Co4–O15	1.882(8)	Co4–O16	1.910(6)
Co4–N7	1.904(9)	Co4–N8	1.883(9)
O1–Co1–N1	95.0(3)	O1–Co1–O3	89.5(3)
N1–Co1–O3	89.7(3)	O1–Co1–O4	91.3(3)
N1–Co1–O4	89.1(4)	O3–Co1–O4	178.6(3)
O1–Co1–N2	89.2(3)	N1–Co1–N2	174.1(4)
O3–Co1–N2	94.5(3)	O4–Co1–N2	86.8(3)
O1–Co1–O2	178.7(3)	N1–Co1–O2	84.8(4)
O3–Co1–O2	91.8(3)	O4–Co1–O2	87.4(3)
N2–Co1–O2	90.9(3)	N4–Co2–O7	94.4(3)
N4–Co2–O5	91.0(3)	O7–Co2–O5	89.5(3)
N4–Co2–N3	174.6(4)	O7–Co2–N3	87.1(3)
O5–Co2–N3	94.2(3)	N4–Co2–O6	88.7(3)
O7–Co2–O6	91.9(3)	O5–Co2–O6	178.6(3)
N3–Co2–O6	86.0(3)	N4–Co2–O8	85.7(3)
O7–Co2–O8	176.8(3)	O5–Co2–O8	87.3(3)
N3–Co2–O8	93.0(3)	O6–Co2–O8	91.2(3)
O11–Co3–O9	90.7(3)	O11–Co3–N6	95.2(3)
O9–Co3–N6	87.4(3)	O11–Co3–O10	90.5(3)
O9–Co3–O10	178.7(3)	N6–Co3–O10	92.5(3)
O11–Co3–N5	89.2(3)	O9–Co3–N5	95.1(3)
N6–Co3–N5	174.9(3)	O10–Co3–N5	84.9(3)
O11–Co3–O12	178.6(3)	O9–Co3–O12	89.7(3)
N6–Co3–O12	86.2(3)	O10–Co3–O12	89.0(3)
N5–Co3–O12	89.4(3)	O15–Co4–N8	94.5(4)
O15–Co4–O13	89.9(4)	N8–Co4–O13	90.0(4)
O15–Co4–N7	87.8(4)	N8–Co4–N7	174.7(4)
O13–Co4–N7	94.7(4)	O15–Co4–O16	178.2(4)
N8–Co4–O16	86.0(4)	O13–Co4–O16	88.3(3)
N7–Co4–O16	91.8(3)	O15–Co4–O14	90.4(4)
N8–Co4–O14	90.1(4)	O13–Co4–O14	179.7(3)
N7–Co4–O14	85.2(4)	O16–Co4–O14	91.4(3)

Symmetry code for A: –1 + *x*, *y*, *z*.

The electronic spectra of the complexes exhibit typical bands centered at 320–360 nm which can be assigned to ligand to metal charge transfer.[14] The bands at 220–250 nm and 260–280 nm are attributed to the π–π^* and n–π^* transitions.[15]

3. 3. Structure Description of Complex 1

Molecular structure of complex **1** is shown in Fig. 1. The two [ZnL^1] units are linked by two phenolate O atoms. The Zn atoms are coordinated in distorted square pyramidal geometry as evidenced by the τ values of 0.24 for Zn1 and 0.33 for Zn2.[16] The basal planes of the square pyramidal coordination are defined by the imino N, amino N and phenolate O atoms of the Schiff base ligands. The apical positions of the square pyramidal coordination are occupied by the Br ligands. The Zn1 and Zn2 atoms deviate from the corresponding basal planes by 0.645(2) and 0.659(2) Å, respectively. The square pyramidal coordination is distorted from ideal model, as evidenced by the bond angles. The *cis* and *trans* angles in the basal plane are in the ranges of 75.09(13)–100.58(17)° and 135.37(18)–

