ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2015, Vol. 41, No. 3, pp. 197–201. © Pleiades Publishing, Ltd., 2015.

Synthesis, Structures, and Biological Activity of Terbium(III) and Cobalt(III) Complexes Derived from Tripodal Schiff Bases[1]

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Received August 8, 2014

Abstract—Terbium(III) (**I**) and cobalt(III) (**II**) complexes derived from tripodal Schiff bases tris(2-((5-chlorosalicylidene)amino)ethyl)amine (H_3L^a) and tris(2-((4-methoxysalicylidene)amino)ethyl)amine (H_3L^b), respectively, have been prepared and characterized by elemental analyses, IR, and single crystal X-ray crystallographic determination (CIF files CCDC nos. 1021371 (**I**) and 1021372 (**II**)). The crystal of $[Tb(L^a)_3]$ (**I**) is monoclinic: space group $P2_1/n$, $a = 12.689(1)$, $b = 15.301(1)$, $c = 15.099(1)$ Å, $\beta = 110.484(2)°$, $V = 2746.2(4)$ Å^3, $Z = 4$, $R_1 = 0.0314$, $wR_2 = 0.0801$. The crystal of $[Co(L^b)_3)]_2 \cdot$ MeCN (**II**) is triclinic: space group $P\bar{1}$, $a = 12.3031(6)$, $b = 13.7209(7)$, $c = 17.884(1)$ Å, $\alpha = 83.785(2)°$, $\beta = 88.144(2)°$, $\gamma = 87.873(1)°$, $V = 2998.0(3)$ Å^3, $Z = 2$, $R_1 = 0.0669$, $wR_2 = 0.1538$. The tripodal Schiff base ligands coordinate to the metal atoms through three phenolate O and three imine N atoms. The Tb atom in complex **I** is in a monocapped octahedral coordination, and the Co atom in complex **II** is in octahedral coordination. The effects of the complexes on the antimicrobial activity against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* were studied.

DOI: 10.1134/S1070328415030045

INTRODUCTION

Schiff bases bearing C=N double bonds are a kind of important ligands in coordination chemistry [1–3]. Metal complexes with Schiff bases have attracted considerable attention due to their versatile biological activity, such as antifungal, antibacterial and antitumor [4–6]. It has been shown that the Schiff base complexes derived from salicylaldehyde and its derivatives have interesting biological activities [7–10]. Tripodal Schiff bases are interesting because of their special coordination sphere [11–13]. In the present paper, the preparation, characterization and antimicrobial activity of a new terbium(III) complex, $[Tb(L^a)_3]$ (**I**), and a new cobalt(III) complex, $[Co(L^b)_3)]_2 \cdot$ MeCN (**II**), where L^a and L^b are the deprotonated forms of tris(2-((5-chlorosalicylidene)amino)ethyl)amine (H_3L^a) and tris(2-((4-methoxysalicylidene)amino)ethyl)amine (H_3L^b), respectively, are reported.

EXPERIMENTAL

Material and methods. 5-Chlorosalicylaldehyde, 4-methoxysalicylaldehyde and tris(2-aminoethyl)amine 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 PerkinElmer 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 $[Tb(L^a)_3]$ (I). 5-Chlorosalicylaldehyde (0.47 g, 3.0 mmol) and tris(2-aminoethyl)amine (0.15 g, 1.0 mmol) were reacted in methanol (30 mL) at ambient temperature for 30 min. Then, terbium(III) nitrate hexahydrate (0.45 g, 1.0 mmol) dissolved in methanol (10 mL) was added dropwise to the solution. The mixture was stirred at room temperature for 1 h to give yellow solution. The solution was allowed to slow evaporate in an uncapped vial. Several days later, block crystals of the complex were obtained. The yield was 28%.

For $C_{27}H_{24}N_4O_3Cl_3Tb$

anal. calcd., %:	C, 45.18;	H, 3.37;	N, 7.81.
Found, %	C, 44.97;	H, 3.45;	N, 7.72.

