Chapter 1

General Aspects of the Cobalt Chemistry

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Additional information is available at the end of the chapter

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Abstract

This chapter aims to collect and summarize the chemical properties of cobalt and some new cobalt compounds. It deals with the progress of cobalt chemistry. Cobalt has been substantial in both chemical reactions and within many compounds. Some of them are heterocyclic reactions, cobalt-based catalyst and cobalamin. Also, it discusses variety of applications of cobalt in a wide range of areas and toxicity of cobalt. The studies carried out in this area so far have enabled and will be continued to be responsible for producing unknown and difficult reactions. This survey of the recent literature illustrates the fact that many different approaches on cobalt and new cobalt compounds are being used in many different areas.

Keywords: cobalt compounds, cobalamin, synthesis, catalyst, areas of usage

1. Introduction

The word cobalt is derived from the sixteenth century German term kobold. Glass, glazes and blue dyes for pottery were the oldest known uses of cobalt. For instance, cobalt compounds were used to dyeing pottery by Egyptians and Babylonians in 1450BC. Cobalt was set apart from copper ore by Swedish chemist Georg Brandt in 1735. After 1900, a new corrosion resistant alloy was invented, which is referred to as Stellite. Furthermore, aluminum-nickel-cobalt (*AlNiCo*) magnets caused an important evolution in 1940. They were used as the first electromagnet [1].

By 2000, scientists had carried out lots of experiments related to the synthesis of new cobalt compounds, examination of antibacterial properties of cobalt compounds and cobalt-catalysed reactions. For example, Kumar and Garg synthesized cobalt(II) complexes of tetradentate Schiff bases of the type [2].

Nowadays, cobalt and cobalt compounds possess a variety of applications from industry to medicine. This is because of its unique properties such as a high-melting point (1493°C) and retaining its strength to a higher temperature, being ferromagnetic with high thermostability and multivalent. Cobalt is one of the abundant metals in the Earth. Global reserves of cobalt are approximately around 7 million tons [3].

This chapter aims to collect and summarize the chemical properties of cobalt and some new cobalt compounds. The studies carried out in this area so far have enabled and will be continued to be responsible for producing unknown and difficult reactions. This survey of the recent literature illustrates the fact that many different approaches on cobalt and new cobalt compounds are being used in many different areas.

In order to briefly discuss about cobalt chemistry in this section, we begin with cobalt electron configuration. Cobalt has the chemical configuration $[Ar]4s^2 3d^7$ and has oxidation states Co(II) and Co(III). Other properties of cobalt are summarized in **Table 1** [4].

Cobalt has some inorganic compounds and complexes. Some chemical and physical properties of cobalt and several inorganic cobalt compounds are mentioned in the following statements.

Dilute sulphuric or hydrochloric acid dissolves slowly, but nitric acid rapidly dissolves and produces the cobalt-II ions [5]

$$3Co + 8HNO_3 \rightarrow 3Co\,(NO_3)_2 + 2NO + 4\,H_2O \tag{1}$$

Cobalt gives cobalt(II) chloride by dissolving in dilute hydrochloric acid [4].

$$Co + 2HCl \rightarrow CoCl_2 + H_2 \tag{2}$$

It is insoluble because it acquires passivity in concentrated nitrate and sulphuric acid [6].

Another oxidation number of cobalt is +3. But this ion can only be found in the complex. Bare cobalt releases oxygen from acidic and neutral environment. All cobalt oxides dissolve in hydrochloric acid [5].

Cobalt generally forms cobalt(II) and cobalt(III) compounds, but there are cobalt compounds, which have $4+, 1+, 0, 1-$ oxidation states [4]. It is more stable than those compounds which

Atomic number	27	Atomic mass	58.93
Electron Distribution	$[Ar]3d^7\,4s^2$	Oxidation Number	+2,+3
Melting Point	1495°C	Boiling Point	2870°C
Electronegativity	1.8	Isotope	59
Density	8.9 g/cm^3	Atomic Volume	6.7
Ionization Energy	757.6 kJ/mol		

Table 1. Other properties of cobalt.

consist of cobalt-III ions. In general, cobalt-II compounds dissolve in water; however, CoS, $CoCO_3$, $Co(OH)_2$, $Co(CN)_2$ *and* CoC_2O_4 are insolvables. Cobalt-II is quite a little hydrolysis. Both cobalt ions do not have amphoteric properties [5].

It is known that all common cobalt compounds have octahedrally coordinated to nitrogen or oxygen ions, all of which include three cobalt ions, two of which are 3+ and one of which is 2+, similar to the title compound.

$Co_3(1-Hdatrz).6(H_2O)_6.\ (NO_3)_8.4H_2O.(Hdartz-3,5-diamino-1,2,4-triazole$ [7], was the most attractive of these that include three cobalt ions. Two of these ions are 3+ and one of these ions was 2+ [8].

Cobalt is found together with iron, copper, nickel, silver and arsenic in nature. Cobalt closely resembles nickel so that they are being identified as “twins.” Although cobalt is used in practice to plate iron, doing alloy is the most significant practice of cobalt. Important cobalt alloys and its uses are summarized in **Table 2**.

The most known minerals are linnaeite, Co_3S_4 *or* $(CoNi)_3S_4$; smaltite, $CoAs_2$ *or* $(CoNi)As_2$ and cobaltite, $CoAsS$. Cobalt oxides are utilized in ceramics as smalt, a cobalt potassium silicate [9]. Important cobalt alloys and its uses are shown in **Table 2** [10].

Cobalt compounds which give blue color to glasses can also be made radioactive and can be used for treatment of some cancers. Further, it is used for the treatment of deep-rooted tumors. This shows that radioactive cobalt can be used as a tracer [11].

It is commonly known that salts and complexes of cobalt are catalysts for the selective oxidation of alkanes and selective epoxidation of alkenes. Scientists have performed several experiments on these catalysts. Several of them are discussed in this chapter [12].

In order to make liquid fuel, cobalt catalyst is used in the Fischer-Tropsch process. Also, cobalt and molybdenum are utilized as a catalyst in hydrodesulphurization of petroleum. These processes make use of refining of liquid fuels [13].

Nickel-cobalt-boride ($Ni-Co-B$) catalysts are used to design an efficient hydrogen generator for portable fuel cell applications [14].

The chemistry of cobalt complexes has attracted a lot of attention in recent years on account of their applications, among others, in biological systems such as antimicrobial agents and antibacterial agents.

Alloy name	Percentage composition	Features	Places used
Stellite	50–60 Co, 30 Cr,20 W,Mn, C	Hard and pourable	Cutting and drilling tools and mould
Vitallium	65 Co, 25 Cr, 5Mo	Resistant to wear and tear	Gas turbine wings
Magnet steel	35–60 Co, 10–25 Ni,Fe	Can be magnetized	Magnet

Table 2. Important cobalt alloys and uses.

To design novel drugs, medicinal chemistry has benefited from the properties of metal ions. Hence, this has caused to have clinical application of chemotherapeutic agents for cancer treatment, such as cisplatin [15].

Some of these works were mentioned as follows. In 1952, the first biological activity of cobalt compounds was acquainted where cobalt(III) compounds of bidentate mustard move as if it were hypoxia selective agents [16].