149.77(19)° for Zn1, and 75.01(13)–99.64(17)° and 132.01(16)–151.69(17)° for Zn2, respectively. The bond angles among the apical and basal donor atoms are in the ranges of 102.37(15)–111.83(12)° for Zn1 and 101.41(14)–116.62(11)° for Zn2. The distortion is mainly caused by the strain created by the four- and five-membered chelate rings Zn1-O1-Zn2-O2, Zn1-N3-C19-C20-N4 and Zn2-N1-C8-C9-N2. The Zn-O, Zn-N and Zn-Br bond lengths are comparable to those observed in bromide coordinated Schiff base zinc complexes.[17]

As shown in Fig. 2, the complex molecules are linked through C–H···Br hydrogen bonds (Table 3), to form a three dimensional network. In addition, there are π···π interactions among the molecules (Cg1···Cg1[a] 4.423(4) Å, Cg2···Cg2[b] 4.446(4) Å, symmetry codes: a) 1 – *x*, – *y*, 1 – *z*; b) 2 – *x*, 1 – *y*, – *z*; Cg1 and Cg2 are the centroids of C1–C2–C3–C4–C5–C6 and C12–C13–C14–C15–C16–C17, respectively).

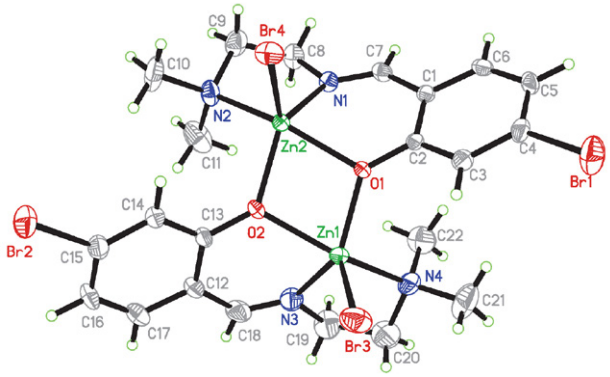

Fig. 1. Molecular structure of complex **1**.

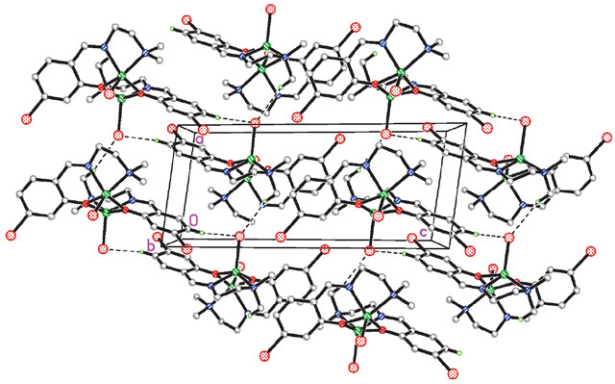

Fig. 2. Molecular packing structure of complex **1**.

3. 4. Structure Description of Complex 2

Molecular structure of complex **2** is shown in Fig. 3. The [ZnL^2] units are linked by $\mu_{1,5}$-dca ligands, to form zigzag chain structure. The Zn atom is coordinated in distorted trigonal bipyramidal geometry as evidenced by the τ value of 0.65.[16] The basal plane of the trigonal bipyramidal coordination is defined by the imino N atom of the Schiff base ligand and two terminal N atoms from two dca ligands. The axial positions of the trigonal bipyramidal coordination are occupied by the phenolate O and hydroxyl O atoms of the Schiff base ligand. The Zn atom deviates from the basal plane by 0.195(2) Å. The trigonal bipyramidal geometry is distorted from ideal model, as evidenced by the bond angles. The angles in the basal plane are in the range of 108.2(3)–128.6(3)°. The bond angles among the axial and basal donor atoms are in the range of 76.8(3)–98.7(3)°. And, the two axial donor atoms form an angle of 167.5(2)° with the Zn atom. The distortion is mainly caused by the strain created by the five-membered chelate ring Zn1-N1-C8-C9-O2. The Zn-O and Zn-N bond lengths are comparable to those observed in dca coordinated Schiff base zinc complexes.[18]

