

Mononuclear Fe(III), Cr(III), Co(II) Metal Complexes Based on Azo-Anthraquinone Moieties: Synthesis, Characterizations and Antibacterial Activities

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Abstract: The coordination properties of anthraquinone ligands bearing *N*-heterocyclic coordination sites to divalent cobalt and trivalent iron and chromium metal complexes have been described and characterized as mono and binuclear complexes. Although 4-(2'-amino benzene sulfonic acid)azo-(2''-*N*-(4''',6'''-dichloro-*s*-triazine)benzene-5''-(β -sulfatoethylsulfonyl)-2-methylanthraquinone was found to form complexes having a ligand to the metal ratio of 2:1 with ferric and cobalt ions, 4-(2'-amino benzene sulfonic acid)azo-(2''-*N*-(4''',6'''-dichloro *s*-triazine) naphthalene-5''-sulfonic acid)-2-methyl anthraquinone gave a complex in a molar ratio of about 1:1 with Fe(III). Spectral results showed that the complexes have octahedral geometry. Antibacterial data showed that the complexes have medium antimicrobial activity against *Staphylococcus aureus* and clinical isolates strains.

Keywords: Anthraquinone, Antibacterial Effect, Azo, Metal Complex, *s*-Triazine

Introduction

Heterocyclic based azo compounds have been employed for the synthesis of dyes there remains much scope for the design and development of new chromophores with the coupling components¹. Anthraquinone and azo derivatives are not only used for dyeing industry² but also semiconductor lasers³, sensor molecules for the Mg²⁺ ion⁴, electrochromism⁵, nonlinear optical elements and printing system⁶.

In recent decades, scores of new antimicrobial agents have been invented to substitute antimicrobial dyes including anthraquinone and azo groups. Cationic anthraquinone dyes, quaternary ammonium salts, demonstrate the excellent antimicrobial ability against both gram-negative and gram-positive bacteria in aqueous solution⁷⁻⁸.

In the present paper, we report potential bidentate ligands bearing N-H bridge binding azo and anthraquinone moieties, their metal complexes with iron(III), chromium(III) and cobalt(II) chlorides, which are the last part of the series of our previous work⁹. Disc diffusion method was used to determine the antibacterial activities of the synthesized compounds.

Experimental

1-Amino-4-bromo-2-methyl anthraquinone (98.8%) used as an initial synthetic material, 2,4,6-trichloro-1,3,5-triazine and primer aromatic amines (2'-amino benzene sulfonic acid, 4-*p*-(β -sulfatoethyl sulfonyl)aniline, 5'-amino naphthalene-3'-sulfonic acid) used as the coupling component in the synthesis of the azo dyes were purchased from Aldrich Chemical Co. and was used without further purification. All other chemicals and solvents were of analytical grade and were used as received.

Instruments

FT-IR spectra was recorded on a Perkin Elmer RX I spectrometer as KBr disc, electronic spectra on Model Shimadzu UVG-54 spectrophotometer in the range 200-400 nm. ¹H-NMR spectra was recorded on a Bruker/XWIN-NMR (400 MHz). UV-Vis spectra were measured on Perkin Elmer Lambda 25 Spectrometer. The metal percents were calculated according to the results of AAS Perkin Elmer Analyst-400. The magnetic measurements were carried out by the Gouy method, Sherwood Scientific Cambridge MS No:MK 1 using CuSO₄.5H₂O as calibrant.

Preparation of the ligands and coupling component

Diazonium salts were synthesized and 1-amino-4-(amino-*p*-(β -sulfatoethyl sulfonic acid)-2-methyl anthraquinone (**2**) and 1-amino-4-(5'-amino naphthalene-3'-sulfonic acid)-2-methyl anthraquinone (**3**) was prepared with a stirred mixture of Pd₂(dbap)₃, BINAP and Cs₂CO₃ as per our previous work⁹.

Preparation of the metal complexes

Fe(III) and Co(II) complexes

The complexes of the ligand were prepared in ethyl alcohol as given in previous work⁹.

Cr(III) complex

3a (0.196 mmol, 23.2 mg) was dissolved in DMF (10 mL) and added to CrCl₃.6H₂O (0.062 mmol, 23.0 mg). NaOAc was added to the mixture and stirred at 5 h in room temperature and cooled. The solution was filtered and dried¹⁰.