Bauer and Drinkard prepared and identified several new cobalt(III) complex compounds of easily oxidized ligands. These were salts of cobalt amines, inner charge complexes, and a variety of cobaltates. The structural formula was $Na_3[Co(CO)_3 3H_2O$ which was the simplest formula [17].

It is commonly known that salts and complexes of cobalt are catalysts for the selective oxidation of alkanes and selective epoxidation of alkenes. Scientists have carried out lots of examination on these catalysts. Several of them are *cobalt (III) acetylacetonate (acac)/*O_2e, *cobalt (II) − (salen complexes/*O_2*/isobutyrylaldehyde,cobalt (II)calix,pyrrole complexes/2 − ethylbutyraldehyde/*O_2*,Schiff base cobalt complexes/aliphatic aldehydes or b − ketoesters, polymer supported cobalt (II)/*O_2*,*H_2O_2*, (N − hydroxyl − phthalimide/*$Co(OAc)_2$*/*O_2*,cobalt (II)phthalocyanine* [18, 19].

Cobalt studies are still continued due to the fact that they have a wide variety of functions and many applications, especially in pharmaceutical technology.

2. Used places

Cobalt has many applications in a wide range of areas. A solution of *cobalt (II)chloride* can be utilized to measure moisture in the air. When the weather is humidity, paper is pink in color. Also, it may be used as an invisible ink [11]. Cobalt II salts are red in the case of complex-ion, that is, solvated with water, and it is dark blue when dehydrated. Invisible ink is made using this feature. If the diluted $CoCl_2.6H_2O$ solution is written on a sheet of paper, nothing can be seen. If the paper is wetted, the blue patch can be read [6]. This color change helps find that gel depletes the amount of time as dryer.

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Exciting results have been obtained from these studies over the last two decades. For example, it was found that there was redox activity of quinone ligands and potential for forming compounds. These formed compounds may involve in a number of electronic states due to the combined electrochemical activity of the cobalt ion and one or more quinone ligands [12].

Cobalt compounds can be made use of treatment of some cancers [11].

Magnetic, wear-resistant, and high-strength alloys are chiefly made by cobalt metal. It is suitable for applications such as desulphurization of hydrocarbons, the removal of nitrous oxide, and the emerging technology of converting natural gas to liquid hydrocarbons due to its unique catalytic properties. Because of allowing manufacture of highly effective cutting tools, it is also suitable for base industry application. It is used in both gas turbines and aggressive working setting owing to high-temperature resistance, hardness and wear characteristics of cobalt while alloyed with other metals. It may be also contributed to improve the operating efficiency by means of durability and wear capacity [3].

Besides, cobalt is generated a significant part of vitamin B12 in biochemistry. Vitamin B12 is a *tetra aza macrocyclic ligand complex of Co*. Therefore, it is a vital mineral for survival. Inorganic form of cobalt is matter that nourishing for bacteria, algae and fungi in chemistry. In addition to all these applications, cobalt is used as a catalyst in some reactions. For instance, cobalt-based catalyst is essential in reactions involving heterocyclic synthesis. Cobalt carboxylates are ordinary catalysts which also utilized in paints, varnishes, and binding resin.

Cobalt catalysts are practiced in many reactions, which are the synthesis of heterocycles. One of them was cobalt-catalyzed oxidative free-radical cyclization of alkyl bromides in 1986 [20].

Another example of these reactions is $3, bis-\{2,2,2-trifluoromethyl-1-[(1R,4S)]-1,7,7-trimethyl-2-(oxo-O)bicycle\,[2.2.1]hept-3-ylidene]ethanolate-O\}-cobalt\,(II)$ that Hartung et al. found.

In order to make liquid fuel, cobalt catalyst is used in the Fischer-Tropsch process. Also, cobalt and molybdenum are utilized as a catalyst in hydrodesulphurization of petroleum. The process made use of refining of liquid fuels [13].

In biochemistry, Vitamin B12 ranked sixth coordination position of Co(III) that is included cyanide ion and so it has another name, cyanocobalamin. Cobalamin complex is joined to $5^{'}deoxy\ adinosl$ unit through the C atom of the CH_2 group that is called Vitamin B12 coenzyme. Both of them are diamagnetic.

Vitamin B12 is indispensable for advanced creatures, but it is not vital for plants. It can only be synthesized by certain bacteria. The living creatures obtain it through the food. Vitamin B12 is digested in the ileum by a mucopolysaccharide, which is present in the gastric juice. If vitamin B12 is lacking or not digested, various diseases come into play. One of them is pernicious anemia. There is no absorption of cobalamin in patients with parenteral anemia. This is shown that it is vital for synthesis of hemoglobin. Besides, all of these indicate the biochemical significance of cobalt [21].

3. Some common cobalt compounds

Cobalt II salts are red in the case of complex-ion, that is, solvated with water, and it is dark blue when dehydrated. Invisible ink is made using this feature. If the diluted $CoCl_2.6H_2O$ solution is written on a sheet of paper, nothing can be seen. If the paper is wetted, the blue color patch can be read [6].

Besides, it is used to say how much moisture present in air. When there is humidity in weather, paper becomes pink [11].

3.1. Cobalt II sulfate, $CoSO_4.7H_2O$

It is dark red that gives double salts with alkali sulfates and is a form of monoclinic prisms [6].

3.2. Cobalt nitrate, $Co(NO_3).6H_2O$

It is separated from water in the form of red monochlorine crystals. If $Co(NO_3)$ is strongly heated it will form cobalt-2,3-oxide (Co_3O_4). With careful heating, Co-3 oxide is obtained [6].

$$2Co(NO_3)_2 \rightarrow Co_2O_3 + 4NO_2 + 1/2O_2 \tag{3}$$

$Co(NO_3)$ wield in treating the certain types of cancer due to it can be made radioctive [11].

3.3. Cobalt-III-sulphate, $Co_2(SO_4)_3.18H_2O$

It is obtained by anodic oxidation of $cobalt - II - sulphate$ and it gives a pair of salts which are opposed to the alum with potassium sulfate. Salts of cobalt-III in aqueous solution are easily converted into salts of cobalt II. On the contrary, salts of cobalt II also readily constitute salts of cobalt-III [6].

4. Synthesized new cobalt compounds

Cobalt was investigated by many scientists over years. These works ended up with many cobalt compounds. For example, Kumar and Garg synthesized cobalt(II) complexes of tetradentate Schiff bases of the type CoL. [$H_2l = C_2OH_{16}N_2O_2$. (H_2dsp), $H_{18}N_2O_2$. (H_2dst), $C_{20}H_{15}N_3O_4$(H_2ndsp) and $C_{16}H_{16}N_2O_2$(H_2salen). They found that $C_{20}H_{14}N_2O_2Co$ complex has the minimum and $C_{16}H_{14}N_2O_2Co$ complex has the maximum activation energy. They found that all the complexes were crystalline, brown-colored substances, non-hygroscopic and insoluble in non-polar solvents unlikely partially soluble in DMF and DMSO. Also, they evaluated complexes by UV-visible, IR, and magnetic studies and figured out various thermodynamic parameters using TG/DTA [2].

The chemistry of cobalt complexes has attracted a lot of attention in recent years on account of their applications, among others, in biological systems such as antimicrobial agents and antibacterial agents (DNA studies and cytotoxicity studies) [22].

