

SYNTHESIS AND CHARACTERIZATION OF $\text{CO}^{+2}, \text{NI}^{+2}, \text{CU}^{+2}, \text{ZN}^{+2}$ AND HG^{+2} COMPLEXES WITH 1,1,2,2-TETRAKIS (SODIUM THIOACTATE) ETHYLENE

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Abstract

The new ligand 1,1,2,2-tetrakis(sodium thiolactate) ethylene, has been prepared from the reaction of disodium salt of thiolactic acid and tetrachloroethylene in (4:1) molar ratio. Di and tetranuclear complexes were obtained by direct reaction of the above ligand with $\text{Co}^{+2}, \text{Ni}^{+2}, \text{Cu}^{+2}, \text{Zn}^{+2}$ and Hg^{+2} metal ion in (1:2) and (1:4) ligand to metal molar ratio.

The prepared complexes were characterized by elemental analysis, spectral studies (FTIR, UV/vis), magnetic measurements, conductivity measurements. Electronic spectra and magnetic moment values indicate the presence of tetrahedral geometric around the metal ions.

Key words: sodium thiolactate, direct reaction, tetranuclear complexes

Introduction

The chemistry poly functional ligands with P-, S-, N- or O-donor atoms are often employed in the synthesis of poly nuclear complexes, mainly due to the versatile bonding feature of the poly functional ligands. Heterobimetallics have received increasing attention as they can be employed as bimetallic compounds or in homogeneous catalysis or heterogeneous catalysis and having increased catalytic properties [Wheatly and Kalck, 1999; Stephan, 1989; Sinfelt 1983].

New metal complexes of the ligand 2-thioacetic acid-5-pyridyl-1,3,4-oxidiazole with the metal ions Co(II), Ni(II) were prepared in alcoholic medium, the prepared complexes were characterized by F-TIR, electronic spectroscopy, elemental analysis, magnetic moment, conductivity measurements [Yousif *et al.* 2011].

Yousif *et al.* [2009 and 2011] prepared new metal complexes of the ligand 2-thioacetic acid benzothiazole with the metal ions Ni(II), Cu(II), Cd(II) and Sn(II). The prepared complexes were characterized by IR, electronic spectroscopy ^1H NMR, magnetic moment and conductivity measurements.

The reaction between InCl_3 with sodium mercapto acetic acid ($\text{NaSCH}_2\text{COOH}$) in 4-methyl pyridine (4Mepy) at 25°C affords $[\text{InCl}(\text{SCH}_2\text{COO})_2]^{-2}[(4\text{-MepyH})_2]^{+2}$. X-ray diffraction studies of the prepared indium compound show it to have a distorted

square pyramidal geometry, with the $[\text{SCH}_2\text{COO}]$ ligands in a trans conformation [Banger, 2004].

The photo stabilization of poly(vinyl chloride) film by 2-thioacetic acid-S-phenyl-1,3,4-oxadiazole with Sn(II), Ba(II), Ni(II), Zn(II), Cu(II) and Ca(II) complexes was investigated [Aydin *et al.* 1998].

Complexes of general formula $[\text{M}(\text{L})]$, $[\text{M}_2(\text{L})]$, $[\text{M}_2(\text{L})\text{Cl}_2(\text{H}_2\text{O})_2]$ and $[\text{Zn}_2\text{M}(\text{L})_2]\text{Cl}_2$ where (M = Co(II), Ni(II), Cu(II) and Zn(II)) were prepared through direct reaction of the 1,4-bis(sodiumthioglycolate) butane (L) with $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ZnCl_2 respectively in (1:1), (1:2) and (2:3) ligand to metal ratio. The prepared complexes were characterized by their metal content, IR, U.V, magnetic and conductivity measurements [Buttrus *et al.*, 2010].

The ligand 1,4-bis(sodiumthiolactate) butane $\text{O}_2\text{CCHCH}_3\text{S}(\text{CH}_2)_4\text{-SCHCH}_3\text{CO}_2^{-2}$, was reacted with $\text{H}[\text{AuCl}_4]$ in 1:1, 1:2 and 2:2 ligand to gold molar ratio. The prepared complexes were characterized by elemental analysis, spectral studies (FTIR and UV-Vis), magnetic measurement and conductivity measurement [Buttrus *et al.*, 2013].

