Scientific paper

Synthesis, Characterization, X-Ray Crystal Structures and Antibacterial Activity of Zinc(II) and Vanadium(V) Complexes Derived from 5-Bromo-2-((2-(methylamino) ethylimino)methyl)phenol

Cheng Liu

School of Medicine, Huaqiao University, Quanzhou 362021, P. R. China

** Corresponding author: E-mail: liucheng_hqu@163.com*

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Abstract

Three new zinc(II) and one vanadium(V) complexes, [$Zn_2Cl_2L_2$] (**1**), [$Zn_2I_2L_2$] (**2**), [$ZnCl_2(HL)$] (**3**), and [$V_2O_2(\mu\text{-}O)_2L_2$] (**4**), where L is 5-bromo-2-((2-(methylamino)ethylimino)methyl)phenolate, have been synthesized and characterized by elemental analyses, IR and UV-Vis spectra, as well as molar conductivity. Structures of the complexes were confirmed by single crystal X-ray diffraction. Complexes **1** and **2** are isostructural dinuclear zinc compounds, with the Zn atoms in square pyramidal coordination. The Zn atoms in the mononuclear complex **3** are in tetrahedral coordination. Complex **4** is a dinuclear vanadium(V) compound, with the V atoms in octahedral coordination. The complexes were assayed for antibacterial activities by MTT method.

Keywords: Schiff base; Zinc complex; Vanadium complex; X-ray diffraction; Antibacterial activity

1. Introduction

Schiff bases are important compounds due to their easy preparation, good coordination, and excellent biological activities.[1] For the past few decades, the coordination chemistry of Schiff base ligands has been the subject of great interest. Schiff bases are capable of forming coordinate bonds with various inorganic metal salts through azomethine group.[2] Recently, metal complexes with biologically active ligands have received considerable attention. The biological activities of the organic ligands can be enhanced during coordination with metal salts.[3] It has been reported that chelation is a good way to cure many diseases like cancer.[4] Zinc is the second most abundant metal in the human body, and zinc homeostasis alterations have been linked to many diseases like neuropsychiatric disorders, bone diseases, and skin disorders.[5] Zinc homeostasis causes a variety of health problems that include growth retardation, immunodeficiency, hypogonadism, and neuronal and sensory dysfunctions.[6] Recently, zinc complexes have attracted much attention in the field of cancer therapy based on the facts that zinc is significantly non-toxic even at higher doses compared with other metals, which is beneficial to biocompatibility.[7] Zinc complexes also show biological activities like anticancer, DNA binding, antioxidant, antibacterial, and antitumor.[8] Moreover, vanadium chemistry has attracted great attention due to its interesting structural features and biological relevance.[9] Many vanadium complexes were synthesized and found to show medicinal properties like insulin mimetic activity.[10] They also show anticancer, antitumor, antifungal and antibacterial activities.[11] Some complexes with tridentate Schiff base ligands have been reported.[12] Herein, we report the synthesis, characterization, and single crystal structures of three new zinc(II) and one vanadium(V) complexes, [$Zn_2Cl_2L_2$] (**1**), [$Zn_2I_2L_2$] (**2**), [$ZnCl_2(HL)$] (**3**), and [$V_2O_2(\mu\text{-}O)_2L_2$] (**4**), where L is 5-bromo-2-((2-(methylamino)ethylimino)methyl)phenolate. The antibacterial activity of the compounds against Gram-positive bacterial strains (*B. subtilis*, *S. aureus* and *St. faecalis*) and 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*-methylethane-1,2-diamine, zinc chloride, zinc iodide, vanadium(IV)oxy acetylacetonate and sodium azide were purchased from

Aldrich. The solvents used in the synthesis and biological assay were obtained from Xiya Chemical Co. Ltd. and used as received. Elemental analyses for C, H and N were performed on a Perkin-Elmer 2400 II analyzer. FT-IR spectra were recorded as KBr pellets on Bruker Tensor-27. UV-Vis spectra were recorded on Lambda 35 spectrophotometer. Single crystal X-ray diffraction was carried out with a Bruker Apex II CCD diffractometer. Molar conductivity was measured in methanol with a DDS-11A molar conductivity meter.

2. 2. Synthesis of 5-Bromo-2-((2-(methylamino)ethylimino)methyl)phenol (HL)

4-Bromosalicylaldehyde (2.0 g, 0.010 mol) and *N*-methylethane-1,2-diamine (0.74 g, 0.010 mol) were stirred at reflux for 30 min in methanol (50 mL). The solvent was removed by distillation under reduced pressure to give yellow product. The solid was re-crystallized from ethanol to give the Schiff base. The yield was 0.22 g (85%). Anal. Calc. (%) for $C_{10}H_{13}BrN_2O$: C, 46.71; H, 5.10; N, 10.89. Found (%): C, 46.55; H, 5.21; N, 10.72. IR data (KBr, cm^{-1}): 3412, 3277, 1638. UV–Vis data [methanol, λ/nm (ε/L mol^{-1} cm^{-1})]: 230, 265, 310, 405. ^1H NMR (500 MHz, DMSO-d_6) δ 10.53 (s, 1H, OH), 10.16 (s, 1H, NH), 8.51 (s, 1H, CH=N), 7.53 (d, 1H, ArH), 7.45 (s, 1H, ArH), 7.11 (d, 1H, ArH), 3.71 (t, 2H, CH_2), 3.23 (d, 3H, CH_3), 2.88 (m, 2H, CH_2).