Some of this works were mentioned as follows. In 1952, the first biological activity of cobalt compounds was acquainted where cobalt(III) compounds of bidentate mustard move as if it were hypoxia selective agents. Then, some compounds demonstrated significant activity against bacterial strains and against leukemia and lymphoma cell lines [20]. Afterward, lots of studies were carried out on anti-microbial, anti-fungal and anti-oxidant activities of cobalt compounds [16].

By 1960, several new cobalt(III) complex compounds of easily oxidized ligands were prepared and identified. These were salts of cobalt amines, inner charge complexes and a variety of cobaltates. The structural formula was $Na_3[(Co(CO])_3]$. $3H_2O$ which was the simplest formula [17].

It was reported that *cobalt* (*II*)*phthalocyanine* (*CoPc*) and its derivatives show catalytic activity for many reactions. They compared the catalytic activities of the *CoPc* species with those of the other first row transition metal phthalocyanine complexes. They were also shown that CoPc-modified glassy carbon electrodes catalyze the oxidation of $o-cresol, m-cresol, p-cresol, 4-chlorophenol$, $2-chlorophenol$ and *pheno*. Coating with *CoPc* species increased stability of GCE (cobalt(II) phthalocyanine-modified glassy carbon electrode) [23].

It was demonstrated that a complex form of cobalt(III) was an active catalyst for the selective oxidation of alkylaromatics using air. The air was used as the source of oxygen in the absence of solvent [24].

Park et al. reported the synthesis of "solid solution" and "core-shell" types of well-defined $Co-Pt$ nanoalloys smaller than 10 nm. The formation of these alloys was carried out by redox transmetalation reactions. $Co_2(CO)_8$ and *Pt*(*hfac*)*hexafluoroacetylacetlacetonate* were generated in the formation of "solid solution" type alloys such as $CoPt_3$ nanoparticles (**Figure 1**). Obtained nanoparticles were moderately monodispersed. Park et al. firstly reported the usage of redox transmetalation reactions for the synthesis of two different types (solid solution and core-shell). Various types of nanoalloys can be synthesized with this kind of redox transmetalation strategy. It is possible to fulfill next generation requirements with magnetic alloys, because of monodispersed particle size of less than 10 nm scales [25].

When pure metals like Fe, Co and Ni and their metal alloys utilized in magnetism, it is difficult to use them because of their oxidation in air. Moreover, this difficulty increases when the particle size gets smaller. So, the stability of particle enhances with a variety of methods. One of them is deposition of insulating shells on the nanoparticles surface. A procedure that leads to air-stable Co nanoparticles was carried out by Gedanken et al. [26]. They pretended that the formation of a carbon shell on the nanoparticle surface increases stability. But, acquired particles were not uniform [27].

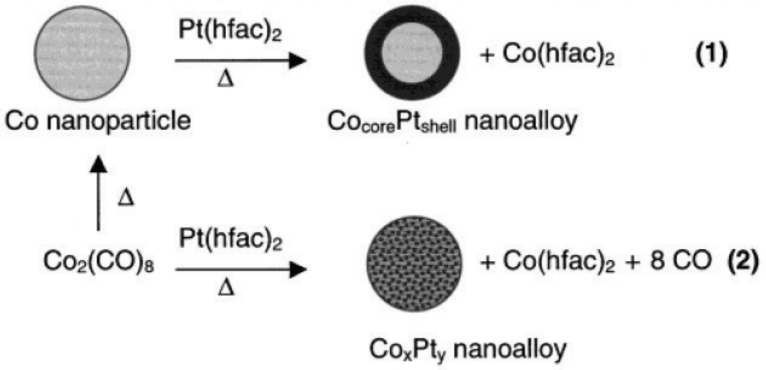

Figure 1. Synthetic routes of core-shell and solid solution type nanoalloys via transmetalation reaction.

Kobayashi et al. informed that it was a procedure, which allows the preparation of Co nanoparticles of various sizes in aqueous solution and their coating with well-defined silica shells. They found an easy chemical method for the synthesis and stabilization of magnetic and amorphous Co nanoparticles. These Co nanoparticles were surrounded by homogeneous shells of silica. This novel type of composite magnetic nanoparticles has potential applications, both in the field of ferrofluids and in magnetic storage media. The controlled assembly of $CoSiO_2$ nanoparticles is currently being studied by Kobayashi et al. [27].

The formation mechanism of the tubular structure of Co_3O_4 was studied by Li et al. and they presented a hypothesis. They prepared Co_3O_4 nanotubes by calcining electrodeposited cobalt nanowires embedded in an anodic alumina template (AAT). Oxidation, phase transition, evaporation and recrystallization processes were once believed that it had played a key role in the formation of Co_3O_4 nanotubes. Scientifically, it was a noteworthy case and these obtained nanotubes also find a wide range of applications in industry [28].

In vitro antimicrobial activity of cobalt(II) complexes was studied. These ligands were $[CoL_2Cl_2]$, where $L_1 = aminobenzimidazole$, $L_2 = 1 - benzyl - 2 - aminobenzimidazole$, $L_3 = 1 - (4 - methylbenzyl) - 2 - aminobenzimidazole$. All of them and their cobalt(II) complexes were examined in vitro antimicrobial activity against *Pseudomonas aeruginosa*, *Bacillus* sp., *Staphylococcus aureus*, *Sarcina lutea* and *Saccharomyces cerevisiae*. They found that none of the compounds were importantly impressive against yeast *Saccharomyces cerevisiae*, but 2-aminobenzimidazole complex was efficient, which moderately restrained the growth of yeast. Similarly, all ligands and their complexes were evaluated for activities one by one and they found that in case of benzimidazole, nucleus had 4-methylbenzyl group at the N1 atom, the antimicrobial activity increased. They concluded that the substituted ligands and cobalt may get a role in the antimicrobial activity [29].

It was reported that synthesis of cobalt nanoparticles using a polymeric microfluidic reactor by the reduction of $CoCl_2$ in tetrahydrofuran (THF) using lithium *hydrotriethylborate* ($LiBH(C_2H_5)_3$ as a reducing agent and $3 - (N, N - dimethyldodecylammonia)propanesulfonate$ (SB_{12}) as a stabilizer. They investigated experimental conditions such as flow rates, growth time and quenching procedure. They found that Co nanoparticles with mainly fcc structures were composed with a high kinetic energy level (e.g., high-flow rate). Co nanoparticles with mainly hcp structures were preferred when it was be conditions with a low kinetic energy level (e.g., low-flow rate) and short-growth time. But, the crystal structure of Co nanoparticles switched to the metastable phase, while Co nanoparticles generated at the low kinetic level grew for a longer time. This submits that by controlling the reaction kinetics, acquired nanoparticles with different structures can utilize as potential application in microfluidic reactors [30].

Ingersoll et al. carried out nickel-cobalt-boride ($Ni - Co - B$) catalysts by a chemical reduction method and their catalytic hydrolysis reaction with alkaline $NaBH_4$ solution. They aimed to design an efficient hydrogen generator for portable fuel cell applications. The reaction temperature in the hydrolysis of alkaline $NaBH_4$ solution, a function of the concentrations of $NaOH$ and $NaBH_4$ were evaluated in their work. The rate of hydrogen generation was surveyed using ($Ni - Co - B$) catalyst. The rate of hydrogen generation was increased with lower $NaOH$ concentrations in the alkaline $NaBH_4$ solution and decreased after reaching a maximum value at 15 wt.% of $NaOH$ [14].

