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芳酰腙铜(Ⅱ)和锌(Ⅱ)配合物的合成、晶体结构及抗菌活性

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摘要:合成了一对结构类似的双核铜和锌配合物,$Cu_2(L^1)_2$ (**1**)和$[Zn_2(L^2)_2(CH_3OH)_2]$ (**2**),其中 L^1 和 L^2 分别是 2-溴-*N*′-(2-羟基-5-甲基苯亚甲基)苯甲酰肼(H_2L^1)和 2-氯-*N*′-(2-羟基-5-甲基苯亚甲基)苯甲酰肼(H_2L^2)的二价阴离子,通过元素分析、红外光谱以及单晶 X 射线衍射表征了它们的结构。配合物 **1** 以三斜晶系 $P\bar{1}$ 空间群结晶,其晶体学参数:a=0.914 11(6) nm,b=1.180 04(7) nm,c=1.359 36(9) nm,α=101.928(2)°,β=91.399(2)°,γ=107.873(2)°,V=1.359 3(2) nm^3,Z=2,R_1=0.054 0,wR_2=0.118 9,GOF=0.970。配合物 **2** 以单斜晶系 $P2_1/c$ 空间群结晶,其晶体学参数:a=1.216 97(9) nm,b=1.214 96(9) nm,c=1.212 83(9) nm,β=110.939(1)°,V=1.674 8(2) nm^3,Z=2,R_1=0.034 1,wR_2=0.068 9,GOF=1.024。X 射线分析表明 2 个化合物都是中心对称的双核配合物,其中配合物 **1** 中的 Cu 原子是平面正方形配位构型,配合物 **2** 中的 Zn 原子是四方锥配位构型。还通过 MTT 法研究了这两个配合物的抗细菌(大肠杆菌,金黄色葡萄球菌,枯草芽孢杆菌和铜绿色假单胞菌)和抗真菌(白假丝酵母菌和黑曲霉菌)活性。

关键词:席夫碱;铜配合物;锌配合物;双核配合物;晶体结构;抗菌活性
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Syntheses, Crystal Structures and Antimicrobial Activity of Copper(Ⅱ) and Zinc(Ⅱ) Complexes with Aroylhydrazones

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Abstract: A pair of structurally similar dinuclear copper(Ⅱ) and zinc(Ⅱ) complexes, $Cu_2(L^1)_2$ (**1**) and $[Zn_2(L^2)_2(CH_3OH)_2]$ (**2**), where L^1 and L^2 are the dianionic form of 2-bromo-*N*′-(2-hydroxy-5-methylbenzylidene)benzohydrazide (H_2L^1) and 2-chloro-*N*′-(2-hydroxy-5-methylbenzylidene)benzohydrazide (H_2L^2), respectively, have been synthesized and characterized by elemental analysis, infrared spectra and single-crystal X-ray diffraction. Complex **1** crystallizes in the triclinic space group $P\bar{1}$, with unit cell parameters: a=0.914 11(6) nm, b=1.180 04(7) nm, c=1.359 36(9) nm, α=101.928(2)°, β=91.399(2)°, γ=107.873(2)°, V=1.359 3(2) nm^3, Z=2, R_1=0.054 0, wR_2=0.118 9, GOF=0.970. Complex **2** crystallizes as the monoclinic space group $P2_1/c$, with unit cell parameters: a=1.216 97(9) nm, b=1.214 96(9) nm, c=1.212 83(9) nm, β=110.939(1)°, V=1.674 8(2) nm^3, Z=2, R_1=0.034 1, wR_2=0.068 9, GOF=1.024. X-ray analysis indicates that the complexes are centrosymmetric dinuclear species, with the Cu atoms in **1** in square planar coordination, and with the Zn atoms in **2** in square pyramidal coordination. The complexes were evaluated for their antibacterial (*B. subtilis*, *S. aureus*, *E. coli* and *P. aeruginosa*) and antifungal (*C. albicans* and *A. niger*) activities by MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide) method. CCDC: 1447054, **1**; 1447056, **2**.

