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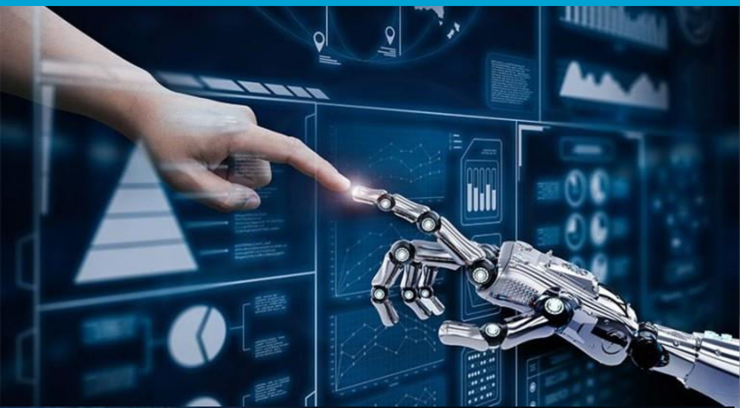

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A Review of Medicinal Uses of Some Transition Metals on Human Health

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ABSTRACT: Transition metals have an important place within medicinal biochemistry. Research has shown significant progress in utilization of transition metal complexes as drugs to treat several human diseases like carcinomas, lymphomas, infection control, anti-inflammatory, diabetes, and neurological disorders. Transition metals exhibit different oxidation states and can interact with a number of negatively charged molecules. This activity of transition metals has started the development of metal-based drugs with promising pharmacological application and may offer unique therapeutic opportunities. Maintenance of human health and vitality requires the ingestion of trace levels of numerous inorganic elements, among them the transition metals iron (Fe), manganese (Mn), zinc (Zn), cobalt (Co), copper (Cu), nickel (Ni), molybdenum (Mo), vanadium (V), and chromium (Cr). In general, transition metals are sequestered in organometallic complexes within our bodies, enabling their properties to be controlled and directed where needed, and their propensity to promote the generation of harmful reactive oxygen species is minimized. Transition metals are key components of numerous enzymes and electron transport proteins as well as the oxygen transport proteins hemoglobin and hemocyanin. Zinc finger motifs provide the DNA-binding domains for many transcription factors, while Fe-S clusters are found in many of the enzymes that participate in DNA replication and repair. Nutritionally or genetically induced deficiencies of these metals are associated with a variety of pathologic conditions including pernicious anemia (Fe), Menkes disease (Cu), and sulfite oxidase deficiency (Mo). When ingested in large quantities, most heavy metals, including several of the nutritionally essential transition metals, are highly toxic and nearly all are potentially carcinogenic.

KEYWORDS: transition metals, medicinal, human health, enzymes, drugs, deficiency, pharmacological

I. INTRODUCTION

There are pharmacological activities of the cheaper and easily available first-row transition metal coordination compounds V(IV), Co(II), Ni(II), Cu(II) and Zn(II) complexes. Moreover, these metal ions are the essential elements present in the biological intracellular environment of living organisms. They are most abundantly found trace elements present in biological systems together with iron and most of the metalloproteins have these elements . These metal ions are nowadays present in several inorganic pharmaceuticals used as drugs against a variety of diseases, ranging from antibacterial and antifungal to anticancer applications . Another fact for targeting these particular metal ions is their less toxic nature which can be further decreased when coordinated with the ligands. [1,2] Though there are innumerable ligands available, the chosen amino acids, N-heterocycles (1,10 Phenanthroline, Bipyridine) and pyrazolones each have an added benefit to their properties which is a major advantage in designing an ideal drug. The amino acids are the building blocks of the human body and when the environment of the drug is similar to that of the functions carried out inside the body, the chance of succeeding in designing a less toxic and cheap drug with high activity is more. In addition to that, the N-heterocycles and pyrazolones as ligands affect the environment of the complex in such a way that their lipophilicity increases which is a major factor in designing a drug.[3,4]

