



زانكۆی سه‌لاحه‌دین - هه‌ولێر
Salahaddin University-Erbil

First row transition metal complexes of saccharine ligand

Submitted to the department of (Chemistry) in partial fulfillment of the
requirements for the degree of **BSc.** in (Chemistry)

Prepared By:

Sara Hamid Awlla

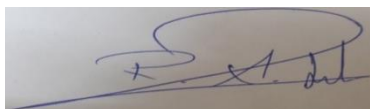
Supervised by:

Rezan Ali Saleh

April-2024

Supervisor recommendation

I am the student's supervisor, **Sara Hamid Awlla**. I support that the student has completed all the requirements for submitting the research drawn entitled ‘First row transition metal complexes of saccharine ligand’ according to the numbered administrative order / / on **oct.**in accordance with the instructions of Salahaddin university quality assurance and it is ready for discussion.



Supervisor

Rezan Ali Saleh

April 6, 2024

Research project lecturer

Dr. Dler D. Kurda

Dedication

To all my family members and friends.

To all my teachers, especially my supervisor.

To all who helped me to learn.

Acknowledgment:

To begin with, I thank (**Allah**) for His blessing, which made me able to complete and perform this study with success, the lord of the universe, blessing, and peace be on **Muhammad** (Allah's peace and prayers be upon him), thanks my parents for being with me and I would like thanks to my supervisors (M. Rezan) for suggesting this topic and giving me useful instruction throughout studying period, I express my deepest appreciation for this academic staff of Chemistry department.

Contents

Dedication.....	II
Acknowledgment:	II
Contents.....	III
Table of Figures	IV
Abstract	V
Part One	1
1. Introduction	1
1.1 Coordination compound.....	1
1.2. Transition metals	2
1.3. Heterocyclic compounds	3
1.4. Saccharinate ligand	4
Part Two	7
2. Literature Review.....	7
2.1 Complexes of saccharine ligand.....	7
Discussion	16
References	17

Table of Figures

Figure 1.1 Periodic table of elements.....	3
Figure 1.2 Coordination modes of saccharinate ligand.....	5
Figure 1.3 Chemical structure of acid saccharin (1), sodium saccharin (2) and calcium saccharin (3)	5
Figure 2.1 Crystal structure of $[\text{Mn}(\text{bipy})_2(\text{sac})(\text{H}_2\text{O})](\text{sac})$	7
Figure 2.2 Proposed structure of $[\text{Cu}(\text{na})_2(\text{sac})_2(\text{H}_2\text{O})]$	8
Figure 2.3 Proposed structure of $[\text{M}(\text{na})_2(\text{H}_2\text{O})_4](\text{sac})_2$, M = Co(II), Ni(II) and Zn(II)...	8
Figure 2.4 Crystal structure of $[\text{Zn}(\text{ea})_2(\text{sac})_2]$	9
Figure 2.5 Crystal structure of $[\text{Cu}_2(-\text{dea})_2(\text{sac})_2]$	9
Figure 2.6 Crystal structure of $[\text{Cu}(\text{N-sac})_2(\text{O-sac})(\text{H}_2\text{O})_2]$	10
Figure 2.7 Crystal structure of $[\text{Zn}(\text{N-sac})_3(\text{H}_2\text{O})]$	10
Figure 2.8 Crystal structure $[\text{Cu}(\text{terpy})(\text{sac})_2]$	11
Figure 2.9 Crystal structure of $[\text{Cd}(\text{dipyr})_2(\text{sac})(\text{H}_2\text{O})](\text{sac})\cdot\text{H}_2\text{O}$	11
Figure 2.10 Crystal structure of $[\text{Hg}(\text{dipyr})(\text{sac})_2]$	12
Figure 2.11 Proposed structure of $[\text{M}(\text{val})_2(\text{Hsac})_2]$	12
Figure 2.12 Crystal structure of $[\text{Cu}(\text{L})\text{sac}(\text{H}_2\text{O})]\text{Hsac}$	13
Figure 2.13 Crystal structure of $[\text{Cu}(\text{sac})(\text{S2AP})_2]$	13
Figure 2.14 Crystal structure of $[\text{Mn}(\text{NO}_3)(\text{sac})(\text{H}_2\text{O})(\text{bzimpy})]\cdot 2\text{DMF}$	14
Figure 2.15 Crystal structure of $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})(\text{bzimpy})]\cdot 2\text{H}_2\text{O}$	14
Figure 2.16 Crystal structure of $[\text{Cu}(\text{sac})_2(\text{bzimpy})]\cdot 3\text{DMF}$	15
Figure 2.17 Crystal structure of $[\text{Co}(\text{bzimpy})_2](\text{sac})_2\cdot 2\text{H}_2\text{O}$	15
Figure 2.18 Crystal structure of $[\text{Ni}(\text{bzimpy})_2](\text{sac})_2\cdot \text{H}_2\text{O}\cdot i\text{-PrOH}$	15
Figure 2.19 Crystal structure of $[\text{Cu}(\text{sac})_2(\text{NCNR}_2)(\text{H}_2\text{O})_2]$	16

First row transition metal complexes of saccharine ligand

Sara Hamid Awlla & Lec. Rezan A. Saleh

Abstract

My research is about first row transition metal complexes of saccharine ligand. Saccharin (o-sulfobenzamide or 1,2-benzothiazole-3(2H)-one 1,1-dioxide, Hsac) are two rings (6-membered and 5-membered ring) compound containing one N, one S and three O-atoms with chemical formula $C_7H_5NO_3S$. Saccharin belong heterocyclic class containing via the imino-nitrogen, carbonyl- or sulfonyl-oxygen atoms and can generate either N- or O- or S-monodentate or (N,O)-bidentate chelating complexes. Research on synthesis and structural analysis of metal-saccharin complexes has been active in the last two decades, because of their potential effectiveness in biological systems and the suspected carcinogenic nature of saccharin. Saccharin is an artificial sweetener with no food energy. Based on the reported literature, the sac ligand form complexes with metals such as Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(I), in which the sac ligand bound to the metal ions through N-atom or N,O-atoms. It has been proven that the sac ligands in some complexes are coordinated to the metal ions, while in some other complexes are uncoordinated and exist as ions outside of the coordination sphere.

Keywords: *Transition Metal complexes, saccharine ligand, review.*

Part One

1. Introduction

1.1 Coordination compound

One definition of a metal complex or coordination compound is ‘a compound formed from a Lewis acid and a Brønsted base’, a Lewis acid being an electron pair acceptor and the Brønsted bases attached to the metal ion in such compounds are called ligands. Ligands which interact with a metal ion through two or more donor atoms are of particular importance in coordination chemistry. The number of donor atoms involved is indicated by the denticity a didentate (or bidentate) ligand interacts with metals through two donor atoms, a tridentate (or terdentate) through three, and so on. If two or more of the donor atoms are interacting with the same metal center, the ligands are described as *chelating* and the complexes as *chelates*. It is generally found that there is an extra stability associated with complexes which contain chelating ligands the so-called *chelate effect*. Where a ligand is bound to a metal ion through a single donor atom, as with Cl^- , H_2O or NH_3 , the ligand is said to be unidentate (the ligand binds to the metal through a single point of attachment as if it had one structure (A. et al., 2010)). Many ligands are found as related neutral and anionic species (for example, water, hydroxide and oxide). Some ligands such as nitrite or thiocyanate can coordinate to a metal ion in more than one way. Where two donor atoms can be used to bind to a metal ion, as with $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, the ligand is said to be bidentate, and where several donor atoms are present in a single ligand as with $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$, the ligand is said to be polydentate. Sometimes ligands can bind to more than one metal ion in a bridging arrangement. Certain polydentate ligands are particularly good at linking together several metal ions and are referred to as polynucleating ligands, ligands which interact with a metal ion through two or more donor atoms are of particular importance in coordination chemistry (Gate et al., 2005).