In view of these interesting results and as continuation of our study on transition metal complexes with sulfur containing ligands [Buttrus N.H. *et al.* 2007; Abdrazag *et al.*, 2011 and Buttrus, 2013]. We have prepared a new ligand 1,1,2,2-tetrakis(sodiumthiolactate)ethylene and

there Co(II),Ni(II),Cu(II),Zn(II)and Hg(II) complexes.

Experimental

All chemical were of reagent grade, purchased from commercial source (BDH and Fluka).

Physical characterization

Elemental analysis of the isolated complexes were accomplished by micro analytical techniques on Perkin Elmer 2400 (IEES) at AL-Abait University (Jordan). Metal estimation were done on PYEUNICAM Spg Atomic Absorption spectrophotometer.

Conductivity measurements for 10^{-3} M solution of the complexes in (DMSO) were carried out on Jenway 4070 conductivity meter. Infrared spectra were recorded on a FTIR Brucker Tensor 27co spectrophotometer in the $250-4000\text{ cm}^{-1}$ range using CsI disc. The UV/Vis spectra were recorded on a Shimadzu UV-160 spectrophotometer for 10^{-3} M solution of the complexes in DMSO using 1 cm quartz cell. Magnetic susceptibilities values were corrected for diamagnetic contribution using Pascal's constants.

Preparation of the ligand

1- preparation of disodium thiolacetate

Thiolactic acid sodium salt (0.15 g,0.001 mol) in (20 ml) ethanol was treated with NaOH (0.40 g,0.001 mol) in (10 ml) ethanol. The mixture was boiled under reflux for 2h. the product was obtained through filtrations, the precipitate was washed with ethanol and diethyl ether and dried under vacuum for several hours.

2- preparation of 1,1,2,2-trakis(sodium thiolactate)ethylene(L)[AL-Allaf *et al.*,1997].

A solution of disodium thiolactate (0.60g,0.004 mol) in (20 ml) of ethanol was added to a solution of tetrachloroethylene (0.17 g,0.001 mol) in (10 ml) ethanol. The mixture was boiled under reflux for 6h., the

precipitate was filtered off, washed several times with ethanol in order to remove the NaCl and then with diethylether and dried under vacuum for 4h.

3- preparation of $[M_2L]$ complexes

$M = \text{Co}^{+2}, \text{Ni}^{+2}, \text{Cu}^{+2}$ and Zn^{+2}

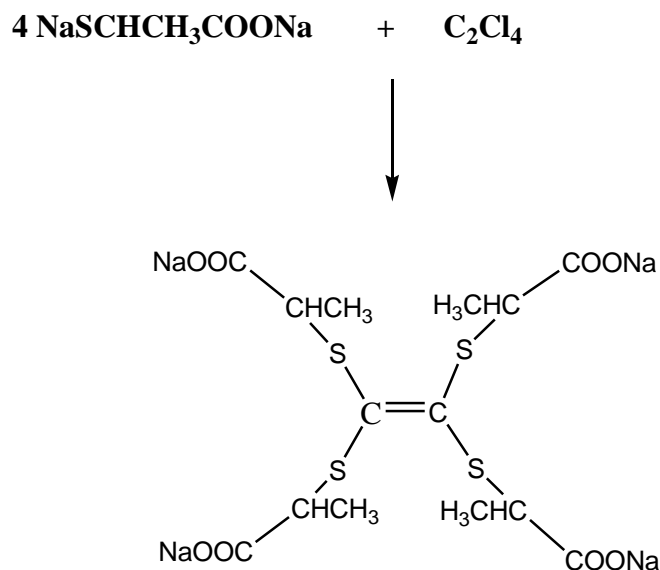
A solution of a metal chloride (0.002 mol) in (10 ml) ethanol was added to a stirred solution of the ligand (L) (0.53 g,0.001 mol) in (10 ml) ethanol. The reaction mixture was refluxed for 3h. The mixture was left 24h. at room temperature to give the precipitate, which was filtered off to remove the NaCl which was dissolved in the filtrate and may be present with the precipitate, washed several times with ethanol and diethylether, then dried under vacuum for several hours.

4-preparation of $[M_2Hg_2(L)Cl_4]$ complexes

A solution of metal chloride (0.002 mol) in (10 ml) ethanol, and mercuric chloride (0.54g, 0.002mol) in (10 ml) ethanol were added to a solution of the ligand (0.53g,0.001mol) in (10 ml) ethanol. the mixture was refluxed for 3h. and the product were obtained as the above procedure.