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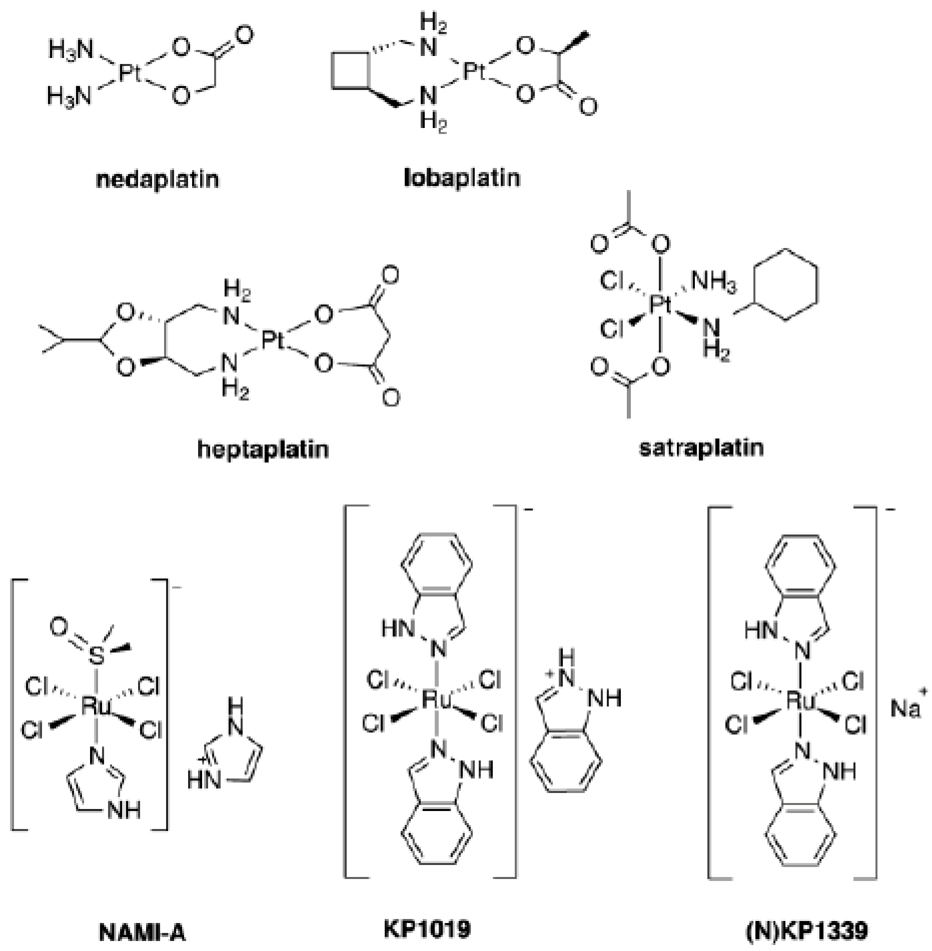

Figure 1: Anticancer platinum and ruthenium metallodrugs in clinical trials in the US.

Platinum (II) complexes has been used as anti cancer drugs since long, among them cisplatin has proven to be a highly effective chemotherapeutic agent for treating various types of cancers (Jamieson 1999). Cisplatin moves into the cell through diffusion and active transport. Inside the cell it causes platination of DNA, which involves interstrand and intrastrand cross-linking as well as formation of adducts, usually through guanine, as it is the most electron rich site and hence, easily oxidized. Formation of cisplatin DNA adducts causes distortion and results in inhibition of DNA replication . Cisplatin DNA adducts also serve as binding site for cellular proteins such as repair enzymes, histones, transcription factors and HMG-domain proteins . The binding of HMGprotein to cisplatin-DNA adduct has been suggested to enhance anticancer effect of the drug . Beside the effectiveness of cisplatin against cancer, [5,6] it has encountered many side effects. Drugs like cisplatin does not specifically affect cancer cells but it also effect the rapidly dividing cells of certain normal tissues, such as those found in hair follicles, bone marrow, and the lining of the gastrointestinal tract. Platinum is not the only transition metal used in the treatment of cancer, various other transition metals have been used in anticancer drugs . Titanium complexes such as Titanocene dichloride had been recognized as active anticancer drug against breast and gastrointestinal carcinomas . Gold complexes also show anti-cancer activity, these complexes act through a different mechanism as compared to cisplatin . The target site of Au complexes is mitochondria not DNA. Certain gold complexes with aromatic bipyridyl ligands have shown cytotoxicity against cancer cells .The 2-[(dimethylamino) methyl] phenyl gold (III) complex has also proven to be anti tumor agent against human cancers. Gold nanoparticles when used in combination with radio therapy or chemotherapy enhance DNA damage and make the treatment target specific . Lanthanum has also been used to treat various forms of cancer [7,8].