As shown in Fig. 4, the [CuL^2] units are bridged by $\mu_{1,5}$-dca ligands, to form zigzag chain along the *a* axis. The chains are further linked through O–H···O hydrogen bonds (Table 3) along the *c* axis to form two dimensional sheets parallel to the *ac* plane. In addition, there are π···π interactions among the molecules (Cg3···Cg3[c] 4.256(5) Å, Cg3···Cg4[c] 3.900(5) Å, Cg3···Cg4[d] 4.245(5) Å, Cg4···Cg4[c] 4.972(5) Å, Cg4···Cg4[d] 4.096(5) Å, symmetry codes: c) 1 – *x*, – *y*, – *z*; d) 2 – *x*, – *y*, – *z*; Cg3 and Cg4 are the centroids of Zn1–O1–C2–C1–C7–N1 and C1–C2–C3–C4–C5–C6, respectively).

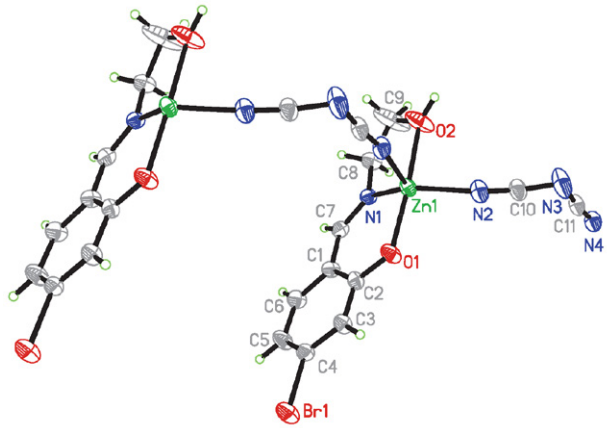

Fig. 3. Molecular structure of complex **2**.

3. 5. Structure Description of Complex 3

Molecular structure of complex **3** is shown in Fig. 5. The Co atom is coordinated by one Schiff base ligand, one 5-bromo-2-formylphenolate ligand and one azide ligand, forming octahedral coordination. The equatorial plane of the octahedral coordination is defined by the phenolate O, imino N and amino N atoms of the Schiff base ligand, and the carbonyl O atom of the 5-bromo-2-formylphenolate ligand. The axial positions of the octahedral coordination are occupied by the phenolate O atom of the 5-bro-