Results and Discussion

The ligand 1,1,2,2-trakis(sodium thiolactate)ethylene is stable, white solid and acts as tetradentate and octadentate from oxygen sulfur and atoms with the metal ions Scheme 1. The complexes were prepared through direct substitution and addition reactions by the relevant thiolactate ligands as oxygen or sulfur that has stronger preferences for metal ions. All complexes are thermally stable and insoluble in organic solvent, however fair solubility in DMSO and DMF. The analytical data (Table 1) of the metal complexes show that all complexes are non electrolytic nature[Geary,1971].



Scheme 1: Preparation of the ligand

The infrared spectrum of the ligand, show a characteristic stretching absorption bands at 1588, 1424 and 884 cm^{-1} assigned to carbonyl $\nu(\text{COO})_{\text{sym}}$ and $\nu(\text{C-S})$ groups respectively. The (COO) stretching vibrations are important to predict the bonding mode of the ligand.

It has also been suggested that the $\Delta\nu(\text{COO})$ value in the chelating mode is less than the $\Delta\nu(\text{COO})$ in a bridging mode [Bhatti *et al.* 2005].

Two bands are observed at 1582-1617 and 1361-1424 cm^{-1} and the difference in $\Delta\nu(\text{COO})$ (187-232) cm^{-1} (Table 2) are indicative of bidentate nature of carboxylate group [AL-Allaf, and Buttrus, 1994].

Further support for this argument came from the IR of the complexes which showed a new bands at 480-510 cm^{-1} and in the region 290-320 cm^{-1} which may be attributable to $\nu(\text{M-O})$ and $\nu(\text{Hg-Cl})$ respectively [Nakamoto, 1997].

The appearance of new bands in the 340-370 cm^{-1} range which is tentatively attributed to $\nu(\text{M-S})$, indicate that the ligand coordinate to the metal ions through the $\nu(\text{C-S})$ [Wenzel *et al.*, 2002].

The experimental magnetic moment for each complex in listed in Table 1. The magnetic measurements give an idea about the electronic state of the metal ion in the complex. The magnetic moments are (4.56 and 4.24) B.M for Co(II) complexes (1 and 5) respectively, while for Ni(II) complexes

(2 and 6) are (3.20 and 3.79) B.M, for Cu(II) complexes (3 and 7) are (1.9 and 2.09) B.M, suggest the presence of one unpaired electron, Zn(II) complexes (4,8) and Hg(II) complexes are diamagnetic.

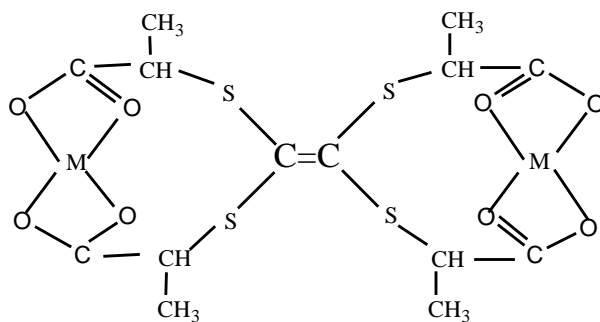
The UV-visible spectra of the ligand and their complexes in 10^{-3} M solution of DMSO were recorded, the results were listed in Table 3. The band observed at 34364,29041 cm^{-1} were due to $\pi-\pi^*$ or $n-\pi^*$ transition within the ligand. The spectrum of cobalt (II) (1 & 5) complexes show a bands at (14641-15974 and 30030-30209) cm^{-1} these bands are assigned to ${}^4\text{A}_2\text{g} \rightarrow {}^4\text{T}_1\text{g}(\text{p})$ transition and charge transfer, which is consistent with proposed tetrahedral symmetry for these complexes. Further the blue and violet colors of these complexes support its proposed tetrahedral geometry [Cotton *et al.*, 1999].

The electronic spectra of Ni(II) complexes No. (2,6) the observed bands at (14124 and 12771) cm^{-1} are due to transition ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{p})$ (ν_3) in tetrahedral symmetry [Patel and Ikekwere, 1981].

