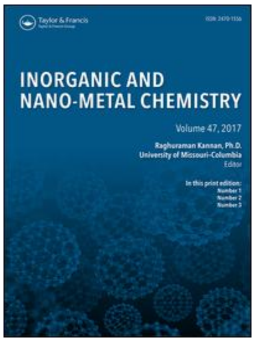

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Copper(II) and cadmium(II) complexes of mono-condensed N,O- or N,N,O-Donor ligands: synthesis, crystal structures, and antibacterial activity

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ABSTRACT
Three new copper(II) and cadmium(II) complexes, $[Cu(L^1)_2]$ (1), $[CuL^2(N_3)]$ (2), and $[Cd(L^3)_2]$ (3), where L^1 = 2-bromo-4-chloro-6-cyclohexylaminomethylphenolate, L^2 = 2-bromo-4-chloro-6-[(2-morpholin-4-ylethylimino)methyl]phenolate, and L^3 = 2-bromo-4-chloro-6-[(3-morpholin-4-ylpropylimino)methyl]phenolate, have been prepared and structurally characterized by X-ray crystallography. The Cu atom in complex 1 is in tetrahedrally distorted square planar geometry. The Cu atom in complex 2 is in square planar geometry. The Cd atom in complex 3 is in octahedral geometry. The complexes exhibited effective activities against *B. subtilis*, *S. aureus*, and *E. coli*.

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KEYWORDS
Schiff base; reduced Schiff base; copper complex; cadmium complex; crystal structure; antibacterial activity

Introduction

Schiff bases represent an important class of compounds in medicinal chemistry with great potential for antibacterial and anticancer applications.[1–3] Metal complexes derived from various Schiff bases and reduced Schiff bases have received much attention in coordination chemistry and bioinorganic chemistry.[4–6] Copper is a human essential element, which has attracted wide interest to explore its complexes with the aim for medical applications, due to its important biological effects.[7,8] A great deal of copper(II) complexes with Schiff bases are reported to possess significant antibacterial activities.[9,10] In addition, cadmium(II) complexes also show interesting biological activities including antibacterial applications.[11,12] In the present work, two new copper(II) complexes, $[Cu(L^1)_2]$ (1) and $[CuL^2(N_3)]$ (2), and a new cadmium(II) complex, $[Cd(L^3)_2]$ (3), where L^1 = 2-bromo-4-chloro-6-cyclohexylaminomethylphenolate, L^2 = 2-bromo-4-chloro-6-[(2-morpholin-4-ylethylimino)methyl]-phenolate, and L^3 = 2-bromo-4-chloro-6-[(3-morpholin-4-ylpropylimino)methyl]phenolate (Scheme 1), were synthesized and characterized by IR, UV-Vis, elemental analysis, and single crystal X-ray diffraction analysis. The antibacterial activities of the complexes were also studied.

Experimental

Materials and measurements

3-Bromo-5-chlorosalicylaldehyde, cyclohexylamine, 2-morpholin-4-ylethylamine, and 3-morpholin-4-ylpropylamine were purchased from Aldrich and used without further purification. Other solvents and reagents were made in China and used as received. C, H and N elemental analyses were performed with a Perkin-Elmer 240 elemental analyzer. Infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm^{-1} region. UV-Vis spectra were recorded on a Lambda 900 spectrometer.

