Scientific paper

Syntheses, Crystal Structures and Antimicrobial Property of Schiff Base Copper(II) Complexes

Shun-Feng Yu, Xiao-Yang Qiu* and Shu-Juan Liu*

College of Science and Technology, Ningbo University, Ningbo 315212, P. R. China

* Corresponding author: E-mail: xiaoyang_qiu@126.com (Xiao-Yang Qiu), lsj_578@163.com (Shu-Juan Liu)

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Abstract

Four new copper(II) complexes, $[CuL^1(\mu_{1,1}-N_3)]_n$ (1), $[CuL^1(\mu_{1,3}-NCS)]_n$ (2), $[Cu(HL^2)_2](SCN)_2$ (3) and $[Cu(L^2)_2]$ (4), where L^1 and L^2 are 2-((2-(dimethylamino)ethylimino)methyl-4,6-difluorophenolate and 2,4-difluoro-6-((3-morpholino-propylimino)methyl)phenolate, respectively, and HL^2 is 2-((2-(dimethylammonio)ethylimino)methyl-4,6-difluorophenolate, were synthesized and characterized by elemental analysis, IR and UV-vis spectroscopy. The structures for the complexes were further confirmed by single crystal X-ray structure determination. Complexes 1 and 2 are polymeric copper(II) complexes, with the Cu atoms in square pyramidal coordination. Complexes 3 and 4 are mononuclear copper(II) complexes, with the Cu atoms in square planar coordination. The complexes were assayed for their antimicrobial properties.

Keywords: Schiff base; copper complex; crystal structure; antimicrobial property

1. Introduction

Schiff base compounds and their metal complexes have attracted much attention due to their interesting biological aspects like antibacterial,1 antifungal,2 and antitumor.³ It has been proved that the compounds with electron-withdrawing substituent groups can enhance their antimicrobial ability.⁴ Rai et al. reported some compounds with fluoro, chloro, bromo, and iodo-substituted groups, and their remarkable antimicrobial property.⁵ Schiff base complexes of copper have potential antibacterial property.6 Recently, our research group has reported some Schiff base complexes with biological properties.⁷ In pursuit of new Schiff base complexes with potential antimicrobial property, in this work, four new copper(II) complexes, $[CuL^{1}(\mu_{1,1}-N_{3})]_{n}$ (1), $[CuL^{1}(\mu_{1,3}-NCS)]_{n}$ (2), $[Cu(HL^{2})_{2}]$ $(SCN)_2$ (3) and $[Cu(L^2)_2]$ (4), where L¹ and L² are 2-((2-(dimethylamino)ethylimino)methyl-4,6-diluorophenolate and 2,4-difluoro-6-((3-morpholinopropylimino)methyl) phenolate, respectively, and HL2 is 2-((2-(dimethylammonio)ethylimino)methyl-4,6-diluorophenolate, and their antimicrobial properties are present.

2. Experimental

2. 1. Materials and Methods

3,5-Difluorosalicylaldehyde, *N*,*N*-dimethylethane-1, 2-diamine, *N*-(3-aminopropyl)morpholine, copper bro-

mide, ammonium thiocyanate and sodium azide were obtained from Sigma-Aldrich. All other chemicals were commercial obtained from Xiya Chemical Co. Ltd. Elemental analyses of C, H and N were carried out in a Perkin-Elmer automated model 2400 Series II CHNS/O analyzer. The molar conductivity was determined using DDS-11A conductor device. FT-IR spectra were obtained on a Perkin-Elmer 377 FT-IR spectrometer with samples prepared as KBr pellets. UV-Vis spectra were obtained on a Lambda 35 spectrometer. Single crystal structural X-ray diffraction was carried out on a Bruker APEX II CCD diffractometer.

Caution! Because of their explosive character, sodium azide and the complexes containing azide ligand should be handled with care and in very low amounts.

2. 2. Synthesis of Complex 1

3,5-Difluorosalicylaldehyde (0.10 mmol, 16 mg), N,N-dimethylethane-1,2-diamine (0.10 mmol, 8.8 mg), sodium azide (0.10 mmol, 6.5 mg) and copper bromide (0.10 mmol, 22 mg) were mixed in methanol (15 mL) to give a clear blue solution. Block blue single crystals of the complex, suitable for X-ray diffraction, were grown from the solution upon slowly evaporation within five days. The crystals were isolated by filtration. Yield 37%. Anal. calc. for $C_{11}H_{13}CuF_2N_5O$: C, 39.70; H, 3.94; N, 21.04; found: C, 39.57; H, 4.03; N, 20.89%. IR data (cm⁻¹): 2045 (s), 1637

(s), 1461 (s), 1255 (m). UV-Vis data (MeOH, $\lambda_{\rm max}$, nm): 215, 265, 376, 572. $\Lambda_{\rm M}$ (10⁻³ M in methanol): 45 Ω^{-1} cm² mol⁻¹.