2. 3. Synthesis of [$Zn_2Cl_2L_2$] (1)

4-Bromosalicylaldehyde (0.20 g, 1.0 mmol) and *N*-methylethane-1,2-diamine (0.074 g, 1.0 mmol) were stirred at reflux for 30 min in methanol (30 mL). Then, zinc chloride (0.14 g, 1.0 mmol) and sodium azide (0.065 g, 1.0 mmol) dissolved in 20 mL methanol were added. The final mixture was further stirred at reflux for 1 h. Diffraction quality single crystals were obtained after a few days by slow evaporation of colorless solution of the complex in open atmosphere. The yield was 0.19 g (53%). Anal. Calc. (%) for $C_{20}H_{24}Br_2Cl_2N_4O_2Zn_2$: C, 33.65; H, 3.39; N, 7.85. Found (%): C, 33.46; H, 3.51; N, 7.73. IR data (KBr, cm^{-1}): 3310, 1649. UV–Vis data [methanol, λ/nm (ε/L mol^{-1} cm^{-1})]: 226 (17,530), 268 (15,540), 333 (5,780). Λ_M (10^{-3} mol L^{-1} in methanol): 35 Ω^{-1} cm^2 mol^{-1}.

2. 4. Synthesis of [$Zn_2I_2L_2$] (2)

This complex was synthesized by the similar method as described for complex **1**, with zinc chloride replaced by zinc iodide (0.32 g, 1.0 mmol). The diffraction quality block like colorless single crystals that deposited over a period of 5 days were collected by filtration and washed

Table 1. Crystallographic data and refinement details for the complexes

	1	**2**	**3**	**4**
Chemical Formula	$C_{20}H_{24}Br_2Cl_2N_4O_2Zn_2$	$C_{20}H_{24}Br_2I_2N_4O_2Zn_2$	$C_{10}H_{13}BrCl_2N_2OZn$	$C_{22}H_{32}Br_2N_4O_8V_2$
Molecular weight	713.89	896.79	393.40	742.22
Crystal color, habit	Colorless, block	Colorless, block	Colorless, block	brown, block
Crystal size, mm	0.25×0.23×0.23	0.22×0.20×0.17	0.20×0.20×0.15	0.19×0.18×0.16
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	*Aba*2	*Aba*2	*P*-1	*C*2/*c*
Unit cell dimensions:				
a, Å	14.6638(18)	15.064(2)	7.3196(18)	25.308(2)
b, Å	21.2929(19)	21.180(2)	14.086(2)	6.8247(17)
c, Å	8.2244(17)	8.739(2)	14.539(2)	16.7172(16)
α, °	90	90	81.282(1)	90
β, °	90	90	76.416(1)	105.867(2)
γ, °	90	90	75.596(1)	90
V, Å^3	2567.9(7)	2788.3(8)	1404.4(5)	2777.4(8)
Z	4	4	4	4
ρ_{calcd}, g cm^{-3}	1.847	2.136	1.861	1.775
μ, mm^{-1}	5.213	6.824	4.959	3.602
θ Range collected, deg	2.36–25.50	2.35–25.50	1.45–25.50	1.67–25.49
T_{min} and T_{max}	0.3557 and 0.3802	0.3152 and 0.3900	0.4371 and 0.5233	0.5477 and 0.5964
Reflections collected/unique	7270/2356	7321/2399	7483/5172	7107/2573
Observed reflections ($I \geq 2s(I)$)	2134	1834	3957	2049
Data/restraints/parameters	2356/1/146	2399/1/146	5172/0/309	2573/0/175
GOOF on F^2	1.056	1.087	1.051	1.073
R_1, wR_2 ($I \geq 2s(I)$)	0.0375, 0.0980	0.0551, 0.1357	0.0406, 0.0954	0.0348, 0.0866
R_1, wR_2 (all data)	0.0443, 0.1065	0.0791, 0.1497	0.0599, 0.1088	0.0494, 0.0928

with methanol. The yield was 0.18 g (40%). Anal. Calc. (%) for $C_{20}H_{24}Br_2I_2N_4O_2Zn_2$: C, 26.78; H, 2.70; N, 6.25. Found (%): C, 26.59; H, 2.63; N, 6.34. IR data (KBr, cm^{-1}): 3310, 1646. UV–Vis data [methanol, λ/nm (ε/L·mol^{-1}·cm^{-1})]: 212 (18,360), 241 (17,460), 268 (15,655), 336 (5,460). Λ_M (10^{-3} mol L^{-1} in methanol): 31 Ω^{-1} cm^2 mol^{-1}.