1.2. Transition metals

The chemistry of the transition elements has been investigated for two centuries. The transition elements comprise groups 3 to 12 and are found in the central region of the standard elements are also, and interchangeably, known as the transition metals in view of their typical metallic properties periodic table (**Fig. 1.1**). This group is further subdivided into those of the first row (the elements scandium to zinc), the second row (the elements yttrium to cadmium) and the third row (the elements lanthanum to mercury). The term 'transition' arises from the elements' supposed transitional positions between the metallic elements of groups 1 and 2 and the predominantly non-metallic elements of groups 13 to 18. Compounds of the transition elements account for the majority of colored inorganic materials, and many pigments are relatively simple derivatives of these elements; however, not all transition-element compounds are colored. A transition element are elements which possessing filled or partially filled valence *d* orbitals in one or more of its oxidation states. This definition excludes the elements in groups 13 to 18. Werner also recognized that in the same way that a metal had one or more characteristic primary valences, a given metal ion also had a number of characteristic secondary valences Werner's key postulate was that a given metal ion could exert *two* different types of valence. The first of these related to the number of anionic groups which was associated with the compound and was termed the primary valence. The crucial observation was that the secondary valence could refer to the attachment of both anionic and neutral groups to the metal center (M. Gerloch et al., 1994)

Periodic table of the elements

group	1*	2											13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
lanthanoid series	6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu			
actinoid series	7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr			

Figure 1.1 Periodic table of elements

1.3. Heterocyclic compounds

Heterocyclic compounds are cyclic organic compounds which contain at least one hetero atom, the most common heteroatoms are nitrogen, oxygen and sulfur but heterocyclic rings containing other hetero atoms are also widely known (Morrison et al., 2002). A heterocyclic compound is one that contains a ring made up of more than one kind of atom. Cyclic compounds such as benzene, naphthalene, cyclohexanol, cyclopentadiene the rings are made up only of carbon atoms; such compounds are called homocyclic compounds. But there are also rings containing, in addition to carbon, other kinds of atoms, most commonly nitrogen, oxygen, or sulfur, are called heterocyclic compounds. The counterparts of heterocyclic compounds are homocyclic compounds, the rings of which are made of a single element. Although heterocyclic compounds may be inorganic, most contain at least one carbon. Since in organic chemistry non-carbons usually are considered to replace carbon atoms, they are called heteroatom, meaning different from carbon and hydrogen (Saini et al., 2013). Carbocyclic compound a cyclic organic compound containing all carbon atoms in ring formation. Heterocyclic compounds considered one of the vital classes of organic compounds, which are used in many biological fields, due to its activity in multiple illnesses. Heterocyclic compounds have a role in most fields of sciences such as medicinal chemistry, biochemistry also

another area of sciences. In this review, we cover most biological active heterocyclic compounds that it's recently synthesized or extracted from the plants such as antifungal, anti-inflammatory, antibacterial, antioxidants, anticonvulsant, antiallergic, herbicidal and anticancer(Al-Mulla, 2017).

1.4. Saccharinate ligand

Saccharin was discovered in 1878 by a Russian chemist named "Constantine Fahlberg"(Mahmood and Al-Juboori, 2020). Saccharin (o-sulfobenzamide or 1,2-benzothiazole-3(2H)-one 1,1-dioxide, Hsac) with chemical formula $C_7H_5NO_3S$, is one of the most well-known and widely used synthetic sweetening agents. Saccharin is a non-caloric sweetener, relatively insoluble in water but soluble in solvents such as ethanol, acetone, and methanol. Saccharin is of much interest in coordination chemistry as a versatile polyfunctional ligand, since the saccharinate anion offers different donor atoms to metal centers, the endocyclic N- and the exocyclic carbonyl or sulfonyl O-atoms. The coordination chemistry of the saccharin anion is very interesting as its donor atoms can chelate to a metallic center in different modes (**Fig. 1.2**), via the imino-nitrogen, carbonyl- or sulfonyl-oxygen atoms and can generate either N- or O- or S-monodentate or (N,O)-bidentate chelating complexes. Mixed-ligand complexes are formed when the metal ion binds to two different ligand moieties. However, there have also been published reports on the coordination of metal cations with the carbonyl- or sulfonyl-oxygen of saccharin. The donor atoms determine the coordination structure of the complexes and subsequently impact their biological properties(**Mokhtaruddin et al., 2017**).

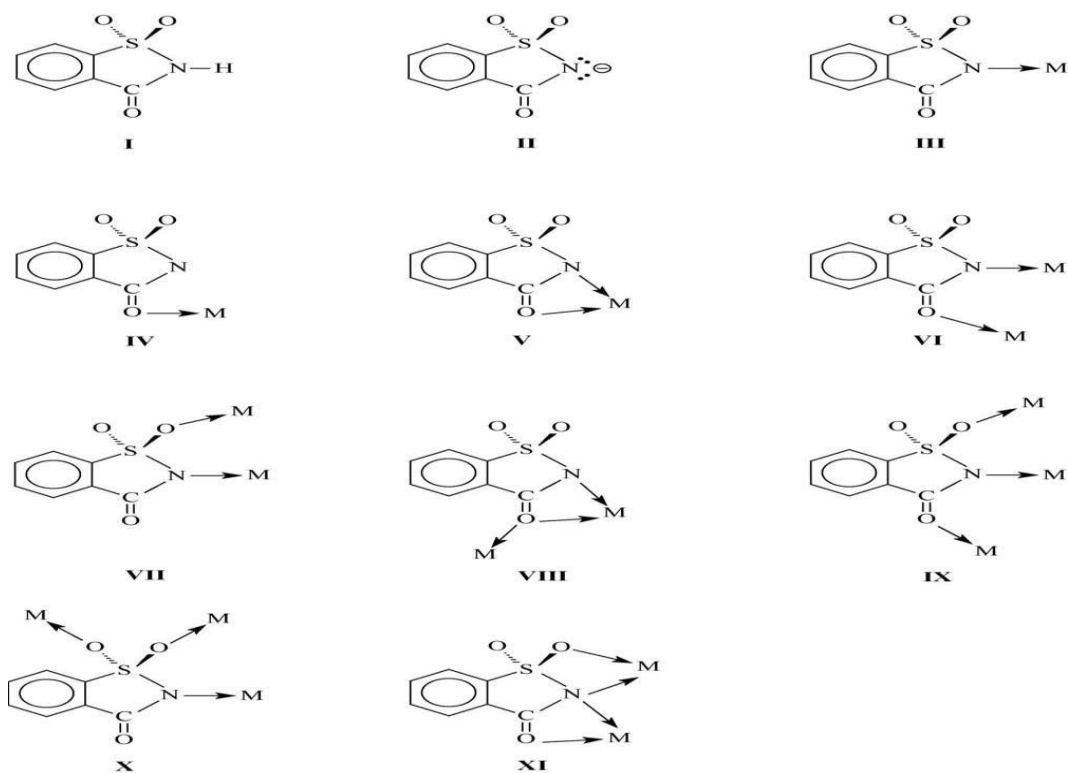


Figure 1.2 Coordination modes of saccharinate ligand

The first studies of saccharin complexes were carried out with the formation of aquo-complexes, due to the ability to coordinate with metals through the nitrogen atom. However, its poly functionality allowed to increase the number of possible complexes and the study of new chemical properties (Galloso et al., 2018). Saccharin is an artificial sweetener with no food energy. It is about 400 times as sweet as sucrose. It is a sulphonamide derivative of toluene, existing as acid saccharin, sodium saccharin and calcium saccharin (**Fig. 1.3**).