4-(2'-Amino benzene sulfonic acid)azo-(2''-N-(4''',6''')-dichloro s-triazine) benzene-5''-(β -sulfatoethyl sulfonyl)-2-methyl anthraquinone (2a)

Ligand was obtained as a light brown powder in 75 % yield. M.p. 211 °C. FT-IR (KBr, cm⁻¹): 3415, 1676, 1592, 1554, 1437, 1300, 1222, 1048, 791. UV-Vis (Ethanol, nm): 252, 337, 480 ϵ (max): 3.95 \times 10³.

4-(2'-Amino benzene sulfonic acid)azo-(2''-N-(4''',6''')-dichloro s-triazine) benzene-5''-(β -sulfatoethyl sulfonyl)-2-methyl anthraquinone-Fe (2a-Fe)

Complex was obtained as an orange powder in 41% yield. M.p. >300 °C. FT-IR (KBr, cm⁻¹): 3316, 1673, 1590, 1551, 1437, 1304, 1262, 1068, 803, 577. UV-Vis (Ethanol, nm): 246, 252, 276, 322, 482 ϵ (max): 4.52 \times 10⁴. ¹H NMR (DMSO-d₆, ppm): 14.1(O-H). AAS:Calc (%): 2.98, Found (%): 3.18, μ_{eff} : 3.22 B.M.

4-(2'-Amino benzene sulfonic acid)azo-(2''-N-(4''',6''')-dichloro s-triazine) benzene-5''-(β-sulfatoethyl sulfonyl)-2-methyl anthraquinone-Co (2a-Co)

Complex was obtained as a brick red powder in 62% yield. M.p.>300 °C. FT-IR (KBr, cm⁻¹): 3315, 1673, 1590, 1551, 1438, 1304, 1261, 1068, 802, 580. UV-Vis (Ethanol, nm): 248, 325, 477 ε (max): 1,30×10⁴. AAS: Calc(%):3.19, Found(%):2.85

4-(2'-Amino benzene sulfonic acid)azo-(2''-N-(4''',6''')-dichloro s-triazine) naphthalene-5''-sulfonic acid)-2-methyl anthraquinone (3a)

Ligand was obtained as a gray powder in 65% yield. M.p. 239,4 °C. FT- IR (KBr, cm⁻¹): 3416, 1674, 1591, 1544, 1451, 1231, 1172, 1046, 796. UV-Vis (Ethanol, nm): 203, 228, 332, 463 ε (max): 6,32×10².

4-(2'-Amino benzene sulfonic acid)azo-(2''-N-(4''',6''')-dichloro s-triazine) naphthalene-5''-sulfonic acid)-2-methyl anthraquinone-Fe (3a-Fe)

Complex was obtained as a black powder in 58% yield. M.p.>300 °C. FT- IR (KBr, cm⁻¹): 3413, 1722, 1611, 1589,1438, 1271, 1116, 1025, 772, 536. UV-Vis (Ethanol, nm): 206, 235, 335, 471 ε (max): 1.0×10³. AAS: Calc(%):5.56, Found(%):5.70

4-(2'-Amino benzene sulfonic acid)azo-(2''-N-(4''',6''')-dichloro s-triazine) naphthalene-5''-sulfonic acid)-2-methyl anthraquinone-Cr (3a-Cr)

Complex was obtained as a dark brown powder in 56% yield. M.p.>300 °C. FT-IR (KBr, cm⁻¹): 3416, 1673, 1591, 1549, 1437, 1269, 1104, 1011, 799, 579. UV-Vis (Ethanol, nm): 204, 250, 342, 443 ε (max): 8,78×10⁴. AAS: Calc(%):2.95, Found(%):2.27, μ_{eff}: 2.36 B.M.

Antibacterial activity process

Disc diffusion method¹¹ with some modification was used to determine the antibacterial activity of the synthesized compounds. *Bacillus subtilis* B-354, *Streptococcus epidermidis* B-4268, *Escherichia coli* B-4269, ARS (NRRL) (Agricultural Research Service Culture Collection), *Staphylococcus aureus* 29213 ATCC (American Type Culture Collection) and *Escherichia coli* K-12 were selected as test organisms. In addition, MRSA (*Methicillin-Resistant Staphylococcus aureus*) and C.D.(*Corynebacterium diphtheriae*) clinical isolate from patients were obtained from Cukurova University Medicine Faculty Balcali Hospital. The synthesized compounds were dissolved in dimethyl sulfoxide at concentrations of 10⁻³ M. Synthesized compound impregnated (10 μL) onto a disc of filter paper was varied to study its effect on the growth test organisms. They were incubated at the 37 °C for 24 h. The antibacterial activity of dyed cotton and wool fabric specimens was tested. Cotton and wool fabric samples (1 cm diameter) were placed on the surface of the inoculated plates and diameter of the inhibition zone (mm) was measured after incubation. Antimicrobial activity of DMSO against the test organisms was also investigated, but was found to have no antimicrobial activity against any of the organisms. Ampicillin (30 μg) was used as a standard antibiotic (S.A) for the antibacterial activities.