Selected IR data (ν, cm^{-1}): 1629 s, ν(C=N).

Synthesis of $[Co(L^b)_3)]_2 \cdot$ MeCN (II). 4-Methoxysalicylaldehyde (0.46 g, 3.0 mmol) and tris(2-aminoethyl)amine (0.15 g, 1.0 mmol) were reacted in methanol (30 mL) at ambient temperature for 30 min. Then, cobalt(II) hexafluoroacetylacetonate (0.47 g, 1.0 mmol) dissolved in methanol and acetonitrile (10 mL,

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Table 1. Crystallographic data and experimental details for **I** and **II**

Parameter	Value	
	I	**II**
Habit; color	Block; yellow	Block; brown
Formula weight	717.8	1250.1
Temperature, K	298(2)	298(2)
Crystal size, mm	0.21 × 0.19 × 0.17	0.25 × 0.23 × 0.20
Radiation (λ, Å)	MoK_{α} (0.71073)	MoK_{α} (0.71073)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions:		
a, Å	12.689(1)	12.3031(6)
b, Å	15.301(1)	13.7209(7)
c, Å	15.099(1)	17.884(1)
α, deg	90	83.785(2)
β, deg	110.484(2)	88.144(2)
γ, deg	90	87.873(1)
V, Å^3	2746.2(4)	2998.0(3)
Z	4	2
ρ_{calcd}, g cm^{-3}	1.736	1.385
F(000)	1416	1308
Absorption coefficient, mm^{-1}	2.904	0.623
θ Range for data collection, deg	2.88–25.50	2.19–25.09
Index ranges, h, k, l	$-15 \le h \le 15, -18 \le k \le 18, -18 \le l \le 18$	$-14 \le h \le 14, -15 \le k \le 16, -21 \le l \le 21$
Reflections collected	24412	27788
Independent reflections (R_{int})	5100 (0.0428)	10589 (0.0465)
Reflections with $I > 2\sigma(I)$	4212	6452
Data/parameters	5100/343	10589/772
Restraints	0	0
Goodness-of-fit on F^2	1.075	1.025
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0314$, $wR_2 = 0.0801$	$R_1 = 0.0669$, $wR_2 = 0.1538$
R indices (all data)	$R_1 = 0.0414$, $wR_2 = 0.0884$	$R_1 = 0.1251$, $wR_2 = 0.1844$
Largest difference peak and hole, e Å^{-3}	0.628, –0.962	0.353, –0.535

$V : V = 1 : 1$) was added dropwise to the solution. The mixture was stirred at room temperature for 1 h to give brown solution. The solution was allowed to slow evaporate in an uncapped vial. Several days later, block crystals of the complex were obtained. The yield was 36%.

For $C_{62}H_{69}N_9O_{12}Co_2$			
anal. calcd., %:	C, 59.57;	H, 5.56;	N, 10.08.
Found, %:	C, 59.38;	H, 5.67;	N, 10.23.

Selected IR data (ν, cm^{-1}): 1623 s, ν(C=N).

X-ray structure determination. Data were collected from selected crystals mounted on glass fibers. The data for the two complexes were processed with SAINT [14] and corrected for absorption using SADABS [15]. Multiscan absorption corrections were applied with ψ-scans [16]. The structures were solved by direct methods using the program SHELXS-97 and refined by full-matrix least-squares techniques on F^2 using anisotropic displacement parameters [17]. Hydrogen atoms were placed at the 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 given in Table 1. Selected bond distances and angles are listed in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 1021371 (**I**) and 1021372 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The Schiff bases H_3L^a and H_3L^b were readily prepared by the condensation of 1 : 3 molar ratio of tris(2-aminoethyl)amine with 5-chlorosalicylaldehyde and 4-methoxysalicylaldehyde, respectively, at ambient temperature. The Schiff bases were not isolated and used directly to the synthesis of the complexes with metal salts. The complexes are very stable at room temperature in the solid state and soluble in common organic solvents, such as methanol, ethanol and acetonitrile. The results of the elemental analyses are in accord with the composition suggested for the complexes.