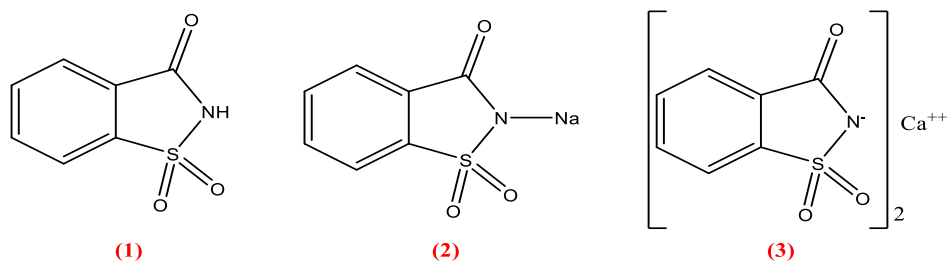


Figure 1.3 Chemical structure of acid saccharin (1), sodium saccharin (2) and calcium saccharin (3)

Saccharin is a weak organic acid, slightly soluble in water. Sodium saccharin has high solubility in water and because of its ease of production, it is the most generally used salt. Also, calcium saccharin is used in different food applications. Imino hydrogen is acidic and, therefore, can easily convert a molecule into a corresponding nitronium. The coordination chemistry of this ion has been shown to be very interesting and versatile, providing different coordination sites for metal nuclei, i.e. one N, one O (carboxylic) and two O (sulfonic) atoms (Al-Obaidi et al., 2022). Research on synthesis and structural analysis of metal-saccharin complexes has been active in the last two decades, because of their potential effectiveness in biological systems and the suspected carcinogenic nature of saccharin. Saccharin in its deprotonated form (sac⁻) interacts with trace elements in the human body and readily forms complexes with a large number of metal ions (Yilmaz et al., 2002). Nowadays, it is generally recognized as safe in the US and it has also been suggested that the importance of sac lies in its potential use as an antidote for metal poisoning (Kumar et al., 2020).

Part Two

2. Literature Review

2.1 Complexes of saccharine ligand

Dillon and coworkers in **1999**, synthesized $[\text{Mn}(\text{bipy})_2(\text{sac})(\text{H}_2\text{O})](\text{sac})$ (**Fig. 2.1**) complex where (bipy = 2,2'-bipyridine; sac = saccharinate). The crystal structure of the synthesized complex reveals that the complex consists of, $[\text{Mn}(\text{bipy})_2(\text{sac})(\text{H}_2\text{O})]^+$ cation and non-coordinated saccharinate (sac^-) anion. The Mn(II) ion constitutes the center of a slightly distorted octahedron, with the water molecule hydrogen bonded to the N atom in the saccharinate counter-ion (Dillon et al., 1999).

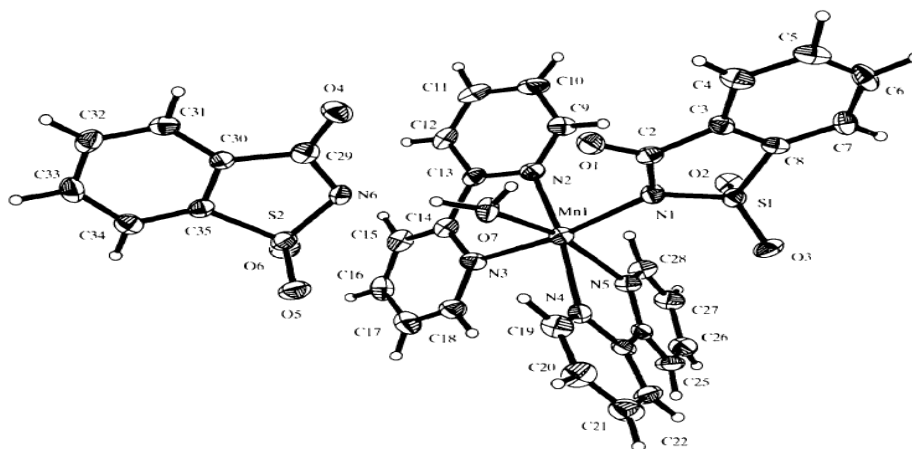


Figure 2.1 Crystal structure of $[\text{Mn}(\text{bipy})_2(\text{sac})(\text{H}_2\text{O})](\text{sac})$

Çakır and coworkers in **2001**, synthesized complexes of the type $[\text{Cu}(\text{na})_2(\text{sac})_2(\text{H}_2\text{O})]$ (**Fig. 2.2**) and $[\text{M}(\text{na})_2(\text{H}_2\text{O})_4](\text{sac})_2$ (**Fig. 2.3**), where M = Co(II), Ni(II) and Zn(II), na = nicotinamide. The complexes are characterized by elemental analysis, FT-IR spectroscopic study, UV-Vis spectrometric and magnetic susceptibility data. The structure of Cu(II) complex is completely different from those of the Co(II), Ni(II) and Zn(II) complexes. It has been proven that the saccharinato ligands in the structure of the Cu complex are coordinated to the metal ion through N-atom, while in the Co(II), Ni(II) and Zn(II) complexes are uncoordinated and exist as ions (Çakır et al., 2001).

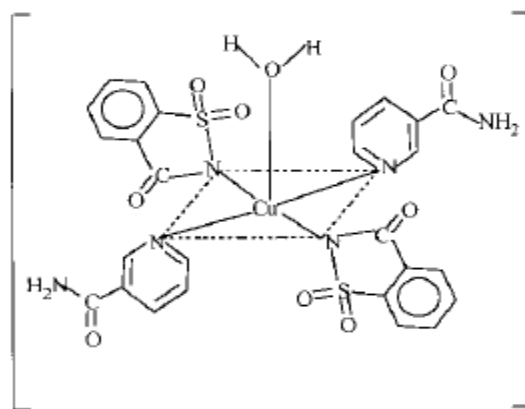


Figure 2.2 Proposed structure of $[\text{Cu}(\text{na})_2(\text{sac})_2(\text{H}_2\text{O})]$