Results and Discussion

The mixed ligands, including azo, anthraquinone and *s*-triazine moieties were synthesized according to previous work⁹ (Figure 1). 2-Amino benzene sulfonic acid, 4-(β-sulfatoethyl sulfonyl) aniline and 5-amino naphthalene-3-sulfonic acid was used for this work (Table 1). The products were obtained in 56-75% yield after purification. The obtained results are supported the proposed structures.

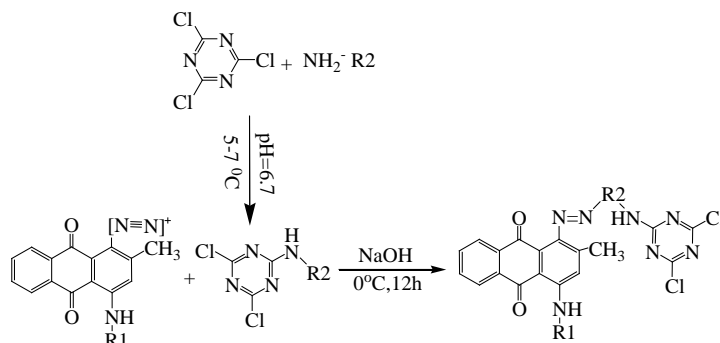


Figure 1. General coupling reaction for the synthesized azo compounds

FT-Infrared spectra

The primary amine asymmetric-symmetric stretching vibration bands at $3400\text{--}3200\text{ cm}^{-1}$ assigned to $\nu(\text{N-H})$ which are belonging to the starting material, 1-amino-4-bromo-2-methyl anthraquinone vanished after diazotization and the sec-amine peaks were observed about 3400 cm^{-1} in the FT-IR spectra of the all ligands. Typically, **2a** and **3a** showed the peaks which assigned to $\nu(\text{S=O})$ band between at $1104\text{--}1262\text{ cm}^{-1}$, $\nu(\text{C=N})$ band at $1544\text{--}1589\text{ cm}^{-1}$ and $\nu(\text{Ar-Cl})$ band between at $1011\text{--}1068\text{ cm}^{-1}$ in *s*-triazine group in Table 1. $\nu(\text{N=N})$ and $\nu(\text{C=O})$ stretching bonds belong to the ligands shifted from $1437\text{--}1451\text{ cm}^{-1}$ to $1437\text{--}1438\text{ cm}^{-1}$ and from $1676\text{--}1674\text{ cm}^{-1}$ to 1673 cm^{-1} in their metal complexes respectively. These shifts indicated coordination of carbonyl oxygen and azo group to the metal ions^{12,13}. The new observing peaks between $536\text{--}580\text{ cm}^{-1}$ could be attributed to metal-oxygen bonds $\nu(\text{M-O})$ in the complexes^{14,15} as shown in Table 2.

Table 1. The synthesized compounds and binding functional groups

Compound	Functional Groups	
	R1	R2
2a	PhSO ₂ CH ₂ CH ₂ OSO ₃ H	PhSO ₃ H
3a	NaphtSO ₃ H	PhSO ₃ H

Table 2. Characteristic bands in the FT-IR spectra (cm^{-1}) of the synthesized compounds

Compound	N=N	N-H	C=N	Ar-Cl	C=C	C=O	CH ₃	S=O	M-O
2a	1437	3415	1554	1048	1592	1676	1300	1222	-
2a-Fe	1437	3316	1551	1068	1590	1673	1304	1262	577
2a-Co	1438	3315	1551	1068	1590	1673	1304	1261	580
3a	1451	3416	1544	1046	1591	1674	1231	1172	-
3a-Fe	1438	3413	1589	1025	1611	1722	1271	1116	536
3a-Cr	1437	3416	1549	1011	1591	1673	1269	1104	579