Synthesis of complex 1

3-Bromo-5-chlorosalicylaldehyde (1.0 mmol, 235 mg) and cyclohexylamine (1.0 mmol, 99.2 mg) were dissolved in ethanol (30 mL). The mixture was stirred at room temperature for 30 min to give a yellow solution. Then, solid $NaBH_4$ (1.5 mmol, 56.6 mg) was slowly added to the solution under ice-water bath. The mixture was reacted until the solution changed to colorless. Then, $Cu(ClO_4)_2\cdot 6H_2O$ (1.0 mmol, 371 mg) was added to the above solution. The mixture was further stirred at room temperature for 30 min to give blue solution. After keeping the solution in air for a few days, blue block-shaped single crystals, suitable for X-ray crystal structure determination, were obtained. The crystals were isolated by filtration and dried in a vacuum desiccator containing anhydrous $CaCl_2$. The yield was 32%. IR data (KBr; ν_{max}, cm^{-1}): 3267, 3053, 3025, 2922, 2871, 1595, 1463, 986, 755. UV-Vis data in acetonitrile (λ, nm (ε, $M^{-1} cm^{-1}$)]: 235 (18,120), 385 (5,050), 670 (180). Anal. Calcd. for $C_{26}H_{32}Br_2Cl_2CuN_2O_2$ (%): C, 44.69; H, 4.62; N, 4.01. Found (%): C, 44.53; H, 4.71; N, 3.92.

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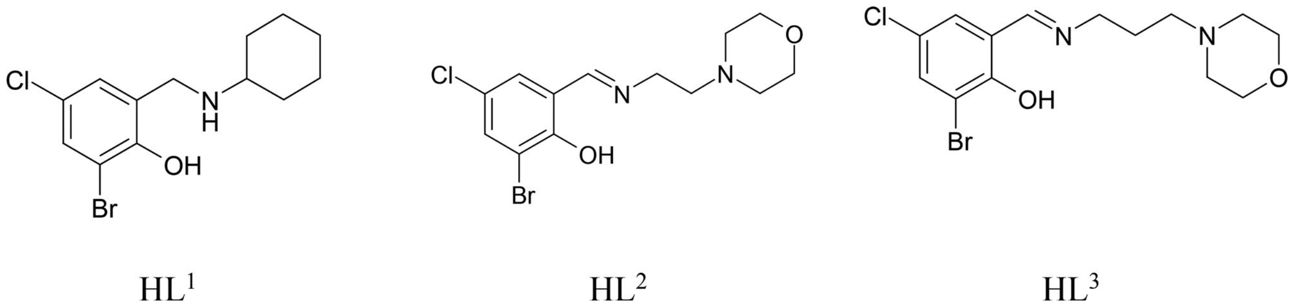

Scheme 1. The ligands.

Synthesis of complex 2

3-Bromo-5-chlorosalicylaldehyde (1.0 mmol, 235 mg) and 2-morpholin-4-ylethylamine (1.0 mmol, 130 mg) were dissolved in ethanol (30 mL). The mixture was stirred at room temperature for 30 min to give a yellow solution. To the solution was added with stirring an ethanolic solution (10 mL) of $Cu(ClO_4)_2{\cdot}6H_2O$ (1.0 mmol, 371 mg) and NaN_3 (1.0 mmol, 65 mg). The mixture was further stirred at room temperature for 30 min to give blue solution. After keeping the solution in air for a few days, blue block-shaped single crystals, suitable for X-ray crystal structure determination, were obtained. The crystals were isolated by filtration and dried in a vacuum desiccator containing anhydrous $CaCl_2$. The yield was 46%. IR data (KBr; ν_{max}, cm^{-1}): 2056, 1635, 1442, 1161, 1076, 948, 858, 745. UV-Vis data in acetonitrile (λ, nm (ε, $M^{-1}cm^{-1}$)]: 275 (20,150), 300 (11,272), 385 (9,370), 665 (210). Anal. Calcd. for $C_{13}H_{15}BrClCuN_5O_2$ (%): C, 34.53; H, 3.34; N, 15.49. Found (%): C, 34.65; H, 3.41; N, 15.32.

