Synthesis and Characterization of Mono and Trinuclear Complexes of Transition and Main Elements with Thioether ligands

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Abstract:
This research involve the preparation of mono and trinuclear compounds and complexes of general formula, $[Sb(SBu^n)_3]$, $[Sb(SFur)_3]$, $[Sn(SBu^n)_4]$, $[Sn(SFur)_4]$ $[Sb(SBu^n)_3(MCl_2)_2]$, $[Sb(SFur)_3(MCl_2)_2]$, $[Sn(SBu^n)_4(MCl_2)_2]$ and $[Sn(SFur)_4(MCl_2)_2]$ where SBu^n=*n*-butanethiol SFur=2-mercaptofurfuryl, M=Co(II), Ni(II) and Cu(II). The compounds and complexes were characterized by conductivity measurements, magnetic measuerments, IR and UV/vis spectral measurements and atomic absorption studies for Co(II), Ni(II) and Cu(II).

Introduction:
Despite the interest in ligands containing sulfur donor atoms, the alkane – or arenethiolate derivatives of main group metals have received much less attention than has been given to the corresponding transition metal compounds. A wide variety of transition metal from complexes with thioether ligands and these ligands have been shown to impart unexpected spectral, electronic or redox properties (1).
Recently some literature information regarding cobalt and nickel complexes with 1,2-dithiolates which exhibit interesting properties and industrial applications (2,3).
The behaviour of marcaptide ion as donor in transiton metal complexes has not been subjected to such detailed study as is true of a number of other donor groups. This arises, in part, because the mercapto group often gives metal ion derivatives that are extremely insoluble, bridged, or even polymeric (4,6).
A series of indium, thiolato compounds have been prepared by direct electrochemical techniques successfully used for the synthesis of thiolates of a number of d^{10} metal ions (7-10).
The synthesis of dihalogenobis (2-pyridinthiolato) tin (IV) by oxidative addition reaction of di-2-pyridyl disulfide to tin(II) halides, an extension of reaction to prepare other dihalogeno dithiolato tin(IV) complexes (10).

Experimental:
Chemicals:
All chemicals as reagent grade (BDH,Fluka) were used as supplied. All solvents were dried by standard methods (11).

Physical Measurements:
Melting point or decomposition temperature were determined by a Buchi 510 melting point apparatus and were uncorrected. Infrared spectra within the range 4000-400 cm^{-1} were recorded on a Burker Tensor 27 Spectrophotometer and Perkin-Elmer 580B spectrophotometer in the 4000-200 cm^{-1} range, as KBr or CsI discs. Electronic spectra were measured with a shimadzu UV/Vis. recording UV-160 spectrophotometer at room temperature, using a concentration of 10^{-3} M of in N,N′-dimethyl formamide (DMF) solution. Conductivity measurements have been carried out with an electrical conductivity measuring set model PCM3-Jenway using 10^{-3}M in(DMF) solution at room temperature. The metal content (Co, Ni, Cu) was estimated spectrophotometrically using Shimadzu AA670. Magnetic measurements were carried out on the solid by the Faraday's method using Bruker BM6 instrument.

Preparation of complexes:

Preparation of $[Sn(SBu^n)_4]$ compound:
Compound (1) was prepared by mixing equivalent amount of KOH (0.48g, 0.004mol) and n-butanetiole (0.48g, 0.004mol) in ($20cm^3$) ethanol and $SnCl_4$ (0.26g,0.001mol) was added to the above mixture,the mixture was heated under stirring for 2 hours. The precipitate was filtered off, washed with ethanol and then dried under vacuum.

$$4HSBu^n + 4KOH + SnCl_4 \xrightarrow{\text{Ethanol}} [Sn(SBu^n)_4] + 4KCl + 4H_2O$$

Preparation of $[Sn(SFur)_4]$ compound:
Compound (2) was obtained following the same procedure as (1) but (SFur) was used in place of (SBu^n).

$$4HSFur + 4KOH + SnCl_4 \xrightarrow{\text{Ethanol}} [Sn(SFur)_4] + 4KCl + 4H_2O$$

Preparation of $[Sb(SBu^n)_3]$ compound:
Compound (3) was prepared by mixing equivalent amount of KOH (0.33g, 0.003mol) and n-butanetiole (0.36g, 0.003mol) in ($20cm^3$) ethanol and $SbCl_3$ (0.21g, 0.001mol) was added to the above mixture, the mixture was heated under stirring for 2 hours.The precipitate was filtered off, washed with ethanol and then dried under vacuum.