2. 3. Synthesis of Complex 2

The complex was prepared with similar method as that described for complex **1**, but with sodium azide replaced with ammonium thiocyanate (0.10 mmol, 7.6 mg). Block blue single crystals of the complex, suitable for X-ray diffraction, were grown from the solution upon slowly evaporation within a week. The crystals were isolated by filtration. Yield 41%. Anal. calc. for $C_{12}H_{13}CuF_2N_3OS$: C, 41.31; H, 3.76; N, 12.05; found: C, 41.13; H, 3.92; N, 12.21%. IR data (cm⁻¹): 2094 (s), 1636 (s), 1462 (s), 1257 (m). UV-Vis data (MeOH, λ_{max} , nm): 215, 265, 380, 575. $\Lambda_{\rm M}$ (10⁻³ M in methanol): 42 Ω^{-1} cm² mol⁻¹.

2. 4. Synthesis of Complex 3

3,5-Difluorosalicylaldehyde (0.10 mmol, 16 mg), N-(3-aminopropyl)morpholine (0.10 mmol, 14 mg), ammonium thiocyanate (0.10 mmol, 7.6 mg) and copper bromide (0.10 mmol, 22 mg) were mixed in methanol (15 mL) to give a clear blue solution. Block blue single crystals of the complex, suitable for X-ray diffraction, were grown from the solution upon slowly evaporation within three days. The crystals were isolated by filtration. Yield 27%.

Anal. calc. for $C_{30}H_{36}CuF_4N_6O_4S_2$: C, 48.15; H, 4.85; N, 11.23; found: C, 48.30; H, 4.92; N, 11.11%. IR data (cm⁻¹): 2056 (s), 1626 (s), 1480 (m), 1265 (m). UV-Vis data (MeOH, λ_{max} , nm): 210, 270, 362, 587. Λ_{M} (10⁻³ M in methanol): 182 Ω^{-1} cm² mol⁻¹.

2. 5. Synthesis of Complex 4

The complex was prepared with similar method as that described for complex 3, but with ammonium thiocyanate replaced with sodium azide (0.10 mmol, 6.5 mg). Block blue single crystals of the complex, suitable for X-ray diffraction, were grown from the solution upon slowly evaporation within a week. The crystals were isolated by filtration. Yield 39%. Anal. calc. for C₂₈H₃₄CuF₄N₄O₄: C, 53.37; H, 5.44; N, 8.89; found: C, 53.23; H, 5.52; N, 8.75%. IR data (cm⁻¹): 1628 (s), 1472 (s), 1268 (m). UV-Vis data (MeOH, $\lambda_{\rm max}$, nm): 210, 270, 360, 595. $\Lambda_{\rm M}$ (10⁻³ M in methanol): 36 Ω^{-1} cm² mol⁻¹.

2. 6. X-ray Crystallography

X-ray diffraction was carried out at a Bruker APEX II CCD area diffractometer equipped with MoK α radiation ($\lambda = 0.71073$ Å). The collected data were reduced with SAINT,⁸ and multi-scan absorption correction was performed using SADABS.⁹ The structures of the complexes were solved by direct method, and refined against F^2 by

