----Raf. Jour. Sci., Vol.17, No. 4 Chemistry, Special Issue, pp.1-14, 2006----

Preparation and Study of Some Effects of γ – Radiation on Some New Copper(II) Complexes Containing Mixed Ligands; Substituted Salicylic Acid and Benzoin semicarbazone

Zuhoor F. Dawood **Younis T. Mahmood**
Department of Chemistry
College of Education
Mosul University

(Received 11/9/2005 , Accepted 27/3/2006)

ABSTRACT

Complexes of the type [Cu(BˋSCH)(AH)]$(NO_3)_2$ and [Cu(BˋSC)(A)] have been prepared in neutral and basic mediam, respectively, (where AH= substituted salicylic acid: salicylic acid-SA and o-acetylsalicylic acid-OASA and 3,5-dinitrosalicylic acid-DNSA or 5-aminosalicylic acid-ASA or 5-sulphosalicylic acid-SSA; A=deprotonated form of the AH ligand; BˋSCH=benzoin semicarbazone; BˋSC=deprotonated form of the ligand BˋSCH).The prepared complexes were characterized by copper ion determination, relative molecular weight determination, magnetic and molar conductance measurements, infrared and electronic spectral data.

The effect of γ-rays have been studied on the aqueous solutions of the complexes under conditions where the hydroxyl radicals were scavenged by 10^{-3} M sodium formate in presence of dinitrogen gas at room temperature (25 ± 2 ^{o}C). Results indicated that copper (II) was reduced to copper (I) and a charge transfer between metal ion and ligands in some complexes were noticed. Some complexes have been completely decomposed while others did not affect by the radiolysis.

التحضير ودراسة بعض تأثيرات أشعة – γ على عدد من المعقدات الجديدة للنحاس (II) الحاوية على مزيج من الليكاندات: حامض السالساليك المعوض وبنزوين سميكاربازون

الملخص

حضرت معقدات ذات صيغ [Cu(BˋSCH)(AH)]$(NO_3)_2$) و [Cu(BˋSC)(A)] في كل من الوسطين المتعادل والقاعدي على التوالي (حيث AH = حامض السالساليك المعوض: حامض السالساليك SA أو أورثو- أسيتيل حامض السالساليك OASA و3،5- ثنائي نيترو حامض السالساليك DNSA و 5- أمينو حامض السالساليك ASA و5- سلفو حامض السالساليك SSA وA = الليكاندات AH مزال منها بروتون وBˋSCH = بنزوين سميكاربازون، BˋSC = الليكاند بنزوين سميكاربازون مزال منه بروتون). شخصت المعقدات بتعيين كمية ايون النحاس والوزن الجزيئي النسبي، وقياس المغناطيسية والتوصيلية المولارية، ودراسة أطياف الأشعة تحت الحمراء والأطياف الالكترونية.

درس تأثير أشعة كاما على هذه المعقدات تحت ظروف حجبت فيها جذور الهيدروكسيل باضافة محلول فورمات الصوديوم (10^{-3} مولار) وبوجود غاز النتروجين وعند درجة حرارة الغرفة (25 ± 2 °م)، دلت النتائج على أن النحاس (II) يختزل إلى النحاس (I) كما تم استنتاج وجود إنتقال الشحنة بين الأيون الفلزي والليكاندات في بعض المعقّدات، فضلا عن تفكك بعض المعقدات تماماً فيما لم يتأثرالبعض الآخر بالإشعاع .

INTRODUCTION

Semicarbazones are organic compounds serve as ligands forming an important class of biologically active ligands and providing models for metal-ligand bonding sites in several enzymes (Campbell et al., 1988). A good deal of work has been reported concerning the preparation and structural investigation of semicarbazones and their complexes (Yin et al., 2000) (Gupta et al., 2003). This is due to their ability to act as a multidentate donor in addition to their importance in biological applications (Kumar and Tolani, 1989) (Kanoongo et al., 1987) (Kasuga et al., 2001).

There has been a growing interest in the formation of ligand chelates involving mixed ligand and transition metals of different oxidation states which could form chelates with ligands containing different donation sites (Afrasiabi et al., 2005). However, coordination compounds of mixed ligands are of a considerable importance in the field of metalloenzymes and other biological activities (Hussain et al., 2000) (Ramesh and Sivagamasundari, 2003). Hence a large body of coordination compounds containing mixed ligands with transition and non-transition metal ions have been reported recently (Yao et al., 2004) (El-ajaily and Maihub, 2003) (Hassan, 2005). Due to the importance of semicarbazone and mixed ligands, we took a humble part in the chemistry of their complexes. Recently some articles have been published concerning their coordination chemistry with transition and non-transition metal ions (Dawood, 2002) (Dawood and Al-Shamaa, 2005) (Dawood et al., 2004).

Copper and it's compounds have been used as an adjunct to radioprotectant treatment to prevent radiation damage of normal tissues. It is known that concentrations of normal plasma copper containing components, e.g. the protein ceruloplasmin which contained 6-8 Cu atoms increased in response to many cancers. This increases in plasma copper has been interpreted as a physiological response which facilitated remission of cancer since it is known that copper complexes had anticancer activity. Copper complexes (eg. tetrakis-μ-3,5-diisopropylsalicylatodiaquodicopper(II)) had in fact anticancer, anticarcinogenic and antimutagenic activities. The contribution of this complex in tumour tissue in radiation therapy, may also having antitumour effect in addition to protecting normal tissue from the effects of ionizing radiation (Sorenson, 1989). Copper complexes may also had other useful applications, an effective compounds would be useful for those people who might experience sudden accidental exposure to higher than normal levels of ionizing radiation, moreover copper complexes are relatively non toxic. German and French physicians had successfully treated patients with arthritic or other degenerative diseases using copper complexes without observing serious toxic effects (Sorenson, 1989). Since some complexes have been involved in biological systems though some of these system involved reducing free radical.

The hydrated electron and hydrogen atoms have been capable to reduce the central metal ions (Sellers, 1981). There has been considerable interest in the radiolysis of copper (II) complexes, recently (Sellers, 1981) (Guldi et. al, 1996) (Sallomi et al., 2002).