Preparation of $[Sb(SFur)_3]$compound:
Compound (4) was obtained following the same procedure as (5) but (SFur) was used in place of (SBu^n) .

Complexes of the type $[Sn(SBu^n)_4(M`Cl_2)_2]$, $[Sn(SFur)_4(M`Cl_2)_2]$, M=Co(II), Ni(II),Cu(II):
Treatment of ethanolic ($15cm^3$) of $[CoCl_2.6H_2O]$ (0.48 g, 0.002 mol) with an ethanolic solution ($15cm^3$) $[Sn(SBu^n)]$ (0.47g,0.001mol) $[Sn(SFur)_4]$ (0.57g,0.001mol).The mixture was refluxed for 1h,cooling gives a colored complexes. It was filtered washed with ethanol and dried under vacuum.
Similar procedure was used to prepare the rest of the complexes.

Complexes of the type $[Sb(SBu^n)_3(M`Cl_2)_2]$, $[Sb(SFur)_3(M`Cl_2)_2]$, M=Co(II), Ni(II),Cu(II):

To an ethanolic solution (15 cm^3) of ($CoCl_2.6H_2O$) (0.48g, 0.002mol) was added to an ethanolic solution (15 cm^3) of $[Sb(SBu^n)_3]$ (0.38g,0.001mol), $[Sb(SFur)_3]$ (0.47g,0.001mol) .The reaction mixture was refluxed for 2h, then reduced to on third of its volume, cooling gives a colored complexes. It was filtered washed with ethanol and dried under vacuum.

Similar procedure was used to prepare the rest of the complexes.

Results and discussion:

The reaction of metal chloride with the Sb or tin compounds in 2:1 molar ratio gave the complexes of general formulas: $[Sn(SBu^n)_4(M'Cl_2)_2]$, $[Sn(SFur)_4(M'Cl_2)_2]$, $[Sb(SBu^n)_3(M'Cl_2)_2]$ and $[Sb(SFur)_3(M'Cl_2)_2]$.

The analytical and physical data of the compounds the complexes are given in Table 1. The values of molar conductance are in the range of (11-20) Ω^{-1} $mol^{-1}cm^{-2}$ in N,N`-dimethyl formamide solution indicate that the complexes are non electrolyte (12). Table 2, shows the characteristic bands of electronic and infrared spectra of the complexes.

The most important bands that appear in the IR spectra of the compounds and complexes are listed in Table 2. The ligands does not show any υ(SH) band in the region 2500-2600cm^{-1}, in which this stretching frequency generally expected (13). The characteristics bands in the infrared spectra of the free ligands occurs at 1015 and 1290cm^{-1} due to stretching vibrations υ(C-S) and υ(C-O-C) respectively (14).

Table 1: Physical properties of the complexes

No.	Complex	Colour	M.P (C^o)	Yield(%)	Molar conductivity $\Omega^{-1}.cm^2.mol^{-1}$	% Metal	μ_{eff} (B.M)
١	$[Sn(SBu^n)_4]$	white	*٢٥٠	٩٠	٢٠		---
٢	$[Sn(Sfur)_4]$	Yellow	*١٩٣	٨٣	٢١		---
٣	$[Sb(SBu^n)_3]$	White	*٢٩٥	٨٠	١٣		---
٤	$[Sb(SFur)_٣]$	Orange	*١٣٠	٧٧	١٠		---
5	$[Sn(SBu^n)_4(CoCl_2)_2]$	Blue	١٠٠	٧٧	١٦	16.03 (15.11)	1.90
6	$[Sn(SBu^n)_4(Ni\ Cl_2)_2]$	Green	*١٩٣	٧٥	١٦	15.98 (15.50)	Dia
7	$[Sn(SBu^n)_4(Cu\ Cl_2)_2]$	Green	١٤٥	٨٠	١٣	17.07 (16.70)	1.80
8	$[Sn(SFur)_٤(CoCl_2)_2]$	Dark beige	*٢٠٠	٦٨	١٠	14.17 (13.69)	4.80
9	$[Sn(SFur)_٤(NiCl_2)_2]$	beige	*١٤٣	٧٥	١٦	14.13 (13.7 0)	2.90
10	$[Sn(SFur)_٤(CuCl_2)_2]$	Brown	٢٥٠	٨٧	١٥	15.12 (14.60)	1.92
11	$[Sb(SBu^n)_3(CoCl_2)_2]$	Violet	١٦٠	٨٠	٢٠	18. 15 (18.66)	1.84
12	$[Sb(SBu^n)_3(NiCl_2)_2]$	Green	٢٣٠	٦٣	٩	18.10 (17.59)	Dia
13	$[Sb(SBu^n)_3(CuCl_2)_2]$	Green	*١٠٠	٧٠	١٠	19.31 (18.77)	1.90
14	$[Sb(SFur)_٣\ (CoCl_2)_2]$	Brown	٩٠	٧٣	١٠	16.34 (15.82)	4.02
15	$[Sb(SFur)_٣(NiCl_2)_2]$	Brown	١٨٠	٦٠	١١	16.29 (15.79)	2.92
16	$[Sb(SFur)_٣(CuCl_2)_2]$	black	٢٥٠	٥٦	١٥	17.40 (16 . 66)	1.70