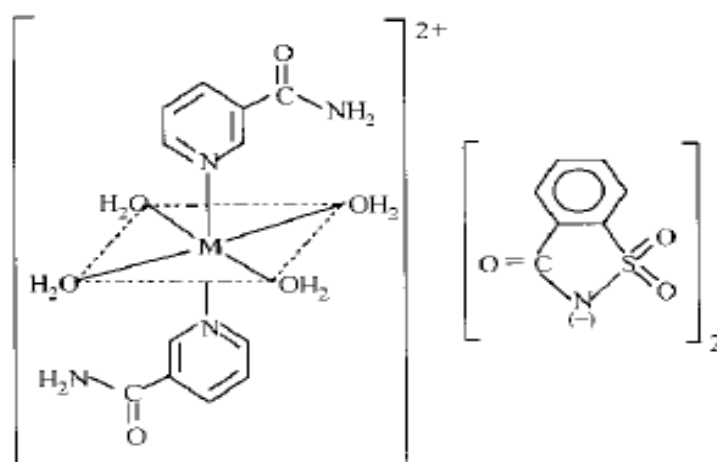


Figure 2.3 Proposed structure of $[\text{M}(\text{na})_2(\text{H}_2\text{O})_4](\text{sac})_2$, $\text{M} = \text{Co}(\text{II}), \text{Ni}(\text{II})$ and $\text{Zn}(\text{II})$

Yilmaz coworkers in **2001**, synthesized new complexes of saccharin with ethanolamine (**ea**) and diethanolamine (**dea**) of the type $[\text{Zn}(\text{ea})_2(\text{sac})_2]$ (**Fig. 2.4**) and $[\text{Cu}_2(\text{dea})_2(\text{sac})_2]$ (**Fig. 2.5**). The crystal structures of the two complexes were determined by single crystal X-ray diffraction. In the Zn(II) complex, the Zn(II) ion is octahedrally coordinated by two bidentate **ea** (N,O) and two monodentate **sac** (N) ligands. The saccharinate anion coordinates to the Cu(II) ion through its N-atom (Yilmaz et al., 2001).

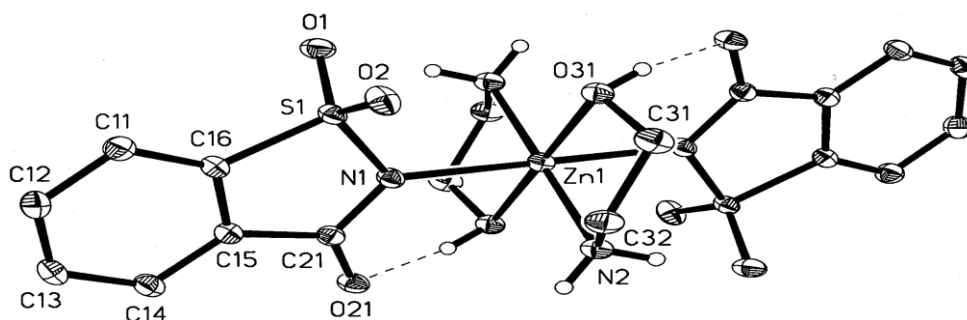


Figure 2.4 Crystal structure of $[\text{Zn}(\text{ea})_2(\text{sac})_2]$

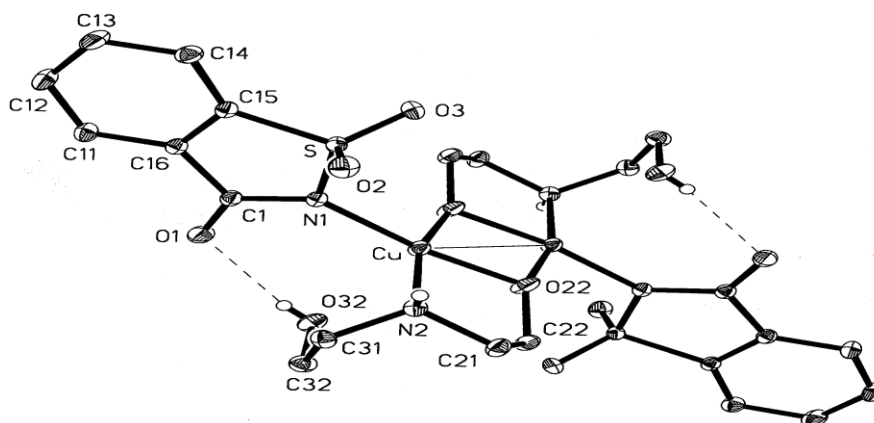


Figure 2.5 Crystal structure of $[\text{Cu}_2(-\text{dea})_2(\text{sac})_2]$

Yilmaz and coworkers in **2005**, synthesized complexes of the type $\text{ApyH}[\text{Cu}(\text{N-sac})_2(\text{O-sac})(\text{H}_2\text{O})_2]$ (**1**) (**Fig. 2.6**) and $\text{ApyH}[\text{Zn}(\text{N-sac})_3(\text{H}_2\text{O})]$ (**2**) (**Fig. 2.7**) as a result of reaction of Schiff base salicylideneaminopyridine (**ApyH**) with $[\text{M}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$, where $\text{M} = \text{Cu}(\text{II})$ or $\text{Zn}(\text{II})$. The crystal structure reveal that, the sac ligands in complex (**1**) exhibit unusual and non-equivalent coordination, behaving as ambidentate ligands. One of them coordinates to the metals through the carbonyl O-atom, while the other two sac ligands are bonded to the metals via the iminoN-atom. However, the zinc(II) ion in (**2**) is tetrahedrally coordinated by three N-donor sac ligands and an aqua ligand(Yilmaz et al., 2005).

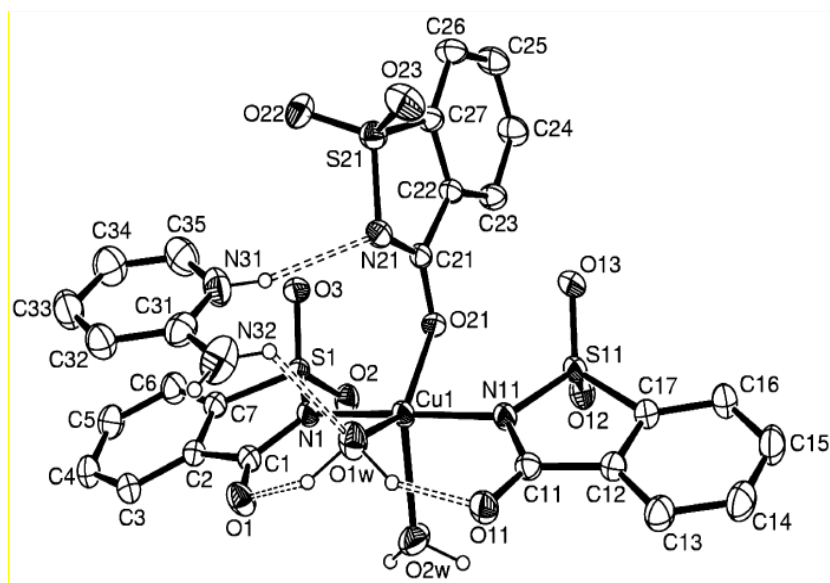


Figure 2.6 Crystal structure of $[\text{Cu}(\text{N-sac})_2(\text{O-sac})(\text{H}_2\text{O})_2]$