Keywords: Schiff base; copper complex; zinc complex; dinuclear complex; crystal structure; antimicrobial activity

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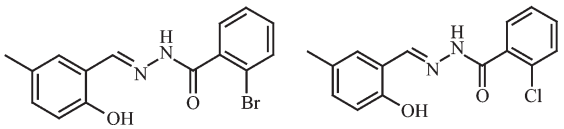
Schiff bases are a kind of biological active compounds bearing the -N =CH- functional groups, which can be prepared by the condensation reactions of carbonyl-containing compounds with primary amines. The compounds have been attracted considerable attention for their wide range of biological activities, such as antibacterial[1-2], antifungal[3], antitumor[4-5], anti-inflammatory[6-7], and cytotoxic[8-9]. Aroylhydrazones bearing the -C (O)-NH-N=CH- functional groups are a kind of special Schiff bases, which possess interesting biological activities[10-13]. It was reported that Schiff bases bearing electron-withdrawing groups can improve their antimicrobial activities[14-15]. Rai and co-workers reported a series of fluoro, chloro, bromo, and iodo-substituted compounds, and found that they have significant antimicrobial activities[16-18]. As a continuation of work on the exploration of novel antimicrobial agents, in this paper, two new dinuclear copper(Ⅱ) and zinc(Ⅱ) complexes, $Cu_2(L^1)_2$ (**1**) and $[Zn_2(L^2)_2(CH_3OH)_2]$ (**2**), where L^1 and L^2 are the dianionic form of 2-bromo-*N*′-(2-hydroxy-5-methylbenzylidene)benzohydrazide (H_2L^1) and 2-chloro-*N*′-(2-hydroxy-5-methylbenzylidene)benzohydrazide (H_2L^2), respectively (Scheme 1), were prepared and their antimicrobial activities were investigated.



H_2L^1　　H_2L^2

Scheme 1　Aroylhydrazones

1　Experimental

1.1　General methods and materials

5-Methylsalicylaldehyde, 2-bromobenzohydrazide, and 2-chlorobenzohydrazide were purchased from Sigma-Aldrich and used as received. All other reagents were of analytical reagent grade. Elemental analyses of C, H and N were carried out in a Perkin-Elmer automated model 2400 Series Ⅱ CHNS/O analyzer. FT-IR spectra were obtained on a Perkin-Elmer 377 FT-IR spectrometer with samples prepared as KBr pellets. Molar conductance was measured with a Shanghai DDS-11A conductometer. X-ray diffraction was carried out on a Bruker SMART 1000 CCD diffractometer.

1.2　Synthesis of the aroylhydrazones

The aroylhydrazones were synthesized as follows. To the methanolic solution (30 mL) of 5-methylsalicylaldehyde (0.02 mol, 2.72 g) was added a methanolic solution (20 mL) of 2-bromobenzohydrazide (0.02 mol, 0.043 g) or 2-chlorobenzohydrazide (0.02 mol, 0.034 g) with stirring. The mixtures were stirred for 30 min at room temperature to give colorless precipitation. The solvent was evaporated to give colorless crystalline product, which was recrystallized from methanol and dried in vacuum containing anhydrous $CaCl_2$.

For H_2L^1: Yield 87%. Characteristic IR data (cm^{-1}): 3 433 (m), 3 217 (w), 1 638 (s). Anal. Calcd. for $C_{15}H_{13}BrN_2O_2$ (%): C, 54.1; H, 3.9; N, 8.4. Found (%): C, 53.9; H, 4.0; N, 8.5. For H_2L^2: Yield 92%. Characteristic IR data (cm^{-1}): 3 441 (m), 3 223 (w), 1 637 (s). Anal. Calcd. for $C_{15}H_{13}ClN_2O_2$(%): C, 62.4; H, 4.5; N, 12.3. Found(%): C, 62.3; H, 4.7; N, 9.6.

