



Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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Synthesis, Crystal Structure and Antimicrobial Activity of Manganese(III) And Iron(III) Complexes Derived from Similar Bis-Schiff Bases

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Abstract

A new manganese(III) complex, [Mn(L¹)(CH₃OH)(dca)] (1), and a new iron(III) complex, [Fe(L²)(CH₃OH)(NCS)] (2), which dca is dicyanoamide anion, and L¹ and L² are the dianionic form of N,N'-3,4-methylphenylenebis(5-methylsalicylaldimine) and N,N'-bis(5-methylsalicylidene)-*o*-phenylenediamine, respectively, have been prepared and characterized by elemental analyses, IR, and single crystal X-ray crystallographic determination. The crystal of complex (1) is orthorhombic: space group *Pna*2₁, *a* = 14.6557(6), *b* = 10.8906(5), *c* = 15.0536(7) Å, *V* = 2402.7(2) Å³, *Z* = 4, *R*₁ = 0.0321, *wR*₂ = 0.0715. The crystal of complex (2) is monoclinic: space group *C*2/*c*, *a* = 14.6798(9), *b* = 11.1306(7), *c* = 27.831(1) Å, *β* = 93.782(2)°, *V* = 4537.6(5) Å³, *Z* = 8, *R*₁ = 0.0423, *wR*₂ = 0.1027. The bis-Schiff base ligands coordinate to the metal center through phenolate O and imine N atoms. Both the Mn and Fe atoms in the complexes are in octahedral coordination, with the equatorial donor atoms come from the Schiff base ligands, and with the axial donor atoms come from a methanol O atom and

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a pseudohalide N atom. The effects of the complexes on the antimicrobial activity against

Staphylococcus aureus, Escherichia coli, and Candida albicans were studied.

Keywords

Schiff base, manganese complex, iron complex, crystal structure, antimicrobial activity

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Introduction

Schiff bases are a kind of important ligands in coordination chemistry and have extensive application in many fields.^[1-3] Schiff bases derived from aromatic carbonyl compounds have been widely studied in connection with metalloprotein models and asymmetric catalysis, due to the versatility of their steric and electronic properties. Schiff bases and their biologically active complexes have been often used as chelating ligands in the coordination chemistry of transition metals as radiopharmaceuticals for cancer targeting, agrochemicals, as model systems for biological macromolecules, as catalysts and as dioxygen carriers.^[4-7] In recent years, metal complexes of Schiff bases have attracted dramatically attention due to their versatile biological activity, such as antifungal, antibacterial and antitumor.^[8--10] It has been shown that the Schiff base complexes derived from salicylaldehyde and its derivatives with primary amines, bearing the N₂O, N₂S, NO₂ or NSO donor sets, have interesting biological activity.^[11-14] In the present paper, the preparation, characterization and antimicrobial activity of a new manganese(III) complex, $[Mn(L^1)(CH_3OH)(dca)]$ (1), and a new iron(III) complex, $[Fe(L^2)(CH_3OH)(NCS)]$ (2), which dca is dicyanoamide anion, and L^1 and L^2 are the dianionic form of N,N'-3,4-methylphenylenebis(5-methylsalicylaldimine) and

N,N'-bis(5-methylsalicylidene)-o-phenylenediamine, respectively, are reported.

Experimental

Material and Methods

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5-Methylsalicylaldehyde, 1,2-diaminobenzene, and 1,2-diamino-4-methylbenzene were purchased from Fluka. Other reagents and solvents were analytical grade and used without further purification. Elemental (C, H, and N) analyses were made on a Perkin-Elmer Model 240B automatic analyser. Infrared (IR) spectra were recorded on an IR-408 Shimadzu 568 spectrophotometer. X-ray diffraction was carried out on a Bruker SMART 1000 CCD area diffractometer.