Table 1. Crystallographic and refinement data for the complexes

Complex	1	2	3	4
Formula	C ₁₁ H ₁₃ CuF ₂ N ₅ O	C ₁₂ H ₁₃ CuF ₂ N ₃ OS	C ₃₀ H ₃₆ CuF ₄ N ₆ O ₄ S ₂	C ₂₈ H ₃₄ CuF ₄ N ₄ O ₄
Formula weight	332.80	348.85	748.31	630.13
T (K)	298(2)	298(2)	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1	P-1
a (Å)	10.074(1)	16.352(1)	6.4118(8)	4.731(1)
b (Å)	6.531(1)	7.563(1)	7.465(1)	11.399(1)
c (Å)	20.322(1)	11.761(1)	17.532(1)	13.749(1)
α (°)	90	90	93.867(1)	68.109(1)
β (°)	101.559(1)	103.849(1)	100.024(1)	81.436(1)
γ (°)	90	90	90.778(1)	84.849(1)
$V(\mathring{A}^3)$	1310.0(3)	1412.2(3)	824.2(2)	679.9(2)
Z	4	4	1	1
$D_{\rm calc}$ (g cm ⁻³)	1.687	1.641	1.508	1.539
μ (Mo K α) (mm ⁻¹)	1.694	1.714	0.857	0.873
F(000)	676	708	387	327
Measured reflections	7376	8002	4867	10251
Unique reflections	2429	2600	3040	2529
Observed reflections $(I \ge 2\sigma(I))$	1790	1625	2396	1913
Parameters	183	183	214	187
Restraints	0	0	0	0
GOOF	1.005	1.001	1.129	1.000
R_1 , $wR_2 [I \ge 2\sigma(I)]^a$	0.0320, 0.0667	0.0581, 0.1471	0.0491, 0.1290	0.0502, 0.1261
R_1 , wR_2 (all data) ^a	0.0552, 0.0736	0.0981, 0.1822	0.0714, 0.1689	0.0719, 0.1381

^a $R_1 = \sum ||F_0| - |F_c||/\sum |F_0|, wR_2 = \{\sum [w(F_0^2 - F_c^2)^2]/\sum [w(F_0^2)^2]\}^{1/2}$

full-matrix least-squares method using SHELXTL.¹⁰ All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data and refinement parameters for the complexes are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

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

1			
Cu1-O1	1.9224(17)	Cu1-N1	1.963(2)
Cu1-N2	2.075(2)	Cu1-N3	1.986(2)
O1-Cu1-N1	92.61(8)	O1-Cu1-N3	89.49(8)
N1-Cu1-N3	170.79(11)	O1-Cu1-N2	176.46(8)
N1-Cu1-N2	83.98(9)	N3-Cu1-N2	93.74(9)
2			
Cu1-O1	1.898(4)	Cu1-N1	1.933(5)
Cu1-N2	2.076(6)	Cu1-N3	1.944(4)
O1-Cu1-N3	90.9(2)	O1-Cu1-N1	92.1(2)
N3-Cu1-N1	168.9(2)	O1-Cu1-N2	171.5(2)
N3-Cu1-N2	91.1(2)	N1-Cu1-N2	84.4(2)
3			
Cu1-O1	1.892(3)	Cu1-N1	2.013(3)
O1-Cu1-O1A	180	O1-Cu1-N1	92.28(12)
O1-Cu1-N1A	87.72(12)	N1-Cu1-N1A	180
4			
Cu1-O1	1.875(2)	Cu1-N1	2.007(3)
O1-Cu1-O1A	180	O1-Cu1-N1A	88.06(10)
O1-Cu1-N1	91.94(10)	N1-Cu1-N1A	180
O1-Cu1-N1	91.94(10)	N1–Cu1–N1A	180

Symmetry code for A: 1 - x, 1 - y, 1 - z.

2. 7. Antimicrobial Assay

The antibacterial property of the complexes was tested against Bacillus subtilis, Staphylococcus aureus, Escherichia coli, and Pseudomonas fluorescence using MH (Mueller–Hinton) medium. The antifungal activities of the compounds were tested against Candida albicans and Aspergillus niger using RPMI-1640 medium. The MIC values of the tested compounds were determined by a colorimetric method using the dye MTT.¹¹ A stock solution of the compound (150 µg mL-1) in DMSO was prepared and graded quantities (75 μ g mL⁻¹, 37.5 μ g mL⁻¹, 18.8 μ g mL⁻¹, $9.4 \ \mu g \ mL^{-1}, 4.7 \ \mu g \ mL^{-1}, 2.3 \ \mu g \ mL^{-1}, 1.2 \ \mu g \ mL^{-1}, 0.59 \ \mu g$ mL⁻¹) were incorporated in specified quantity of the corresponding sterilized liquid medium. A specified quantity of the medium containing the compound was poured into micro-titration plates. Suspension of the microorganism was prepared to contain approximately 1.0×10^5 cfu mL⁻¹ and applied to microtitration plates with serially diluted compounds in DMSO to be tested and incubated at 37 °C for 24 h and 48 h for bacteria and fungi, respectively. Then the MIC values were visually determined on each of the

microtitration plates, 50 μL of PBS (phosphate buffered saline 0.01 mol $L^{-1}, pH=7.4)$ containing 2 mg of MTT mL $^{-1}$ 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 was measured with a microplate reader at 550 nm.