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II. DISCUSSION

The Transition Metals

	1A	2A												3A	4A	5A	6A	7A	8A
	(1)	(2)												(13)	(14)	(15)	(16)	(17)	(18)
			3B		4B	5B	6B	7B	—	8B	—	1B	2B						
			(3)		(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)						
1	H																		He
2	Li	Be												B	C	N	O	F	Ne
3	Na	Mg												Al	Si	P	S	Cl	Ar
4	K	Ca	Sc		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y		Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	—	Uuq	—	—	—	—
6					Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
7					Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

The transition elements or transition metals occupy the short columns in the center of the periodic table, between Group 2A and Group 3A. They are sometimes called the d-block elements, since in this region the d-orbitals are being filled in, and are also referred to as B-group elements since in most numbering systems of the columns on the periodic table the numerals of these groups are followed by the letter B. The period 4 transition metals are scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), and zinc (Zn). The period 5 transition metals are yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), technetium (Tc), ruthenium (Ru), rhodium (Rh), palladium (Pd), silver (Ag), and cadmium (Cd). The period 6 transition metals are lanthanum (La), hafnium (Hf), tantalum (Ta), tungsten (W), rhenium (Re), osmium (Os), iridium (Ir), platinum (Pt), gold (Au), and mercury (Hg). The period 7 transition metals are the naturally-occurring actinium (Ac), and the artificially produced elements rutherfordium (Rf), dubnium (Db), seaborgium (Sg), bohrium (Bh), hassium (Hs), meitnerium (Mt), darmstadtium (Ds), roentgenium (Rg), and the as-yet unnamed ununbiium (Uub).[9,10]

The elements which follow lanthanum (Z=57) and actinium (Z=89) are called the lanthanides and actinides, respectively, and together are known as the inner transition elements.

In the transition metals, the five d orbitals are being filled in, and the elements in general have electron configurations of $(n\text{-}1)d^{1\text{-}10}\ ns^2$, although there are some exceptions when electrons are shuffled around to produce half-filled or filled d subshells. Many of the transition metals can lose two or three electrons, forming cations with charges of 2+ or 3+, but there are some which form 1+ charges, and some which form much higher charges.

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All of the transition metals in their elemental forms are malleable and ductile (except for mercury, which is a liquid at room temperature), and are good conductors of heat and electricity. Many of the transition metal ions have characteristic colors associated with them, and many have biological and industrial significance.

Titanium is a hard, strong, silvery metal. The name is derived from the Titans of Greek mythology. It is found in the Earth's crust at a concentration of 4400 ppm, making it the 9th most abundant element. The most common ores of titanium are rutile (TiO_2, the eighth most common compound on Earth) and ilmenite [$FeTiO_3$].

Titanium melts at 1668°C, has a low density (4.51 g/cm^3), and is as strong as steel, but is 45% lighter: this makes it an ideal metal for use in the aerospace industry. It is used in many applications where both strength and lightness are desirable, such as aircraft frames and engines, bicycles, and golf clubs. Titanium alloyed with aluminum and vanadium forms a metal with a higher strength-to-weight ratio than any other metal.[11,12]

Titanium is resistant to corrosion because its surface becomes coated with a thin, hard oxide film, which is very resistant to further chemical attack. For this reason, titanium can be used in many medical devices. Titanium is used in the pins that hold broken bones together, and in cranial plates; it is a component in hip and knee replacements; and is used in pacemakers and surgical screws. Tissues bond to a titanium oxide layer on the surface of the metal which is formed when the metal is exposed to a plasma arc that exposes a fresh surface of titanium. Titanium's unreactivity also makes it useful in offshore oil rigs, and parts of ships that are exposed to seawater.