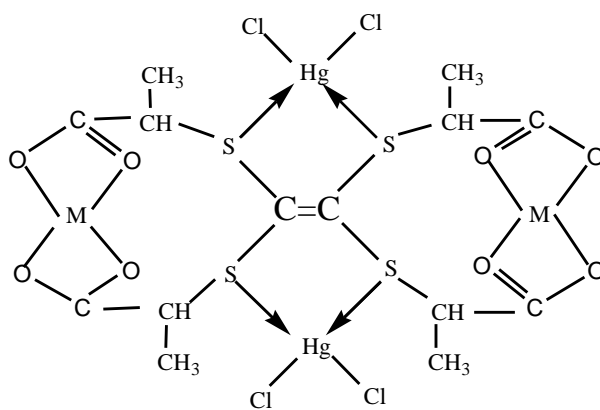
In case of Cu(II) complexes (3 and 7) a band at (15220 and 12903) cm^{-1} were assigned to ${}^2\text{T}_2 \rightarrow {}^2\text{E}$ transition in tetrahedral environment [Konno *et al.* 1994]. The magnetic susceptibility showed that all Zn(II) and Hg(II) complexes (4,5-8) were diamagnetic and the electronic spectra of these complexes do not show any d-d band.

The ligand used in this study, coordinate to the metal ions from the oxygen atoms of the carboxylate groups and the sulfur atoms

of thioether groups acting as tetradentate and octadentate ligand, as show in Fig 1.



(1-4)



(5-8)

M= Co(II),Ni(II),Cu(II) and Zn(II)

Fig 1: Suggested structures for the complexes

Table 1: Physical properties of the complexes

| Seq. | Compound | m.p (°c) | Color | Analysis ,found (calc.) % | | | | | Molar conductivity (Λ) $\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{mol}^{-1}$ | μ_{eff} |
|------|---|----------|-------------|---------------------------|-------------|--------------|--------------|--------------|--|--------------------|
| | | | | C | H | S | M | Hg | | |
| L | $\text{C}_{14}\text{H}_{16}\text{O}_8\text{S}_4\text{Na}_4$ | 238-239 | Bieje | 31.21(31.29) | 3.00(3.01) | 24.01(24.06) | ---- | ---- | ---- | --- |
| 1 | $[\text{Co}_2(\text{L})]$ | >350 | Blue | 30.06(30.10) | 2.79(2.86) | 22.89(22.94) | 21.09(21.15) | ---- | 15 | 4.56 |
| 2 | $[\text{Ni}_2(\text{L})]$ | 290 | Dark brown | 30.09(30.16) | 2.81(2.87) | 22.91(22.98) | 21.00(21.10) | ---- | 12 | 3.20 |
| 3 | $[\text{Cu}_2(\text{L})]$ | 285 | Olive sreen | 29.10(29.16) | 2.79(2.820) | 22.51(22.57) | 22.35(22.40) | ---- | 20 | 1.90 |
| 4 | $[\text{Zn}_2(\text{L})]$ | 272 | White | 29.39(29.43) | 2.75(2.80) | 22.39(22.42) | 22.89(22.92) | ---- | 18 | Dia |
| 5 | $[\text{Co}_2\text{Hg}_2(\text{L})]$ | 180 | Violet | 15.20(15.26) | 1.41(1.45) | 11.59(11.63) | 10.69(10.72) | 36.39(36.43) | 26 | 4.24 |
| 6 | $[\text{Ni}_2\text{Hg}_2(\text{L})]$ | 160 | Green | 15.19(15.27) | 1.40(1.45) | 11.59(11.64) | 10.60(10.64) | 36.40(36.47) | 22 | 3.79 |
| 7 | $[\text{Cu}_2\text{Hg}_2(\text{L})]$ | 130 | Dark yellow | 15.10(15.13) | 1.41(1.44) | 11.51(11.53) | 11.40(11.44) | 35.99(36.14) | 14 | 2.09 |
| 8 | $[\text{Zn}_2\text{Hg}_2(\text{L})]$ | 213 | Yellowish | 15.03(15.08) | 1.40(1.43) | 11.21(11.49) | 11.69(11.74) | 35.97(36.02) | 18 | Dia |

d= decomposition temperature .