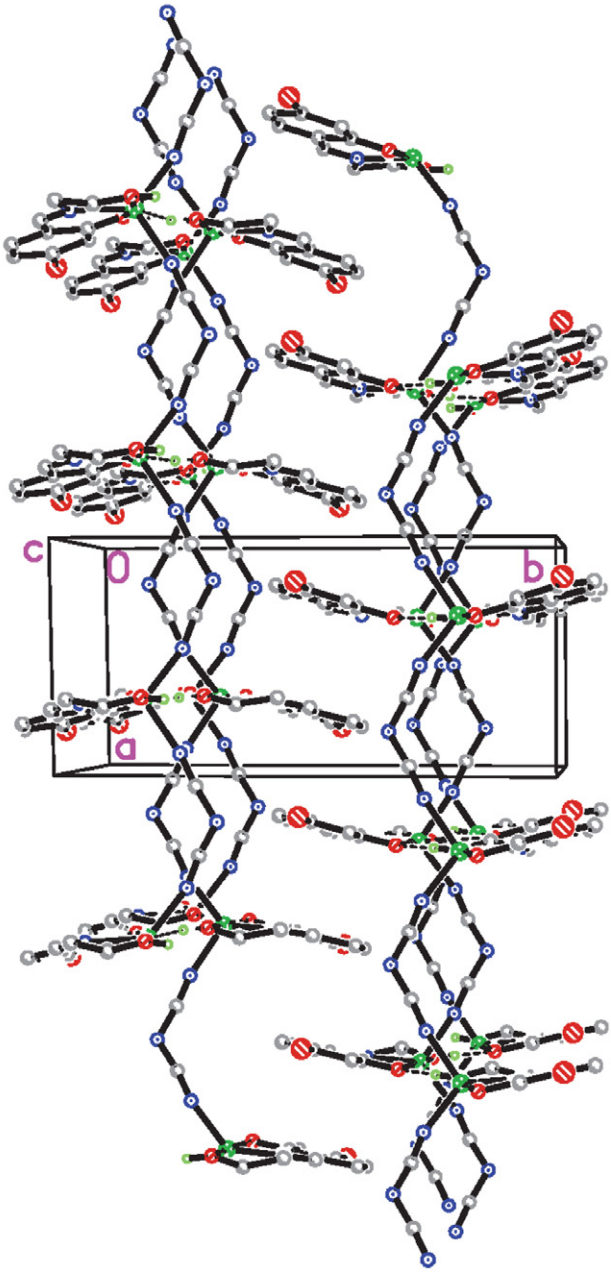

Fig. 4. Molecular packing structure of complex **2**.

mo-2-formylphenolate ligand, and the azide N atom. The Co atom deviates from the equatorial plane by 0.003(2) Å. The octahedral geometry is distorted from ideal model, as evidenced by the bond angles. The *cis* and *trans* angles in the equatorial plane are in the ranges of 86.3(2)–95.0(2) ° and 178.2(2)°, respectively. The bond angles among the axial and equatorial donor atoms are in the range of 87.0(2)–94.0(2)°. And, the two axial donor atoms form an angle of 175.5(2)° with the Co atom. The distortion is mainly caused by the strain created by the five-membered chelate ring Co1-N1-C8-C9-N2. The Co-O and Co-N bond lengths are comparable to those observed in azide coordinated Schiff base cobalt complexes.[19]

As shown in Fig. 6, the molecules are linked through C–H···N hydrogen bonds (Table 3), to form one dimensional chains along the *b* axis. The chains are further linked by weak Br···N interactions along the *c* axis to form a two dimensional sheets parallel to the *bc* plane.

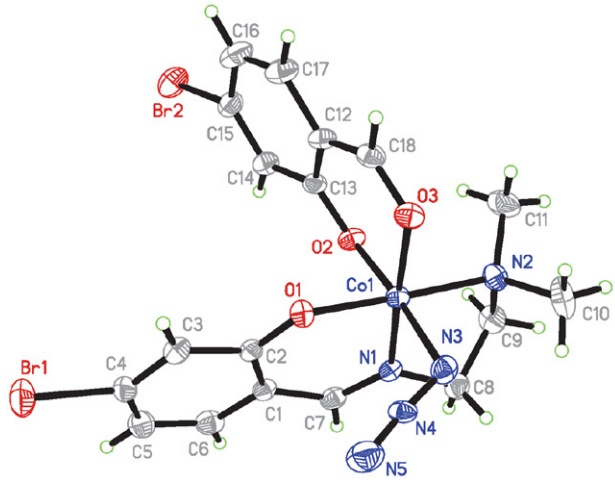

Fig. 5. Molecular structure of complex **3**.

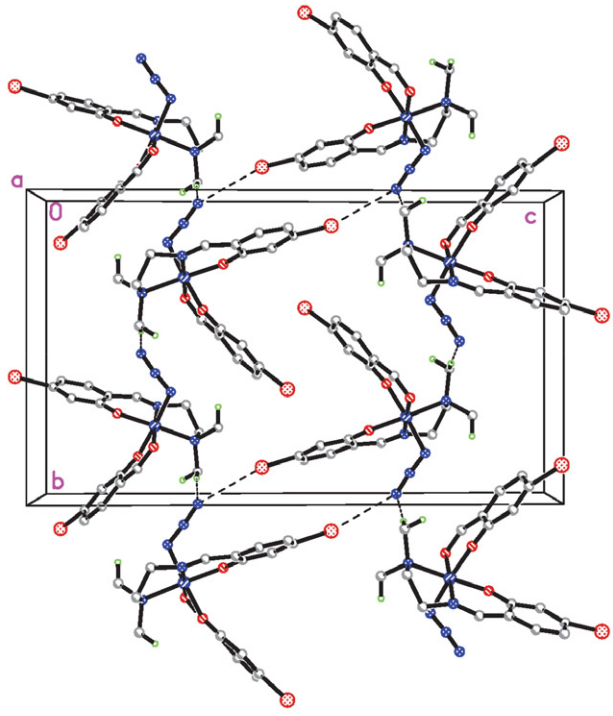

Fig. 6. Molecular packing structure of complex **3**.