UV-Visible spectra

The electronic absorption spectra of the synthesized compounds was recorded at room temperature in EtOH as shown in Table 3. The peaks were observed at 482 and 477 nm for 2a-Fe, 2a-Co respectively. Their molar extinction coefficients at the wavelength of maximum absorption (λ_{peak}) higher than all remain synthesized compounds. The increasing extinction coefficient of anthraquinone compounds indicates their good ability dyeing by chemical modifications¹⁶. The characteristic $n \rightarrow \pi^*$ transition peaks¹⁶ are observed between at

322-342 nm for the azo compounds. Typically, in UV spectrum of -N=N- group, the shoulder is assigned to $n \rightarrow \pi^*$ transition between at 323 -347 nm¹⁷. When the metal attaches to the ligands, small amounts of their absorption intensities and shifts were observed¹⁵.

Table 3. UV Spectra of the synthesized compounds (Solvent Ethanol)

Compounds	λ , nm $\pi \rightarrow \pi^*$	λ , nm _{azo} $n \rightarrow \pi^*$	λ , nm $n \rightarrow \pi^*$	ϵ (Lmol ⁻¹ cm ⁻¹) max
2a	252	337	480	3,88×10 ⁴
2a-Fe	252	322	482	4,52×10 ⁴
2a-Co	248	325	477	1,30×10 ⁴
3a	228	332	463	6,32×10 ²
3a-Fe	235	335	471	1,00×10 ³
3a-Cr	250	342	443	8,78×10 ³

¹H and ¹³C NMR spectra

The NMR spectra of all compounds confirmed the expected structures. The samples measured in DMSO-d⁶ solvent at 25 °C, in Table 4. The singlet signal at δ 2.4 and 2.6 ppm assigned to three protons (-CH₃), at δ 6.7-8.2 ppm multiple peaks of two protons in the quinone ring. The value of a chemical shift for methyl group which is an electron donor moiety indicated shielding effect. The multiple signals belong to (-CH₂) of vinylsulfone group appeared at δ 3.1-4.5 ppm. In the ¹H NMR spectra of ligands, the peak which is belonging to starting material, (NH₂) at δ 3.3 ppm disappeared after the diazotization process. The singlet peak for the (N-H) binding s-triazine ring showed around at δ 10.2 and 10.8 ppm but another contribution was not observed by the heterocyclic structure which has not any proton as shown in Table 4^{13,17}.

Table 4. The ¹H and ¹³C NMR (400 MHz) spectral values of the synthesized compounds, **2a, 3a**

Compds	¹ H NMR (δ , ppm, CDCl ₃ , 25 °C)	¹³ C NMR (δ , ppm, DMSO, 25°C)
2a	δ 2.2(s, SO ₃ H, -OH), δ 2.4 (s, -CH ₃), δ 3.1-4.5 (-CH ₂), δ 6.9-8.2 (m, 9H, Ph), δ 11.2 (s, NH, triazine), δ 10.8 (s, NH, Ph-NH-Ph), ppm.	δ 18.0 (-CH ₃), δ 119.0-150.0 (C, aromatic), δ 143 (C-N=N-Ph), δ 145 (Ph-N=N-C), δ 154 (NH-C-N- (triazine)), δ 162 (N-C(Cl)-N- (triazine)), δ 181 (C=O) ppm.
3a	δ 1.9 (SO ₃ H, -OH), δ 2.6(s, -CH ₃), δ 6.7-8.2 (m, 9H, Ph), δ 11.2 (NH, triazine), δ 10.2 (s, NH, Ph-NH-Ph), ppm.	δ 21.2 (-CH ₃), δ 118.0-151.0 (C, aromatic), δ 140 (NH-C(Ph)), δ 146 (C-N=N-Ph), δ 150 (Ph-N=N-C), δ 152 (NH-C-N- (triazine)), δ 162 (N-C(Cl)-N- (triazine)), δ 187(C=O) ppm.

The carbon peaks belong to (CH₃) group bonding anthraquinone was measured in the range δ 18-21 ppm as singlet in all the ligands. The aromatic carbons belong to anthraquinone ring gave multiple signals near δ 118-151 ppm. Furthermore, the peaks between at δ 145-146 were assigned to (C-N=N-Ph). The carbon peaks of s-triazine were observed at δ 152-154 (NH-C-N- (triazine)). Typically, the signals of carbonyl units (C=O) which are common in all the ligands on a ketone group gave in the range δ 181-187 ppm as singlet^{3,18,19}.