To the best of our knowledge, the preparation and characterization of copper (II) complexes containing mixed ligands (benzoin semicarbazone-B`SCH and substituted salicylic acids SA, OASA, DNSA , ASA or SSA) and study the effect of gamma radiation on such complexes have not yet been reported. It is a matter of interest to study the effect of gamma irradiation on these new complexes.

EXPERIMENTAL

I. Material :

Copper(II) nitrate, benzoin, semicarbazide hydrochloride, salicylic acid, o-acetylsalicylic acid, 3,5-dinitrosalicylic acid, 5-aminosalicylic acid, 5-sulphosalicylic acid, sodium formate, nitric acid, dimethylformamide, ethanol, potassium hydroxide, sodium hydroxide, ammonium ferrous suphate, sulfuric acid, sodium chloride (Fluka, BDH or Alderich) have been used as supplied .

II. Analytical and physical measurements :

Copper contents have been determined by applying gravimetric method (Vogel, 1981). Relative molecular weights of the ligands and their complexes have been determined cryoscopically (Danials, 1962). Conductivity measurements have been carried using an electrolytic conductivity measuring set LF-42 and Multiline F/SET-Z WTW Wissenschaf for 10^{-3} M dimethylformamide solutions at 25 ^{o}C. Infrared spectra has been recorded on a Pye-Unicam 1100 Infrared Spectrophotometer in the 400-4000 cm^{-1} range using KBr pellets. Electronic spectra have been recorded on Shimadzu UV-210A Spectrophotometer and Ultraviolet-Vissible Spectrophotometer Cecil-1021 for 10^{-3} M solutions of the ligands and their complexes in dimethylformamide solvent at 25 ^{o}C. Magnetic susceptibility of the complexes have been measured using Bruker B.M6 instrument at 25 ^{o}C.

III. Synthetic Methods :

Benzoin semicarbazone–B`SCH has been prepared according to a published method (Vogel, 1964). A general procedure has been adopted for the preparation of the complexes in neutral and basic medium . In neutral medium, a solution of 0.0041 mole copper nitrate in 5 ml distilled water has been added to the solution of 0.0041 mole benzoin semicarbazone and 0.0041 mole of the substituted salicylic acids in 15 ml. hot ethanol. The mixtures have been refluxed for three hours followed by evaporation to half of their volumes then cooled in ice-bath. The products were separated by filteration, followed by washing with petroleum ether (b.p. 60-80 ^{o}C) and dried at 90 ^{o}C. In basic medium, complexes have been prepared by applying same amounts used in a neutral medium, and after mixing the metal salts with the ligands and heating on a water bath, potassium hydroxide solution (1M) has been added until pH of the solutions reach 8-9. The mixtures have been heated on a water bath for half an hour then allowed to stand and cooled in ice-bath. The products were filtered, washed with petroleum ether (b.p. 60-80 ^{o}C) and dried at 90 ^{o}C .

IV. Radiolysis of the Complexes :

All the solutions (10^{-4}M) of the metal salt, ligands and complexes have been prepared using 10^{-3} M formate solution in triply distilled water (neutral medium) or 10^{-3} M formate and 10^{-1} M sodium hydroxide solution in triply distilled water (basic medium). The solutions were saturated with nitrogen gas. All gamma irradiations have been carried out using gamma cell-220 perchased from the Canadian Atomic Energy. The absorbed dose has been determined using Fricke dosimeter (Fricke and Hart, 1935). The dose rate was $2.7x10^{16}$ ev. ml^{-1} min^{-1}.

RESULTS AND DISCUSSION

The reaction of copper (II) nitrate, benzoin semicarbezone and the substituted salicylic acids in 1:1:1 molar ratio in both neutral and basic medium can be represented by the following reactions:

$Cu(NO_3)_2.3H_2O + B^{\backprime}SCH + AH \rightarrow [Cu(B^{\backprime}SCH)(AH)](NO_3)_2 + 3\ H_2O$ (in neutral med.)
$Cu(NO_3)_2.3H_2O+B^{\backprime}SCH+AH+2KOH \rightarrow [Cu(B^{\backprime}SC)(A)] + 2KNO_3+5H_2O$ (in basic med.)
(where AH = substituted salicylic acid SA or OASA or DNSA or ASA or SSA; A^- = deprotonated AH ligands, $B^{\backprime}SCH$=benzoin semicarbazone; $B^{\backprime}SC^-$ = deprotonated $B^{\backprime}SCH$ ligand).

The resulted complexes were colored, solid, slightly soluble in water, ethanol and soluble in dimethylformamide. Copper contents and relative molecular weights revealed that the complexes had the general formula $[Cu(B^{\backprime}SCH)(AH)](NO_3)_2$ and $[Cu(B^{\backprime}SC)(A)]$ in neutral and basic medium, respectively (Table 1). The values of the molar conductivities shown in Table (1), approached those expected for 1:2 and non electrolytes (Geary, 1971), for complexes prepared in neutral and basic medium, respectively. The room temperature magnetic moments of copper (II) complexes were in the range of 1.1-2.2 B.M. (Table 1), indicating the presence of one unpaired electron and assigned to a monomeric structure having distorted octahedral geometries (Hafez et al., 1986).