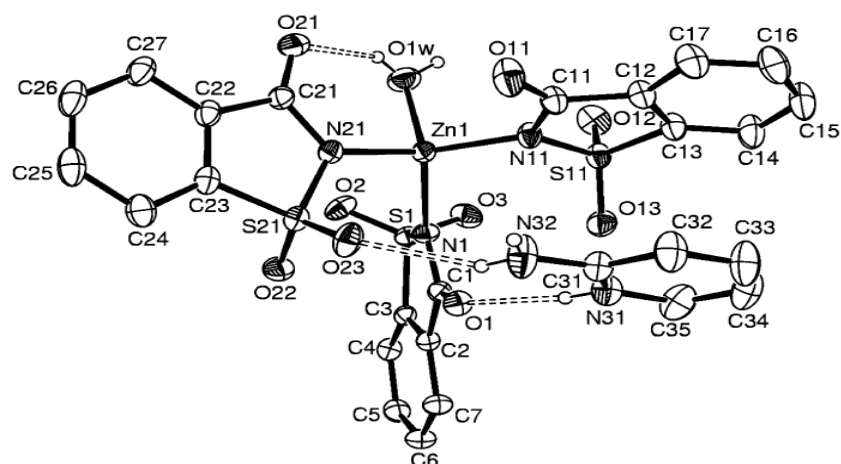


Figure 2.7 Crystal structure of $[\text{Zn}(\text{N-sac})_3(\text{H}_2\text{O})]$

Deng and coworkers in **2007**, synthesized complex of the type $[\text{Cu}(\text{terpy})(\text{sac})_2]$ (**Fig. 2.8**), where **terpy**= 2,2',6,2''-terpyridine. The crystal structure of the synthesized complex reveals that the sac ligand behaved as a monodentate fashion that coordinated to the copper ion through N-atom with one terpy ligand in a five coordinated arrangement (Deng et al., 2008).

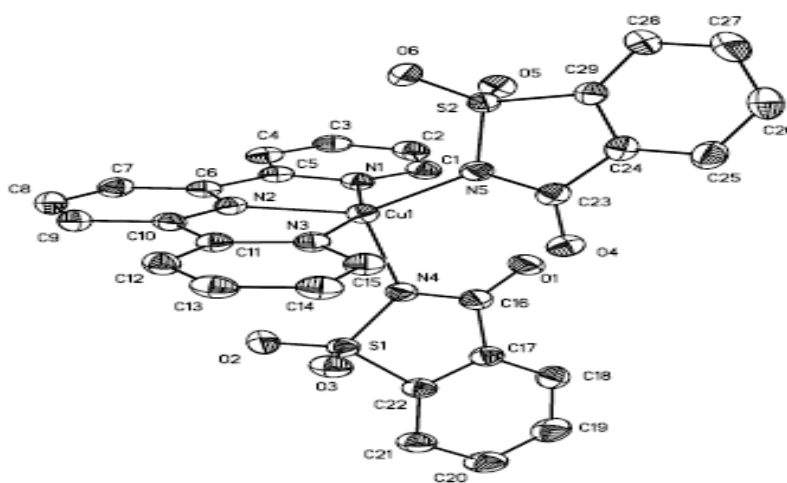


Figure 2.8 Crystal structure $[\text{Cu}(\text{terpy})(\text{sac})_2]$

Deng and coworkers in **2009**, synthesized $[\text{Cd}(\text{dipyr})_2(\text{sac})(\text{H}_2\text{O})]\text{sac}\cdot\text{H}_2\text{O}$ (**1**) (**Fig. 2.9**) and $[\text{Hg}(\text{dipyr})(\text{sac})_2]$ (**2**) (**Fig. 2.10**) complexes, where **dipyr** = dipyridylamine. Both complexes have been fully characterized by single-crystal X-ray diffraction. The geometry around Cd in **1** is approximately octahedral, with the metal coordinated by two bidentated**dipyr** ligands, one N-bonded sac and one H_2O molecule; the second sac forms the counter-ion, and there is also a water of crystallisation. In the anhydrous Hg complex **2**, the metal has approximately tetrahedral geometry, with coordination from a bidentated**dipyr** ligand and two N-bonded sac groups (Deng et al., 2009).

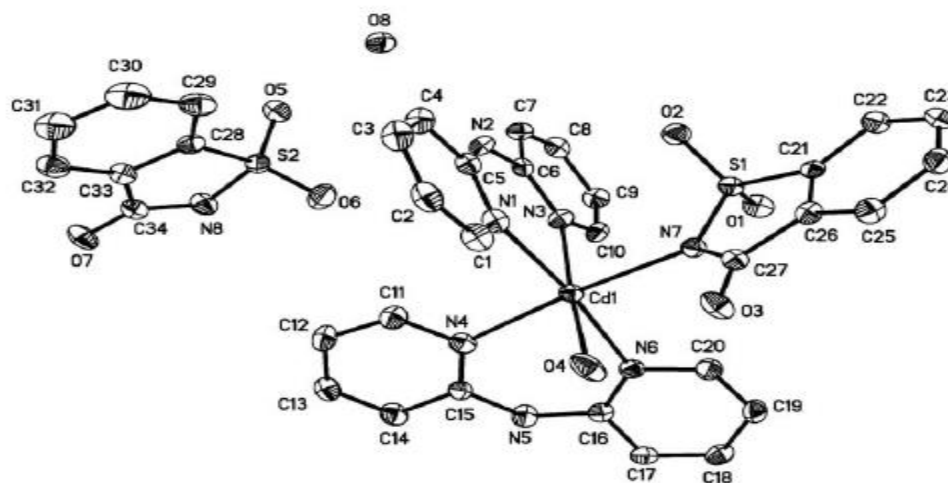


Figure 2.9 Crystal structure of $[\text{Cd}(\text{dipyr})_2(\text{sac})(\text{H}_2\text{O})](\text{sac})\cdot\text{H}_2\text{O}$

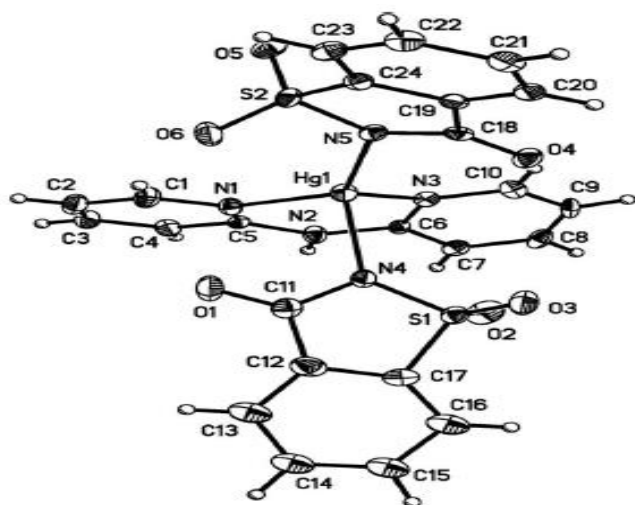


Figure 2.10 Crystal structure of $[\text{Hg}(\text{dipyr})(\text{sac})_2]$

Fayad and coworkers in **2012**, synthesized a series of mixed ligand complexes of the type $[\text{M}(\text{val})_2(\text{Hsac})_2]$ (**Fig. 2.11**) where $\text{M} = \text{Mn}(\text{II}), \text{Fe}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II}), \text{Zn}(\text{II})$ and $\text{Cd}(\text{II})$ and **val** = L-valine. All complexes have been characterized by molar conductance, magnetic susceptibility, infrared, electronic spectral and elemental analysis. According to characterization data, all complexes are formed as an octahedral geometry in which the sac ligand behaved as a monodentate N-donor fashion (Fayad et al., 2012).