By 2008, cobalt nanoparticles using thermal decomposition of $[bis(salicylidene)cobalt\ (II)]$ in the presence of *TPP* and *oleylamine was studied*. The obtained cobalt particles were stable in hydrocarbon solvents to air oxidation and had cubic cobalt crystallinity. The hysteresis loops of the obtained samples were found to have soft magnetic behavior, enhanced coercivity (Hc) and decreased saturation magnetization (Ms) in comparison to bulk materials. After having contact with air, the hysteresis loop of Co nanoparticles also revealed ferromagnetic property saturation magnetization (Ms) and coercivity (Hc) values of about 56.2 emu/g [31].

Bruijnincx and Sadler investigated the design of modernist metal-based anticancer drugs that include recent literature. Many novel chances for anti-cancer drugs were gained low systemic toxicity and ability of coming from the top of the drug resistance. In their work was been presented with different examples of promising offer. These studies caused expansion toolbox of medical inorganic chemistry [15].

It had been studied with three species of bacteria, in order to found the activity of the schiff base and their complexes. In this work, it was found best results with diameters (30 mm), due to the inclusion of Co(II) ion. This was shown that the complexes have more antibacterial activities than the free Schiff bases [32].

Kumar and Chandra synthesized cobalt compounds that exhibit significant antifungal activity [33].

Pannu et al. synthesized $[CoLCl_2]_2$ and $[Co(L)_2(H_2O)_4][CoLBr_3]_2 2H_2O$. They found that latter compound has magnetic response [34].

The research was carried out in cobalt catalysis and they obtained cost-effective catalysts and milder conditions for existing C–H functionalization. Their studies also paved the way for unrivaled chemical transformations. They found two answers for two questions in this study. First, low-valent cobalt catalysts may imitate the reactivity of noble transition metal catalysts to C–H activation. Second, in C − H functionalization, cobalt catalysts may present matchless reactivity and selectivity and these properties provide a way for undergoing mysterious and hard synthesis transformations, up to now. Given examples were branched-selective hydroarylation of styrenes, ortho-alkylation of aryl imines with secondary alkyl halides and migratory arylzincation of alkynes. Their work brought out novel difficulties and possibilities. It was necessary to fully understand the reaction mechanism and the nature of the catalyst due to further growth in this area [35].

Gaëlle et al. synthesized and investigated two complexes, a cobalt(II) complex $[Co(phen)_3(NO_3)_2]2H_2O$ (1) and a novel Co(III) complex with mixed ligand $[diazido\ bis(1,10-phenanthroline-k2N,N')cobalt\ (III)]nitrate[Co(phen)_2(N_3)_2]NO_3(2)$. They examined their antimicrobial activities in vitro against eight pathogens (four bacteria and four fungal species). **Figure 2** showed the histogram of MIC against bacterial species. The results showed that the complexes were very active; however, complex 1 is more active toward the bacteria, but complex 2 is more active toward the fungi. The MICs values for complexes are summarized in **Table 3**.

Both of them may stand for decent nominees as an antibacterial (1) and antifungal agent (2). However, Gaëlle et al. continued the relevant works [17].

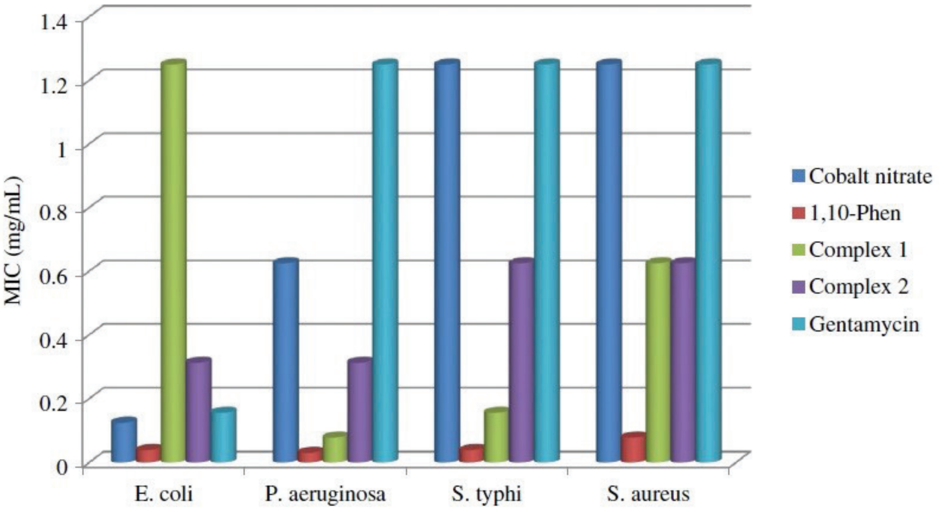

Figure 2. Histogram of MIC against bacteria species.

Three new cobalt(II) coordination compounds were reported (i.e., $Co(HL_1)Cl$ (1), $Co(HL_2)Cl$ (2) and $[Co(HL_3)Cl\ (CH_3)_2CHOH]$ (3) by Morcelli et al. [36]. Structures of complexes (2) and (3) involved the naphthyl group and contained α and β-naphthyl groups, respectively. Also, complexes (2) and (3) possess more activity than complex (1). The results of this work showed that there was effect of the isomerism on the antitumour activity. Moreover, complexes (2) and (3) paved the way for the death of cancer cells without affecting the normal cells. In this chapter, it is significant to determine the kind of the structure of the ligand and the kind of metal center on cytotoxicity [36].

	Species	**MIC(mg/mL)**						
		$Co(NO_3)_2 6H_2 0$	**O-Phen**	N_3^-	**Complex 1**	**Complex 2**	**Gentamycin**	**Nystatin**
Bacteria	*E. coli*	0.125	0.039	1.156	1.25	0.313	0.156	>2.5
	P. aeruginosa	0.625	0.039	0.078	0.078	0.313	1.25	>2.5
	S. typhi	1.25	0.039	0.156	0.156	0.625	1.25	>2.5
	S. aureus	1.25	0.078	0.625	0.625	0.625	1.25	>2.5
Fungi	*C. albicans* ATCC 12C	0.625	0.039	1.25	0.156	1.25	>2.5	>2.5
	C. albicans ATCC P37037	0.625	0.078	0.625	0.156	0.313	>2.5	>2.5
	C. albicans ATCC P37039	0.625	0.156	1.25	0.156	1.25	>2.5	>2.5
	C. neoformans	1.25	0.039	2.5	0.078	1.25	>2.5	>2.5

Table 3. MIC (mg/mL) of the complexes.

In 2016, three homospin compounds of chain structures that were linked to pentagonal bipyramidal Co(II) units were synthesized (**Figure 3**). Moreover, this work demonstrated the preparation of higher dimensional coordination polymers [37].

Cody et al. synthesized two new metal thiophosphate anions, $[Co(Co(P_3S_8)_2)_2]^{4-}$ and $[Cr(P_3S_9)_2]^{3-}$. These new compounds indicated that it is the applicability of ionothermal synthesis to two new metals in the thiophosphate system. Both syntheses demonstrate the versatility of ionothermal synthesis for preparing new thiophosphate compounds [8].