2. 5. Synthesis of [$ZnCl_2$(HL)] (3)

This complex was synthesized by the similar method as described for complex **1**, but without sodium azide. The diffraction quality block like colorless single crystals that deposited over a period of 5 days were collected by filtration and washed with methanol. The yield was 0.20 g (51%). Anal. Calc. (%) for $C_{10}H_{13}BrCl_2N_2OZn$: C, 30.53; H, 3.33; N, 7.12. Found (%): C, 30.40; H, 3.41; N, 7.27. IR data (KBr, cm^{-1}): 3122, 1632. UV–Vis data [methanol, λ/nm (ε/L·mol^{-1}·cm^{-1})]: 225 (19,210), 245 (17,830), 268 (13,380), 365 (5,110). Λ_M (10^{-3} mol L^{-1} in methanol): 40 Ω^{-1} cm^2 mol^{-1}.

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

1			
Zn1-O1	2.030(4)	Zn1-N1A	2.080(5)
Zn1-O1A	2.103(4)	Zn1-N2A	2.215(6)
Zn1-Cl1	2.268(2)		
O1-Zn1-N1A	140.3(2)	O1-Zn1-O1A	75.84(16)
O1-Zn1-N2A	96.1(2)	O1-Zn1-Cl1	108.37(17)
N1-Zn1-Cl1A	110.86(18)	O1-Zn1-Cl1A	113.16(17)
N2-Zn1-Cl1A	103.84(17)		
2			
Zn1-O1	2.000(7)	Zn1-N1A	2.037(12)
Zn1-O1A	2.117(7)	Zn1-N2A	2.193(10)
Zn1-I1	2.5873(19)		
O1-Zn1-N1A	135.6(5)	O1-Zn1-O1A	76.1(3)
O1-Zn1-N2A	94.8(4)	O1-Zn1-I1	108.8(3)
N1-Zn1-I1A	114.9(4)	O1-Zn1-I1A	109.9(3)
N2-Zn1-I1A	105.1(3)		
3			
Zn1-O1	1.950(3)	Zn1-N1	2.007(4)
Zn1-Cl1	2.2447(16)	Zn1-Cl2	2.2158(15)
Zn2-O2	1.940(4)	Zn2-N3	2.009(4)
Zn2-Cl3	2.2377(17)	Zn2-Cl4	2.2095(17)
O1-Zn1-N1	96.33(15)	O1-Zn1-Cl2	111.63(12)
N1-Zn1-Cl2	113.18(13)	O1-Zn1-Cl1	108.65(13)
N1-Zn1-Cl1	111.15(13)	Cl2-Zn1-Cl1	114.42(6)
O2-Zn2-N3	96.77(17)	O2-Zn2-Cl4	109.71(13)
N3-Zn2-Cl4	113.77(14)	O2-Zn2-Cl3	110.72(13)
N3-Zn2-Cl3	109.38(13)	Cl4-Zn2-Cl3	115.02(7)
4			
V1-O1	1.875(2)	V1-O2	1.6529(19)
V1-O3	1.574(2)	V1-N1	2.140(3)
V1-N2	2.113(2)	V1-O2A	2.2764(19)
O3-V1-O2	106.43(11)	O3-V1-O1	101.21(11)
O2-V1-O1	99.09(9)	O3-V1-N2	92.27(11)
O2-V1-N2	94.48(10)	O1-V1-N2	157.25(10)
O3-V1-N1	96.48(11)	O2-V1-N1	155.66(9)
O1-V1-N1	84.11(10)	N2-V1-N1	76.15(10)
O3-V1-O2A	171.10(10)	O2-V1-O2A	79.35(9)
O1-V1-O2A	84.26(8)	N2-V1-O2A	80.39(8)
N1-V1-O2A	76.96(8)		

2. 6. Synthesis of [$V_2O_2(\mu\text{-}O)_2L_2$] (4)

4-Bromosalicylaldehyde (0.20 g, 1.0 mmol) and *N*-methylethane-1,2-diamine (0.074 g, 1.0 mmol) were stirred at reflux for 30 min in methanol (30 mL). Then, vanadium(IV)oxy acetylacetonate (0.26 g, 1.0 mmol) dissolved in 20 mL methanol was added. The final mixture was further stirred at reflux for 1 h. Diffraction quality single crystals were obtained after a few days by slow evaporation of brown solution of the complex in open atmosphere. The yield was 0.26 g (70%). Anal. Calc. (%) for $C_{22}H_{32}Br_2N_4O_8V_2$: C, 35.60; H, 4.35; N, 7.55. Found (%): C, 35.75; H, 4.23; N, 7.46. IR data (KBr, cm^{-1}): 3251, 1650, 934, 848. UV–Vis data [methanol, λ/nm (ε/L·mol^{-1} cm^{-1})]: 223 (16,630), 252 (15,120), 363 (4,330). Λ_M (10^{-3} mol L^{-1} in methanol): 27 Ω^{-1} cm^2 mol^{-1}.

2. 7. 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.[13] Structures of the complexes were solved by direct and Fourier methods and refined by full-matrix least-squares based on F^2 using SHELXL.[14] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms have been placed at geometrical positions with fixed thermal parameters. Crystallographic data of the complexes are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

2. 8. 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.[15] Penicillin and Kanamycin were tested as reference drugs. A stock solution of the Schiff base ligand and the complexes (50 μg mL^{-1}) in DMSO was prepared and quantities of the compounds were incorporated in specified quantity of sterilized liquid medium. 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.