* = decomposition temperature

Table 2:Electronic and infrared data of the compounds

No.	λ_{max} (cm^{-1})	υ(C -S)	υ(C -O-C)	υ(M-S)	υ(M`–S)	υ(M'–O)	υ(M`–Cl)
١	-	999		325	-	-	-
٢	-	1000		340	-	-	-
٣	-	998		330	-	-	-
٤	-	990		326	-	-	-
٥	12422, 16420	1001		335	360	-	320
٦	14930, 24630	990		330	390	-	300
٧	10974	995		350	380	-	310
٨	11186, 20450, 26230	996	1260	345	375	440	290
٩	11198, 16900, 26178	1000	1250	333	365	460	295
١٠	13021	991	1265	340	-	470	300
١١	11198, 16393, 23497	989		325	370	-	295
١٢	16808, 124814	990		328	385	-	300
١٣	13587, 18990	995		340	384	-	311
١٤	11198, 21979, 26230	994	1265	350	370	480	320
١٥	11919, 16051, 29499	1002	1255	345	380	465	300
١٦	19881, 18939	1000	1250	330	385	450	290

M= Sn or Sb
M`= Co(II), Ni(II) and Cu(II)

In the Sb and Sn compounds of these ligands, it was found that the υ(C-S) band show lowering in frequency, indicating that this band is involved in the coordination. The infrared of Sb(II) and Sn(II) show new bands of 325-350cm^{-1} assigned to υ(Sb-S) or υ(Sn-S). In the complexes similar observation was found, due to the donation of ion pair electrons on the sulfur atoms to the metal ions, also the υ(C-O-C) band in the complexes (8-10) and (14-16) was found at lower frequencies by about 30-40cm^{-1}, which indicates that it was shared in coordination with metal ions. The infrared of the complexes show new bands at 440-480, 360-390 and 320-290cm^{-1} assigned to υ(M`-O) (15), υ(M`-S) (16) and (M`-Cl) (17) respectively.

The magnetic moments values at room temperature of Co(II) complexes (5 and 11) are (1.9, 1.8) B.M., these values are in turn with a low spin configuration and shows the presence of square planer geometry (18), whereas the Co(II) complexes (8 and 14) show magnetic moment of (4.8-4.82) B.M. indicating an octahedral geometry of the complexes (19).

The electronic spectra Co(II) complexes (5 and 11) display absorption in the region 11198-12422 and 16393-23479cm^{-1} at the band to $^2A_1g \rightarrow {}^2Eg(\upsilon_1)$ and $^2A_1g \rightarrow {}^2T_1g(\upsilon_2)$ transition and could be assigned to a square planer structure (20).

The electronic spectra of cobalt complexes (8 and 14) shows three bands at 11186-11198, 20450-21979, 26230-27174cm^{-1}, corresponding to the transitions $^4T_1g(F) \rightarrow {}^4T_2g$ $(F)(\upsilon_1)$, $^4T_1g \rightarrow {}^4A_2g$ (υ_2) and $^4T_1g(F) \rightarrow {}^4T_1g(P)(\upsilon_3)$ respectively. The position of these band indicates that these complexes have an octahedral geometry (23).

The Ni(II) complexes (6 and 12) are diamagnetic and they show square planer geometry (23). The Ni(II) complexes (9 and 15) shows a magnetic moments (2.90 and 2.92) B.M. These values are in turn with a high spin configuration and shows the presence of an octahedral environment around Ni(II) ions in the complexes (24).