Two new mono- and dinuclear Co(II) complexes namely $Co(tdmpp)Cl_2]_2.2H_2O$ (1) and $[Co_2(tdmpp)Cl_4]$ (2) (where $tdmpp \frac{1}{4} 1,1,3,3-tetrakis\,(3,5-dimethyl-1-pyrazolyl)propane\big)$ were prepared by Azizolla Beheshti et al. [38]. This work showed that bacterial inhibition ability of these compounds increases from tdmpp to the dinuclear complex 2 (**Figure 4**). Furthermore, it is demonstrated that the metal complexes are more active than free ligands [38].

Also, cobalt is used as a catalyst in some reactions. For instance, cobalt-based catalysts are essential in reactions involving heterocycle synthesis. Adam et al. carried out catalytic hydrogenation of nitriles to primary amines. They used $Co(acac)_3$in combination with $tris\ [2\ (dicyclo\ hexylphosphino)ethyl]phosphine$ as a catalyst. It catalyzes the selective hydrogenation of nitriles to give the corresponding amines [39].

The $[Co(2-hydroxy-1-naphthaldehyde_2(DMF)_2]$ complex 1 was synthesized by Zeinab Asgharpour et al. and successfully supported on modified Fe_3O_4nanoparticles using *tetraethylorthosilicate* (*TEOS*) and (3 − *aminopropyl*)*trimethoxysilane* (*APTMS*). Moreover, it was stated as $Fe_3O_4SiO_2APTMS\ complex$ nanocatalyst (**Figure 5**). It was a useful heterogeneous catalysis system that there were properties of solid catalyst candidates as $Fe_3O_4SiO_2APTMS\ complex$ 1 such as easy preparation, mild reaction conditions, high yield, ease of catalyst separation and recyclability [12].

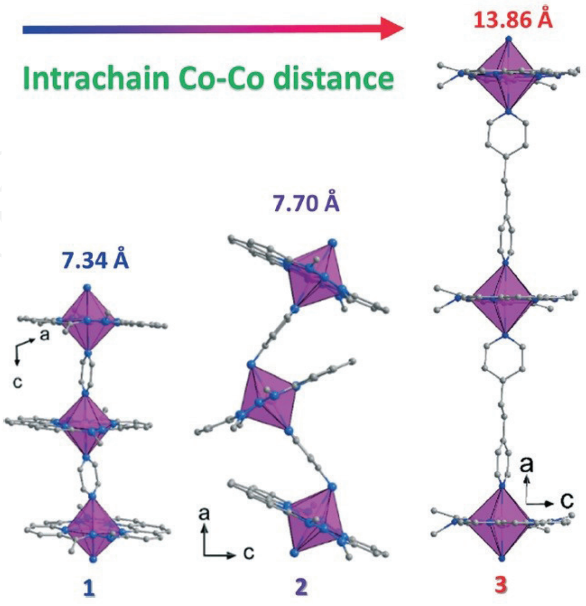

Figure 3. The 1D chain structures of complexes **1**–**3**. Hydrogen atoms are omitted for clarity.

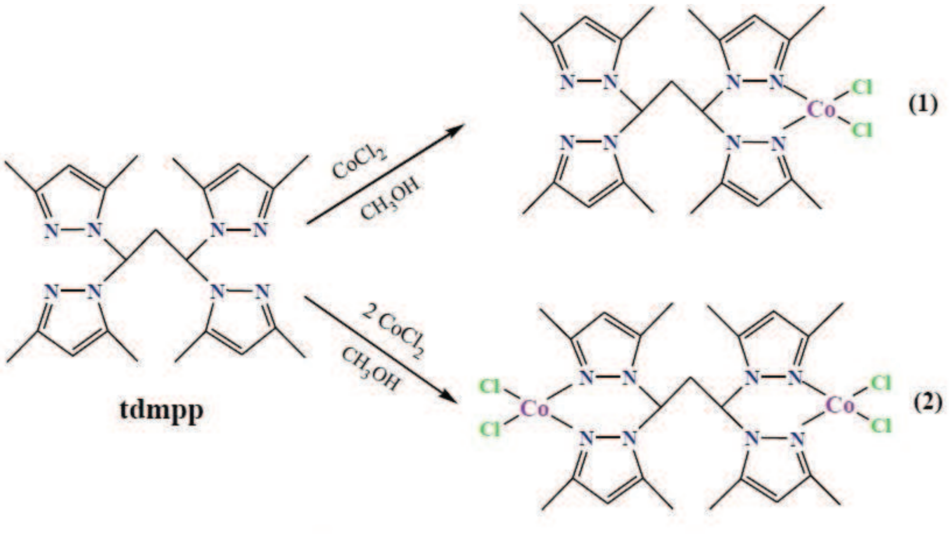

Figure 4. Synthesis procedure for compounds **1** and **2**.

Ko et al. carried out the preparation of hollow cobalt oxide and cobalt selenide microspheres and their Na-ion storage properties. Hollow cobalt selenide microspheres were classed with the hollow cobalt oxide microspheres. Hence, it was applied as an anode material for NIBs. Selenide microspheres showed high initial discharge capacity and high initial Coulombic efficiency as well as good cycling and rate performances for Na-ion storage. Also, they had structures that improve electrochemical properties by means of optimizing the electrolyte system used for Na-ion storage. On the other hand, hollow cobalt oxide microspheres were favorable from the point of their high initial capacity and low voltages for Na-ion storage as anode material for NIBs. They had leveragable cycling and rate performances. So, both of these microspheres were act as a promising anode material for NIBs [40].

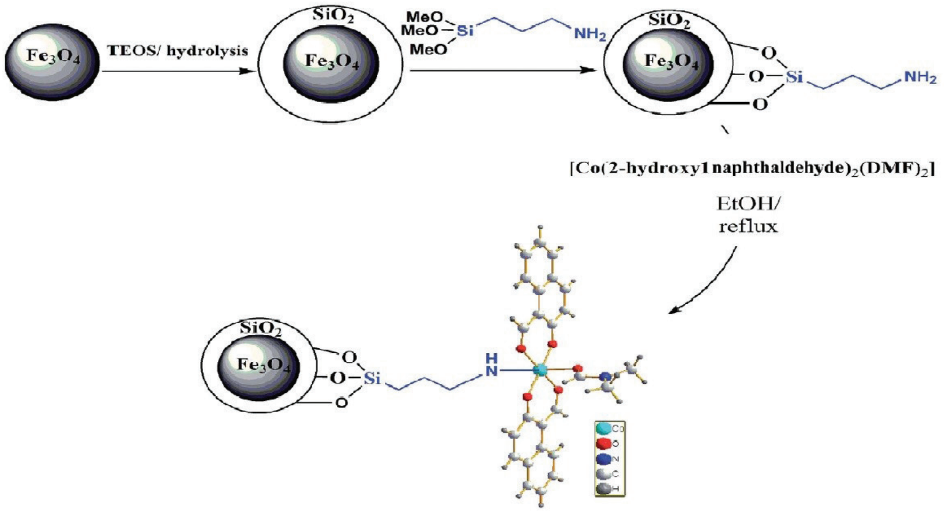

Figure 5. Preparation steps of Fe_3O_4@SiO_2@APTMS@complex 1.

Mondal et al. prepared mixed $NiCoMn - Oxide$ nanorods, which was a new class substance for supercapacitor application. They carried out process for synthesis of mixed $NiCoMn - Oxide$ through a facile hydrothermal technique and their electrochemical capacitive properties. Structures were characterized by XRD and SEM. A variety of measurement showed that there was potential to utilize as electrodes for supercapacitor devices in this substance. Moreover, it was considered that there were cost-effective methods for extraction of raw materials. Therefore, mixed oxide was preferred as raw materials for large-scale applications such as supercapacitor electrodes [41].