Synthesis of complex 3

3-Bromo-5-chlorosalicylaldehyde (1.0 mmol, 235 mg) and 3-morpholin-4-ylpropylamine (1.0 mmol, 144 mg) were dissolved in ethanol (30 mL). The mixture was stirred at room temperature for 30 min to give a yellow solution. To the solution was added with stirring an ethanolic solution (10 mL) of $Cd(CH_3COO)_2{\cdot}2H_2O$ (1.0 mmol, 266 mg). The mixture was further stirred at room temperature for 30 min to give colorless solution. After keeping the solution in air for a few days, colorless block-shaped single crystals, suitable for X-ray crystal structure determination, were obtained. The crystals were isolated by filtration and dried in a vacuum desiccator containing anhydrous $CaCl_2$. The yield was 31%. IR data (KBr; ν_{max}, cm^{-1}): 1631, 1453, 1272, 1153, 1046, 987, 955, 837, 756, 643. UV-Vis data in acetonitrile (λ, nm (ε, $M^{-1}cm^{-1}$)]: 275 (19,310), 298 (9,565), 360 (6,120). Anal. Calcd. for $C_{28}H_{34}Br_2CdCl_2N_4O_4$ (%): C, 40.34; H, 4.11; N, 6.72. Found (%): C, 40.26; H, 4.03; N, 6.85.

X-ray crystallography

Diffraction intensities for the complexes were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å). The collected data were reduced using SAINT,[13] and multi-scan absorption corrections were performed using SADABS.[14] Structures of the complexes were solved by direct methods and refined against F^2 by full-matrix least-squares methods using SHELXTL.[15] All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms in the complexes were placed in idealized positions and constrained to ride on their parent atoms. Crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

Antibacterial assay

The antibacterial activity of the complexes was tested against *B. subtilis*, *S. aureus*, *E. coli*, and *P. aeruginosa* using LB medium (Luria-Bertani medium: Tryptone 10 g, Yeast extract 5 g, NaCl 10 g, distilled water 1000 mL, pH 7.4). The IC_{50} (half inhibitory concentration) of the test compounds were determined by a colorimetric method using the dye MTT (3-(4,5-di-methylth-iazol-2-yl)-2,5-diphenyl tetrazolium bromide).

A stock solution of the synthesized compound (1000 μg mL^{-1}) in DMSO was prepared and graded quantities of the test compounds were incorporated in specified quantity of sterilized liquid LB medium. Suspension of the microorganism was prepared and applied to 96-well assay plate with serially diluted compounds to be tested. 10 μL of tested samples at pre-set concentrations were added to wells with Penicillin as a positive reference and with the solvent control (5% DMSO) in medium and incubated at 37 °C for 24 h.

After 24 h exposure, 10 μL of PBS (phosphate buffered saline 0.01 mol L^{-1}, pH 7.4) containing 4 mg mL^{-1} of MTT was added to each well. After 4 h, the medium was replaced by 150 μL DMSO to dissolve the complexes. The absorbance at 492 nm of each well was measured with an ELISA plate reader. The IC_{50} value was defined as the concentration at which 50% of the bacterial strain could survive.

Results and discussion

Chemistry

The complexes were prepared by the reaction of the ligands and metal salts in ethanol. Crystals of the complexes are soluble in DMF, DMSO, methanol, ethanol, and acetonitrile.

Table 1. Crystallographic data and refinement parameters for the complexes.