1.3　Synthesis of complex 1

H_2L^1 (0.1 mmol, 33.3 mg) and copper nitrate trihydrate (24.2 mg, 0.1 mmol) were mixed in methanol (10 mL). The mixture was refluxed for 1 h and then cooled to room temperature. Single crystals of the complex, suitable for X-ray diffraction, were grown from the solution upon slow evaporation within a few days. The crystals were isolated by filtration, washed with methanol and dried in vacuum containing anhydrous $CaCl_2$. Yield: 41%. Characteristic IR data (cm^{-1}): 1 623 (s). Anal. Calcd. for $C_{30}H_{22}Br_2Cu_2N_4O_4$ (%): C, 45.6; H, 2.8; N, 7.1. Found (%): C, 45.8; H, 2.7; N, 7.0%.

1.4　Synthesis of complex 2

Complex **2** was prepared and crystallized by the similar method as described for complex **1**, with H_2L^1 replaced by H_2L^2 (0.1 mmol, 28.9 mg), and copper nitrate trihydrate replaced by zinc nitrate hexahydrate (29.7 mg, 0.1 mmol). Yield 52%. Characteristic IR data (cm^{-1}): 3 453 (m), 1 621 (m). Anal. Calcd. for $C_{32}H_{30}Cl_2N_4O_6Zn_2$ (%): C, 50.0; H, 3.9; N, 7.3. Found (%): C, 49.8; H, 4.1; N, 7.3.

1.5 X-ray crystallography

X-ray diffraction analysis was carried out at a Bruker SMART 1000 CCD area diffractometer equipped with Mo $K\alpha$ radiation (λ=0.071 073 nm). The diffraction data were collected with SMART and reduced with SAINT[19], and multi-scan absorption correction was performed using SADABS[20]. The structures of the complexes were solved by direct method, and refined against F^2 by full-matrix least-squares method using SHELXTL[21]. All of the non-hydrogen atoms were refined anisotropically. The methanol hydrogen of complex **2** was located from a difference Fourier map, and refined isotropically with O-H distance restrained to 0.085(1) nm. The remaining hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. The methanol ligand in complex **2** disordered over two sites, with occupancies of 0.638(2) and 0.362(2). The crystallographic data and refinement parameters for the compounds are listed in Table 1. Selected bond lengths and angles are listed in Table 2.

CCDC: 1447054, **1**; 1447056, **2**.

1.6 Antimicrobial assay

The antibacterial activities of the synthesized compounds was tested against *B. subtilis*, *S. aureus*, *E. coli*, and *P. aeruginosa* using LB medium. The antifungal activities of the compounds were tested against *C. albicans* and *A. niger* using RPMI-1640 medium. The IC_{50} (half inhibitory concentration) of the test compounds were determined by a colorimetric

Table 1 Crystallographic information for the complexes

Complex	**1**	**2**
Formula	$C_{30}H_{22}Br_2Cu_2N_4O_4$	$C_{32}H_{30}Cl_2N_4O_6Zn_2$
Formula weight	789.42	768.24
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a / nm	0.914 11(6)	1.216 97(9)
b / nm	1.180 04(7)	1.214 96(9)
c / nm	1.359 36(9)	1.212 83(9)
α / (°)	101.928(2)	90
β / (°)	91.399(2)	110.939(1)
γ / (°)	107.873(2)	90
V / nm^3	1.359 3(2)	1.674 8(2)
Z	2	2
D_c / (g·cm^{-3})	1.929	1.523
μ / mm^{-1}	4.550	1.640
F(000)	780	784
θ range / (°)	2.82~25.50	2.45~25.49
Index range (h, k, l)	−11~11, −12~14, −16~16	−14~10, −12~14, −14~14
Measured reflections	10 721	8 620
Unique reflections	4 929	3 117
Observed reflections [$I \geqslant 2\sigma(I)$]	3 328	2 393
Absorption correction	Multi-scan	Multi-scan
Min. and max. transmission	0.463 0 and 0.494 7	0.714 2 and 0.756 7
Data, restraints, parameters	4 929, 0, 380	3 117, 2, 219
Goodness-of-fit on F^2	0.970	1.024
R_1, wR_2 [$I \geqslant 2\sigma(I)$][a]	0.054 0, 0.118 9	0.034 1, 0.068 9
R_1, wR_2 (all data)[a]	0.086 4, 0.136 9	0.054 6, 0.075 2