3. 6. Structure Description of Complex 4

Molecular structure of complex **4** is shown in Fig. 7. The asymmetric unit of the compound contains four [$CoL^2(HL^2)$] units, which are linked together by O–H···O hydrogen bonds (Table 3). The Co atom in each unit is coordinated by one monoanionic and one dianionic Schiff

base ligands, forming octahedral coordination. The equatorial plane of the octahedral coordination is defined by the phenolate O, imino N and the deprotonated hydroxyl O atom of the the dianionic Schiff base ligand, and the imino N atom of the monoanionic Schiff base ligand. The axial positions of the octahedral coordination are occupied by the phenolate O and hydroxyl O atoms of the monoanionic Schiff base ligand. The Co atoms deviate from the corresponding equatorial planes by 0.040(2) Å for Co1, 0.017(2) Å for Co2, 0.024(2) Å for Co3 and Co4. The octahedral geometry is distorted from ideal model, as evidenced by the bond angles. The *cis* and *trans* angles in the equatorial planes are in the ranges of 86.8(3)–94.5(3)° and 174.1(4)–178.6(3)° for Co1, 85.7(3)–94.4(3)° and 174.6(4)–176.8(3)° for Co2, 86.2(3)–95.2(3)° and 174.9(3)–178.6(3)° for Co3, and 86.0(4)–94.5(4)° and 174.7(4)–178.2(4)° for Co4, respectively. The bond angles among the axial and equatorial donor atoms are in the ranges of 84.8(4)–95.0(3)° for Co1, 86.0(3)–94.2(3)° for Co2, 84.9(3)–95.1(3)° for Co3, and 85.2(4)–94.7(4)° for Co4. And, the two axial donor atoms form angles of 178.7(3)° with Co1 and Co3 atoms, 178.6(3)° with Co2 atom, and 179.7(3)° with Co4 atom. The distortion is mainly caused by the strain created by the five-membered chelate rings Co1-N1-C8-C9-O2, Co1-N2-C17-C18-O4, Co2-N3-C26-C27-O6, Co2-N4-C35-C36-O8, Co3-N5-C44-C45-O10, Co3-N6-C53-C54-O12, Co4-N6-C65-C64-O16, and Co4-N7-C62-C63-O14. The Co-O and Co-N bond lengths are comparable to those observed in Schiff base cobalt complexes.[20]

As shown in Fig. 8, the molecules are linked through O–H···O hydrogen bonds (Table 3), to form one dimensional chains along the *a* axis. The chains are further linked by C–H···Br hydrogen bonds, to form two dimensional sheets parallel to the *bc* plane. In addition, there are π···π interactions among the molecules (Cg5···Cg6[e] 4.619(5) Å, Cg7···Cg5[f] 4.881(5) Å, symmetry codes: e) –1 + *x*, *y*, *z*; f) 1 + *x*, *y*, *z*; Cg5, Cg6 and Cg7 are the centroids of Co3–O11–C47–C46–C52–N6, Co4–O13–C56–C55–C61–N7 and C55–C56–C57–C58–C59–C60, respectively).

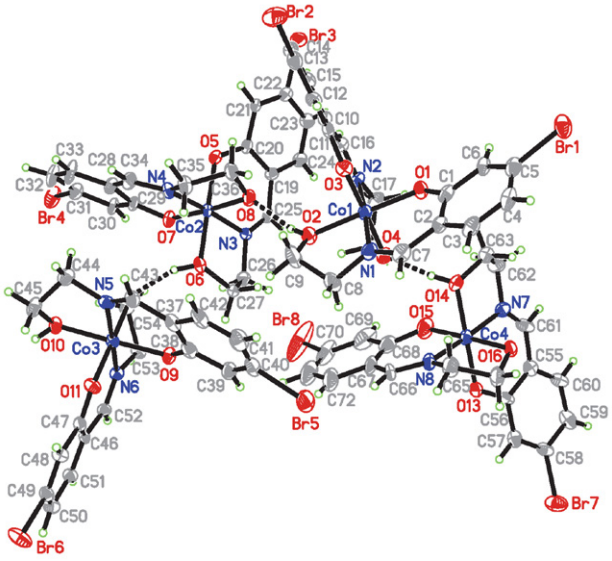

Fig. 7. Molecular structure of complex **4**.