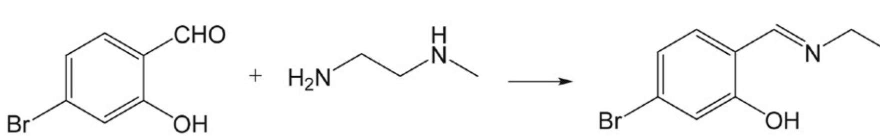
3. Results and Discussion

3. 1. Chemistry

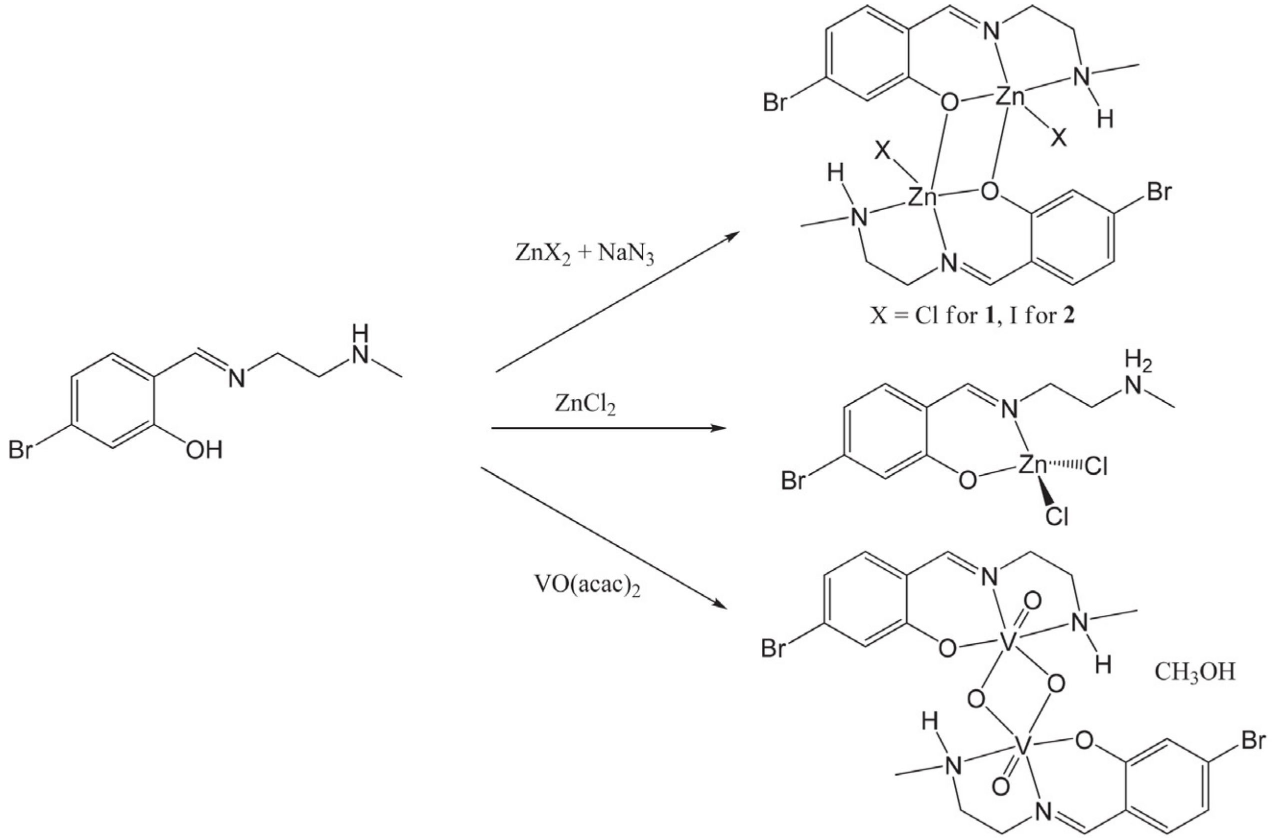
The Schiff base HL was facile synthesized by the reaction of 4-bromosalicylaldehyde with *N*-methylethane-1,2-diamine in methanol (Scheme 1). The complexes were prepared in a similar method, by the reaction of HL with various inorganic salts (Scheme 2). The dinuclear zinc complexes **1** and **2** were prepared in the presence of sodium azide, even though it is not a component of the compounds. Interestingly, the mononuclear complex **3** was obtained with no sodium azide presented during the synthesis. The solubility values of complexes **1**, **2**, **3** and **4** in methanol are 63, 54, 47 and 61 mg/mL, respectively. The conductivity values of the complexes (27–40 Ω^{-1} cm^2 mol^{-1}) indicated that they are non-electrolytes in methanol solution.[16]

3. 2. IR and UV-Vis Spectra Study

The weak absorptions at 3310-3122 cm^{-1} for complexes **1**-**3**, and 3251 cm^{-1} for complex **4** are assigned to $\nu_{N\text{-}H}$. The characteristic imine stretching for the complexes **1**-**4** is observed at 1632-1650 cm^{-1}.[17] The Schiff base ligand coordination through the phenolate oxygen is indicated by the absorption bands of the Ar–O bonds at 1178-1205 cm^{-1} in the complexes **1**-**4**.[18] In general, the infrared spectra of complexes **1** and **2** are similar to each other, due to the isostructural nature. The V=O bonds of complex **4** are indicated by the absorption at 848 and 934 cm^{-1}, which may be assigned to symmetric and asymmetric ν(O=V=O) vibration.[19]



Scheme 1. The synthetic procedure for HL.