Atomic absorption spectra and magnetic susceptibilities

The calculations of metal percentages showed the mole ratios were estimated as 2:1 and 1:1 for the metal complexes as given in experimental section. These values were supported by the obtained results of Job's method. The synthesized metal complexes which have octahedral geometry include one and two chloride atoms in their outer sphere the resultant of argentometric titration data for the complexes of **2a** and **3a** respectively²⁰, as shown in Figure 2.

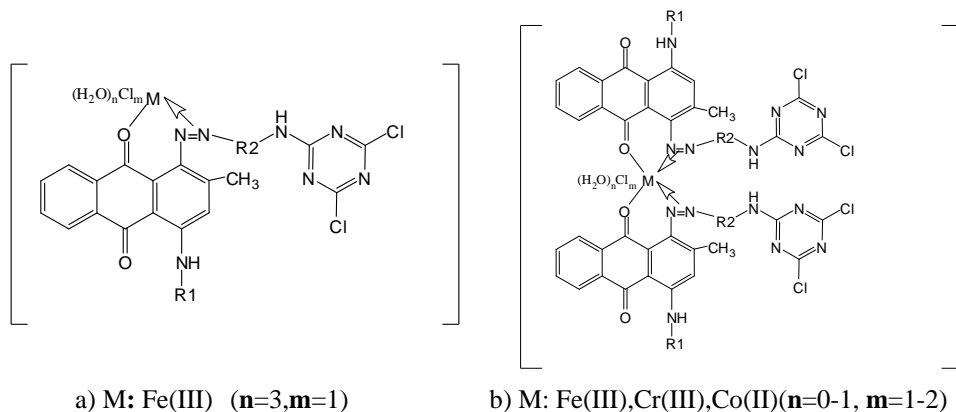


Figure 2. Plausible structures for the synthesized metal complexes (L:M), a) 1:1 b) 2:1 ratios (coordination number 6)

The magnetic moment of **2a-Fe** was measured as 3.22 BM and indicated the low spin complex Fe(III) state in room temperature. The magnetic interaction between ligand and metal caused a deviation in magnetic susceptibility value²¹. **3a-Cr** was determined as 2.36 BM for d^1 electron configuration. The mononuclear complexes exhibited the strong field ligand effects^{22,23}.

Antibacterial activities

Escherichia coli, is a gram-negative bacteria, *Staphylococcus aureus*, *Bacillus subtilis*, *Streptococcus epidermidis* and *Corynebacterium diphtheriae*, are gram-positive bacteria, and was test bacteria. *Staphylococcus aureus* is the major cause of cross-infection in hospitals, and it is the most frequently evaluated species. The results of antimicrobial screening of the synthesized compounds, metal salts and standard antibiotic are given in Table 5 and 7 respectively. Only one compound (**3a-Fe**) showed activity while other showed no activity. MRSA used in the present study are responsible for many hospital infections. The antibacterial activities of compounds against MRSA strains and C.D. are shown in Table 6 and 8, which indicates the antibacterial activity is strengthened metal containing compounds on MRSA. Among the Fe-complex series of compounds tested, **2a-Fe** was found active against only one C.D. The same compounds were also tested against MRSA, but there was not any activity detected. However, among Fe-complex compounds, **3a-Fe** affected all MRSA and *Staphylococcus aureus*. **3a-Cr** compound was showing the same antimicrobial activity as **2a-Fe** compound. **3a** from synthesized compounds was found active against three MRSA strains. In particular, synthesized compounds with metal complex showed more bacterial activity than the others against these strains. It is obvious that antibacterial properties are closely related to the dye structure, especially the presence of functional groups on it²⁴. The similar results indicate that the synthesized compounds can inactivate both gram-negative and gram-positive bacteria effectively²⁵. Remaining compounds exhibited no antibacterial activity at all. The zone of bacterial inhibition was not found for DMSO.