3. Results and Discussion

3. 1. Synthesis and Characterization

The complexes were readily prepared by the reaction of equimolar quantities of 3,5-difluorosalicylaldehyde, N,N-dimethylethane-1,2-diamine or N-(3-aminopropyl)morpholine, sodium azide or ammonium thiocyanate, and copper bromide in methanol. Single crystals of the complexes were obtained by slow evaporation of their methanolic solution. The azide and thiocyanate coordinate to the Cu atoms in complexes 1 and 2, respectively. However, the thiocyanate acts as a counteranion in complex 3, and the azide is absent in complex 4. Without sodium azide, complex 4 can also be obtained by the reaction of equimolar quantities of 3,5-difluorosalicylaldehyde, N-(3-aminopropyl)morpholine, and copper bromide in methanol. Elemental analyses of the complexes are in accordance with the molecular structures determined by the single crystal X-ray analysis. Molar conductivity for 10⁻³ mol L⁻¹ sample/methanol solutions for ionic electrolytes at 25 °C indicates the non-electrolytic nature of complexes 1, 2 and 4, and 1:2 electrolytic nature of complex.12

3. 2. Spectroscopic Studies

The typical and strong absorptions at 1626–1637 cm⁻¹ of the complexes are generated by the vibrations of the C=N bonds, indicating the formation of the Schiff bases from the condensation reaction of the 3,5-difluorosalicylaldehyde and the amines during the coordination. The intense absorption at 2045 cm⁻¹ for complex 1 is attributed to the stretching vibration of the azide, ¹³ and those at 2094 cm⁻¹ for complex 2 and 2056 cm⁻¹ for complex 3 are assigned to the stretching vibrations of CN bond in thiocyanate. The difference of the absorption bands of the thiocyanate groups, indicates different modes in the complexes. The thiocyanate in complex 2 coordinates to the Cu atom, while that in complex 3 is free. ¹⁴

In the UV-Vis spectra of the complexes, the bands at 360–380 nm are attributed to the azomethine chromophore $\pi \rightarrow \pi^*$ transition.¹⁵ The bands at higher energies (210–215 and 265–270 nm) are associated with the benzene $\pi \rightarrow \pi^*$ transition.¹⁵ The weak and less well-defined broad bands found at 570–600 nm are assigned to the d-d transitions.¹⁶

3. 3. Structure Description of Complex 1

Molecular structure of the end-on azido bridged polymeric copper complex 1 is shown in Figure 1. The asymmetric unit of the complex contains a [CuL1(N3)] unit. The Cu atom is coordinated in a square pyramidal geometry, with the phenolate O1, imino N1, amino N2 atoms of the Schiff base ligand L¹, and the azido N3 atom defining the basal plane, and with the azido N3A atom located at the apical position. The Schiff base ligand, acts as a tridentate ligand, chelate the Cu atom by generating one five and one six-membered rings with bite angles of 83.98(9)° and 92.61(8)°, respectively. The displacement of the Cu atom from the plane defined by the four basal donor atoms toward the apical azido N atom by 0.087(2) Å. The azide ligand bridges Cu atoms with an end-on bridging mode, generating a Cu-Cu distance of 4.156(3) Å. The bond lengths and angles in the square pyramidal coordination are similar to those in the reported azido bridged Schiff base copper complexes.¹⁷ In the crystal structure of the complex, the [CuL¹] units are linked by the azide bridges, to form one-dimensional chains along the *b* axis (Figure 2).

3. 4. Structure Description of Complex 2

Molecular structure of the end-to-end thiocyanato bridged polymeric copper complex 2 is shown in Figure 3.

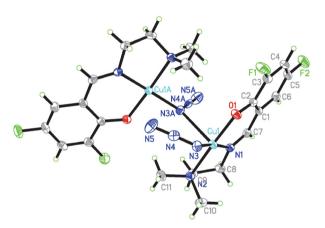


Figure 1. A perspective view of complex **1** with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

The asymmetric unit of the complex contains a [CuL¹(NCS)] unit. The Cu atom is coordinated in a square pyramidal geometry, with the phenolate O1, imino N1, amino N2 atoms of the Schiff base ligand L¹, and the thio-

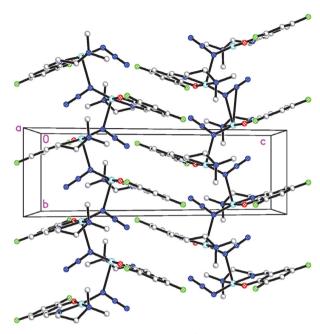


Figure 2. Molecular packing structure of complex 1, viewed along the b axis.