Scheme 2. The synthetic procedure for the complexes.

The absorption spectral data of the complexes were measured in methanol. In the complexes, peaks between 212–245 nm, 252–268 nm and 333–363 nm are assigned to π→π*, n→π* and ligand to metal charge transfer transitions, respectively.[20]

3. 3. Structure Description of Complexes 1 and 2

Molecular structures of complexes **1** and **2** are shown in Figs. 1 and 2, respectively. The complexes are phenolate O bridged dinuclear zinc compounds. The molecules of the complexes possess crystallographic two fold rotation symmetry. The Zn atom is in square pyramidal coordination, with the basal plane defined by the phenolate O, imino N and amino N atoms of one Schiff base ligand, and one phenolate O atom of the other Schiff base ligand, and with the apical position occupied by one chloride ligand, *viz.* Cl for **1** and I for **2**. In general, the coordination geometry around the Zn atoms in both complexes displays distortion, as evidenced by the coordinate bond lengths and angles. The Zn−O and Zn−N bonds in both complexes are similar and range from 2.030(4) to 2.215(6) Å for complex **1**, and range from 2.000(7) to 2.193(10) Å for complex **2**. The *cis* and *trans* bond angles in the basal planes are 75.84(16)-96.1(2)° and 140.3(2)-142.8(2)° for complex **1**, and 76.1(3)-94.8(4)° and 135.6(5)-144.9(4)° for complex **2**. The bond angles among the apical and basal donor atoms are 103.84(17)-113.16(17)° for complex **1**, and 105.1(3)-114.9(4)° for complex **2**. All the bond angles indicate that the square pyramidal coordination is distorted from ideal

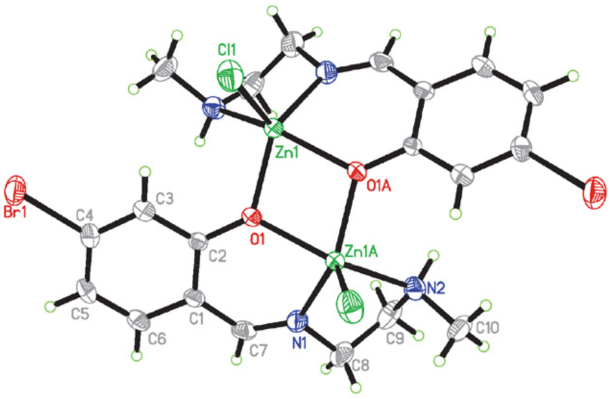


Fig. 1. Molecular structure of complex **1**. Atoms labeled with the suffix A are related to the symmetry operation 1 – *x*, 1 – *y*, *z*.

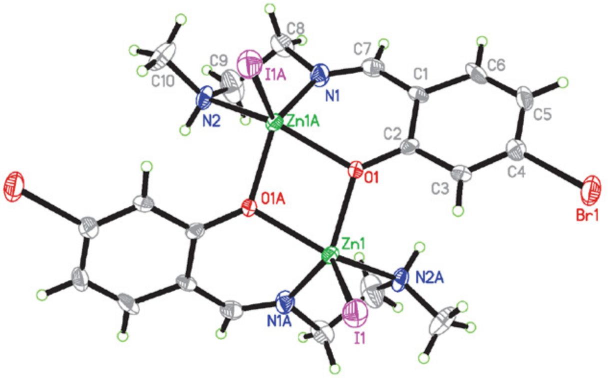


Fig. 2. Molecular structure of complex **2**. Atoms labeled with the suffix A are related to the symmetry operation 1 – *x*, 1 – *y*, *z*.

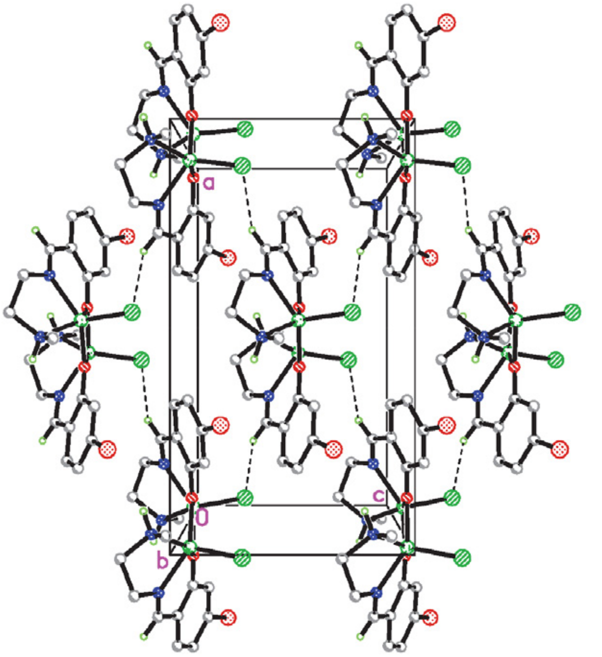


Fig. 3. Molecular packing diagram of complex **1**, viewed along the *b* axis. Hydrogen bonds are drawn as dashed lines.