Infrared spectra of semicarbazone ligand (Table 2), showed a strong band at 1700 cm^{-1} which was attributed to $\upsilon_{(C=O)}$. This value shifted towards a lower frequency (1640-1650 cm^{-1}) on coordination, in neutral medium, indicating a coordination of the oxygen of the C=O group to the metal ion (Kumar and Tolani, 1989) (Yin et al., 2000). Whereas, in a basic medium, this band was disappeared in the complexes and a new band was observed at 1400 cm^{-1} due to bending enolic OH thereby establishing coordination of the ligand through the enolic oxygen atom (Singh et al., 1981). The appearance of strong bands at 1635-1640 cm^{-1} and 1575-1585 cm^{-1} which were attributed to $\upsilon_{(C=N)} + \upsilon_{(O-C=N)}$ and azine chromophore C=N-N=C, respectively, supported the formation of enolic structure in a basic medium (Kanoongo et al., 1987). The strong band at 1620 cm^{-1} attributed to $\upsilon_{(C=N)}$ has been shifted towards a lower frequency on coordination due to the decrease of the bond order as a result of metal nitrogen bond formation (Kumar et al., 1989). The band in the region 3200-3300 cm^{-1} was attributed to $\upsilon_{(NH)}$, the broadening of this band was due to the hydrogen bonding phenomenon. By complexation, this phenomenon becomes more complicated due to different factors such as the effect of hydrogen bonding and the coordination and also the presence of other groups (NH_2, OH) situated at the same position (Yin et al., 2000) (Kanoongo et al., 1987). The $\upsilon_{(NH)}$ band remained unchanged in the spectra of the complexes prepared in a neutral medium indicating that the NH group was uncoordinated. Meanwhile in a basic medium, it was more difficult to notice the absence of NH group due to the presence of hydrogen bonding, but it is well known that this band has been disappeared (Kanoongo et al., 1987) due to the enolic form. The strong bands appeared at 3390, 3410 cm^{-1} and 1450 cm^{-1} due to $\upsilon_{(NH2)}$ and $\delta_{(NH2)}$, respectively (Kumar and Tolani, 1989) (Kanoongo et al., 1987) remained unchanged on complexation indicated the uncoordination of this group with the metal ion.

Infrared spectra of the substituted salicylic acid ligands (Table 2), showed two bands at 1375-1390 cm^{-1} and 1575-1595 cm^{-1} assigned to the symmetric and asymmetric stretching frequency of the carboxylic group, respectively. On complexation these bands were shifted to 1400-1420 cm^{-1} and 1510-1590 cm^{-1}, respectively (Nakamoto, 1976) (Wilkinson et al., 1987). The difference between these bands ($\Delta\upsilon$=110 cm^{-1}) indicated that CO_2^- group coordinated to the central metal ion in a bidentate manner. The next wide bands at 3500-3600 and 2900 cm^{-1} were attributed to the stretching vibration of the carboxylic OH and the phenolic OH, respectively which indicated the formation of hydrogen bonds. In the spectra of the complexes it was more difficult to observe the coordination of these groups due to the interaction of other groups in the same region and the presence of hydrogen bonding. Whatever, in the complexes prepared in neutral medium this wide band was shifted to lower frequency, whereas for complexes prepared in basic medium it has been very difficult to observe the disappearance of this band, but it is well known that this band has been disappeared due to the deprotonation of the acid and the formation of ionic form (Nakamoto, 1976) (Palaskar et al., 1975). The band observed at 1730 cm^{-1} in OASA ligand was attributed to $\upsilon_{C=O}$ remained unaltered in the complexes indicating that there was no coordination through this group (Nakamoto, 1976) (Ali, 2002).

The complexes prepared in a neutral medium showed a band at 1385 cm^{-1}due to the ionic bonding of NO_3^- group (Nakamoto, 1976) (Wilkinson et al., 1987). Whereas the complexes prepared in basic medium did not showed this band indicating the absence of NO_3^- group. On the other hand the spectra of all the complexes showed new bands at 525-575 and 600-750 cm^{-1} due to $\upsilon_{(Cu-N)}$ and $\upsilon_{(Cu-O)}$, respectively (Wilkinson et al., 1987) (Ali, 2002).

The electronic spectra of the complexes, showed one broad band centered at 13793-14285 cm^{-1} due to two or three transitions $^2B_{1g} \rightarrow {}^2E_g$, $^2B_{1g} \rightarrow {}^2A_{1g}$ (Shrivastava et al., 1986). This band has been comparable both in position and width with the earlier reported octahedral complexes. Since the eg state has been highly affected by Jahn Taller effect, therefore, copper (II) complexes had distorted octahedral geometry (Gahlot et al., 1986).

The radiolysis of copper (II) nitrate in presence of nitrogen gas and sodium formate solution (Table 4), caused a decrease in the conductivity and a change in electronic spectra at 5 min in neutral medium, this may be due to the following reaction:

$CO_2^{\cdot-}/e^-_{aq} + Cu_{aq}^{2+} \rightarrow Cu_{aq}^{+1} + CO_2$

Increasing the time of irradiation, the conductivity has been changed which may be due to the reaction of .OH with copper (I), after the consumption of formate solution, and forming copper (II). Continuous irradiation caused a reversible reaction. The results in basic medium (Table 4), indicated that .OH radicals reacted with OH^- forming $O^{\cdot-}$

(Draganic and Draganic, 1971) (Al-Tayy, 1998) (Sallomi et al., 2002) which interacted with $HCOO^-$ as follows:
$O^{\cdot -} + HCOO^- \rightarrow OH^- + CO_2^{\cdot -}$
and hence $CO_2^{\cdot -}$ and e^-_{aq} reduced copper (II) to copper (I) leading to a decrease in conductivity and change in electronic spectra. Increasing time of irradiation copper (I) oxidized to copper (II) at 50 min. The results of gamma irradiation of the ligands (Tables 4, 5), in formate solution and in presence of nitrogen gas have been lead to a slight changes in conductivities and in absorbance but the wave lengths have been not changed except for the salicylic acid. The general reaction that may be happened can be represented as follows:
$L + CO_2^{\cdot -}/e^-_{aq} \rightarrow L^- + CO_2$
$L \rightarrow X + Y$ (the increase in conductivity lead to suggest the decomposition of the ligand)
$L^- + L \rightarrow (L\text{-}L^-)$ (decrease in conductivity lead to suggest the occurance of association, i.e. dimerization).