Parameters	1	2	3
Molecular formula	$C_{26}H_{32}Br_2Cl_2CuN_2O_2$	$C_{13}H_{15}BrClCuN_5O_2$	$C_{28}H_{34}Br_2CdCl_2N_4O_4$
Mr	698.80	452.20	833.71
Crystal color, habit	Blue, block	Blue, block	Colorless, block
Crystal size, mm^3	0.23 × 0.23 × 0.19	0.32 × 0.32 × 0.29	0.30 × 0.28 × 0.27
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	*Pccn*	$P2_1/n$
a, Å	20.547(2)	9.4879(6)	9.6015(13)
b, Å	12.356(2)	37.327(2)	15.8070(17)
c, Å	24.224(2)	9.1166(9)	20.1719(18)
α, °	90	90	90
β, °	105.475(2)	90	90.013(2)
γ, °	90	90	90
V, Å^3	5927.0(12)	3228.7(4)	3061.5(6)
Z	8	8	4
ρ_{calcd}, g cm^{-3}	1.566	1.861	1.809
μ, mm^{-1}	3.639	4.009	3.539
F(000)	2808	1800	1656
Number of unique data	34580	9221	12915
Number of observed data ($I > 2\sigma(I)$)	11009	2997	4924
Independent reflections	5194	2133	2641
Parameters	631	208	370
Restraints	0	0	0
R_1, wR_2 ($I > 2\sigma(I)$)	0.0539, 0.1039	0.0511, 0.0955	0.0390, 0.0885
R_1, wR_2 (all data)	0.1525, 0.1483	0.0811, 0.1075	0.0762, 0.0983
Goodness of fit on F^2	0.994	1.071	0.849
Largest difference peak and hole, *e* Å^{-3}	0.552 and −0.573	0.465 and −0.489	0.340 and −0.379

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

1			
Cu1-O1	1.896(5)	Cu1-O2	1.890(4)
Cu1-N1	2.016(6)	Cu1-N2	2.032(5)
O2-Cu1-O1	158.50(19)	O2-Cu1-N1	83.9(2)
O1-Cu1-N1	94.8(2)	O2-Cu1-N2	93.2(2)
O1-Cu1-N2	92.8(2)	N1-Cu1-N2	166.1(2)
2			
Cu1-O1	1.885(3)	Cu1-N1	1.925(4)
Cu1-N2	2.083(4)	Cu1-N3	1.950(5)
O1-Cu1-N1	93.22(16)	O1-Cu1-N3	93.05(17)
N1-Cu1-N3	169.3(2)	O1-Cu1-N2	170.23(16)
N1-Cu1-N2	84.46(17)	N3-Cu1-N2	90.75(18)
3			
Cd1-O1	2.213(5)	Cd1-O3	2.203(5)
Cd1-N1	2.228(5)	Cd1-N2	2.589(5)
Cd1-N3	2.263(5)	Cd1-N4	2.602(5)
O3-Cd1-O1	173.08(14)	O3-Cd1-N1	105.05(19)
O1-Cd1-N1	81.41(18)	O3-Cd1-N3	80.43(18)
O1-Cd1-N3	93.16(18)	N1-Cd1-N3	174.4(2)
O3-Cd1-N2	84.15(17)	O1-Cd1-N2	94.90(17)
N1-Cd1-N2	78.43(17)	N3-Cd1-N2	103.56(17)
O3-Cd1-N4	95.15(18)	O1-Cd1-N4	86.10(18)
N1-Cd1-N4	99.36(18)	N3-Cd1-N4	78.77(17)
N2-Cd1-N4	177.39(16)		

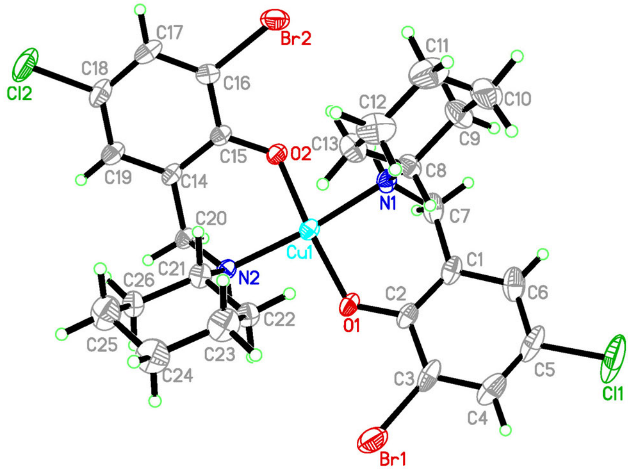

Figure 1. Molecular structure of complex 1, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Structure description of compound 1