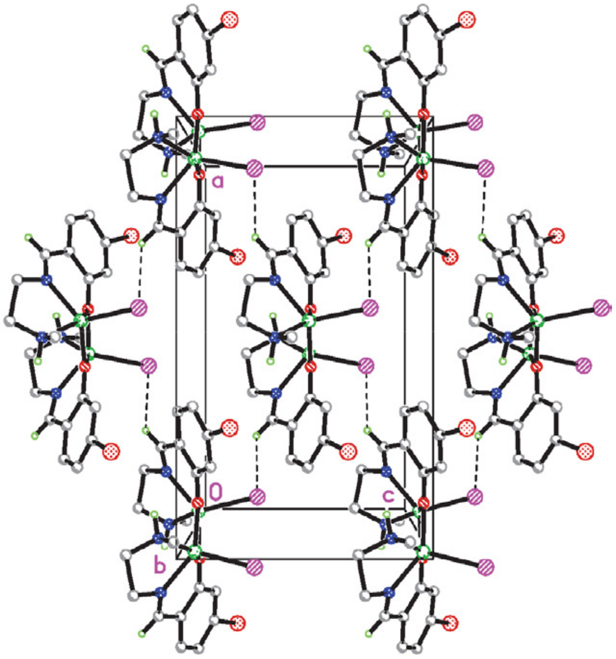


Fig. 4. Molecular packing diagram of complex **2**, viewed along the *b* axis. Hydrogen bonds are drawn as dashed lines.

model. Even though, the coordinate bond values are comparable to those observed in similar Schiff base zinc complexes with square pyramidal coordination.[21] The average deviation (0.001(5) Å for complex **1**, 0.051(5) Å for complex **2**) of the four basal donor atoms and the displacement (0.681(3) Å for complex **1** and 0.695(3) Å for complex **2**) of the Zn atoms from the least-squares planes defined by the four donor atoms indicate that the O_2N_2 cavities afford almost perfect planes to the Zn centers. The two benzene rings of the Schiff base ligands form a dihedral angle of 56.4(5)° for complex **1**, and 65.2(5)° for complex **2**.

In the crystal structures of complexes **1** and **2** (Figs. 3 and 4), the complex molecules are linked through C-H···Cl and C-H···I hydrogen bonds (Table 3), respectively, to form two dimensional network.

3. 4. Structure Description of Complex 3

Molecular structure of complex **3** is shown in Fig. 5. The complex is a mononuclear zinc compound. The asymmetric unit of the compound contains two independent molecules. The Schiff base ligand adopts zwitterionic form, with the H atom of the phenol group transfer to the amino group. The Zn atom is coordinated by the phenolate O and imino N atoms of the Schiff base ligand, and two Cl ligands, forming tetrahedral geometry. The coordination geometry around the Zn atoms displays distortion, as evidenced by the coordinate bond lengths and angles. The Zn–O and Zn–N bonds in the molecules are similar and range from 1.940(4) to 2.009(4) Å. The bond angles are 96.33(15)-114.42(6)° for Zn1, and 96.77(17)-115.02(7)° for Zn2. The coordinate bond values are comparable to those observed in similar Schiff base zinc complexes with tetrahedral coordination.[22]

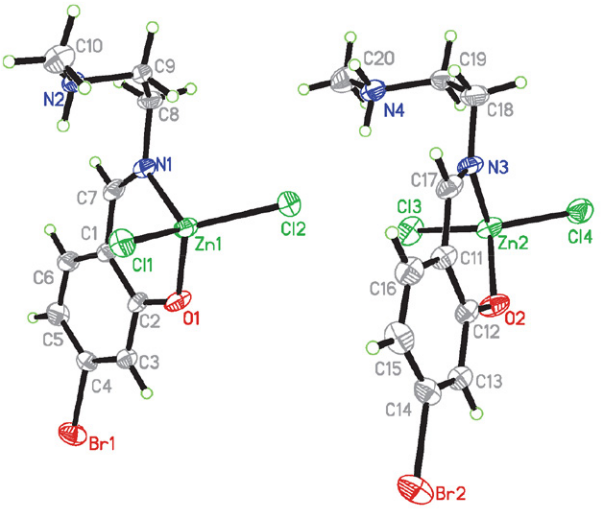


Fig. 5. Molecular structure of complex **3**. Atoms labeled with the suffix A are related to the symmetry operation 1 – *x*, 1 – *y*, *z*.

In the crystal structure of the complex (Fig. 6), the complex molecules are linked through C-H···Cl, N-H···Cl and N-H···O hydrogen bonds (Table 3), to form two dimensional network.