The reducing radicals $CO_2^{\cdot -}$ and e^-_{aq} have been attacked the ligands and the reduced ligands may be either decomposed or dimerized leading to an increase or a decrease in the conductivities, respectively (Draganic and Draganic, 1971) (Al-Tayy, 1998). In basic medium (Tables 4, 5), the so formed $O^{\cdot -}$ reacted with $HCOO^-$ as indicated before. $CO_2^{\cdot -}$ and e^-_{aq} which may be reacted with the ligands forming either molecular association or decompotion of the ligands which caused either a decrease or increase in the conductivities, respectively. Gamma irradiation of the complexes in N_2-saturated aqueous solutions and in presence of formate caused changes in conductivity and electronic spectra for complexes (1- 4). This may be represented by the following equation:
$[Cu^{11}(B`SCH)(AH)]^{2+} + CO_2^{\cdot -}/e^-_{aq} \rightarrow [Cu^{I}(B`SCH)(AH)]^{+} + CO_2$

Continuation of irradiation caused changes in the values of conductivities and electronic spectra data indicating the continuity of redox reaction with the time of irradiation (Belteheim and Faraggi, 1977) (Sellers, 1981)· Irradiation of the complexes (5) and (6) did not showed any changes in the electronic spectra and only a very slight changes in the conductivities was noticed which could be neglected. This supported the resistance of such complexes to the effect of gamma radiation during the time of radiation. Irradiation of the complexes (7-10), caused an increase in the values of the conductivities indicating the decomposition of the complexes which may be represented by the following equation:
$[Cu^{II}(B`SCH)(AH)]^{+2} \sim\rightarrow [Cu^{II}(B`SCH)(AH)]^{\cdot} \rightarrow Cu^{II} + B`SCH + AH$
$[Cu^{II}(B`SC)(A)] \sim\rightarrow [Cu^{II}(B`SC)(A)]^{\cdot} \rightarrow Cu^{II} + B`SC^- + A^-$

CONCLUSSION

According to the physico-chemical studies, some observations have been achieved leading to establish the following points:

1. Benzoin semicarbazone (Fig. 1), acted as tridentate chelating ligand coordinated to copper (II) ion through the azomethine-nitrogen and the two oxygen atoms of the carbonyl and alcoholic groups.
2. Substituted salicylic acids (Fig. 1), acted as tridentate chelating ligands.
3. Nitrate group joint in an ionic manner to the metal ion.

4. Copper (II) ion has been probably hexacoordinated, forming a distorted octahedral geometry (Fig. 2).
5. The effect of gamma rays could be caused either:
   I-Reduction of the complexes (1-4).
   II-Complexes 5 and 6 did not affect.
   III-Decomposition of the complexes (7-10).

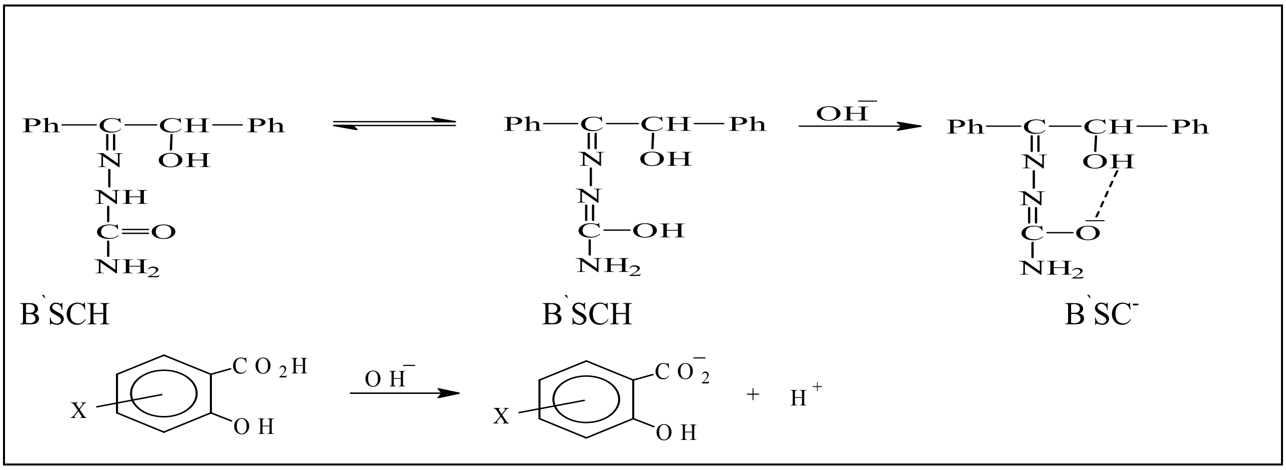

Fig. 1 : Structures of the ligands.