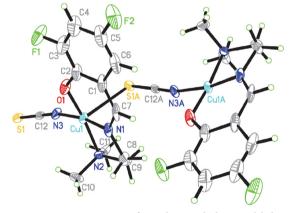


Figure 3. A perspective view of complex **3** with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level.

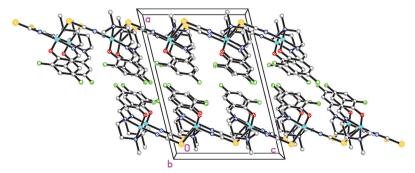


Figure 4. Molecular packing structure of complex **2**, viewed along the *c* axis.

cyanate N3 atom defining the basal plane, and with the thiocyanato S1A atom located at the apical position. The Schiff base ligand, acts as a tridentate ligand, chelate the Cu atom by generating one five and one six-membered rings with bite angles of 84.4(2)° and 92.1(2)°, respectively. The displacement of the Cu atom from the plane defined by the four basal donor atoms toward the apical thiocyanato S atom by 0.160(2) Å. The thiocyanate ligand bridges Cu atoms with an end-to-end bridging mode, generating a Cu···Cu distance of 6.077(4) Å. The bond lengths and angles in the square pyramidal coordination are similar to those in the reported thiocyanate bridged Schiff base copper complexes. In the crystal structure of the complex, the [CuL¹] units are linked by the thiocyanate bridges, to form one-dimensional chains along the *c* axis (Figure 4).

3. 5. Structure Description of Complex 3

Molecular structure of the mononuclear copper complex 3 is shown in Figure 5. The complex contains a $[Cu(HL^2)_2]^{2+}$ cation and two thiocyanate anions. The molecule possesses crystallographic inversion center symmetry. The Cu atom, located at the center, is coordinated in a square planar geometry by the phenolate O1 and O1A and imino N1 and N1A atoms. The Schiff base ligand, acts as a bidentate ligand, chelate the Cu atom by generating one

six-membered ring with bite angle of 92.3(1)°. The morpholine N atom is protonated, and forms a hydrogen bond with the thiocyanate anion (N2–H2···N3: N2–H2 = 0.91 Å, H2···N3 = 1.92 Å, N2···N3 = 2.806(7) Å, N2–H2···N3 = 165(3)°). The bond lengths and angles in the square planar coordination are similar to those in the reported Schiff base copper complexes. ¹⁹ In the crystal structure of the complex, the molecules are stack along the *a* axis *via* weak π ··· π interactions (Figure 6).

3. 6. Structure Description of Complex 4

Molecular structure of the mononuclear copper complex **4** is shown in Figure 7. The complex contains a $[Cu(L^2)_2]$ molecule. The molecule possesses crystallographic inversion center symmetry. The Cu atom, located at the center, is coordinated in a square planar geometry by the phenolate O1 and O1A and imino N1 and N1A atoms. The Schiff base ligand, acts as a bidentate ligand, chelate the Cu atom by generating one six-membered ring with bite angle of 88.1(1)°. The bond lengths and angles in the square planar coordination are similar to those in the reported Schiff base copper complexes.¹⁹ In the crystal structure of the complex, the molecules are stack along the a axis via weak $\pi \cdots \pi$ interactions (Figure 8).

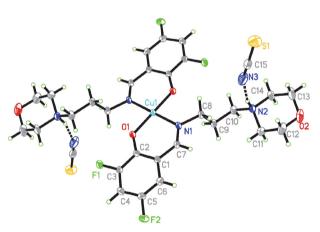


Figure 5. A perspective view of complex **3** with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen bonds are shown as dashed lines.

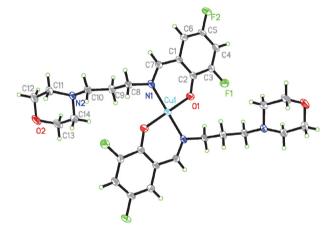


Figure 7. A perspective view of complex **4** with the atom labeling scheme. Thermal ellipsoids are drawn at the 30% probability level

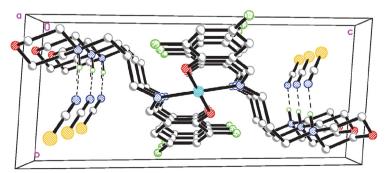


Figure 6. Molecular packing structure of complex 3, viewed along the a axis. Hydrogen bonds are shown as dashed lines.