3. 5. Structure Description of Complex 4

Molecular structure of complex **4** is shown in Fig. 7. The complex is an oxo O bridged dinuclear vanadium compound, with V···V separation of 3.050(1) Å. There are two methanol molecules of crystallization, which connect to the complex molecule through O-H···O hydrogen bonds (Table 3). The molecule of the complex possesses crystallographic inversion center symmetry. The V atom is in octahedral coordination, with the equatorial plane defined by the phenolate O, imino N and amino N atoms of one Schiff base ligand, and one bridging O atom (O2), and with the axial positions occupied by terminal O atom (O3) and the other bridging O atom (O2A). The coordination geometry around the V atoms displays distortion, as evidenced by the coordinate bond lengths and angles. The V–O and V–N bonds in the equatorial plane are range from 1.653(2) to 2.140(3) Å, and the axial bonds are 1.574(2) and 2.276(2) Å. The obvious difference of the axial bonds from the equatorial bonds is caused by the Jahn-Teller effects. The *cis* and *trans* bond angles in the equatorial plane are 76.15(10)-99.09(9)° and 155.66(9)-157.25(10)°. The

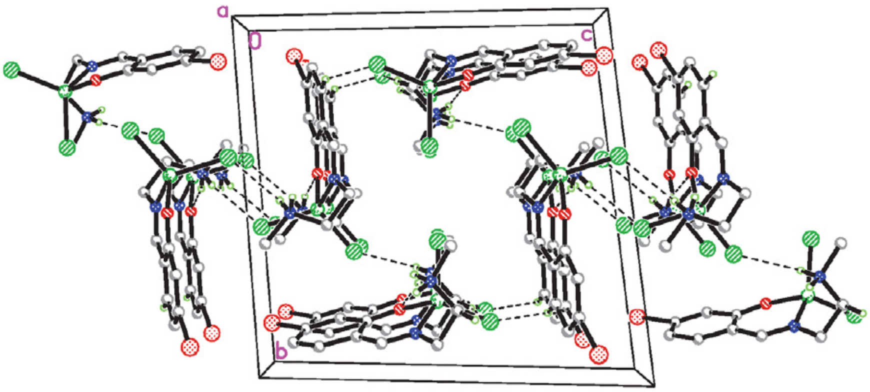


Fig. 6. Molecular packing diagram of complex **3**, viewed along the *a* axis. Hydrogen bonds are drawn as dashed lines.

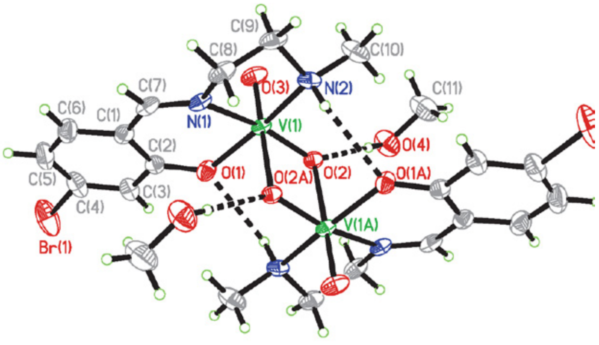


Fig. 7. Molecular structure of complex **4**. Atoms labeled with the suffix A are related to the symmetry operation 1/2 – *x*, 1/2 – *y*, 1 – *z*.

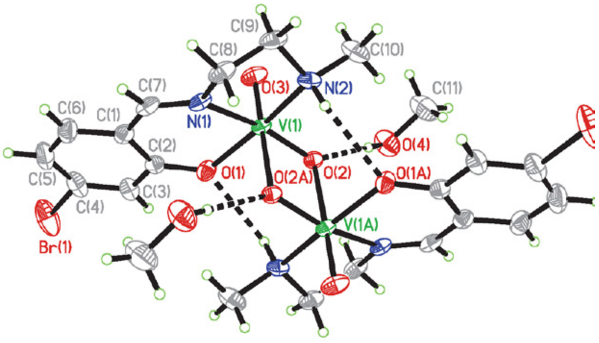


Fig. 8. Molecular packing diagram of complex **4**, viewed along the *b* axis. Hydrogen bonds are drawn as dashed lines.

bond angles among the axial and equatorial donor atoms are 79.96(8)-106.43(11)°. All the bond angles indicate that the octahedral coordination is distorted from ideal model. Even though, the coordinate bond values are comparable to those observed in similar Schiff base vanadium complexes.[23] The average deviation (0.063(5) Å) of the four equatorial donor atoms and the displacement (0.315(2) Å) of the V atom from the least-squares plane defined by the four donor atoms indicate that the O_2N_2 cavity afford somewhat distortion to the V center.

In the crystal structure of the complex (Fig. 8), the complex molecules are linked through C-H···O and N-H···O hydrogen bonds (Table 3), to form two dimensional network.