L= 1,1,2,2-tetrakis(sodium thiolactate) ethylene

Table 2: IR spectra and electronic spectral data of the ligand and their complexes

| Compl. no. | Band maxima (λ_{max}) cm^{-1} | $\nu_{as}(\text{COO})$ | $\nu_{sy}(\text{COO})$ | $\Delta\nu = (\nu_{as} - \nu_s)$ | $\nu(\text{C-S})$ | $\nu(\text{M-Cl})$ | $\nu(\text{Hg-S})$ | $\nu(\text{M-O})$ |
|------------|---|------------------------|------------------------|----------------------------------|-------------------|--------------------|--------------------|-------------------|
| L | 34364,26041 | 1588 _s | 1424 _s | --- | 884 _m | --- | --- | --- |
| 1 | 14727 | 1583 _s | 1362 _s | 221 _w | 880 _w | --- | --- | 500 _m |
| 2 | 14124 | 1616 _s | 1409 _m | 305 _s | 881 _m | --- | --- | 520 _w |
| 3 | 15226 | 1617 _m | 1430 _w | 187 _m | 882 _m | --- | --- | 510 _m |
| 4 | 29940 | 1616 _s | 1384 _s | 232 _m | 884 _w | --- | --- | 525 _w |
| 5 | 14814 | 1616 _s | 1400 _m | 216 _w | 832 _s | 325 _s | 380 _w | 530 _s |
| 6 | 12771 | 1594 _s | 1361 _s | 233 _m | 835 _m | 310 _s | 370 _m | 496 _w |
| 7 | 12903 | 1622 _m | 1411 _m | 211 _s | 846 _s | 320 _m | 390 _m | 504 _m |
| 8 | 28653 | 1582 _m | 1364 _s | 218 _m | 845 _m | 312 _s | 404 _s | 514 _m |

s= strong, m=medium, w= we

References

- Abd alrazaq E.A., Buttrus N.H., Al-Kattan W., Jbarah A. A. and Almatarneh M., (2011), Reaction of Pd^{+2} and Pt^{+2} with pyrrolidinedithio carbamate and cystine ligands, synthesis and DFT calculation, *J. Sulfur Chem.*,32(2),159-169.
- AL-Allaf T.A.K. and Buttrus N. H., (1994), Coordination complexes of Uranium (VI),Thorium(IV),Cerium (III) and Lanthanum (III) with various multidentate ligands, *ABATH AL-YAEMOK* 3,101-110.
- AL-Allaf T.A.K.; Buttrus N.H. and Hitchcock P.B.,(1997),Palladium and Platinum (II) complexes with arylthioethene, *Asia.J. Chem.*, 9(2), 187-194.
- Aydin, M., Arsu N.,Yagci Y., Jackusch S. and Turro N.J. (2005), Mechanistic study of photoinitiated free radical polymerization using thioxathone thio acetic acid, *Macromolecules*, 38,4133-4138
- Banger K.K., Duraj S.A., Fanwick P.E., Hehemann D.G., Hepp A. F. and Matrok R.A., (2004), Synthesis and structural characterization of novel indium mercapto derivative $[\text{ClIn}(\text{SCH}_2(\text{COO})_2)^2[4\text{-MePyH}]_2]^{+2}$, *NASAITM*,212289.
- Bhatti M.,Ali S.,Huma F. and Shahazadi S., (2005), Organo tin (IV) derivatives of N-maleonyl amino acids. Their synthesis and structural elucidation, *Turk J.Chem.*,29,463-470.
- Buttrus N.H. and Saeed F.T.,(2012),Bis (N-methyl benzimidazolium-2-thio) ethane,propane or butane and its Co(II),Ni(II),Cu(II) and Zn(II) ionic salts, *International J.Chem.*,22(2),117-122.
- Buttrus N.H., Abd alrazaq E.A.and AL-Sger A.K., Synthesis and characterization of some new semiconducting dinuclear platinum (II) complexes containing 1,1,2,2-tetrakis-(substituted phenylthio) ethylene, (2007) *Int.J.Chem.Sci.*, 5(3), 1111-1120,(2007).
- Buttrus N.H.,AL-Smaan S.H.and AL-Asalli S.M.,(2010),Mono,di- and tri-nuclear complexes of Co(II), Ni(II), Cu(II) and Zn(II) with 1,4 bis(sodium thioglycolate) butane, 20(1), 37-42.
- Buttrus N.H., AL-Smaan S.H.and AL-Asalli S.M.,(2013),Gold(III)complexes with thiolactate and bis(1,4-sodium thiolactate) butane ligands, *International J. Chem.*, accepted (2013).
- Buttrus N.H., Mohamed S.M, Sabah A.A and Abdalrazaq E.A., *Asian (2013)*, Synthesis and characterization of Ni^{+2} , Cu^{+2} and Zn^{+2} complexes with benzimidazole-2-thionate, diphosphene and their reaction with iodine, *J.Chem.*, 25(9), 14125, (2013).
- Cotton F.A.; Wilkinson G.; Murillo C.A. and Bochmann M., (1999) "Advance Inorganic Chemistry", 6th Ed., Joh. Wiley and Sons, New York, 810-842
- Geary W.J.(1971),The use conductivity measurements in organic solvents for characterization of coordination compounds, *Coord. Chem.Rev.*,7,8-81.
- K.Nakamoto,(1997),"Infrared of inorganic and coordination compounds", 6th Edition, John Wiley New York.
- Konno T., Yonenobu K.,Hidaka J. and Okamoto K., (1994), A New class of s-bridged hexanuclear complexes with amino thiolate ligands. Formation and structural characterization of $[\text{Pd}^{\text{II}}_2\{\text{Ni}^{\text{II}}(\text{aet})_2\}_x\{\text{Pd}^{\text{II}}(\text{aet})_2\}_{4-x}]\text{Br}_4$ ($x = 0-4$; aet = 2-aminoethanethiolate), *Inorg.Chem.*,33, 538.
- Patel K.S. and Ikekwere P.O,1981,Magnetic and spectral properties of Cu(II) cyanobenzoates, *J. Inorg. Nucl. Chem.*, 43,51-55
- Sinfelt J. H., (1983), "Bimetallic Catalysis", Wiley, New York, (1983).
- Stephan D.W., (1989), Early late heterobimetallics, *Coord. Chem. Rev.*, 95, 41.
- Wenzel B.,Lonnecke P., Stender M. and Hey Hawkins E., (2002), Early/ Late heterobimetallic, unusual tetranuclear Zr/Ni and octanuclear Zr/Pd complexes with bridging bifunctional sulfide acetate ligands, *J. Chem. Soc. Dalton Trans.*,478-480.
- Wheatly N. and Kalck P.,(1999),Structure and reactivity of early- late heterobimetallic complexes, *Chem. Rev.*, 99,3379.