Synthesis of Complex (1)

5-Methylsalicylaldehyde (0.272 g, 2 mmol) and 1,2-diamino-4-methylbenzene (0.122 g, 1 mmol) were reacted in methanol (30 mL) at ambient temperature for 1 h. Then, manganese perchlorate hexahydrate (0.362 g, 1 mmol) and sodium dicyanoamide (0.089 g, 1 mmol) were added to the mixture. The mixture was further stirred at room temperature for 30 min to give a deep brown solution. The solution was kept still in air for a few days, generating deep brown single crystals. Yield, 287 mg. Analysis Calc. (%) for $C_{26}H_{24}MnN_5O_3$: C, 61.30; H, 4.75; N, 13.75. Found (%): C, 61.17; H, 4.82; N, 13.62. Selected IR data (v, cm⁻¹): 2283 s, 2228 s, 2181 s, v(dca), 1607 s, v(C = N).

Synthesis of Complex (2)

5-Methylsalicylaldehyde (0.272 g, 2 mmol) and 1,2-diaminobenzene (0.108 g, 1 mmol) were reacted in methanol (30 mL) at ambient temperature for 1 h. Then, iron perchlorate hexahydrate (0.462 g, 1 mmol) and ammonium thiocyanate (0.065 g, 1 mmol) were added to the mixture. The

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mixture was further stirred at room temperature for 30 min to give a red solution. The solution was kept still in air for a few days, generating red single crystals. Yield, 216 mg. Analysis Calc. (%) for $C_{24}H_{22}FeN_3O_3S$: C, 59.03; H, 4.54; N, 8.60. Found (%): C, 59.18; H, 4.62; N, 8.45. Selected IR data (v, cm⁻¹): 2107 s, v(N₃), 1605 s, v(C = N).

X-Ray Diffraction

Data were collected from selected crystals mounted on thin glass fibers. The data for the complexes were processed with SAINT^[15] and corrected for absorption using SADABS.^[16] Multi-scan absorption corrections were applied with ψ -scans.^[17] The structures were solved by direct method using SHELXS-97 and refined by full-matrix least-squares techniques on F^2 using anisotropic displacement parameters.^[18] The methanol hydrogen atoms were located from difference Fourier maps and refined isotropically, with O–H distances restrained to 0.85(1) Å. The remaining hydrogen atoms were placed at calculated positions. Idealized H atoms were refined with isotropic displacement parameters set to 1.2 (1.5 for methyl groups) times the equivalent isotropic U values of the parent carbon atoms. The crystallographic data for the complexes are listed Table 1.

Results and Discussion

The Schiff bases were readily prepared by the condensation of 2:1 molar ratio of 5-methylsalicylaldehyde with 1,2-diamino-4-methylbenzene and 1,2-diaminobenzene, respectively, in methanol at ambient temperature. The Schiff bases were not isolated and used directly to the synthesis of the complexes. Crystals of the complexes are very stable at room

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temperature. The results of the elemental analyses are in accord with the composition suggested for the complexes.

Infrared Spectra

In order to compare the IR spectrum of the complexes with the free Schiff bases, small quantity of the Schiff bases was prepared. The IR spectra of the Schiff bases contain medium C--O absorption bands at about 1235 cm⁻¹. The bands disappeared on complexation, and new C--O absorption bands appeared at about 1090 cm⁻¹ in the spectra of the complexes, indicating that the Schiff bases coordinate to the metal atoms through deprotonated form. The infrared spectra of the complexes displays intense absorption bands at 1607 cm⁻¹ for complex (1) and 1605 cm⁻¹ for complex (2), which can be assigned to the C = N stretching frequencies of the Schiff base ligands, whereas for the free Schiff bases the corresponding absorption bands are observed at higher wave numbers. The shift of the bands on complexation indicates the coordination of the imine nitrogen to the metal centers.^[19] In the spectrum of complex (1), strong bands observed at 2283, 2228, and 2181 cm⁻¹ are assigned to the absorption of the dca ligand,^[20] and in the spectrum of complex (2), strong band observed at 2107 cm⁻¹ is assigned to the absorption of the thiocyanate ligand.^[21]

Crystal Structure Description

The molecular structures of the complexes are shown in Figures 1 and 2. Selected bond distances and angles are listed in Table 2. The complexes are structurally similar mononuclear compounds. The Mn atom in complex (1) is coordinated by two phenolate O and two imine N