In order to compare the IR spectra of the complexes with the free Schiff bases, small quantities of H_3L^a and H_3L^b were prepared. The IR spectra of the Schiff bases contain strong C–O absorption bands in the region 1240–1255 cm^{-1}. The bands disappeared on complexation, and new C–O absorption bands appeared in the region 1085–1112 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 complexes **I** and **II** display intense absorption bands at 1629 and 1623 cm^{-1}, respectively, 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, 1630–1650 cm^{-1}. The shift of these bands on complexation towards lower wave number indicates coordination of the imine nitrogen to the metal center [18].

The molecular structure of complex **I** is shown in Fig. 1. The Schiff bases coordinated as heptadentate ligands with the Tb atom encapsulated within the N_4O_3 cavity. The Tb atom is seven coordinate and its geometry can be considered as a mono-capped octahedron with the tertiary amine nitrogen N(4) capped on the triangular face formed by the three imino nitrogen atoms, N(1), N(2), and N(3). The Tb–N distance of the capped tertiary nitrogen (Tb(1)–N(4) 2.748(3) Å) is longer than those of the imino nitrogens. In general, the Tb–O and Tb–N distances are similar to those observed in rare earth metal complexes with tripodal Schiff base ligands [19, 20]. The dihedral angles among the three benzene rings of the Schiff base ligands are 107.2(3)°, 87.8(3)°, and 85.8(3)°.

Table 2. Selected bond distances (Å) and angles (deg) for **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
		I	
Tb(1)–O(1)	2.219(3)	Tb(1)–O(2)	2.206(3)
Tb(1)–O(3)	2.208(3)	Tb(1)–N(1)	2.508(3)
Tb(1)–N(2)	2.510(4)	Tb(1)–N(3)	2.495(3)
		II	
Co(1)–O(1)	1.886(3)	Co(1)–O(5)	1.909(3)
Co(1)–O(3)	2.091(3)	Co(1)–N(2)	2.042(3)
Co(1)–N(3)	2.340(4)	Co(1)–N(4)	2.074(3)
Co(2)–O(7)	1.898(3)	Co(2)–O(9)	1.981(3)
Co(2)–O(11)	1.991(3)	Co(2)–N(6)	2.191(4)
Co(2)–N(7)	2.194(4)	Co(2)–N(8)	2.053(4)
Angle	ω, deg	Angle	ω, deg
		I	
O(2)Tb(1)O(3)	87.87(12)	O(2)Tb(1)O(1)	95.89(11)
O(3)Tb(1)O(1)	93.67(11)	O(2)Tb(1)N(3)	160.17(11)
O(3)Tb(1)N(3)	72.82(11)	O(1)Tb(1)N(3)	89.96(11)
O(2)Tb(1)N(1)	91.70(11)	O(3)Tb(1)N(1)	165.89(12)
O(1)Tb(1)N(1)	72.33(11)	N(3)Tb(1)N(1)	108.13(11)
O(2)Tb(1)N(2)	73.34(11)	O(3)Tb(1)N(2)	87.09(12)
O(1)Tb(1)N(2)	169.18(12)	N(3)Tb(1)N(2)	100.56(11)
N(1)Tb(1)N(2)	106.30(12)	O(2)Tb(1)N(4)	124.30(10)
O(3)Tb(1)N(4)	124.91(10)	O(1)Tb(1)N(4)	121.29(12)
N(3)Tb(1)N(4)	66.75(10)	N(1)Tb(1)N(4)	66.32(10)
N(2)Tb(1)N(4)	66.12(12)		
		II	
O(1)Co(1)O(5)	89.06(12)	O(1)Co(1)N(2)	169.24(13)
O(5)Co(1)N(2)	84.41(12)	O(1)Co(1)N(4)	90.74(13)
O(5)Co(1)N(4)	173.91(13)	N(2)Co(1)N(4)	96.66(13)
O(1)Co(1)O(3)	86.07(12)	O(5)Co(1)O(3)	100.46(12)
N(2)Co(1)O(3)	86.72(13)	N(4)Co(1)O(3)	85.60(13)
O(1)Co(1)N(3)	83.85(13)	O(5)Co(1)N(3)	84.07(13)
N(2)Co(1)N(3)	103.90(14)	N(4)Co(1)N(3)	89.86(13)
O(3)Co(1)N(3)	168.88(12)	O(7)Co(2)O(9)	88.20(13)
O(7)Co(2)O(11)	92.43(13)	O(9)Co(2)O(11)	91.74(13)
O(7)Co(2)N(8)	175.70(15)	O(9)Co(2)N(8)	88.71(14)
O(11)Co(2)N(8)	84.68(13)	O(7)Co(2)N(6)	82.35(13)
O(9)Co(2)N(6)	169.89(13)	O(11)Co(2)N(6)	85.12(14)
N(8)Co(2)N(6)	100.53(15)	O(7)Co(2)N(7)	87.05(15)
O(9)Co(2)N(7)	83.40(14)	O(11)Co(2)N(7)	175.13(14)
N(8)Co(2)N(7)	95.56(15)	N(6)Co(2)N(7)	99.60(15)