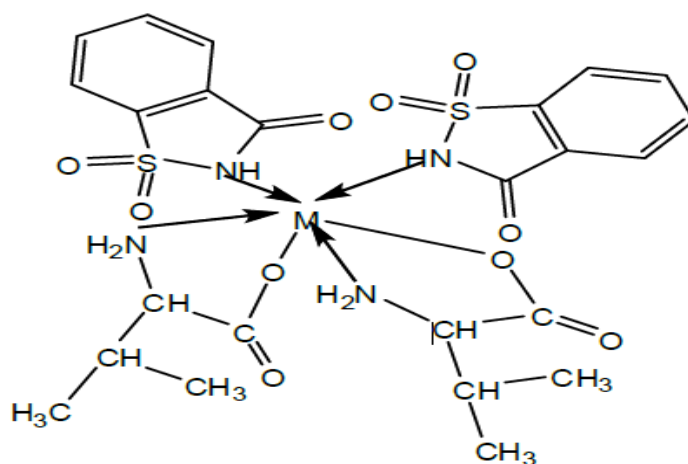


Figure 2.11 Proposed structure of $[\text{M}(\text{val})_2(\text{Hsac})_2]$

Omer and coworkers in **2014**, synthesized $[\text{Cu}(\text{L})(\text{sac})(\text{H}_2\text{O})]\text{Hsac}$ (**Fig. 2.12**) complex, where $\text{L} = (\text{E})\text{-N-Methyl-2-(1-(5-methylpyridin-2-yl)ethylidene)hydrazinecarbothioamide}$. The molecular structure of the synthesized complex, reveal that the complex has distorted square-pyramidal structure and one sac ligand is coordinated to copper metal through N-atom with a non-bonded saccharin molecule present in the outer coordination sphere(Omar et al., 2014).

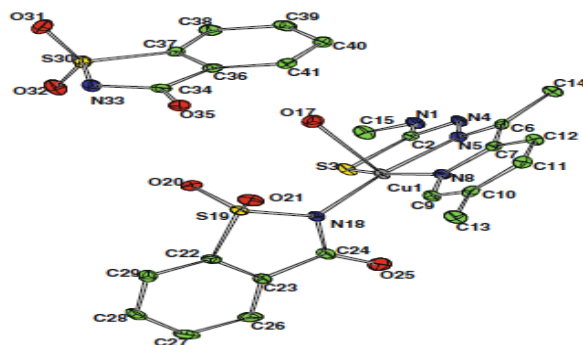


Figure 2.12 Crystal structure of $[\text{Cu}(\text{L})\text{sac}(\text{H}_2\text{O})]\text{Hsac}$

Mokhtaruddin and coworkers in **2017**, synthesized, $[\text{Cu}(\text{sac})(\text{S}_2\text{AP})]_2$ (**Fig. 2.13**) when $\text{S}_2\text{APH} = 2\text{-acetyl-4-methylpyridine}$, The crystal structure of the synthesized complex showed that the $\text{Cu}(\text{II})$ atom was coordinated to the thiolate-S, azomethine-N and pyridyl-N donors of the S_2AP Schiff base and to the saccharinate-N from one anion, as well as to the carbonyl-O atom from a symmetry related saccharinate anion yielding a square pyramidal geometry(Mokhtaruddin et al., 2017).

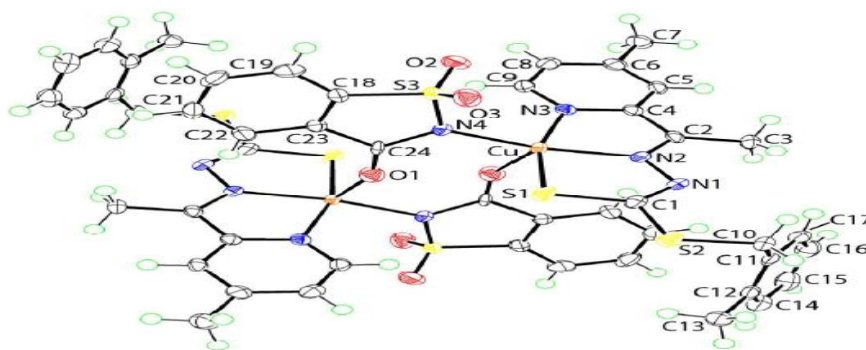


Figure 2.13 Crystal structure of $[\text{Cu}(\text{sac})(\text{S}_2\text{AP})]_2$

Icsele and coworkers in 2020, synthesized complexes $[\text{Mn}(\text{NO}_3)(\text{sac})(\text{H}_2\text{O})(\text{bzimpy})]\cdot 2\text{DMF}$ (Fig. 2.14), $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})(\text{bzimpy})]\cdot 2\text{H}_2\text{O}$ (Fig. 2.15), $[\text{Cu}(\text{sac})_2(\text{bzimpy})]\cdot 3\text{DMF}$ (Fig. 2.16), $[\text{Co}(\text{bzimpy})_2](\text{sac})_2\cdot 2\text{H}_2\text{O}$ (Fig. 2.17) and $[\text{Ni}(\text{bzimpy})_2](\text{sac})_2\cdot \text{H}_2\text{O}\cdot i\text{-PrOH}$ (Fig. 2.18) (where $\text{bzimpy} = 2,6\text{-bis}(2\text{-benzimidazolyl})\text{pyridine}$). The crystal structure reveals that the sac ligand functions as a monodentate N-donor ligand while in $[\text{Cu}(\text{sac})_2(\text{bzimpy})]\cdot 3\text{DMF}$, the two- sac ligand coordinated through N and O-atoms. In $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ complexes the sac ligand is located out of the coordination sphere. The $\text{Mn}(\text{II})$, $\text{Fe}(\text{II})$, $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ ions have a distorted octahedral geometry (Icsele et al., 2020).

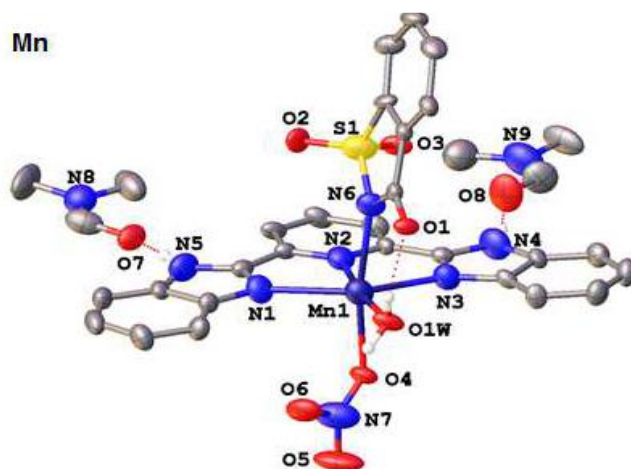


Figure 2.14 Crystal structure of $[\text{Mn}(\text{NO}_3)(\text{sac})(\text{H}_2\text{O})(\text{bzimpy})]\cdot 2\text{DMF}$