Molecular structure of compound 1 is shown in Figure 1. The asymmetric unit of the compound contains two mononuclear copper(II) complexes. The Cu atom in the compound is coordinated by two amino nitrogen atoms and two phenolato oxygen atoms from two L^1 ligands, forming a tetrahedrally distorted square planar geometry. The Cu1 and Cu2 atoms deviate from the least-squares planes defined by the corresponding donor atoms by 0.061(3) and 0.046(3) Å, respectively. The coordinate bond lengths in the complex are similar to those observed in copper complexes with reduced Schiff base ligands.[16,17] The distortion of the square planar coordination can be observed from the coordinate bond angles, ranging from 83.9(2)° to 94.8(2)° for the perpendicular angles, and from 158.5(2)° to 172.3(2)° for the diagonal angles. The dihedral angle between the planes defined by Cu1-O1-N1 and Cu1-O2-N2 is 24.1(5)°, and that defined by Cu2-O3-N3 and Cu2-O4-N4 is 15.2(5)°. In the crystal structure of the compound, molecules are linked through N–H···O hydrogen bonds [N3–H3 = 0.90 Å, H3···O1 = 2.53(2) Å, N3···O1 = 3.3154(5) Å, N3–H3···O1 = 146(3)°; N2–H2 = 0.90 Å, H2···O4 = 2.50(2) Å, N2···O4 = 3.1879(5) Å, N2–H2···O4 = 134(3)°], to form dimers (Figure 2).

Structure description of compound 2

Molecular structure of compound 2 is shown in Figure 3. The Cu atom in the complex is coordinated by the phenolate oxygen atom, imino nitrogen atom, and amino nitrogen atom of the L^1 ligand, and one azido nitrogen atom,

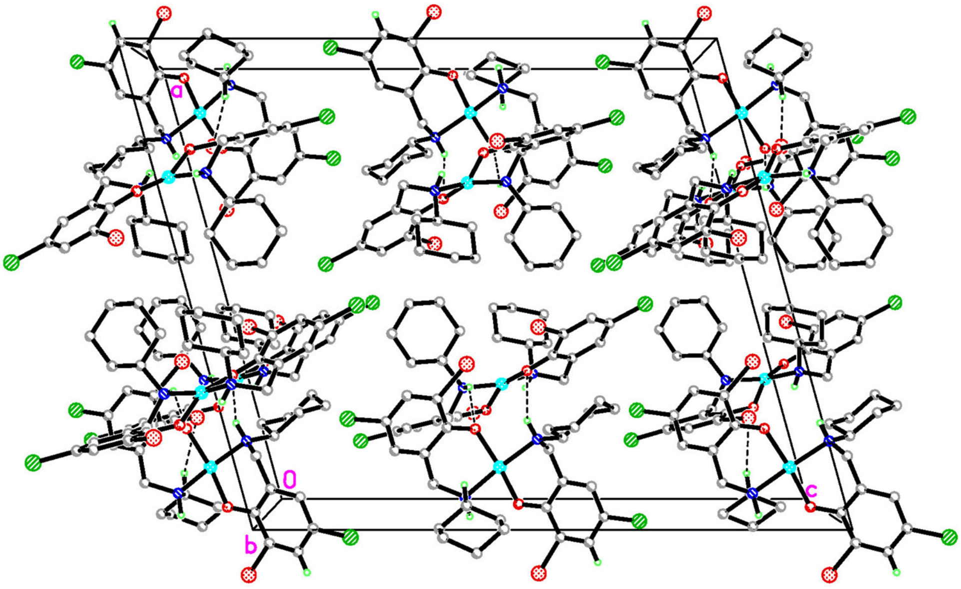

Figure 2. Crystal packing structure of complex 1, viewed along the *b* axis. Hydrogen bonds are shown as dashed lines.