The molecular structure of complex **II** is shown in Fig. 2. The asymmetric unit of the compound contains two mononuclear cobalt(III) complex molecules and one acetonitrile molecule. The Schiff bases coordinated as hexadentate ligands with the Co atom encapsulated within the N_3O_3 cavity. The Co atom is six coor-

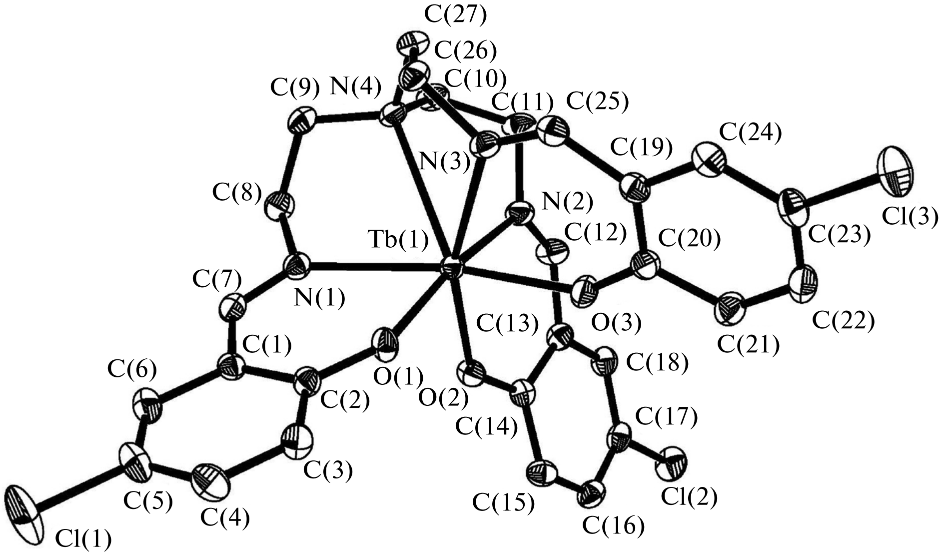

Fig. 1. Perspective view of complex **I** with 30% probability thermal ellipsoids.