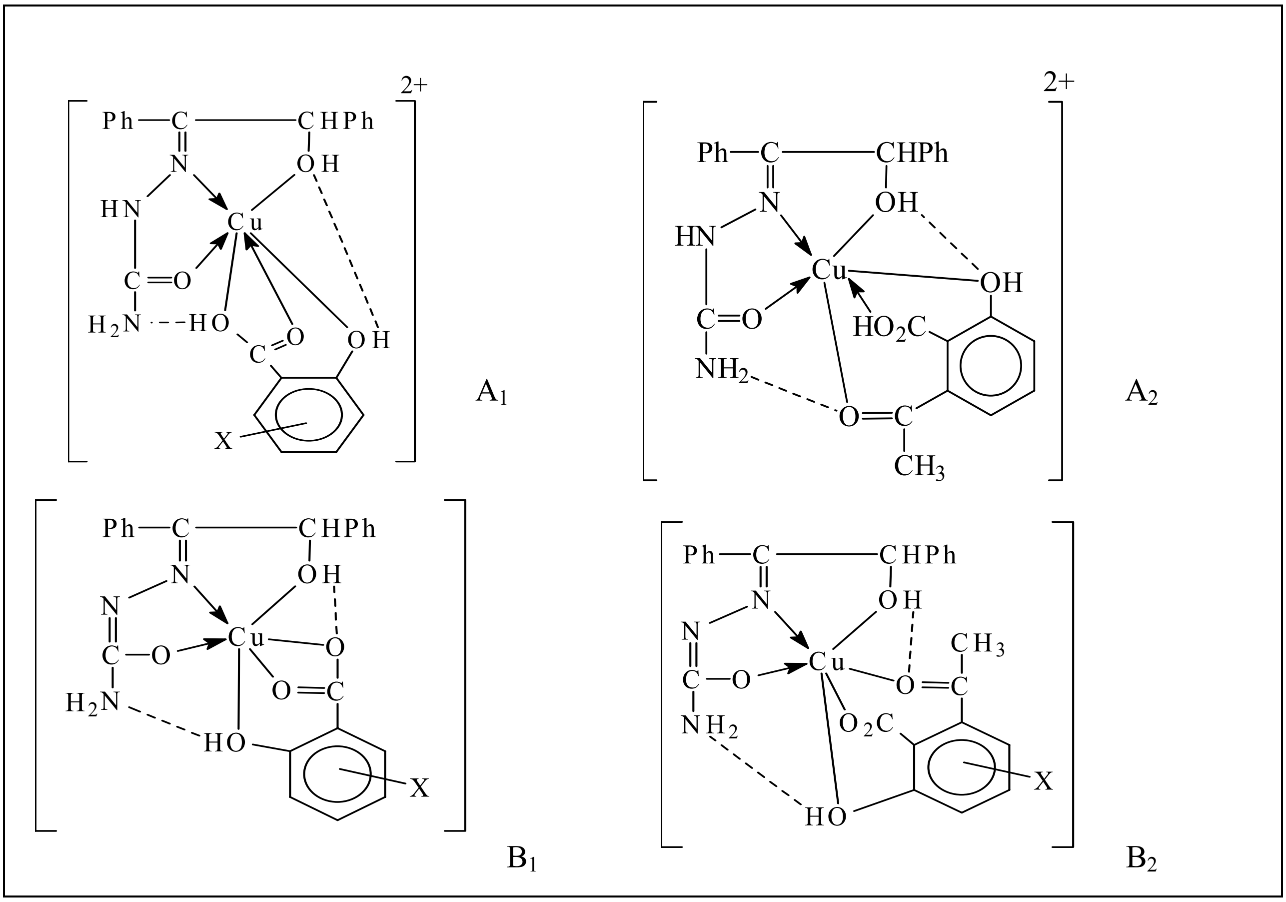

Fig. 2 : Proposed structures of the complexes; A$_1$,A$_2$ in neutral med.; B$_1$,B$_2$ in basic med.

Table 1 **:** Amounts, physical and analylical results of the prepared complexes (1-10)**.**

No.	**Complex**	**Medium**	**% yield**	**Color**	**m.p or d ^{0}C**	**$\wedge_M$ ***	**Cu Cal/ (obs)**	**m.wt Cal / (obs)**	**μ_{eff}**
1	[Cu(B`SCH)(SA)]$(NO_3)_2$	Neutral	97	Grey	206	139.7	10.0 (10.7)	594.5 (584.0)	1.9
2	[Cu(B`SC)(SA)]	Basic	97	Pale brown	212d	31.0	16.8 (17.2)	468.5 (453.0)	1.8
3	[Cu(B`SCH)(OASA)]$(NO_3)_2$	Neutral	96	Grey	142	138.7	10.5 (10.0)	636.5 (625.0)	1.7
4	[Cu(B`SC)(OASA)]	Basic	96	Dark green	214	20.0	14.6 (15.5)	510.5 (490.0)	2.2
5	[Cu(B`SCH)(DNSA)]$(NO_3)_2$	Neutral	95	Yellowish brown	180	125.0	8.6 (9.3)	684.5 (681.0)	1.1
6	[Cu(B`SC)(DNSA)]	Basic	96	Green	212	28.0	13.2 (13.9)	558.5 (533.0)	1.9
7	[Cu(B`SCH)(ASA)]$(NO_3)_2$	Neutral	96	Dark brown	100	130.7	9.9 (10.4)	609.5 (584.0)	1.7
8	[Cu(B`SC)(ASA)]	Basic	95	Dark brown	219	30.0	15.9 (16.6)	383.5 (350.0)	1.5
9	[Cu(B`SCH)(SSA)]$(NO_3)_2$	Neutral	96	Yellowish brown	141	130.7	10.1 (9.4)	674.5 (645.0)	2.2
10	[Cu(B`SC)(SSA)]	Basic	96	Green	196	27.0	11.2 (11.6)	448.5 (409.0)	1.7

* $\wedge_M$ = molar conductivity in Ω^{-1} cm^2 mol^{-1} ; d = decomposition point

Table 2 **:** IR spectral data of the ligands and their complexes (values in cm^{-1})**.**

Compd no.	$\upsilon_{(C=N)}$ **Semi**	$\upsilon_{(NH2)}$ **Semi**	$\upsilon_{(C=O)}$ **Semi**	$\upsilon_{(C-O)}$ **Semi**	$\upsilon_{(CO2)}$ **Sym.**	$\upsilon_{(CO2)}$ **Asym.**	$\Delta\upsilon$	**υ(NH) υ(O-H) acid**	**υ(Cu-N)**	**υ(Cu-O)**
B`SCH AH	1620	1455	1700	-	1390	1595	205	3200-3300 3500-3600	-	-
1	1510	1455	1650	-	1410	1520	110	3200-3300 3500-3600	550	600, 700
2	1540	1455	-	1275	1400	1510	110	3500-3600	550	650, 725
3	1530	1455	1640	-	1410	1590	110	3200-3300 3500-3600	575	650, 750
4	1540	1455	-	1230	1420	1590	110	3500-3600	575	650, 750
5	1510	1455	1640	-	1420	1530	110	3200-3300 3500-3600	525	625, 700
6	1520	1455	-	1275	1400	1510	110	3500-3600	525	650, 700
7	1540	1455	1650	-	1410	1520	110	3200-3300 3500-3600	550	650, 700
8	1530	1455	-	1275	1410	1520	110	3500-3600	550	675, 700
9	1540	1455	1650	-	1410	1520	110	3200-3300 3500-3600	525	600, 700
10	1530	1455	-	1240	1410	1520	110	3500-3600	525	625, 725

Table 3 : Electronic spectral data of the complexes (1-10).