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

Table 2　Selected bond lengths (nm) and angles (°) for the complexes

			1		
Cu1-N1	0.190 6(4)	Cu1-O1	0.193 5(3)	Cu1-O2	0.192 9(3)
Cu1-O1A	0.195 4(4)	Cu2-N3	0.190 2(4)	Cu2-O3	0.194 6(3)
Cu2-O4	0.193 8(4)	Cu2-O3B	0.195 8(4)		
N1-Cu1-O2	81.17(17)	N1-Cu1-O1	94.12(16)	O2-Cu1-O1	174.86(15)
N1-Cu1-O1A	172.71(16)	O2-Cu1-O1A	106.09(15)	O1-Cu1-O1A	78.66(15)
N3-Cu2-O4	80.87(17)	N3-Cu2-O3	93.32(16)	O4-Cu2-O3	173.38(16)
N3-Cu2-O3B	171.66(15)	O4-Cu2-O3B	107.38(16)	O3-Cu2-O3B	78.51(15)
			2		
Zn1-O1A	0.198 0(2)	Zn1-O3	0.200 0(2)	Zn1-N1	0.205 1(2)
Zn1-O2	0.207 1(2)	Zn1-O1	2.075 6(18)		
O1-Zn1-O3A	105.31(9)	O1-Zn1-N1A	145.34(9)	O3-Zn1-N1	108.15(9)
O1-Zn1-O2A	107.46(7)	O3-Zn1-O2	97.17(9)	N1-Zn1-O2	77.21(8)
O1-Zn1-O1A	78.10(8)	O3-Zn1-O1	103.71(9)	N1-Zn1-O1	85.42(8)
O2-Zn1-O1	156.18(8)				

Symmetry codes: A: 1−*x*, −*y*, 1−*z*; B:−*x*, 2−*y*, 1−*z* for **1**; A: 1−*x*, −*y*, 1−*z* for **2**.

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 (1 mg·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 G as a positive reference and the solvent control (5% DMSO) in medium and incubated at 37 ℃ 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 purple formazan crystals produced. The absorbance at 492 nm of each well was measured with an ELISA plate reader.

2　Results and discussion

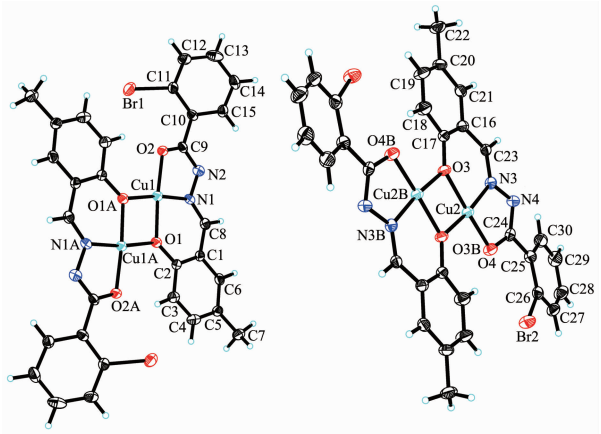
2.1　Synthesis and characterization

The aroylhydrazones H_2L^1 and H_2L^2 were readily prepared by the condensation reaction of 1:1 molar ratio of 5-methylsalicylaldehyde with 2-bromobenzohydrazide and 2-chlorobenzohydrazide, respectively, in methanol. Complexes **1** and **2** were prepared by the reaction of the aroylhydrazones with copper nitrate and zinc nitrate, respectively, in methanol, followed by recrystallization. Elemental analyses of the complexes are in accordance with the molecular structures proposed by the X-ray analysis. FT-IR spectra of both complexes are of similar type. The complexes show typical C=N absorptions at 1 623 cm^{-1} for **1** and 1 621 cm^{-1} for **2**. Both complexes are stable in air at room temperature. The molar conductivity of the complexes measured in absolute methanol at concentration of 1 mmol·L^{-1} are 18.0 Ω^{-1}·cm^2·mol^{-1} for **1** and 22 Ω^{-1}·cm^2·mol^{-1} for **2**, indicating the non-electrolytic nature of the complexes in solution[22].