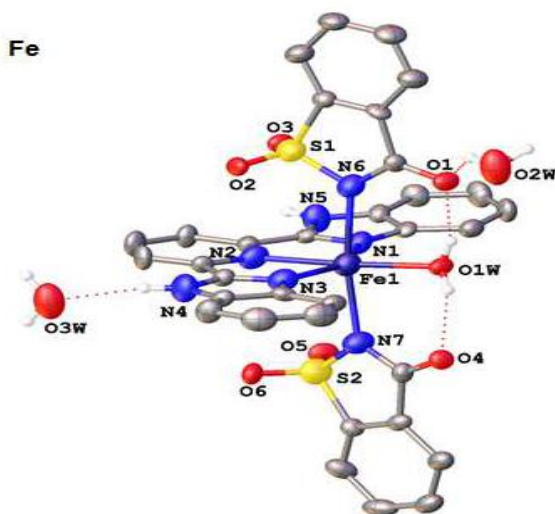


Figure 2.15 Crystal structure of $[\text{Fe}(\text{sac})_2(\text{H}_2\text{O})(\text{bzimpy})]\cdot 2\text{H}_2\text{O}$

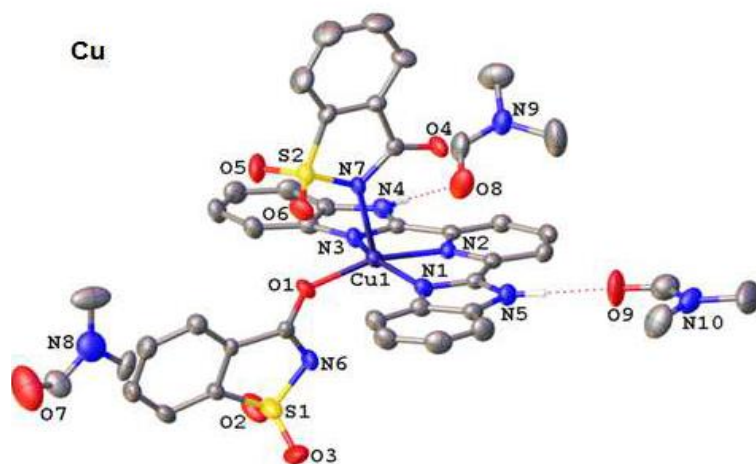


Figure 2.16 Crystal structure of $[\text{Cu}(\text{sac})_2(\text{bzimpy})]\cdot 3\text{DMF}$

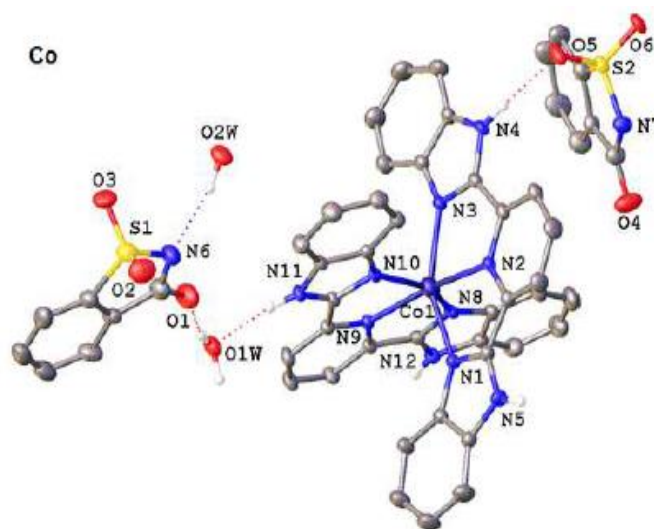


Figure 2.17 Crystal structure of $[\text{Co}(\text{bzimpy})_2](\text{sac})_2\cdot 2\text{H}_2\text{O}$

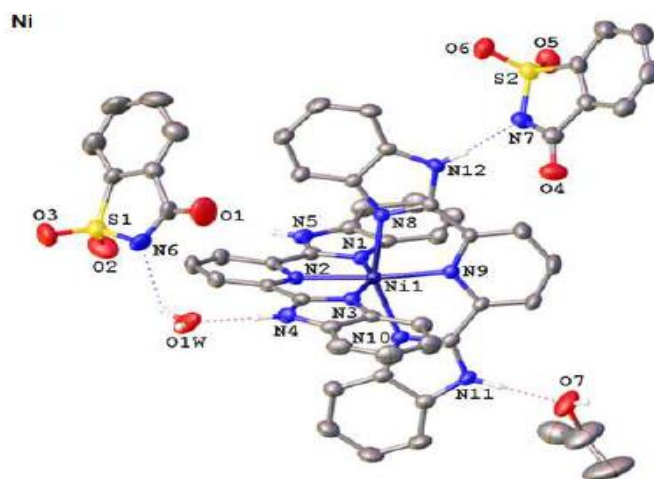


Figure 2.18 Crystal structure of $[\text{Ni}(\text{bzimpy})_2](\text{sac})_2\cdot \text{H}_2\text{O}\cdot i\text{-PrOH}$

Toikka and coworkers in 2021, synthesized $[\text{Cu}(\text{sac})_2(\text{NCNMe}_2)(\text{H}_2\text{O})_2]$ (Fig. 2.19) (NCNMe_2 = dimethyl cyanamide). Molecular structure of the complex displayed that the sac ligand coordinated to the metal ion through N-atom (Toikka et al., 2021).

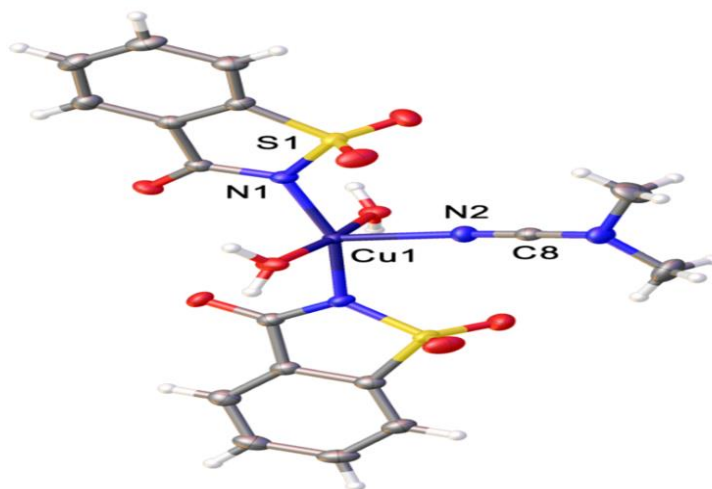


Figure 2.19 Crystal structure of $[\text{Cu}(\text{sac})_2(\text{NCNR}_2)(\text{H}_2\text{O})_2]$

Discussion

This study is a review project, aims to collect first raw transition metal complexes of saccharinate ligand. According to the reported literature, sac ligand form complexes with metals such as Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(I) in a tetrahedral, square pyramidal, distorted square pyramidal, octahedral or distorted octahedral coordination geometry. Characterization data as well as X-ray structure of the reported complexes reveal that the sac ligand functions as a monodentate ligand coordinating to the metal ions through either N or O atom. While in some complexes it exist as ions outside of the coordination sphere.