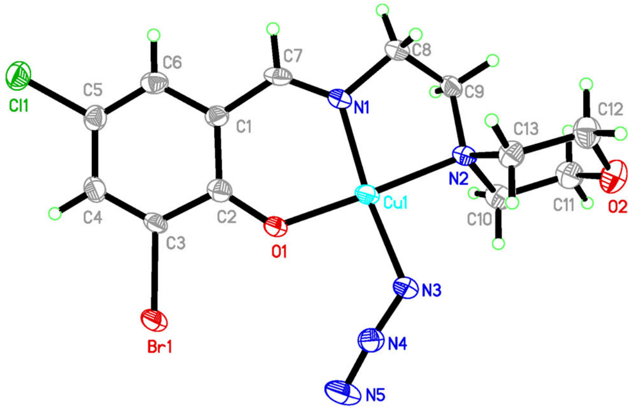

Figure 3. Molecular structure of complex 2, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

forming a square planar geometry. The Cu atom deviates from the least-squares plane defined by the donor atoms by 0.003(3) Å. The coordinate bond lengths in the complex are similar to those observed in Schiff base copper(II) complexes with azido ligand.[18,19] The distortion of the square planar coordination can be observed from the coordinate bond angles, ranging from 84.5(2)° to 93.2(2)° for the perpendicular angles, and from 169.3(2)° to 170.2(2)° for the diagonal angles. In the crystal structure of the complex, molecules are linked through C–H···O, C–H···N and C–H···Cl hydrogen bonds [C4–H4 = 0.93 Å, H4···Cl1^{i} = 2.72(5) Å, C4···Cl1^{i} = 3.586(5) Å, C4–H4···Cl1^{i} = 156(5)°; C10–H10A = 0.97 Å, H10A···O2^{ii} = 2.55(3) Å, C10···O2^{ii} = 3.283(3) Å, C10–H10A···O2^{ii} = 133(4)°; C10–H10B = 0.97 Å, H10B···N3 = 2.47(3) Å, C10···N3 = 3.061(3) Å, C10–H10B···N3 = 119(4)°; symmetry codes: i: 1/2+*x*,-*y*,-1/2-*z*; ii: *x*. 1/2-*y*, −1/2+*z*], to form a network (Figure 4).

Structure description of compound 3

Molecular structure of compound 3 is shown in Figure 5. The Cd atom in the complex is coordinated in an octahedral geometry, with the two phenolate oxygen atoms and two imino nitrogen atoms from two L^3 ligands defining the equatorial plane, and with the two amino nitrogen atoms from two L^3 ligands occupying the axial positions. The Cd atom deviates from the least-squares plane defined by the equatorial donor atoms by 0.012(2) Å. The coordinate bond lengths in the complex are similar to those observed in Schiff base cadmium(II) complexes.[20,21] The distortion of the octahedral coordination can be observed from the coordinate bond angles, ranging from 78.4(2)° to 105.0(2)° for the perpendicular angles, and from 173.1(2)° to 177.4(2)° for the diagonal angles.

IR and UV-Vis spectra of the complexes

The $\nu(C=N)$ absorptions are observed at 1635 cm^{-1} for complex 2 and 1631 cm^{-1} for complex 2.[22] The typical band indicative of the azide ligand in complex 2 is observed at 2056 cm^{-1}.[23] The weak absorption at 3267 cm^{-1} can be assigned to the vibration of the N–H groups of complex 1. The weak peaks in the low wave numbers in the region 450–750 cm^{-1} may be attributed to M–O and M–N bonds in the complexes.

The UV-Vis spectra of the complexes were recorded in 10^{-5} mol L^{-1} in acetonitrile, in the range 200–800 nm. The bands in the range of wavelength 350–400 nm arise mainly due to the nitrogen to metal charge transfer transition (LMCT).[24] The bands at about 300 nm in the spectra of complexes 2 and 3 are attributed to the azomethine chromophore π-π^* transition. The bands at higher energies (235–275 nm) are associated with the benzene π-π^* transition.[25]

Antibacterial activities

The complexes were screened for antibacterial activities against two Gram-positive bacterial strains (*B. subtilis* and *S. aureus*) and two Gram-negative bacterial strains (*E. coli* and