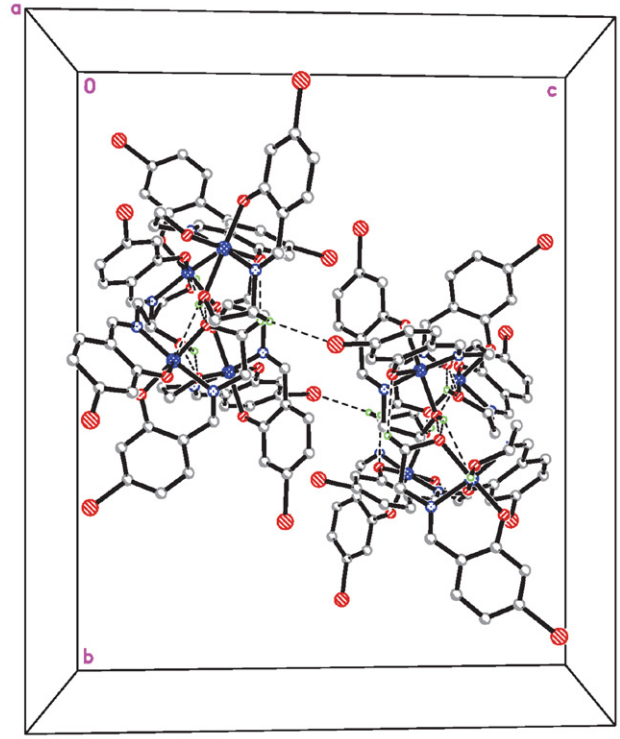

Fig. 8. Molecular packing structure of complex **4**.

Table 3. Hydrogen bond distances (Å) and bond angles (°) for the complexes

D–H···*A*	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	Angle (*D*–H···*A*)
		1		
C16–H16···Br3^{i}	0.93	2.88	3.700(3)	148(5)
C21–H21C···Br3	0.96	2.92	3.590(3)	127(5)
C22–H22A···Br3^{ii}	0.96	2.90	3.815(3)	161(5)
		2		
O2–H2···O1^{iii}	0.85(1)	1.82(4)	2.647(9)	164(14)
		3		
C10–H10C···N3	0.96	2.41	2.801(4)	104(5)
C11–H11A···O2	0.96	2.39	2.970(4)	118(5)
C11–H11C···N5^{iv}	0.96	2.61	3.565(4)	171(5)
		4		
O10–H10···O16^{v}	0.85(1)	1.61(2)	2.445(9)	169(4)
O14–H14···O4^{vi}	0.85(1)	1.65(5)	2.45(1)	156(13)
O6–H6···O12^{vii}	0.85(1)	1.66(6)	2.436(9)	150(11)
O2–H2···O8	0.85(1)	1.69(7)	2.419(9)	143(11)
C18–H18B···O15^{vi}	0.97	2.56(7)	3.300(9)	133(11)
C54–H54A···O7^{vii}	0.97	2.56(7)	3.252(9)	129(11)
C62–H62B···Br4^{viii}	0.97	2.84(7)	3.756(9)	158(11)

Symmetry codes for i): 2 – *x*, 1 – *y*, – *z*; ii): –1 + *x*, *y*, *z*; iii): *x*, 3/2 – *y*, –1/2 + *z*; iv): 1/2 – *x*, 1/2 + *y*, 1/2 – *z*; v): –1 + *x*, *y*, *z*; vi): 1 – *x*, 1/2 + *y*, 1/2 – *z*; vii): 1 – *x*, –1/2 + *y*, 1/2 – *z*; viii): *x*, 1/2 – *y*, 1/2 + *z*.