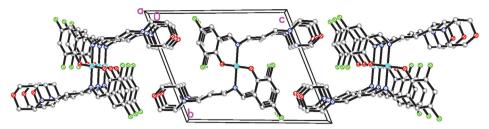


Figure 8. Molecular packing structure of complex **4**, viewed along the *a* axis.

Table 3. Antimicrobial activities of the complexes with minimum inhibitory concentrations ($\mu g \ mL^{-1}$)

Tested material	B. subtilis	S. aureus	E. coli	P. fluorescence
1	2.3	9.4	4.7	37.5
2	2.3	9.4	4.7	37.5
3	1.2	2.3	9.4	75
4	1.2	2.3	9.4	75
Penicillin G	2.3	4.7	>150	> 150

3. 7. Antimicrobial Activity

The complexes were screened for antibacterial activities against two Gram (+) bacterial strains (Bacillus subtilis and Staphylococcus aureus) and two Gram (-) bacterial strains (Escherichia coli and Pseudomonas fluorescence) by MTT method. The MIC (minimum inhibitory concentration, µg mL⁻¹) values of the compounds against four bacteria are listed in Table 3. Penicillin G was used as the standard drug. Interestingly, complex 1 has the same activities against all the bacteria as complex 2. And, complex 3 has the same activities against all the bacteria as complex 4. Thus, the azide and thiocyanate ligands or anions in the complexes do not have obvious influence on the antibacterial activity. Complexes 1 and 2 show strong activity against B. subtilis and E. coli, and medium activity against S. aureus and P. fluorescence. Complexes 3 and 4 show strong activity against B. subtilis and S. aureus, medium activity against E. coli, and weak activity against P. fluorescence. The complexes have strong or similar activities against B. subtilis, S. aureus and E. coli which comparable to Penicillin G. However, all the complexes have no activity on the fungal strains Candida albicans and Aspergillus niger. The antimicrobial activities of the complexes are comparable to the copper complex derived from 2-hydroxy-5-methylbenzaldehyde oxime.²⁰

4. Conclusion

In summary, an end-on azide bridged polymeric copper(II) complex, an end-to-end thiocyanate bridged polymeric copper(II) complex, and two mononuclear copper(II) complexes derived from the Schiff bases 2-((2-(dimethylamino)ethylimino)methyl-4,6-diluorophenol and

2,4-difluoro-6-((3-morpholinopropylimino)methyl)phenol were obtained. The Cu atoms in the polymeric complexes are in square pyramidal geometry, and those in the mononuclear complexes are in square planar geometry. One compound has ionic structure ([Cu(HL²)₂]²+ cation, two thiocyanate anions) in others the molecules are present. The results of the conductivity measurements are in agreement with that determined by the single crystal X-ray analysis. The complexes have strong activities against the bacteria *B. subtilis, S. aureus* and *E. coli*.

Supplementary Data

CCDC 2021453–2021456 (1–4) contain the supplementary crystallographic data for the compounds. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Povzetek

Sintetizirali smo štiri nove bakrove(II) komplekse, $[CuL^1(\mu_{1,1}-N_3)]_n$ (1), $[CuL^1(\mu_{1,3}-NCS)]_n$ (2), $[Cu(HL^2)_2]$ (\$\frac{3}{2}]\$ (\$\frac{1}{2}\$), kjer sta \$L^1\$ in \$L^2\$ 2-((2-(dimetilamino)etilimino)metil-4,6-difluorofenolat in 2,4-difluoro-6-((3-morfolino-propilimino)metil)fenolat, HL^2 pa je 2-((2-(dimetilammonio)etilimino)metil-4,6-difluorofenolat. Okarakterizirali smo jih z elementno analizo ter IR in UV-vis spektroskopijo. Strukture kompleksov smo potrdili z monokristalno rentgensko difrakcijo. Kompleksa 1 in 2 sta polimerna bakrova(II) kompleksa s kvadratno piramidalno geometrijo okoli Cu atoma. Kompleksa 3 in 4 sta enojedrna bakrova(II) kompleksa s kvadratno planarno geometrijo okoli Cu atoma. Kompleksom smo določili antimikrobne lastnosti.



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