2.2　Structure description of complex 1

The molecular structure of complex **1** is shown in Fig.1. The asymmetric unit of the complex contains two independent molecules. The complex is a centrosymmetric dinuclear copper (Ⅱ) species, with the inversion center located at the midpoint of the two Cu atoms. The Cu…Cu distances are 0.300 9(2) and 0.302 3(2) nm. Each Cu atom of the complex is coordinated by the phenolate oxygen, imino nitrogen and enolate oxygen of the aroylhydrazone ligand, and the

phenolate oxygen of the symmetry related aroylhydrazone ligand, forming square planar geometry. The distortion of the square planar coordination can be observed from the bond distances and bond angles. The *cis* bond angles are from 81.2(2)° to 106.1(2)° for Cu1, and from 78.5(2)° to 107.4(2)° for Cu2, and the *trans* bond angles are 172.7(2)° and 174.9(2)° for Cu1, and 171.7(2)° and 173.4(2)° for Cu2. The Cu-O and Cu-N bonds in the complex are comparable to those observed in copper(Ⅱ) complexes with aroylhydrazone ligands[23-24]. The two benzene rings of the aroylhydrazone ligand form dihedral angle of 25.7(3)°.

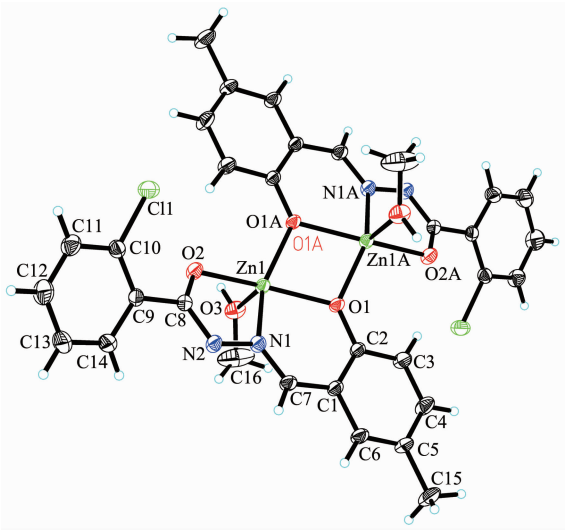


Thermal ellipsoids are drawn at the 30% probability level; Symmetry operations to generate related atoms: A: 1−*x*, −*y*, 1−*z*; B: −*x*, 2−*y*, 1−*z*

Fig.1 A perspective view of complex **1** with the atom labeling scheme

2.3 Structure description of complex 2

The molecular structure of complex **2** is shown in Fig.2. The complex is a centrosymmetric dinuclear zinc(Ⅱ) species, with the inversion center located at the midpoint of the two Zn atoms. The Zn ⋯ Zn distance is 0.315 0(2) nm. Each Zn atom of the complex is coordinated in a square pyramidal geometry, with the phenolate oxygen, imino nitrogen and enolate oxygen of the aroylhydrazone ligand, and the phenolate oxygen of the symmetry related aroylhydrazone ligand, defining the basal plane, and with the methanol oxygen occupying the apical position. The Zn atom deviates from the least-squares plane defined by the four basal donor atoms by 0.046 8(2) nm. The distortion of the square pyramidal coordination can be observed from the bond distances and bond angles. The *cis* bond angles in the basal plane are from 77.21(8)° to 108.15(9)°, and the *trans* bond angles are 145.34(9)° and 156.18(8)°. The angles among the apical and basal donor atoms are in the range of 97.17(9)°~105.31(9)°. The Zn-O and Zn-N bonds in the basal plane of the complex are comparable to those observed in zinc(Ⅱ) complexes with aroylhydrazone ligands [25-26]. The two benzene rings of the aroylhydrazone ligand form dihedral angle of 28.3(5)°.