3. 7. Antibacterial Activities

The two complexes and the free Schiff base were screened for antibacterial activities against three Gram-positive bacterial strains (*B. subtilis*, *S. aureus*, and *St. faecalis*) and three Gram-negative bacterial strains (*E. coli*, *P. aeruginosa*, and *E. cloacae*) by MTT method. The MICs of the compounds against the bacteria are presented in Table 4. Penicillin and Kanamycin were tested as reference drugs. Complex **1** show strong activities against *B. subtilis*, *S. aureus* and *St. faecalis*, moderate activity against *P. aeruginosa*, and weak activities against *E. coli* and *E. cloacae*. Complex **2** show strong activities against *B. subtilis*, *S. aureus* and *St. faecalis*, and weak activities against *P. aeruginosa*, *E. coli* and *E. cloacae*. Complexes **3** and **4** show moderate or weak activities against the bacteria except for *E. coli*. Obviously, the two zinc complexes have better activities than the two cobalt complexes. Interestingly, complexes **1** and **2** are excellent agents for *B. subtilis* and *St. faecalis*, which even comparable to the effects of Penicillin and Kanamycin.

Table 4. MICs (μg mL^{-1}) of the compounds and related materials

Tested material	Gram positive			Gram negative		
	B. subtilis	*S. aureus*	*St. faecalis*	*P. aeruginosa*	*E. coli*	*E. cloacae*
1	0.78	3.12	0.39	6.25	25	12.5
2	1.56	3.12	1.56	12.5	25	25
3	6.25	6.25	25	25	> 50	6.25
4	6.25	12.5	25	25	> 50	25
Penicillin	1.56	1.56	1.56	6.25	6.25	3.12
Kanamycin	0.39	1.56	3.12	3.12	3.12	1.56

4. Conclusion

In summary, two new polynuclear zinc(II) complexes and two new mononuclear cobalt(III) complexes with tridentate Schiff base ligands have been synthesized. Single crystal structures of the complexes were confirmed by X-ray diffraction method and described. The antibacterial assay of the complexes indicates that the zinc complexes are prospective antibacterial agents for *B. subtilis* and *St. faecalis*.

5. Supplementary Materials

X-ray crystallographic data for the complexes have been deposited with the Cambridge Crystallographic Data Centre (The Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK; e-mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk; fax: +44-(0)1223–336033) and are available free of charge on request, quoting the deposition numbers CCDC 2060468 for **1**, 2060469 for **2**, 2060470 for **3** and 2060472 for **4**.

Acknowledgments

This project was supported by the Henan Province Universities and Colleges Funded Scheme (21A530010).

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Povzetek

Sintetizirali in karakterizirali smo nov večjedrni cinkov kompleks, $[Zn(\mu_{1,5}\text{-dca})L^1]_n$ (**1**) in dva nova enojedrna kobaltova kompleksa $CoL^2N_3(Brsal)]$ (**2**) ter $[CoL^1(HL^1)]$ (**3**), kjer je L^1 = 5-bromo-2-(((2-hidroksietil)imino)metil)fenolat, L^2 = 5-bromo-2-(((2-dimetilamino)etil)imino)metil)fenolat, dca = dicianoamid, Brsal = 5-bromo-2-formilfenolat. Spojine smo analizirali z elementno analizo, IR, UV-VIS spektroskopijo, meritvami molarne prevodnosti in monokristalno rentgensko analizo. Strukturna analiza kaže, da se cinkov atom v spojini **1** nahaja v popačeni trigonalno bipiramidalni koordinaciji, medtem ko so atomi kobalta v spojinah **2** in **3** oktaedrično koordinirani. Molekule so medsebojno povezane z vodikovimi vezmi in π···π interakcijami. Testirali smo antibakterijsko učinkovitost kompleksov na treh grampozitivnih (*B. subtilis*, *S. aureus* in *St. faecalis*) in treh gramnegativnih rodovih bakterij (*E. coli*, *P. aeruginosa* in *E. cloacae*) z metodo MTT.