Table 5. Antibacterial activities of compounds on standard bacteria

	<i>Escherichia coli</i> K-12	<i>Bacillus subtilis</i> B-354	<i>Escherichia coli</i> B-4269	<i>Streptococcus epidermidis</i> B-4268	<i>Staphylococcus aureus</i> 29213
Metal salts	0	0	0	0	0
Ligands					
2a	0	0	0	0	0
3a	0	0	0	0	0
Fe ²⁺					
2a-Fe	0	0	0	0	0
3a-Fe	0	0	0	0	9
Co ²⁺					
2a-Co	0	0	0	0	0
Cr ⁶⁺					
3a-Cr	0	0	0	0	0
DMSO	0	0	0	0	0
S.A.	22	24	19	21	0

Table 6. Antibacterial activities of compounds on MRSA and C.D

	MRSA 02	MRSA 03	MRSA 09	MRSA 38	MRSA 59	MRSA 87	MRSA 313	MRSA 12	MRSA 13	MRSA 57	C.D. 557	C.D. 111
Metal salts	0	0	0	0	0	0	0	0	0	0	0	0
Ligands												
2a	0	0	0	0	0	0	0	0	0	0	0	0
3a	0	0	8	7	0	0	0	0	0	9	0	0
Fe ²⁺												
2a-Fe	0	0	0	0	0	0	0	0	0	0	7	0
3a-Fe	8	9	9	9	9	9	7	9	8	9	0	0
Co ²⁺												
2a-Co	0	0	0	0	0	0	0	0	0	0	0	0
3a-Cr	0	0	0	0	0	0	0	0	0	0	8	0
DMSO	0	0	0	0	0	0	0	0	0	0	0	0
S.A.	0	0	0	0	0	0	0	0	0	0	18	18

Table 7. Antibacterial activities of compounds on standard bacteria at concentrations of 10⁻³ M

	<i>Escherichia coli</i> K-12	<i>Bacillus subtilis</i> B-354	<i>Escherichia coli</i> B-4269	<i>Streptococcus epidermidis</i> B-4268	<i>Staphylococcus aureus</i> 29213
Metal salts	0	0	0	0	0
Ligands					
3a	0	0	0	0	0
Fe ²⁺					
2a-Fe	0	9	0	0	9
3a-Fe	0	9	0	0	9
Cr ⁶⁺					
3a-Cr	0	7	0	0	0
DMSO	0	0	0	0	0
S.A.	22	24	19	21	0

Table 8. Antibacterial activities of compounds on MRSA and C.D. at concentrations of 10^{-3} M

	MRSA 02	MRSA 03	MRSA 09	MRSA 38	MRSA 59	MRSA 87	MRSA 313	MRSA 12	MRSA 13	MRSA 57	C.D. 557	C.D. 111
Metal salts	0	0	0	0	0	0	0	0	0	0	0	0
Ligands												
3a	7	8	0	0	0	0	0	0	0	0	0	0
Fe ²⁺												
2a-Fe	7	8	9	10	7	0	9	9	7	8.5	0	0
3a-Fe	9	9.5	10	9.5	10	0	10.5	10	9.5	11.5	0	11
Cr ⁶⁺												
3a-Cr	0	0	7	7	7	0	0	0	0	0	0	0
DMSO	0	0	0	0	0	0	0	0	0	0	0	0
S.A.	0	0	0	0	0	0	0	0	0	0	18	18

Many of the phyto origin anthraquinones compounds are affected to *Pseudomonas aeruginosa*²⁶, *Bacillus subtilis*, *Escherichia coli*, *Micrococcus luteus*²⁷. In this study, synthesized compounds were showing no antibacterial activity against gram-negative bacterium *Escherichia coli*. The antimicrobial activities of quinones may be linked to their properties to be complex irreversibly with nucleophilic amino acids in proteins often leading to inactivation of the protein and loss of biological function²⁸.

Conclusion

In this work, we have prepared new mixed ligand materials composed of Cr(III), Fe(III) and Co(II)-substituted s-triazine and primer amine compounds as inorganic building blocks and 1-amino-4-bromo-2-methyl anthraquinone as the organic ligand. The structures of the synthesized compounds were characterized with UV-visible, FT-IR, ¹³C and ¹H NMR, AAS, magnetic susceptibility and argentometric titration techniques. Single crystals of the synthesized compounds could not be isolated from any solution; thus no definite structure may be described. However, our proposed structural formula is given in Figure 1 and 2. The octahedral structures were supported by using characterization techniques. The divalent Co complexes, trivalent iron and chromium complex exhibited as 2:1 and 1:1 molar ratio. They have one and two chloride atoms in their outer sphere according to argentometric methods for the metal complexes of **2a** and **3a** respectively.

As a result, the synthesized compounds were determined more active against MRSA strains, especially the values belong to **3a-Fe** indicated that it could be used to prevent the infection although the merely metal salts have not any protective properties significantly. Therefore, the results obtained in this study can be accepted as promising new antibacterial agent compounds on MRSA.

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