Thermal ellipsoids are drawn at the 30% probability level; Symmetry operation to generate related atoms: A: 1−*x*, −*y*, 1−*z*

Fig.2 A perspective view of complex **2** with the atom labeling scheme

2.4 Fluorescence character of complex 2

The fluorescence property of complex **2** was studied at room temperature (Fig.3). The emission spectrum of the complex is from 420 to 500 nm, with λ_{max}=465 nm (λ_{ex}=266 nm). For zinc(Ⅱ) complexes, no

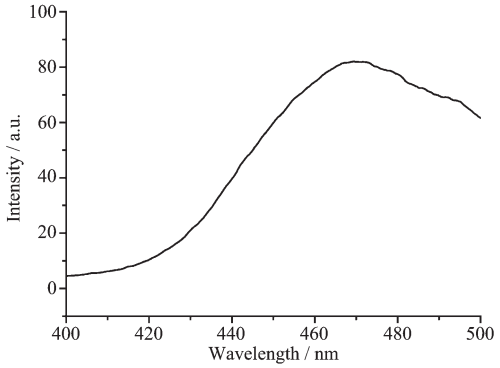


Fig.3 Emission spectrum of complex **2**

emission originating from metal-centered MLCT/LMCT excited states are expected, since zinc (Ⅱ) ion is difficult to oxidize or reduce due to its stable d^{10} configuration. Thus, the emission observed in the complex is tentatively assigned to the π-π^* intra-ligand fluorescence.

2.5 Antimicrobial activity

The complexes and the free aroylhydrazones were screened for antibacterial activity against two Gram (+) bacterial strains (*B. subtilis* and *S. aureus*) and two Gram (−) bacterial strains (*E. coli* and *P. aeruginosa*) by MTT method. The IC_{50} values of the compounds against four bacteria are listed in Table 3. Penicillin G was used as the standard drug. The aroylhydrazone H_2L^1 showed medium activity against the bacteria *B. subtilis*, while no activity against the other bacteria. The aroylhydrazone H_2L^2 showed medium activities against the bacteria *B. subtilis*, *S. aureus*, and *E. coli*, while no activity against *P. aeruginosa*. Thus, the Cl-substitute group is better than the Br-substitute group for the antibacterial activity of *S. aureus* and *E. coli*. The copper complex has strong activity against *B. subtilis*, medium activity against *S. aureus*, and no activity against the other bacteria. The zinc complex has medium activity against *B. subtilis*, and no activity against the other bacteria. From the results, it is difficult to give a definite conclusion about which one is good for the antibacterial activities of the aroylhydrazone and the complexes. For example, complexes **1** and **2** have stronger activities against *B. subtilis* than the aroylhydrazones. However, as for *S. aureus*, complex **1** has stronger activity than H_2L^1, yet, H_2L^2 has stronger activity than complex **2**. As for *E. coli*, both H_2L^1 and complexes **1** and **2** have no activity, while H_2L^2 has effective activity. The particular interest is that complex **1** showed the most effective activity against *B. subtilis*, which is even more effective than Penicillin G.

The antifungal activities of the complexes and the aroylhydrazones were also evaluated against two fungal strains (*C. albicans* and *A. niger*) by MTT method. Ketoconazole was used as a reference drug. It is interesting that complex **1** has effective activity, with IC_{50} value of 7.27 $\mu g \cdot mL^{-1}$. However, both the aroylhydrazone and the zinc complex have no activity against the fungal strains.

Table 3　IC_{50} values of the tested material

$\mu g \cdot mL^{-1}$

Tested material	*B. subtilis*	*S. aureus*	*E. coli*	*P. aeruginosa*	*C. albicans*	*A. niger*
H_2L^1	21.30	>50	>50	>50	>50	>50
H_2L^2	16.25	32.27	10.28	>50	>50	>50
1	1.02	23.25	>50	>50	7.27	>50
2	8.85	>50	>50	>50	>50	>50
Penicillin G	2.35	0.75	17.51	17.49	>50	>50
Ketoconazole	>50	>50	>50	>50	2.76	9.15

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