- Yousif E., Farina Y., Kasar K., Grasia A. and Ayid K., (2009), Complexes of 2-thioacetic acid benzothiazole with some metal ions, Am. J. Appl. Sci., 6(4), 582-585.
- Yousif E., Muaiad F. and Adil H., (2011), Synthesis and characterization of Fe(II), Mn(II), Co(II), Hg(II) and Cr(II) complexes of benzothiazol-2-yl-sulfanyl)-acetic acid ligand, J. AL-Nahrain Univ., 14(1), 44.
- Yousif E., Farnia Y., Grasia A., Salih N. and Salimon J., (2011), Structure and Fungicidal activity of some diorganotin (IV) with 2-thioacetic acid -5-phenyl-1, 3, 4-oxodiazole and benzamidophenyl alanine, Iran J. Chem. Chem. Eng., 30, 67-72.

تحضير وتشخيص معقدات Hg^{+2} و Zn^{+2} ، Cu^{+2} ، Ni^{+2} ، Co^{+2} مع 2,2,1,1 تتراس (صوديوم ثايولاكتيت) اثيلين

الخلاصة

تم تحضير الليكاند 2,2,1,1 تتراس (صوديوم ثايولاكتيت) اثيلين من خلال مفاعلة الملح ثنائي الصوديوم لحمض لثايولاكتيك ورباعي كلورواثيلين بنسبة مولية (1:4). تم تحضير معقدات ثنائية ورباعية النوى من خلال التفاعل المباشر لليكاند اعلاه مع الايونات الفلزية Hg^{+2} و Zn^{+2} ، Cu^{+2} ، Ni^{+2} ، Co^{+2} و بنسب مولية (1:2) و (1:4) فلز الى ليكاند.

تم تشخيص المعقدات المحضرة بواسطة التحليل العنصري الدقيق، الدراسات الطيفية (الاشعة تحت الحمراء وفوق البنفسجية) والمغناطيسية وقياسات التوصيلية. أظهرت القياسات المغناطيسية (العزم المغناطيسي) والطيف الالكتروني بان المعقدات تمتلك بنية رباعي السطوح حول الايونات الفلزية.