No.	**C.T (cm^{-1})**	**υ (cm^{-1})**	**10Dq**	**C.F.S.E**
1	29500	14285	14285	8571.0
2	29000	14285	14285	8571.0
3	28600	13888	13888	8332.8
4	28500	13793	13793	8275.8
5	31050	13888	13888	8332.8
6	31000	14084	14084	8450.4
7	30050	14084	14084	8450.4
8	30000	14084	14084	8450.4
9	30000	13793	13793	8275.8
10	29950	13888	13888	8332.8

Table 4 : Radiolytical results of copper nitrate and the ligand B`SCH in a formate solution (N_2 gas) in neutral and basic medium.

	$CuNO_3$ Neutral			**$CuNO_3$ Basic**			**B`SCH Neutral**			**B`SCH Basic**		
T*	$\wedge_M$	λ nm	A	$\wedge_M$	λ nm	A	$\wedge_M$	λ nm	A	$\wedge_M$	λ nm	A
0	1.5	760 300	0.04 0.52	8.6	315	0.98	3.3	325	0.96	2.0	275	0.81
5	1.3	310	0.60	8.0	325	0.61	3.2	325	0.95	2.1	275	0.81
10	1.4	310	0.60	5.1	315	0.90	3.9	325	0.95	2.6	275	0.82
15	0.4	690 309	0.06 0.85	7.9	330	0.55	3.8	325	0.96	2.6	275	0.80
20	1.5	310	0.60	6.6	315 305	0.92 0.48	3.8	325	0.94	2.6	275	0.80
30	1.3	310	0.60	6.9	315	0.88	1.6	305	0.85	1.1	275	0.70
40	1.6	310	0.60	7.2	315	0.90	3.0	305	0.85	1.5	275	0.72
50	1.5	310	0.60	8.1	700 315	0.05 0.95	3.1	305	0.85	1.5	275	0.72
60	1.6	310	0.60	8.3	700 315	0.05 0.90	3.1	305	0.85	1.6	275	0.71

* T = Time of radiation , $\wedge_M$ = molar conductivity *10^4 in Ω^{-1} Cm^2 mol^{-1} , λ=wave length , A= absorbence

Table 5 : Radiolytical results of SA and OASA, formate solution (N_2 gas) in neutral and basic medium.

	SA Neutral			**SA Basic**			**OASA Neutral**			**OASA Basic**		
T^*	^ M	λ (nm)	A	^ M	λ (nm)	A	^M	λ (nm)	A	^M	λ (nm)	A
0	1.30	270	0.63	1.10	230	0.72	1.60	280	0.62	1.00	220	0.90
5	1.20	270	0.63	1.00	230	0.72	1.50	280	0.60	1.00	220	0.88
10	1.00	275	0.60	1.00	230	0.71	1.30	280	0.61	0.80	220	0.90
15	0.90	275	0.61	0.80	230	0.7	1.00	280	0.61	0.70	220	0.89
20	0.90	310 270	0.51 0.60	0.70	290 230	0.42 0.70	1.90	280	0.60	0.70	220	0.89
30	0.75	310 270	0.50 0.60	0.65	290 230	0.42 0.70	0.75	280	0.62	0.50	220	0.90
40	0.50	310 270	0.50 0.60	0.40	290 230	0.42 0.70	0.60	280	0.62	0.40	220	0.90
50	0.40	310 270	0.50 0.60	0.30	290 230	0.42 0.70	0.50	280	0.62	0.20	220	0.90
60	0.20	310 270	0.50 0.60	0.20	290 230	0.42 0.70	0.40	280	0.62	0.20	220	0.90

Table 6 : Radiolytical results of DNSA and ASA, formate solution (N_2 gas) in neutral and basic medium

	DNSA Neutral			**DNSA Basic**			**ASA Neutral**			**ASA Basic**		
T^*	^ M	λ nm	A	^ M	λ nm	A	^ M	λ nm	A	^ M	λ nm	A
0	2.50	300	0.60	1.10	240	0.85	2.10	270	0.8	1.7	290	0.65
5	2.50	300	0.60	1.00	240	0.85	2.00	270	0.8	1.5	290	0.65
10	2.30	300	0.60	1.00	240	0.85	2.00	270	0.8	1.2	290	0.65
15	2.50	300	0.60	1.20	240	0.85	1.80	270	0.8	1.2	290	0.65
20	2.40	300	0.60	1.10	240	0.85	1.70	270	0.8	1.0	290	0.65
30	2.40	300	0.60	1.10	240	0.85	1.70	270	0.8	0.9	290	0.65
40	2.50	300	0.60	1.00	240	0.85	1.50	270	0.8	0.6	290	0.65
50	2.50	300	0.60	1.10	240	0.85	1.20	270	0.8	0.4	290	0.65
60	2.50	300	0.60	1.10	240	0.85	1.20	270	0.8	0.2	290	0.65

Table 7 : Radiolytical results of SSA, complex 1 and complex 2, formate solution (N_2 gas) in neutral and basic medium.

	SSA Neutral			**SSA Basic**			**Complex 1**			**Complex 2**		
T^*	$\wedge_M$	λ nm	A	$\wedge_M$	λ nm	A	$\wedge_M$	λ nm	A	$\wedge_M$	λ nm	A
0	1.1	210	0.45	1.0	230	0.3	6.3	808 285	0.065 0.810	3.9	860 240	0.530 0.950
5	1.3	210	0.45	1.2	230	0.3	5.5	285	0.800	3.2	860 240	0.051 0.920
10	1.3	210	0.45	1.2	230	0.3	5.0	285	0.810	2.8	860 240	0.052 0.920
15	1.6	210	0.45	1.2	230	0.3	4.2	285	0.820	2.4	860 240	0.052 0.940
20	1.8	210	0.45	1.3	230	0.3	3.1	285 304	0.820 0.690	1.9	240 290	0.950 0.760
30	1.8	210	0.45	1.5	230	0.3	2.5	285 304	0.810 0.700	1.5	240 290	0.940 0.750
40	2.1	210	0.45	1.9	230	0.3	1.9	285 304	0.800 0.710	1.2	240 290	0.940 0.750
50	2.5	210	0.45	2.2	230	0.3	1.5	285 304	0.800 0.710	0.9	240 290	0.910 0.760
60	3.0	210	0.45	2.4	230	0.3	0.8	285 304	0.820 0.700	0.3	240 290	0.940 0.760