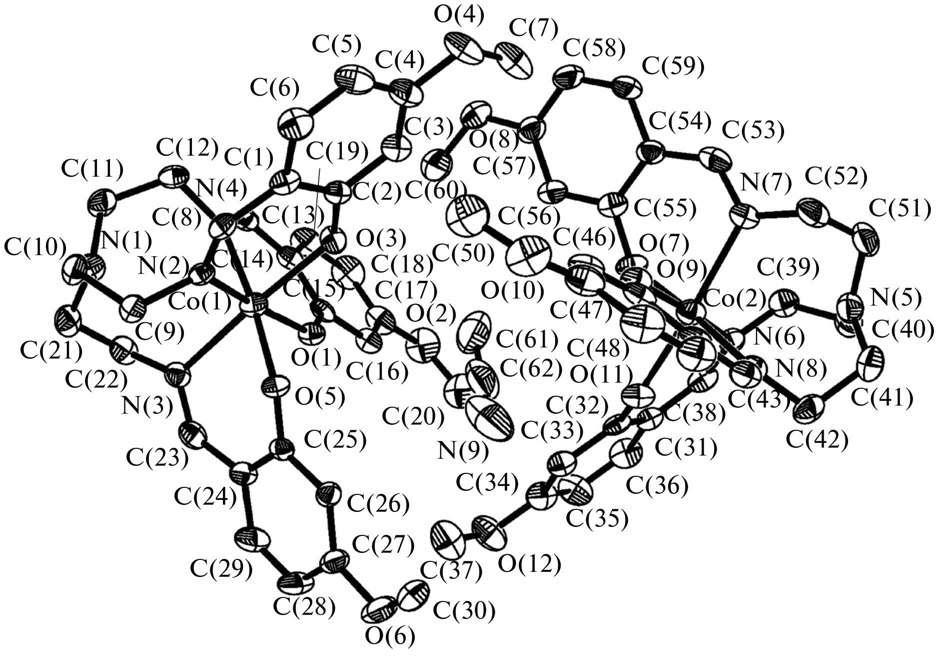

Fig. 2. Perspective view of complex **II** with 30% probability thermal ellipsoids.

dinate and its geometry can be considered as a typical octahedron with the tertiary amine nitrogen N(4) not coordinate to the metal. The Co–O and Co–N distances are much shorter than those in complex **I**, but similar to those observed in other cobalt(III) complexes with Schiff base ligands [21–23]. The dihedral angles among the three benzene rings of the Schiff base ligands in Co(1) complex molecule are 97.3(3)°, 65.7(3)°, and 79.3(3)°. The dihedral angles among the three benzene rings of the Schiff base ligands in Co(2) complex molecule are 75.8(3)°, 95.3(3)°, and 101.9(3)°. The acetonitrile molecule is embraced by the two cobalt complex molecules.

Qualitative determination of antimicrobial activity was done using the disk diffusion method [24, 25]. The results are summarized in Table 3. A comparative study of minimum inhibitory concentration (MIC) values of the Schiff bases and the complexes indicate that the two complexes have more effective activity than the free Schiff bases. Generally, this is caused by

Table 3. MIC values (μg/mL) for the antimicrobial activities of the tested compounds

Compound	*Staphylococcus aureus*	*Escherichia coli*	*Candida albicans*
H_3L^a	32	32	512
H_3L^b	128	256	>1024
I	8	16	128
II	16	64	128
Tetracycline	0.30	2.15	>1024

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 [26]. 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 microorganisms.

From the results, it can be seen that in general complex **I** shows greater antibacterial and antifungi activities against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* when compared to complex **II**. Moreover, H_3L^a has greater antibacterial and antifungi activities against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans* when compared to H_3L^b. This phenomenon obvious indicates that the chloro-substitute groups are better than the methoxy-substituted groups in the Schiff bases for the biological activity. For *Staphylococcus aureus* and *Escherichia coli*, the activities of the complexes are less than the control drug Tetracycline. But for *Candida albicans*, both complexes have stronger activities than Tetracycline.

In summary, a new terbium(III) and a new cobalt(III) complexes with tripodal Schiff base ligands have been prepared and characterized. The crystal structures of the complexes were confirmed by X-ray single crystal structure determination. The biological test shows that the complexes have some activities against *Staphylococcus aureus*, *Escherichia coli*, and *Candida albicans*.

ACKNOWLEDGMENTS

This research was supported by the National Sciences Foundation of China (nos. 20676057 and 20877036) and Top-class foundation of Pingdingshan University (no. 2008010).