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				
C7–H7···Cl1^{i}	0.93	2.74	3.583(6)	151
2				
C7–H7···I1^{ii}	0.93	3.00	3.719(13)	136
3				
N2–H2A···Cl1^{iii}	0.90	2.53	3.274(4)	140(6)
N2–H2A···Cl1	0.90	2.92	3.551(4)	128(6)
N2–H2B···O1^{iv}	0.90	1.91	2.793(5)	166(6)
N4–H4A···Cl2	0.90	2.51	3.277(5)	144(6)
N4–H4A···Cl3	0.90	2.87	3.444(5)	123(6)
N4–H4B···O2^{iv}	0.90	1.97	2.856(6)	168(6)
C6–H6···Cl4^{v}	0.93	2.83	3.647(6)	148(6)
C19–H19B···Cl4^{iv}	0.97	2.73	3.628(6)	154(6)
4				
O4–H4···O2	0.82	1.93	2.738(3)	170(5)
N2–H2···O4^{vi}	0.91	2.60	3.169(4)	121(5)
N2–H2···O1^{vii}	0.91	2.34	3.007(3)	130(5)
C3–H3···O4^{viii}	0.93	2.52	3.400(5)	157(5)
C7–H7···O3^{ix}	0.93	2.58	3.020(4)	109(5)
C8–H8B···O3^{ix}	0.97	2.57	3.240(4)	126(5)
C9–H9B···O4^{vi}	0.97	2.54	3.217(5)	127(5)

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

3. 6. Antibacterial Activity of the Compounds

The Schiff base ligand and the complexes 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. The Schiff base ligand has weak activity against *B. subtilis*, *S. aureus* and *E. coli*, while no activity against the remaining bacteria. In general, the complexes have higher activity than the Schiff base ligand. The zinc complexes **1** and **2** have equal activities against all the bacterial strains. Both complexes showed strong activity against *B. subtilis*, *S. aureus* and *E. coli* (MICs

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*
HL	25	12.5	> 50	> 50	12.5	> 50
1	3.12	1.56	25	> 50	6.25	> 50
2	3.12	1.56	25	> 50	6.25	> 50
3	1.56	0.39	6.25	> 50	12.5	> 50
4	12.5	6.25	12.5	> 50	12.5	> 50
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

= 1.56-6.25 μg mL^{-1}), weak activity against *St. faecalis* (MIC = 25 μg mL^{-1}), and no activity against *P. aeruginosa* and *E. cloacae*. Complexes **1** and **2** have similar activity against *S. aureus* and *E. coli* when compared with the reference drugs Penicillin and Kanamycin. In general, complex **3** has better activity against the Gram positive bacteria than complexes **1** and **2**. However, complex **3** has worse activity against the Gram negative bacteria than **1** and **2**. Complex **3** has higher activity against *S. aureus* and similar activity against *B. subtilis* when compared with the reference drugs. Complex **4** has effective activity against *S. aureus*, but weak or no activity against the remaining bacteria.

As a comparison with the zinc complexes derived from 4-fluoro-2-((pyridin-2-ylmethylimino)methyl)phenol and 4-fluoro-2-((2-(hydroxymethyl)phenylimino) methyl)phenol, the current zinc complexes have weaker activity against *B. subtilis*, *St. faecalis*, *P. aeruginosa* and *E. coli*, but higher activity against *S. aureus*.[24] The complexes have similar activities against *S. aureus* and *E. coli* when compared with the zinc complexes derived from 5-bromo-2-((2-(diethylammonio)ethylimino)methyl)phenol.[12f]

4. Conclusion

Two new dinuclear zinc(II) complexes, one new mononuclear zinc complex, and one new dinuclear vanadium(V) complex have been synthesized and characterized. Crystal structures of the complexes are determined and described. The Zn atoms in the dinuclear zinc complexes are in square pyramidal coordination. The Zn atom in the mononuclear zinc complex is in tetrahedral coordination. The V atom in the dinuclear vanadium complex is in octahedral coordination. The three zinc complexes have effective antibacterial activities against *B. subtilis* and *S. aureus*, which deserve further study.

5. Supplementary Materials

The crystal data for the complexes have been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 2111648 (**1**), 2111649 (**2**), 2111650 (**3**) and 2111651 (**4**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Povzetek

Sintetizirali smo tri nove koordinacijske spojine cinka(II) in eno vanadija(V), [$Zn_2Cl_2L_2$] (**1**), [$Zn_2I_2L_2$] (**2**), [$ZnCl_2(HL)$] (**3**), and [$V_2O_2(\mu\text{-}O)_2L_2$] (**4**), kjer je L = 5-bromo-2-((2-(metilamino)etilimino)metil)fenolat, ter produkte karakterizirali z elementno analizo, IR in UV-Vis spektroskopijo ter meritvami molarne prevodnosti. Strukture produktov smo določili z monokristalno rentgensko analizo. Produkta **1** in **2** sta izostrukturni dvojedrni cinkovi spojini s cinkovimi atomi v kvadratno piramidalni koordinaciji. Cinkovi atomi v enojedrni spojini **3** so tetraedrično koordinirani. Spojina **4** je dvojedrna z vanadijevimi atomi v oktaedrični koordinaciji. Antibakterijsko učinkovitost produktov smo preverili z metodo MTT.