Table 8 : Radiolytical results of the complexes 3 - 6, formate solution (N_2 gas) in neutral and basic medium

	Complex 3			**Complex 4**			**Complex 5**			**Complex 6**		
T^*	$\wedge_M$	λ nm	A	$\wedge_M$	λ nm	A	$\wedge_M$	λ nm	A	$\wedge_M$	λ nm	A
0	7.9	750 325	0.055 0.600	6.1	800 310	0.030 0.820	4.0	730 270	0.030 0.630	1.5	670 300	0.060 0.720
5	7.1	325	0.590	5.6	800 310	0.030 0.800	4.0	730 270	0.030 0.630	1.4	670 300	0.060 0.700
10	6.5	325	0.610	5.0	310	0.810	4.1	730 270	0.030 0.630	1.4	670 300	0.060 0.700
15	5.8	325 340	0.630 0.500	4.2	310	0.800	3.9	730 270	0.030 0.620	1.4	670 300	0.060 0.700
20	5.1	325 340	0.590 0.510	3.8	310	0.800	3.9	730 270	0.030 0.620	1.6	670 300	0.060 0.710
30	4.8	325 340	0.610 0.500	3.1	310 330	0.810 0.700	4.1	730 270	0.030 0.610	1.5	670 300	0.060 0.710
40	4.0	325 340	0.600 0.500	2.4	310 330	0.800 0.69	4.0	730 270	0.030 0.620	1.5	670 300	0.060 0.700
50	3.4	325 340	0.600 0.500	2.0	310 330	0.790 0.700	4.0	730 270	0.030 0.620	1.4	670 300	0.060 0.720
60	2.9	325 340	0.600 0.500	1.1	310 330	0.800 0.700	4.0	730 270	0.030 0.630	1.5	670 300	0.060 0.720

Table 9 : Radiolytical results of the complexes 7 - 10, formate solution (N_2 gas) in neutral and basic medium

	Complex 7			Complex 8			Complex 9			Complex 10		
T^*	$^\wedge{}_M$	λ nm	A	$^\wedge{}_M$	λ nm	A	$^\wedge{}_M$	λ nm	A	$^\wedge{}_M$	λ nm	A
0	3.9	650 275	0.040 0.880	1.6	625 300	0.100 0.670	3.1	680 270	0.020 0.710	1.3	740 300	0.015 0.560
5	4.4	650 275	0.040 0.900	2.0	625 300	0.110 0.650	3.6	680 270	0.022 0.700	1.9	740 300	0.016 0.540
10	5.0	650 275	0.042 0.860	2.5	625 300	0.100 0.650	3.9	680 270	0.021 0.720	2.4	740 300	0.015 0.550
15	5.4	650 275	0.039 0.800	3.2	625 300	0.090 0.650	4.5	680 270	0.020 0.700	2.9	740 300	0.016 0.540
20	6.0	650 275	0.044 0.880	3.7	625 300	0.100 0.64	5.1	680 270	0.021 0.710	3.7	740 300	0.015 0.550
30	6.3	650 275	0.038 0.850	4.5	625 300	0.100 0.660	5.9	680 270	0.020 0.700	4.5	740 300	0.014 0.540
40	7.0	650 275	0.041 0.830	5.1	625 300	0.110 0.660	6.7	680 270	0.022 0.720	5.2	740 300	0.015 0.550
50	7.6	650 275	0.042 0.800	5.8	625 300	0.120 0.650	7.7	680 270	0.020 0.710	6.1	740 300	0.015 0.540
60	8.1	650 275	0.040 0.800	6.2	625 300	0.100 0.660	8.9	680 270	0.020 0.700	7.5	740 300	0.016 0.540

REFERENCES

Afrasiabi, Z., Sinn, E., Lin, W., Ma, Y., Campana, Ch. and Padhye, S., 2005. Nickel (II) complexes of naphthaquinone thiosemicarbazone and semicarbazone: synthesis, structure, spectroscopy and biological activity, J. Inorg. Biochem.

Ali, M.W.I., 2002. Preparation of cobalt (II) and nickel (II) complexes containing mixed ligands and their radiolytical study, M. Sc. Thesi , Mosul University, 33, 42, 48, pp.50-53.

Al-Tayy, Z.F.D., 1998.Preparation, characterization of some Schiff base metal complexes and their radiolytical studies, Ph. D. Thesis, Mosul University, pp.92-114.

Bindu, P.,.Kurup, M.R.P. and Satyakeerthy, T.R., 1998. EPR, cyclic voltametric and biological studies of copper (II) complexes of salicylaldehyde N(4)-substituted thiosemicarba- zone and heterocyclic bases, Polyhedron, 18, 321 p.

Bindu, P., Kurup, M.R.P. and Satyakeerthy, T.R., 1997. Synthesis, spectral characterization and biological activity of copper (II) complexes containing mixed ligands, National Seminar on metal in Biological Science, Department of Chem., Indian Institute of Technology. Madras, March 21-23.

Campbell, M., Elizabeth, C. and Verno, N.R., 1988. The synthesis and spectroscopic properties of some (π-allyl) dicarbonyl semicarbazonato halogen molybdenum (II) complexes, Polyhedron, 7(18), pp.1719 -1724.

Danials, F., William, J.W., Bender, P., Alberty, R.A., and All, 1962. Experimental physical chemistry, McGraw-Hill, 6th ed., 81 p.

Dawood, Z.F., 2002. Zr(IV) complexes of some nitrogen-oxygen donor ligands (semicarbazone and salicylaldazine), Sci. and Tech., 17, pp.35-38 .

Dawood, Z.F., Hussein, S.H., and Al-Shamaa, M.A., 2004. Some complexes Ni(II) containing mixed ligands, Sci. and Tech. A, 21, pp.71-75.