It was made with fabrication of Ni NWs decorated with Co NPs by using two-step etching and deposition technique in 2016. This study showed that nanoparticles dispersed on the surface of nanoparticles as shown in **Figure 6**. They declared in this study that this technique has been used for the first time in order to manufacture nickel nanowires which are adorned with cobalt nanoparticles [42].

Montazerozohori et al. synthesized a new nanostructured cobalt(II) bromide complex with a bidentate Schiff base ligand. Particles' size of complex in nanodimension size by XRD and SEM analyses is shown in **Figures 7** and **8** [43].

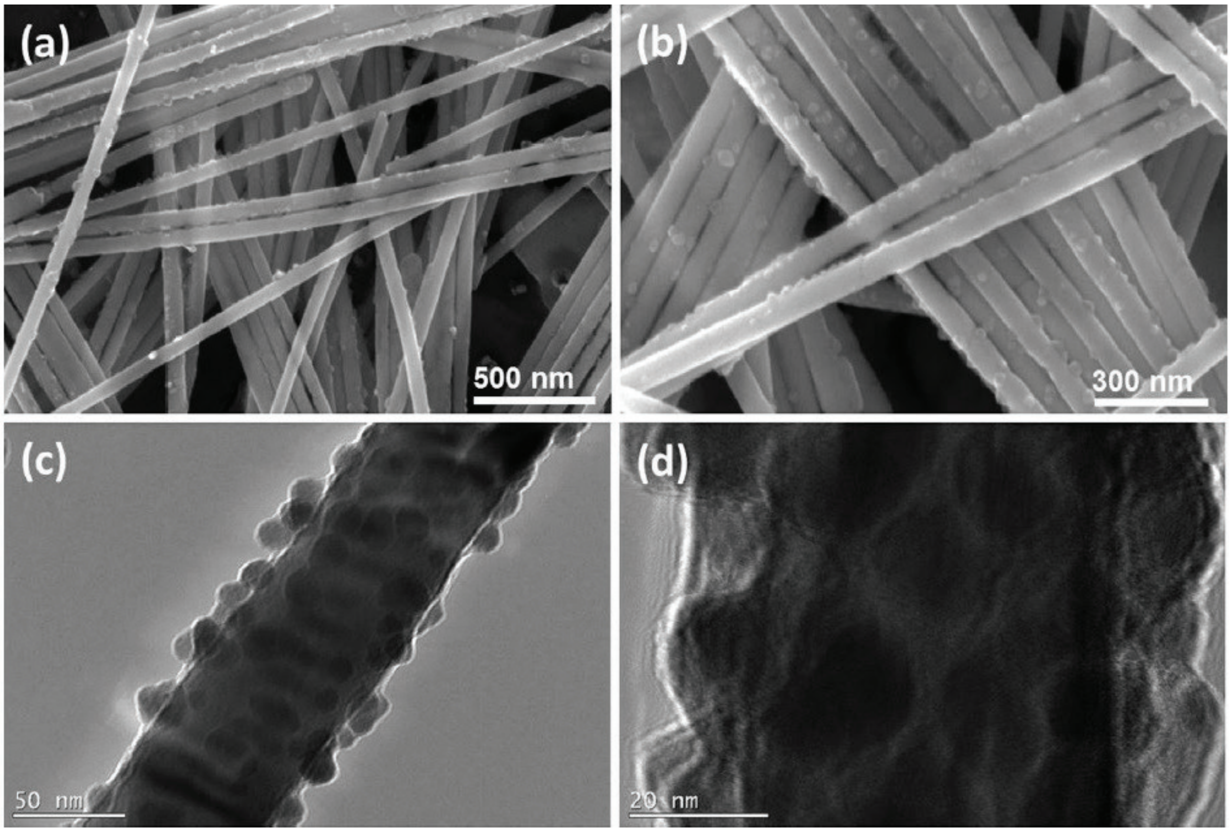

Figure 6. SEM images of nanoparticle-decorated NWs shown in (a) and (b). TEM images of the NWs at different resolutions are presented in (c) and (d), which confirm the successful fabrication of Co nanoparticle-decorated Ni nanowires with diameter of ~60 nm.

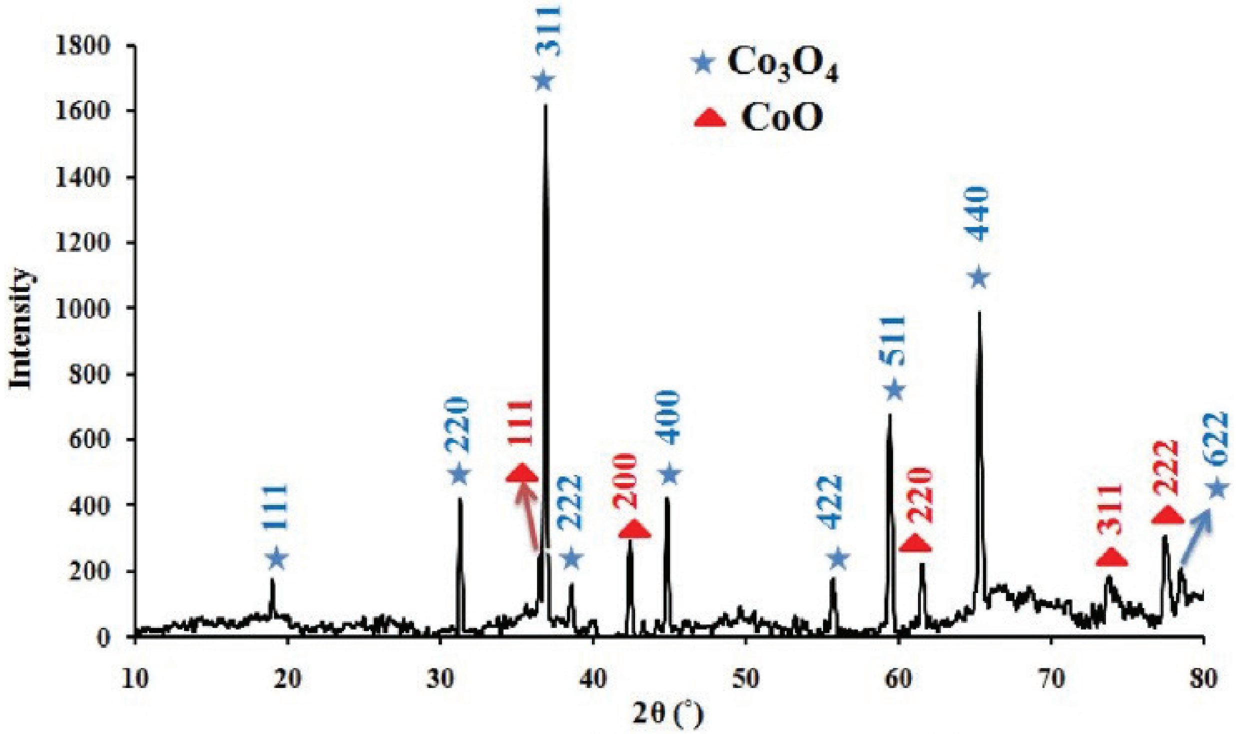

Figure 7. XRD pattern of CoO/Co_3O_4 nanoparticles.