REFERENCES

1. Pradeep, C.P. and Das, S.K., *Coord. Chem. Rev.*, 2013, vol. 257, nos. 11–12, p. 1699.
2. Qian, S.-S., Li, H.-H., Zhu, H., et al., *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, 2013, vol. 43, no. 4, p. 412.
3. Moradi-Shoeili, Z., Amini, Z., Boghaei, D.M., et al., *Polyhedron*, 2013, vol. 53, p. 76.
4. Li, J.-N., *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, 2013, vol. 43, no. 7, p. 826.
5. Chityala, V.K., Kumar, K.S., Subhashini, N.J.P., et al., *J. Coord. Chem.*, 2013, vol. 66, no. 2, p. 274.
6. Mukherjee, T., Pessoa, J.C., Kumar, A., et al., *Dalton Trans.*, 2013, vol. 42, no. 7, p. 2594.
7. Yuan, C.X., Lu, L.P., Gao, X.L., et al., *J. Bio. Inorg. Chem.*, 2009, vol. 14, no. 6, p. 841.
8. Sonmez, M., Celebi, M., and Berber, I., *Eur. J. Med. Chem.*, 2010, vol. 45, no. 5, p. 1935.
9. Xue, L.W., Zhao, G.Q., Han, Y.J., et al., *Russ. J. Coord. Chem.*, 2011, vol. 37, no. 4, p. 262.
10. Xue, L.W., Han, Y.J., Zhao, G.Q., et al., *Russ. J. Coord. Chem.*, 2012, vol. 38, no. 1, p. 24.
11. Mizukami, S., Houjou, H., Kanesato, M., et al., *Chem. Eur. J.*, 2003, vol. 9, no. 7, p. 1521.
12. Archibald, S.J., Blake, A.J., Schroder, M., et al., *Chem. Commun.*, 1994, no. 14, p. 1669.
13. Chandra, S.K., Chakraborty, P., and Chakravorty, A., *Dalton Trans.*, 1993, no. 6, p. 863.
14. Bruker, *SMART and SAINT*, *Area Detector Control and Integration Software*, Madison (WI, USA): Bruker Analytical X-ray Instruments Inc., 1997.
15. Sheldrick, G.M., *SADABS*, *Program for Empirical Absorption Correction of Area Detector Data*, Göttingen (Germany): Univ. of Göttingen, 1997.
16. North, A.C.T., Phillips, D.C., and Mathews, F.S., *Acta Crystallogr., A*, 1968, vol. 24, no. 3, p. 351.
17. Sheldrick, G.M., *SHELXL-97*, *Program for the Refinement of Crystal Structures*, Göttingen (Germany): Univ. of Göttingen, 1997.
18. Habibi, M.H., Askari, E., Amirnasr, M., et al., *Spectrochim. Acta A*, 2011, vol. 79, no. 3, p. 666.
19. Avecilla, F., Platas-Iglesias, C., Rodriguez-Cortinas, R., et al., *Dalton Trans.*, 2002, no. 24, p. 4658.
20. Wong, W.-K., Liang, H.Z., Guo, J.P., et al., *Eur. J. Inorg. Chem.*, 2004, no. 4, p. 829.
21. Elerman, Y., Kabak, M., Svoboda, I., et al., *Acta Crystallogr., C*, 1994, vol. 50, no. 11, p. 1694.
22. Xue, L.-W., Han, Y.-J., Zhao, G.-Q., et al., *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, 2012, vol. 42, no. 2, p. 154.
23. Souza, E.T., Maia, P.J.S., Azevedo, E.M., et al., *J. Inorg. Biochem.*, 2011, vol. 105, no. 12, p. 1767.
24. Barry, A., In: *Antibiotics in Laboratory Medicine*, Lorian, V., Ed., Baltimore: Williams and Wilkins, 1991, p. 403.
25. Rosu, T., Negoiu, M., Pasculescu, S., et al., *Eur. J. Med. Chem.*, 2010, vol. 45, no. 2, p. 774.
26. Searl, J.W., Smith, R.C., and Wyard, S., *J. Proc. Phys. Soc.*, 1961, vol. 78, no. 505, p. 1174.