Dawood, Z.F. and Al-Shamaa, M.A., 2005. Preparation of Si(IV) complexes with mixed ligands, Al-Takani J., 18(5), Accepted.

Draganic, I.G. and Draganic, Z.D., 1971. The radiation chemistry of water, Academic Press, New York, Ch. 1-4.

El-Ajaily, M.M. and Maihub, A.A., 2003. Preparation and spectroscopic investigation of new mixed ligand chelates, Jerash Res. Stud., 8(1), pp.7-12.

Frick, H. and Hart, F.J., 1935. The oxidation Fe^{2+} to Fe^{3+} by the irradiation with x-rays of solution of ferrous sulfate in sulfuric acid, J. Chem. Phys., 30, 60 p.

Gahlot, A., Sharma, S. and Mehta, R.K., 1986. Cobalt(II), nickel(II), opper(II), zinc(II), cadmium(II), dioxouranium(VI) and oxovanadium(IV) complexes with 2-(N-a-benzyl-2-hydroxy benzylidine imino) ethane sulphonic acid, J. Indian Chem. Soc., 63, 198 p.

Geary, W.J., 1971. Use of conductivity measurements in organic solvents for the characterization of coordination compounds, Coord. Chem. Rev., 7, 81 p.

Guldi, D.M., Neta, P. and Vogel, E., 1996. Radiolytic reduction of tetrapropylporphycene and its iron, cobalt, nickel, copper and tin complexes, J. Phys. Chem., 100, pp.4097-4103.

Gupta, P., Basuli, F., Peng, S.M., Lee, G.H. and Bhattacharya, S., 2003. Unpreceedented chemical transformation of benzaldehyde semicarbazone mediated by osmium, Inorg. Chem., 42(6), 2069 p.

Hafez, M.A.H., Taha, F.I.M. and Moussa, M.N.H., 1986. Transition metal complexes of diacetylcarbohydrazonemethyltrimethyl ammonium chloride, J. Indian Chem. Soc., Vol. 63, pp.651-653.

Hassan, F.S.M., 2005. Formation of mixed ligand complexes of Ni(II), Pd(II) and Pt(II) involving salicylidine-3-amino-1,2,4-trizole (Schiff base) as a primary ligand and cystein as secondary ligand, Arabian J. Sci. and End., 30(1A), pp.29-37.

Hussain, R.K., Sambasiva, R.P. and Ravindra, B.P., 2000. Nuclease activity of mixed ligand complexes of copper (II) with heteroaromatic derivatives and picolin, Transit. Met. Chem., 25(5), pp.505-510.

Kanoongo, N., Singh, R.V. and Tandon, J.P., 1987. Synthesis and structural studies of oxo- vanadium (V) complexes of semicarbazone, J. Synth. React. Inorg. Met-Org. Chem., 17(8 and 9), pp.837-847.

Kasuga, N.C., Sekino, K., Koumo, C., Shimada, N. and Nomiya, K., 2001. Synthesis, structural characterization and antimicrobial activities of 4-coordinate nickel (II) complexes with the three thiosemicarbazones and semicarbazone ligands, J. Inorg. Biochem., 84(1-2), pp.55-56 .

Kumar, Y. and Tolani, S.P., 1989. Pd(II), Pt(II), Rh(III), Ir(III) and Ru(III) complexes of some nitrogen-oxygen donor ligand, Croat. Chem. Acta, 62, 73 p.

Nakamoto, K., 1976. Infrared and Raman Spectra of Inorganic and Coordination Compound, 2nd ed., Wiley-Interscience, pp.222, 223.

Palaskar, N.G., Jahagirdar, D.V. and Khanolkar, D.D., 1975. Physico-chemical studies of copper (II)-phthalic acid system, J. Indian Chem. Soc., 14, 134 p.

Ramesh, R. and Sivagamasundari, M., 2003. Synthesis, spectral and antifungal activity of mixed ligand complexes, Synth. React. Inorg. Met-Org. Chem., 33(5), pp.899-910.

Saeed, A.A., 1983. Radiation Chemistry, Basrah University, Basrah, Iraq, 29, 117, 215 p.

Salomi, I.J., Al-Obaydi, A.A. and Dawood, Z.F., 2002. Radiolysis of some copper(II) complexes in non-oxygenated aqueous solutions (formate, N_2 gas), Raf. Jour. Sci., 13(1), pp.7-14.

Sellers, R.M., 1981. Metal ions in unusual valency state, J. Chem. Educ., 58, 114 p.

Shrivastava, V.S., Bhasin, C.P. and Saxena, G.C., 1986. Spectral, magnetic and antibacterial studies of some newly synthesized manganese(II), cobalt(II), nickel(II) and copper(II) complexes, J. Indian Chem. Soc., 63, 865 p.

Singh, P.K., Koacher, J.K. and Tandon, J.P., 1981. Boron complexes of some oxygen nitrogen and sulphur-nitrogen containing chelating agents, J. Inorg. Nucl. Chem., 43, 1775 p.

Sorenson, J.R.J., 1989. Copper complexes as radiation recovery agents, Chem. Brit., pp.170-172 .

Vogel, A.I., 1964. Textbook of Practical Organic Chemistry, Longman Green, London, 3rd ed., 344 p.

Vogel, A.I., 1981. Textbook of Quantitative Inorganic Analysis, Longman Inc., New York, 4th ed., 427, 463 p.

Wilkinson, G.A., Gillard, R.D. and McCleverty, J.A., 1987. Comprehensive Coordination chemistry, 1st ed., Pergamon Press Oxford , England , Vol. 5, p. 534; Vol. 2, 447 p.

Yao, Y., Cai, Q., Kou, H., Li, H., Wang, D., Yu, R., Chen, Y. and Xing, X., 2004. Self-assembed of a novel manganiferous coordination polymer with mixed ligands, Chem. Soc. Japan, 33, pp.1270-1271 .

Yin, D.D., Wang, Z. and Shan, L., 2000. Synthesis and characterization of semicarbazone metal complexes of Sn(IV) and Zr(IV), Chinese Chem., 18(3), 364 p.