The electronic spectra of Ni(II) complexes (6 and 12) shows two bands at 14930-16808 and 24630-24814cm^{-1} correspond to the transitions $^1A_1g \rightarrow {}^1A_2g$ (υ_1) and $^1A_1g \rightarrow {}^1B_1g$ (υ_2) respectively. An examination of these bands indicates that the complexes has square planer geometry (25).

The electronic spectra of the complexes (9 and 15) shows three bands at 11198-11919, 16051-16807, and 26178-29499cm^{-1} these may be assigned to the transitions $^3A_2g(F) \rightarrow {}^3T_2g$ $(F)(\upsilon_1)$, $^3A_2g(F) \rightarrow {}^3T_1g(F)(\upsilon_2)$ and $^3A_2g(F) \rightarrow {}^3T_1g$ $(P)(\upsilon_3)$. The position of these bands indicate that these complexes have octahedral geometry (24).

The magnetic moment measurements of Cu(II) complexes (7, 10, 13 and 16) have magnetic moment values (1.8, 1.92, 1.84 and 1.7) B.M. corresponding to the presence of one unpaired electron (26). The electronic spectra of Cu(II) complexes (7 and 10) show one band at 10974-13021cm^{-1} corresponding to the transition $^2B_1g(F) \rightarrow {}^2Eg$ arising from square planer geometry.

The electronic spectrum of Cu(II) complexes (13 and 16) show two bands appear at 13587-14881 and 18931-18990cm^{-1} which may be assigned to $^2B_1g \rightarrow {}^2A_1g$, $^2B_1g \rightarrow {}^2B_2g$ transition this show that the Cu(II) complexes have distorted octahedral geometry.

On the basis of the above discussion we propose the following structures for the compounds and metal complexes, as in Fig. 1

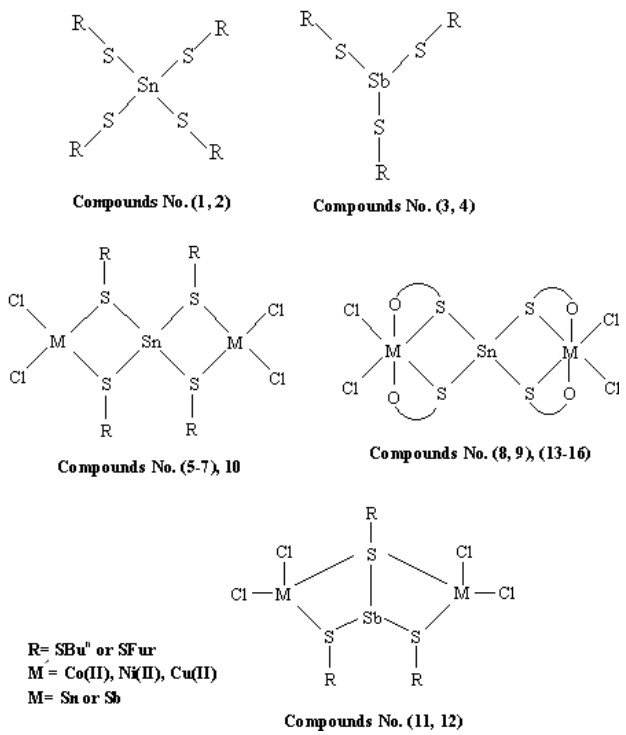

Fig. 1: Suggested structures for the compounds and compleces

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تحضير وتشخيص معقدات احادية وثلاثية النوى من العناصر الرئيسية والانتقالية الاولى مع ليكاندات الثايو ايثر

ليلى جمعة نجم

قسم الكيمياء، كلية العلوم، جامعة الموصل، الموصل، جمهورية العراق

الملخص:

يتضمن البحث تحضير معقدات ومركبات جديدة ذوات الصيغ العامة $[Sn(SFur)_4]$, $[Sn(SBu^n)_4]$, $[Sb(SFur)_3]$, $[Sb(SBu^n)_3]$, $[Sb(SFur)_3(MCl_2)_2]$, $[Sb(SBu^n)_3(MCl_2)_2]$, $[Sn(SFur)_4(MCl_2)_2]$, $[Sn(SBu^n)_4(MCl_2)_2]$ حيث SBu^n = ١- بيوتان ثايوليت ، SFur = فورفورايل ثايوليت ، M= Co ، Ni و Cu.

تم تشخيص المعقدات بقياسات التوصيلية الكهربائية وقياسات المغناطيسية وقياسات الأطياف الالكترونية وطيف الأشعة تحت الحمراء والامتصاص الذري للمعقدات.