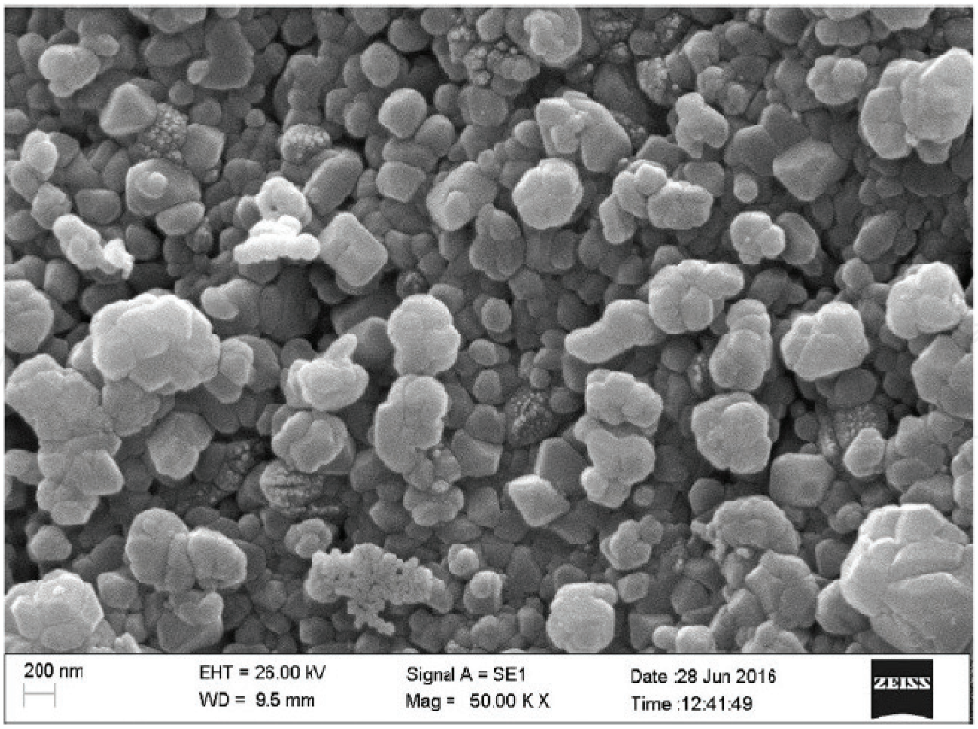

Figure 8. SEM image of CoO/Co_3O_4 nanoparticles.

It was shown, in another work in 2017, a novel dry coating technology for Co/Al_2O_3 catalyst synthesis without solvents and heating treatment. The dry-coated catalysts were presented as comparable to conventional chemical impregnated catalysts. **Figure 9** shows a spherical shape of Co/Al_2O_3 [44].

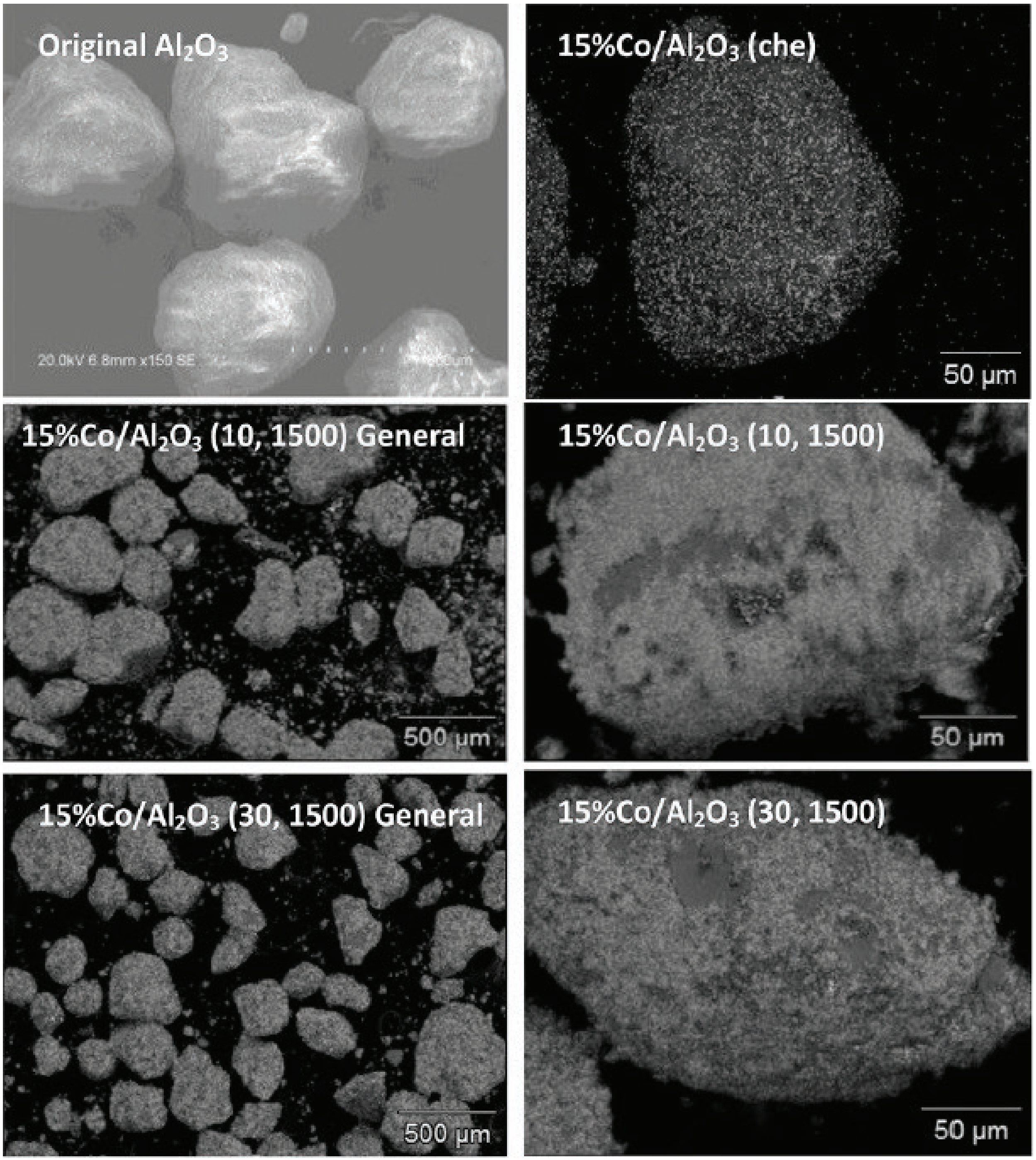

Figure 9. Morphology of the catalysts prepared in "Picomix" and by conventional impregnation: Al (blue color) and Co (green color).

Przyojski et al. synthesized two new complexes of cobalt(II) with 7-azaindole. They have Co(II) in a distorted tetrahedral environment. Asymmetric units of complexes are shown in **Figures 10** and **11** [45].