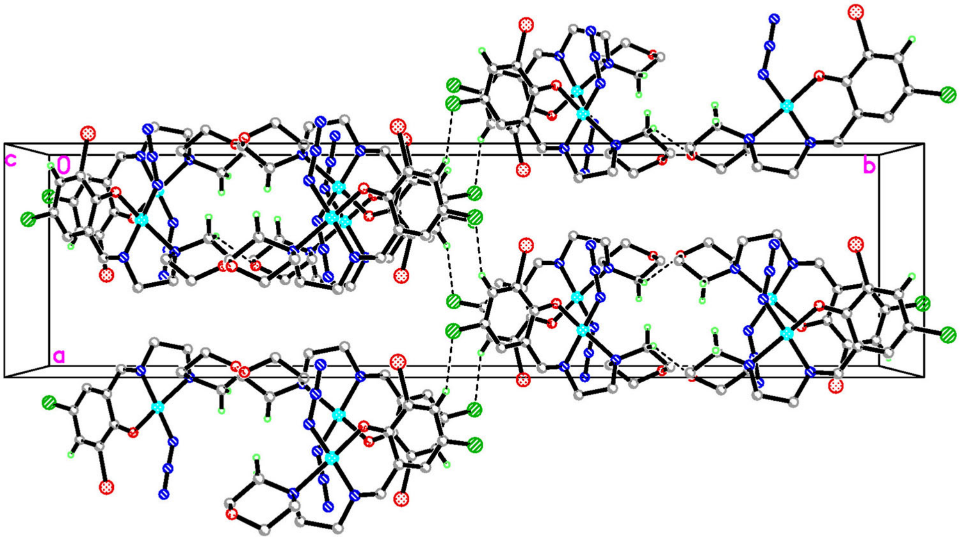

Figure 4. Crystal packing structure of complex 2, viewed along the *c* axis. Hydrogen bonds are shown as dashed lines.

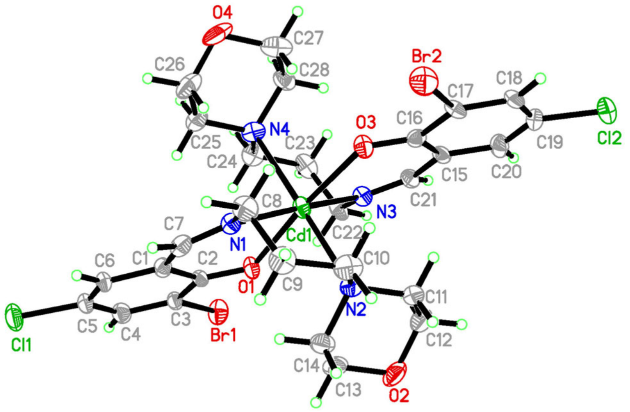

Figure 5. Molecular structure of complex 3, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 3. Antibacterial results (IC_{50}, $\mu g\ mL^{-1}$).

	Gram-positive		Gram-negative	
Compound	*B. subtilis*	*S. aureus*	*E. coli*	*P. aeruginosa*
1	3.31	0.38	12.20	>50
2	4.56	2.05	21.54	>50
3	8.87	5.73	17.18	32.37
Penicillin G	2.35	0.75	17.51	17.49

P. aeruginosa) by MTT method. The IC_{50} values of the complexes against the bacteria are presented in Table 3. Penicillin G was tested as a reference drug. Complexes 1 and 2 exhibited effective activities against *B. subtilis*, *S. aureus*, medium activity against *E. coli*, and no activity against *P. aeruginosa*. Complex 3 exhibited effective activity against *S. aureus*, medium activities against *B. subtilis* and *E. coli*, and weak activity against *P. aeruginosa*. It is interesting that complex 1 has the most active activity against *S. aureus*, with IC_{50} value of 0.38 $\mu g\ mL^{-1}$, which is stronger than Penicillin G.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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