Titanium dioxide, TiO_2, is commonly used in paints because of its intensely white color. (Since titanium compounds are nontoxic, its use has largely replacing that of lead in paints.) It is also used in sunscreens to scatter away ultraviolet light before it burns the skin. Titanium tetrachloride, $TiCl_4$, reacts with moisture in the air to produce titanium dioxide and hydrochloric acid, generating a dense white vapor; it is used in skywriting and smoke-screen devices.

Tantalum is a hard, gray metal, with a melting point of 3017°C, which is very resistant to corrosion. It is named after a character in Greek mythology, Tantalus (father of Niobe). Tantalus killed his son, Pelops, and served him to the gods at a feast; the gods were not amused, and punished Tantalus in Hades by being made to stand in a pool of water surrounded by trees laden with fruit, but whenever he stooped to drink the water, it receded from him, and whenever he reached out for the fruit, the branches withdrew out of reach, leaving him forever thirsty and hungry. (This is also the derivation of the word "tantalize.") Titanium was difficult to isolate from the chemically-similar niobium (see above), and it was some time before the "tantalizingly" elusive element could be isolated in a pure form. It is found in the Earth's crust at a concentration of 2 ppm, making it the 51st most abundant element. The primary ores of tantalum are tantalite [$(Fe,Mn)(Nb,Ta)_2O_6$, called columbite if there is more niobium than tantalum], samarskite [$(Y,Ce,U,Fe)_3(Nb,Ta,Ti)_5O_{16}$], and euxenite [$(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$].

Tantalum is used in some medical implants, such as pins in bone fractures, and in plating to replace damaged skull bone. It is also used in surgical and dental tools, in electronic capacitors, and in some turbine blades and rocket nozzles.

Tantalum carbide, TaC, is an extremely hard material, and is used in some cutting tools. A composite of tantalum carbide and graphite has been made at Los Alamos National Laboratory, and is one of the hardest materials known, with a melting point of 3738°C.

Technetium is a radioactive element; the pure metal is silvery-gray in appearance, although it usually used as a grey powder. It is named for the Greek word technetos, meaning "artificial," because it was the first element to be produced artificially. Trace amounts of technetium are found in uranium ores, where it is produced by spontaneous fission of uranium-238, but the element is not present in large enough quantities to be practically mined (the concentration is estimated at about 1 nanogram per kilogram of ore). It is also obtained from spent uranium-235 fuel rods in nuclear reactors.[13]

Technetium is produced by the neutron bombardment of molybdenum-98 to produce molybdenum-99, which then undergoes beta-decay with a half-life of 67 hours to produce technetium-99m, a metastable, excited nuclear state with a half-life of 6 hours, which emits gamma rays to form ground-state technetium-99. Technetium-99 is also radioactive, and is a beta-particle emitter with a half-life of 211,000 years.

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There are about 56 isotopes of technetium (including metastable states), and all of them are radioactive. The longest-lived isotope, technetium-98, has a half-life of 4.2 million years. That may seem like a long time, but compared to the age of the Earth — 4.5 billion years — that is enough time for any technetium that had originally been in the Earth's crust to have decayed. In 1952, traces of technetium were discovered in the spectra of some types of red giant stars; this was one of the first pieces of evidence to support the theory that heavy elements were produced in stars.