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atoms of the Schiff base ligand L¹, defining the equatorial plane, and by one methanol O atom and one dicyanoamide N atom, occupying the two axial positions, generating an octahedral geometry. The Fe atom in complex (2) is coordinated by two phenolate O and two imine N atoms of the Schiff base ligand L², defining the equatorial plane, and by one methanol O atom and one thiocyanate N atom, occupying the two axial positions, generating an octahedral geometry. The axial bonds are much longer than the basal bonds, which is caused by the Jahn--Teller effects. The equatorial bond distances subtended at the Mn atoms in complex (1) are shorter than those subtended at the Fe atoms in complex (2), while the axial bond distances related to the Mn atom in complex (1) are longer than those related the Fe atom in complex (2). The coordinate bond lengths in both structures are comparable to those observed in similar manganese (III) or iron(III) complexes with Schiff bases.^[22-26] The dihedral angles between the two benzene rings of the Schiff base ligands are 14.6(3)^o for complex (1) and 21.6(3)^o for complex (2).

In the crystal structure of complex (1), the complex molecules are linked through intermolecular O--H…N hydrogen bonds (Table 3), generating 1D chains along the axis-*a* direction (Figure 3). In the crystal structure of complex (2), the complex molecules are linked through intermolecular O--H…O hydrogen bonds (Table 3), generating dimers (Figure 4).

Antimicrobial Activity

Qualitative determination of antimicrobial activity was done using the disk diffusion method.^[27--29] The results are summarized in Table 4. A comparative study of minimum inhibitory concentration (**MIC**) values of the free Schiff bases and the complexes indicated that

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the complexes have more effective activity than the free Schiff bases. Generally, this is caused by the greater lipophilic nature of the complexes than the ligands. Such increased activity of the metal chelates can be explained on the basis of chelating theory.^[30] On chelating, the polarity of the metal atoms will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of the metal atoms with donor atoms. Further, it increases the delocalization of *p*-electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and blocks the metal binding sites on enzymes of micro-organisms.

From Table 4, it can be seen that complex (1) has greater antibacterial and antifungi activities against the bacteria than complex (2). Complex (1) has a similar activity against *Escherichia coli* to the reference drug Tetracycline. Both complexes are more effective against *Candida albicans* than Tetracycline, however, for *Staphylococcus aureus*, the activities of the complexes are much weak.

Conclusion

In summary, a new manganese(III) complex and a new iron(III) complex derived from bis-Schiff bases have been prepared and characterized. The crystal structures of the complexes were confirmed by X-ray single crystal structure determination. The Mn and Fe atoms in the complexes are in octahedral coordination. The biological test showed that the complexes have effective activities against *Escherichia coli* and *Candida albicans*.

Supplementary Material

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A full detail of data collections and structure determinations has been deposited with the Cambridge Crystallographic Data Centre (no. 1424596 (1) and 1424568 (2); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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Table 1. Crystallographic data and experimenta	l details for the complexes
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Parameter	Value		
	(1)	(2)	
Habit; color	Block; deep brown	Block; red	
Formula	C ₂₆ H ₂₄ MnN ₅ O ₃	C ₂₄ H ₂₂ FeN ₃ O ₃ S	
Formula weight	509.4	488.4	
Temperature, K	298(2)	298(2)	
Crystal size, mm	$0.30 \times 0.29 \times 0.26$	$0.27 \times 0.27 \times 0.23$	
Radiation (λ, Å)	Μο <i>K</i> _α (0.71073)	Μο <i>K</i> _α (0.71073)	
Crystal system	Orthorhombic	Monoclinic	
Space group	Pna2 ₁	C2/c	
Unit cell dimensions:			
<i>a</i> , Å	14.6557(6)	14.6798(9)	
<i>b</i> , Å	10.8906(5)	11.1306(7)	
<i>c</i> , Å	15.0536(7)	27.831(1)	

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β, deg		93.782(2)
V, Å ³	2402.7(2)	4537.6(5)
Ζ	4	8
$\rho_{calcd}, g \text{ cm}^{-3}$	1.408	1.430
<i>F</i> (000)	1056	2024
Absorption coefficient, mm ¹	0.588	0.788
θ Range for data collection,	3.0925.50	2.9325.49
deg		
Index ranges, <i>h</i> , <i>k</i> , <i>l</i>	$15 \le h \le 17;12 \le k \le$	$17 \le h \le 15;13 \le k \le$
	13;17 $\leq l \leq 18$	$11;33 \le l \le 32$
Reflections collected	8133	13129
Independent reflections	3962 (0.0233)	4207 (0.0312)
$(R_{\rm int})$		
Reflections with $I > 2\sigma(I)$	3453	3362
Reflections with $I > 2\sigma(I)$ Parameters	3453 322	3362 294