Conclusion

Saccharin (o-sulfobenzoimide or 1,2-benzothiazole-3(2H)-one 1,1-dioxide, H₅CO₂S) with chemical formula C₇H₅NO₃S, is one of the most well-known and widely used synthetic sweetening agents. Saccharin is of much interest in coordination chemistry as a versatile polyfunctional ligand, since the saccharinate anion offers different donor atoms to metal centers, the endocyclic N- and the exocyclic carbonyl or sulfonyl O-atoms.

Characterization data as well as X-ray structure of the reported complexes reveal that the sac ligand functions either as a monodentate ligand coordinating to the metal ions through either N or O atoms. While in some complexes it exists as ions outside of the coordination sphere.

References

- A., G., AND & LAWRENCE 2010. *Introduction to Coordination Chemistry, First edition* A John Wiley and Sons, Ltd., .
- AL-MULLA, A. 2017. A review: biological importance of heterocyclic compounds. *Der Pharma Chemica*, 9, 141-147.
- AL-OBAIDI, N. S., AHMED, A. A. & ABD, A. N. 2022. Synthesis, Characterization And Evaluation Antibacterial Activity For Mixed-Ligand Complexes Of Saccharine and Acetylacetonato. *Synthesis*, 140.
- ÇAKIR, S., BULUT, I., NAUMOV, P., BIÇER, E. & ÇAKIR, O. 2001. Synthesis and spectroscopic studies of novel Cu (II), Co (II), Ni (II) and Zn (II) mixed ligand complexes with saccharin and nicotinamide. *Journal of Molecular Structure*, 560, 1-7.
- DENG, R. M., DILLON, K. B., GOETA, A. E., MAPOLELO, M. & SHEPHERD, H. J. 2009. The synthesis, crystal and molecular structures of two saccharinate–metal complexes with dipyr as a co-ligand. *Inorganica Chimica Acta*, 362, 5109-5112.

- DENG, R. M., DILLON, K. B., GOETA, A. E. & SEKWALE, M. S. 2008. Synthesis and structural characterisation of four saccharinate–Metal complexes with 2, 2': 6, 2''-terpyridine (terpy) as a co-ligand. *Inorganica Chimica Acta*, 361, 1542-1546.
- DILLON, K. B., BILTON, C., HOWARD, J. A., HOY, V. J., DENG, R. M. & SETHATHO, D. T. 1999. The first manganese (II) compound with the saccharinate ligand present both in the complex cation and as the counter-ion: [Mn (bipy) 2 (sac)(H₂O)]⁺. sac⁻. *Acta Crystallographica Section C: Crystal Structure Communications*, 55, 330-332.
- FAYAD, N., AL-NOOR, T. H. & GHANIM, F. 2012. Synthesis, characterization, and antibacterial activities of manganese (II), cobalt (II), iron (II), nickel (II), zinc (II) and cadmium (II) mixed-ligand complexes containing amino acid (L-Valine) and saccharin. *Adv. Phys. Theor. Appl*, 9, 1-13.
- GALLOSO, M. C., ANGULO-CORNEJO, J. R., LINO-PACAHECO, M. N., HUERTA, C. C. V., SORIANO, E. M. C. & ANGULO-CORNEJO, J. R. 2018. Synthesis and characterization of mixed-ligand silver (I) saccharinate complex containing (2-(2-pyridyl) benzimidazole. *Revista Colombiana de Química*, 47, 73-78.
- GATE, E., AND & HARLOW 2005. *INORGANIC CHEMISTRY, second edition* Library of Congress Cataloging.
- ICSEL, C., YILMAZ, V. T., AYDINLIK, Ş. & AYGUN, M. 2020. New manganese (II), iron (II), cobalt (II), nickel (II) and copper (II) saccharinate complexes of 2, 6-bis (2-benzimidazolyl) pyridine as potential anticancer agents. *European Journal of Medicinal Chemistry*, 202, 112535.
- KUMAR, P., BUTCHER, R. J. & PATRA, A. K. 2020. Ternary Co (II), Ni (II) and Cu (II) complexes containing dipyrrophenazine and saccharin: Structures, reactivity, binding interactions with biomolecules and DNA damage activity. *Inorganica Chimica Acta*, 506, 119532.
- M. GERLOCH, AND & CONSTABLE, E. G. 1994. *Transition Metal Chemistry, first edition* VCH Verlagsgesellschaft mbH.
- MAHMOOD, A. A. R. & AL-JUBOORI, S. B. 2020. A Review: Saccharin Discovery, Synthesis, and Applications. *Ibn AL-Haitham Journal For Pure and Applied Sciences*, 33, 43-61.
- MOKHTARUDDIN, N. S. M., YUSOF, E. N. M., RAVOOF, T. B., TIEKINK, E. R., VEERAKUMARASIVAM, A. & TAHIR, M. I. M. 2017. Unusual saccharin-N, O (carbonyl) coordination in mixed-ligand copper (II) complexes: Synthesis, X-ray crystallography and biological activity. *Journal of Molecular Structure*, 1139, 1-9.

- MORRISON, R. T., AND & BOYD, R. N. 2002. *organic chemistry, SIXTH EDITION*, Prentice-Hall of Indis.
- OMAR, S. A., RAVOOF, T. B., TAHIR, M. I. M. & CROUSE, K. 2014. Synthesis and characterization of mixed-ligand copper (II) saccharinate complexes containing tridentate NNS Schiff bases. X-ray crystallographic analysis of the free ligands and one complex. *Transition Metal Chemistry*, 39, 119-126.
- SAINI, M. S., KUMAR, A., DWIVEDI, J. & SINGH, R. 2013. A review: biological significances of heterocyclic compounds. *Int. J. Pharm. Sci. Res*, 4, 66-77.
- TOIKKA, Y. N., SPIRIDONOVA, D. Y. V., NOVIKOV, A. S. & BOKACH, N. A. 2021. Copper (II) Prevents the Saccharine-Dialkylcyanamide Coupling by Forming Mononuclear (Saccharinate)(Dialkylcyanamide) copper (II) Complexes. *Inorganics*, 9, 69.
- YILMAZ, V., KARADAG, A. & THOENE, C. 2002. Metal complexes of saccharin with the N-(2-hydroxyethyl)-ethylenediamine ligand: Synthesis, characterization and spectroscopic examination. Crystal structures of trans-bis (saccharinato) bis {N-(2-hydroxyethyl)-ethylenediamine} copper (II) and cadmium (II). *Journal of Coordination Chemistry*, 55, 609-618.
- YILMAZ, V. T., TOPCU, Y., YILMAZ, F. & THOENE, C. 2001. Saccharin complexes of Co (II), Ni (II), Cu (II), Zn (II), Cd (II) and Hg (II) with ethanolamine and diethanolamine: synthesis, spectroscopic and thermal characteristics. Crystal structures of [Zn (ea) 2 (sac) 2] and [Cu₂ (μ-dea) 2 (sac) 2]. *Polyhedron*, 20, 3209-3217.
- YILMAZ, V. T., YILMAZ, F. & KAZAK, C. 2005. The first tris (saccharinato) complexes. Syntheses, spectral, thermal and structural characterization of ApyH [Cu (N-sac) 2 (O-sac)(H 2 O) 2] and ApyH [Zn (N-sac) 3-(H 2 O)](ApyH= 2-aminopyridinium and sac= saccharinate). *Transition metal chemistry*, 30, 95-102.