The existence of technetium was predicted from the gap in the periodic table between the elements molybdenum (Z=42) and ruthenium (Z=44), but element 43 proved to be extremely elusive. Many early reports of its discovery turned out to be mistaken, being instead impure samples of other, known elements. The element was finally discovered in 1937 by Emilio Segre and Carlo Perrier at the University of Palermo in Italy, in a sample of molybdenum-96 that had been bombarded with deuterium (hydrogen-2), producing technetium-97. The element may have been discovered earlier by Walter Noddack, Otto Berg, and Ida Tacke in 1925, who bombarded a sample of columbite [$(Fe, Mn)(Nb, Ta)_2O_6$] with a beam of electrons, and reported an X-ray signal that they believed to be element 43, which they named "masurium" after after Masuria in eastern Prussia (now a part of Poland). However, their results could not be reproduced, and their claim was not accepted; recent research indicates they they may indeed have been able to produce very small amounts of element 43 by this method after all.

Technetium is used in several applications in nuclear medicine as a radioactive tracer, since it emits gamma rays that are detectable by imaging devices. It is obtained from a technetium-99m generator, also known as a "technetium cow," in which radioactive molybdenum-99 (with a half-life of 67 hours) is adsorbed onto an alumina chromatography column; the molybdenum-99 decays to water-soluble technetium-99m, which is extracted from the column by passing a saline solution through it (the process is naturally referred to as "milking"), whereupon it can be mixed with the reagent that is appropriate for the particular imaging technology to be used. In immunoscintigraphy, radioactive technetium-99m is incorporated into a monoclonal antibody which binds to cancer cells; this technique is used to detect intestinal cancers, which are difficult to locate by other techniques. In combination with tin compounds, technetium-99m binds to red blood cells, and can be used to map the circulatory system; this is particularly useful in diagnosing some types of congestive heart failure and in determining the damage done to the heart muscle by a heart attack.[14]

Ammonium pertechnate, NH_4TcO_4, and other technetium salts, can be used as corrosion inhibitors for steel, however, because of the radioactivity of technetium, this is useful only in closed systems.

III. RESULTS

Iron is an essential nutrient for almost all living organisms. Of the 4 grams of iron in the average human adult, about 65% is incorporated into the protein hemoglobin, which carries oxygen in the bloodstream from the lungs to the cells. The hemoglobin protein consists of four subunits, each of which contains a molecule called heme, a porphyrin ring which binds an iron in the +2 oxidation state; oxygen molecules "stick" to the iron ion, allowing transport of oxygen from the lungs to the various tissues of the body. Iron is also involved in the function of many of the body's enzymes, including those which synthesize DNA and those which metabolize carbohydrates. Iron is also bound by the transferrin protein, which carries iron between various cells in the body; it also acts as an antibiotic by preventing the uptake of iron by invading bacteria. Iron is easily obtained in the diet, from foods such as red meat, fish, poultry, liver, breakfast cereals, wine, lentils, beans, black-eyed peas, leafy vegetables, tofu, peanut butter, raisins, bread, and eggs. Despite the nutritional recommendations from the "Popeye" cartoons, spinach is not actually a good source of iron — even though it contains 2.7 mg per 100 g of spinach leaves, the oxalate ions ($C_2O_4^{2-}$) that are also found in spinach bind the iron very tightly, decreasing the amount that the body can extract.

In its compounds, the most common oxidation states of platinum are +2 and +4, but +3 and +6 states are also known.

Cisplatin, $PtCl_2(NH_3)_2$, also known as Platinol, Peyrone's chloride, and more formally as cis-diamminedichloroplatinum(II), is used in the chemotherapeutic treatment of some cancers. It works by attaching itself to sections of DNA which contain two guanine units next to each other; since it affects healthy cells as well as cancer cells, it causes a number of side effects, but many of these effects can be treated with other medications.

Colloidal silver is a suspension of silver used in "alternative" medicine as a antibiotic. However, prolonged use, or overdoses, of colloidal silver can lead to a condition called argyria, in which silver becomes deposited in tissues

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throughout the body, causing the skin to become bluish-gray. Although this is not harmful in itself, it is disfiguring, and it may not be possible to reverse the condition.