Four novel complexes $[Co(H_2O)_4(sul)_2]$ 1,$[Co(2-ampy)_2(sul)_2]_2$,$[Co(H_2O)_2(1,10-phen)(sul)_2]_3$ and $[Co(2,9-dimephen)(sul)_2]_4(sul = sulindac, 2-ampy = 2-aminopyridine,$ $1,10-phen = 1,10-phenanthroline$ and $2,9-dimeph = 2,9-dimethyl-1,10-phenanthroline$ were prepared and characterized by Shalash and Abu Ali [16]. This novel complexes were evaluated to determine activity against Gram-positive (*Staphylococcus epidermidis*, *S. aureus*) and Gram-negative (*Bordetella*, *Escherichia coli*) bacteria and Yeast species (*Saccharomyces* and *Candida*) using agar well-diffusion method. The results indicated that only complex 4 have been effective against yeast. Also, all of them have more antibacterial activity against Gram-positive bacteria than Gram-negative bacteria [16].

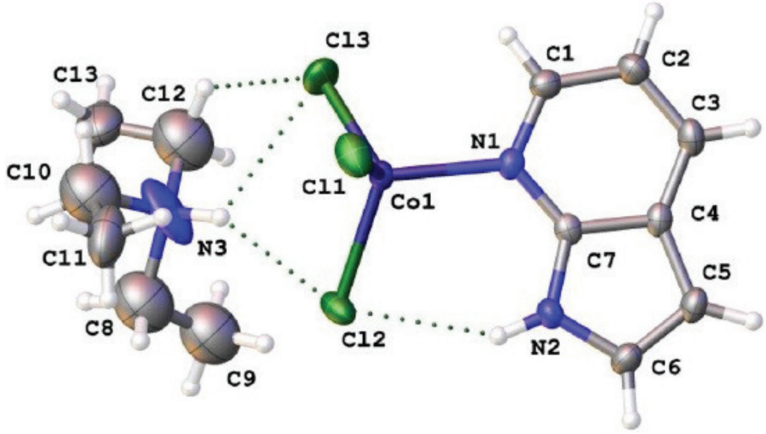

Figure 10. Asymmetric unit of $[(C_2H_5)_3NH]$ $[Co(Haza)Cl_3]$, **1**. Thermal ellipsoids are shown at 50% probability. Color code: *C, gray; Cl, green; Co, dark blue; H, white; N, blue.*

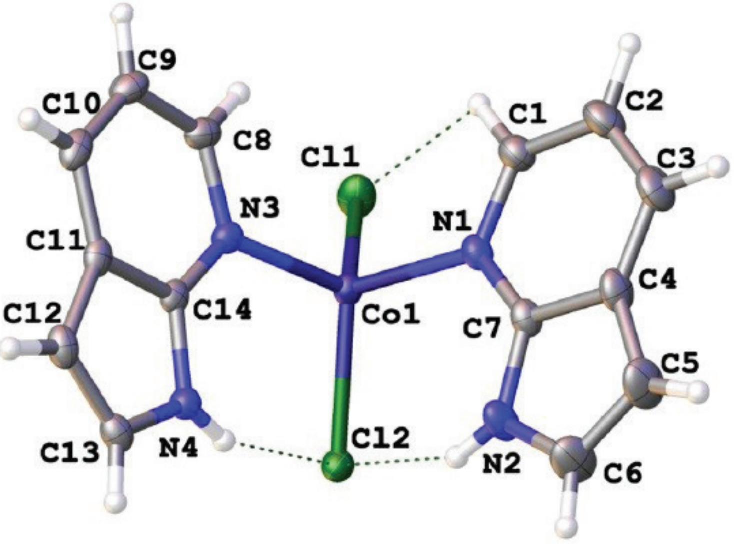

Figure 11. Asymmetric unit of $[Co(Haza)_2Cl_2]$, **2**. Thermal ellipsoids are shown at 50% probability. Color code: *C, gray; Cl, green; Co, dark blue; H, white; N blue.*

Hassanzadeh et al. investigated the cobalt Schiff base complex-modified CPE containing cationic surfactant. This complex could increase resolution and selectivity of voltammetric responses of DA and AA. Also, it was challenging to distinguish the voltammetric peaks of DA and AA. It obtained the better of resolution than previous reported works. This makes it suitable for simultaneous detection of these compounds. Moreover, it was simple preparation, acceptable selectivity and sensitivity, had low-detection limit and reproducibility. All of them made the prepared system very effective in manufacturing [46].

$[(Co(bdmpzm)_2(NCS)_2](bdmpzm = bis(3, 5 - dimethylpyrazol - 1 - yl\ methan$ was synthesized and was integrated with single-walled carbon nanotubes (SWCNT) and nafion on a screen printed carbon electrode (SPCE) by Nagles et al. [47]. They investigated its electrocatalytic activity for dopamine (DA) oxidation. The measurements were made with or without the cobalt complex and compared with the modified electrode. DA in human urine was measured by obtained new sensor in the range of 83, 0–93, 0. Owing to cobalt complex in this electrode, there was an increase in anodic current and change in oxidation potential for DP. Also, unlike other conventional methods, analysis had been done in short time [47].

Studies on cobalt are continuing due to the fact that they have a wide variety of functions and many applications, especially in health sector. Unfortunately, cobalt derivatives have not been studied as pharmaceutical, yet. Up to now, the only cobalt-based drug is Doxovir that is Co(III) Schiff base complex and its mechanism is not also completely understood [36].

5. Toxicity of cobalt

Physical contact with cobalt is not the only way to expose to a substance. You may be exposed by lot of routes such as breathing, eating or drinking the substance, or by skin contact. Metal poisonings occur because of different reasons. For example, cobalt toxicity depends on oral intake and inhalation. Cobalt exposure related to using vitamin B12 is considered as there is low toxicity due to fast rate of renal excretion and limited oral intake. Mostly, absorbed cobalt (50–88%) eliminated by renal excretion rest by feces.

Just as other metals, cobalt is also a multiple organ poison. $CuSO_4$ inhibits many key enzyme systems and prevents the beginning phase of protein synthesis.

It is brought to attention that cobalt may inhibit aerobic metabolism with increasing glycolysis while $CoCl_2$ reduce the consumption of oxygen [48].

Cobalt poisoning causes gastrointestinal distress and heart failure. Chelating agents are used in the treatment of those poisonings [49].

Cobalt also prevents Krebs cycle by generating reduced α-lipoic acid. Besides, cobalt salts inhibit dihydrolipoic acid by forming complex with dihydrolipoic acid sulfhydryl groups.

Result of this reaction, it is not enough pyruvate convert to acetyl co-A and α-ketoglutarate convert to succinyl-coA.

Moreover, $CoCl_2$ inhibit tyrosineiodinase enzyme. This causes the reduction of triiodothyronine (T3) and thyroxine (T4) [48].

6. Conclusion

In this chapter, chemical properties of cobalt and some new cobalt compounds were discussed. It deals with the progress of cobalt chemistry. Cobalt is substantial in both chemical reactions and within many compounds. Some of them are heterocycle reactions, cobalt-based catalyst and cobalamin. Cobalt studies are continuing due to the fact that they have a wide variety of functions and many applications, especially in pharmaceutical technology. These studies caused appearance of medicinal bioorganometallic chemistry and expanding of medical inorganic chemistry. The studies so far in this area carried out have enabled producing unknown and difficult reactions and they will be continued to be responsible for them. This survey of the recent literature illustrates the fact that many different approaches on cobalt and new cobalt compounds are being used in many different areas. For example, one of them is that many different new creative approaches are being taken toward the design of innovative metal-based anticancer drugs.

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