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Goodness-of-fit on F^2	1.061	1.050
Final <i>R</i> indices $(I > 2\sigma(I))$	$R_1 = 0.0321, wR_2 =$	$R_1 = 0.0423, wR_2 =$
	0.0715	0 1027
	0.0715	0.1027
<i>R</i> indices (all data)	$R_1 = 0.0424, wR_2 =$	$R_1 = 0.0576, wR_2 =$
	0.0778	0 1133
	0.0770	0.1155
Largest difference peak and	0.195,0.233	0.712,0.481
hole $e^{\dot{\Delta}^{-3}}$		
1010, 0 11		

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Table 2. Selected bond distances (\AA) and angles (deg) for the complexes

(1)			
Bond lengths			
Mn1O1	1.8748(18)	Mn1O2	1.870(3)
Mn1N1	1.992(3)	Mn1N2	1.994(2)
Mn1O3	2.347(2)	Mn1N3	2.271(3)
Bond angles			
O2Mn1O1	93.56(10)	O2Mn1N1	174.62(10)
O1Mn1N1	91.80(10)	O2Mn1N2	92.92(9)
O1Mn1N2	170.61(10)	N1Mn1N2	81.70(10)
O2Mn1N3	90.46(11)	O1Mn1N3	93.88(10)
N1Mn1N3	89.69(11)	N2Mn1N3	92.86(9)
O2Mn1O3	87.93(11)	O1Mn1O3	90.72(9)
N1Mn1O3	91.50(10)	N2Mn1O3	82.73(8)
N3Mn1O3	175.21(8)		
(2)			

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Bond lengths			
Fe1O1	1.888(2)	Fe1O2	1.9326(17)
Fe1N1	2.123(2)	Fe1N2	2.118(2)
Fe1O3	2.146(2)	Fe1N3	2.033(3)
Bond angles			
01Fe1O2	104.52(8)	01Fe1N3	93.66(11)
O2Fe1N3	95.20(9)	01Fe1N2	165.71(8)
O2Fe1N2	89.05(8)	N3Fe1N2	89.47(11)
01Fe1N1	88.85(9)	O2Fe1N1	164.01(9)
N3Fe1N1	92.60(9)	N2Fe1N1	77.08(9)
01Fe1O3	90.04(9)	O2Fe1O3	83.80(8)
N3Fe1O3	176.29(11)	N2Fe1O3	86.94(9)
N1Fe1O3	87.52(8)		

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<i>D</i> H··· <i>A</i>	d(DH, Å)	d(H…A, Å)	d(<i>D</i> … <i>A</i> , Å)	$\omega(DH\cdots A, \deg)$
(1)				
O3H3…N5 ⁱ	0.85(1)	1.97(1)	2.800(4)	170(4)
(2)				
O3H3…O2 ⁱⁱ	0.85(1)	1.90(1)	2.732(3)	169(4)

Table 3. Hydrogen geometries for the complexes

Symmetry codes : (i) 1/2 + x, 1/2 - y, z; (ii) - x, y, 1/2 - z.

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Table 4. MIC values (μ g/mL) for the antimicrobial activities of the tested compounds

Compound	Staphylococcus	Escherichia coli	Candida albicans
	aureus		
H_2L^1	128	256	> 1024
H_2L^2	128	512	> 1024
Complex (1)	8.0	2.0	256
Complex (2)	32	16	512
Tetracycline	0.30	2.15	> 1024

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Figure 1. Perspective view of complex (1) with 30% probability thermal ellipsoids.

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Figure 2. Perspective view of complex (2) with 30% probability thermal ellipsoids.

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Figure 3. Molecular packing structure of complex (1). Hydrogen bonds are drawn as dashed lines.

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Figure 4. Molecular packing structure of complex (2). Hydrogen bonds are drawn as dashed lines.

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