Gold salts are used in some treatments for arthritis, when non-steroidal anti-inflammatory drugs do not work. Because there are side effects from having gold build up in the body, this kind of treatment can only be used for a few years. Gold is also used in dentistry to fill cavities and make crowns; the gold is alloyed with silver, palladium, and zinc to harden the amalgam. Over 60 tons of gold per year are used in this fashion.[15]

Bioinorganic chemistry is a fast growing emerging field of science bridging inorganic chemistry and biology. Since long the importance of metal ions in biological systems has been known, though systematic study of their chemical and biochemical roles has started only in recent times. Metal ions such as sodium, magnesium, potassium, calcium etc., are present in living organisms in relatively large quantities and many other metal ions such as iron, copper, zinc, manganese, molybdenum, chromium, vanadium etc., occur in trace amounts. Though the total metal ion content in an adult man is nearly 2.5% of the body weight, (several of these are present in 'mg' quantities only) yet without these, life cannot sustain. So, the role of metal ions and metal complexes in biological processes has become very important. Since human body contains various metal ions as nutrients and micronutrients, it is important to study the coordinating ability of various metals. Most of the metals that are necessary in trace amount but essential for various body functions. Proteins containing transition metals are important to the living organisms due to their biological action. The transition metals have great importance in our lives. The transition metals and some of their alloys shaped the Bronze Age and Iron Age. Now due to the advancement of technology and aerospace industry, metals with high conductivity and greater strength are at top demand. Without these valuable metals, life simply would not exist. Transition metals are found everywhere on this Earth in various quantities. Most are not occur in a pure substance in the Earth's crust. Some metals that are rare can be sold at extremely high prices, like gold. Other metals are seen right in front of us.The computer is made up of transition metals. It has metals to send electrical currents. The chair we use, has metal ball-bearings in the wheels. The pictures hanging on the wall, they are hanging by nails, which are made up of metal alloys. Almost everything around us have been made from transition metals. Titanium is a relatively new transition metal which is in high demand due to its light weight, good strength, high temperature and corrosion resistance. It is used to make airplane bodies and engines.
Metals are in today's society have the highest demand. Metals are used to make bicycles, electrical toothbrushes, wires and refrigerators. Steel is used to make bridges and buildings. Anything that needs electricity has metal components because metals are electrical conductors. Transition metals are used as catalysts in many ways. Many times transition metals can be used to simply speed up a reaction. This is used because it is often economically quite cheaper to add some metal rather than waste time waiting for the reaction to occur. An example of this would be the use of a vanadium oxidizing catalyst in the process the making sulfuric acid. Metals are also the key ingredient in automobiles because of their strength, durability and extreme resistance to heat and fire. The main problem with transition metals is their easy way of oxidation. Due to oxidation the metals get corroded and become brittle. This can be overcome by making alloys. For example, alloys of chromium, has a higher corrosion resistance. Transition metals are also found in our bodies. They are key elements in life and evolution. The bronze, iron and steel ages would never have happened leaving us in the Stone Age. Research has shown significant progress in utilization of transition metal complexes as drugs to treat several human diseases. Transition metals exhibit different oxidation states and can interact with a number of negatively charged molecules. Humans excrete about 1 mg of iron every day and must constantly have 3 gm of iron in their bodies. The iron is mostly used as hemoglobin that transports oxygen to the brain and muscles. Iron deficiency or anemia, occurs when our body don't have enough iron and causes to become chronically tired. Cobalt is another transition metal our bodies need. It is a component of vitamin B_{12} which human need in their diet. Without iron, oxygen would not make it to the brain and life would not exist. Transition metals have become of utmost importance due to our every growing population and economy. Their demand will continue as long as life as we know it continues.[14]

Conclusions

Coordination chemistry being an important branch of inorganic chemistry, is undergoing an unprecedented pace of development both experimentally and theoretically. Since metals are endowed with unique properties the positive aspects in drug discovery can be continued for the design of new drugs. The therapeutic application of metal complexes is still to be explored in the area of research and useful to develop novel therapeutic agents. The exploration of transition metal complexes and their activation strategies, should continue further for future generations of drugs which may overcome some of the disadvantages associated with present drug therapies, including the unwanted side-effects. Therefore metal based drugs will surely take a key part of drug development to improve the quality of life of patients.[15]

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