

Synthesis and characterization of new complexes of Mn^{+2} , Co^{+2} , Ni^{+2} , Ca^{+2} and Zn^{+2} with 1,2-bis (sodium cystienate) ethane ligand

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Abstract: A new multidentate ligand 1,2-bis (sodium cystienate) ethane (L) was prepared from the reaction between 1,2-dibromoethane and disodium cystienate in ethanol. Complexes of general formula $[M(L)]$ and $[M_2(L)Cl_2]$ where (M=Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)) were prepared through the reaction of the above ligand with $MnCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$ and $ZnCl_2$ respectively in (1:1) and (1:2) ligand to metal molar ratio. The prepared complexes were characterized by their elemental analysis, metal content, infrared, UV-Visible spectra, magnetic measurements and conductivity measurements. The results of electronic spectra and magnetic measurements indicate that the complexes $[Co(L)]$ and $[Ni(L)]$ have square planer geometry while the rest of the complexes show the presence of tetrahedral geometry.

Keywords : 1,2-bis(sodium cystienate) ethane, square planer complexes.

Introduction

Thiocarboxylic acids, cysteine, amino acid and their transition metal complexes have attracted attention not only because they contain both "soft" sulfur and "hard" oxygen sites, but also because of their wide variety of technological applications⁽¹⁻⁴⁾. A perusal of the literature reveals that this carboxylate complexes of nickel, palladium, copper, zinc, silver, cadmium and mercury⁽⁵⁾ have been studied in view of the fact that these complexes are widely used as homogeneous catalyst in many reaction like hydrogenation, hydrogen transfer, hydrosilylation and hydroformylation. The reaction of the mercapto carboxylic acids $HOOC(CH_2)_nSH$ ($n=1,2$) with $HAuCl_4$ followed by treatment with PMe_2Ph led to the (phosphane) gold thiolates $[Au(SCH_2)_nCOOH(PMe_2Ph)]$ $n=1(1),2(2)$, which can act as metallo ligands, towards complex fragments of a second metal. Compound (1) and (2) react with $[Cp^o_2ZrMe_2]$, ($Cp^o=C_5EtMe_4$) to give the trinuclear Zr/Au complexes $[Cp^o_2Zr\{k^1-OOC(CH_2)_nSAu(PMe_2Ph)\}\{k^2o,o'-OOC(CH_2)_nSAu(PMe_2Ph)\}]$, $n=1(3)$, $n=2(4)$.

Compounds 1-4 were characterized by 1H , ^{13}C , ^{31}P NMR and IR spectroscopy. The crystal structure of (4) shows mono and bi dentate coordination of metallo ligands to one zirconocene fragment⁽⁶⁾. The interaction of cis-platin with different amino acids methionine, pencillamine and glutathione has been studied. To elucidate the mechanisms involved in the inhibition of toxicity⁽⁷⁾. Studied the behavior of Pd(II) and Pt(II) complexes containing ligand with -S-S- bond cleavage such as tetra methylthiura disulfide.

Mono and di nuclear complexes of the type $[M(Cys)]$, $[M(PTD)_2]$ and $[M_2(PTD)_4]$, where M=Pd(II) or Pt(II), Cys=($SCH_2CH(NH_2)-COOH$)₂, PTD= pyrrolidinethiocarbonyldisulfide have been prepared through oxidative addition reaction. They are characterized by microanalyses of metal content, molar conductance magnetic measurements, infrared and UV-visible spectral studies⁽¹⁾. The reaction between $InCl_3$ with sodium mercaptoacetic acid $NaSCH_2COOH$ in 4-methyl pyridine affords $[InCl(SCH_2COO)_2][4Me-pyH]_2$ X-ray diffraction study of the complex, show it to have a distorted square pyramidal geometry with - SCH_2COO - ligands in the trans conformation⁽⁸⁾.

A new multidentate ligand 1,4-(sodium thioglycolate) butane (L) was prepared from the reaction between 1,4-dichlorobutane and disodium thioglycolate in ethanol. Complexes of the general formula $[M(L)]$, $[M_2(L)Cl_2(H_2O)_2]$ and $[Zn_2M(L)_2Cl_2]$ where M=Co(II), Ni(II), Cu(II) and Zn(II) were prepared through direct reaction of the above ligand with $CoCl_2 \cdot 6H_2O$; $NiCl_2 \cdot 6H_2O$; $CuCl_2 \cdot 2H_2O$ and $ZnCl_2$ in (1:1), (1:2) and (2:3) metal to ligand ratio. The prepared complexes were characterized by their metal contents, infrared, UV-visible spectra, magnetic measurements and conductivity measurement⁽⁹⁾. Unexpectedly the zirconocene metalloligand $[Cp^o_2Zr(OOCH_2SH-K^1o,o)]$ ($(1)Cp^o=C_5EtMe_4$) reacts with $[NiCl_2(PMe_2Ph)_2]$ or $[PdCl_2(P^nBu_3)_2]$ in the presence of NEt_3 (ratio 1:1:2) to give the tetra nuclear Zr(IV)-Ni(II) complex (2) and the octa nuclear Zr(IV)-Pd(II) complex (3) respectively. The structure of the complexes (2) and (3) were studied by X-ray crystallography⁽¹⁰⁾.

As extension to our studied on transition metal complexes with multifunction ligands⁽¹¹⁻¹³⁾ we are presenting have the preparation new ligand result from the reaction of disodium cystienate with 1,2-dibromoethane and their complexes with M=Mn(II),Co(II), Ni(II),Cu(II) and Zn(II) metal ions.

Experimental

All starting materials used were of Analar grade were purchased from Aldrich or Fluke and used as supplied.

Physical measurements:

C,H,N data were obtained using a C,H,N elemental analyzer type Perkin Elmer 2400 at AL-Bait University (Jordan). The metal content was estimated spectrometric ally using Shimadzu Atomic Absorption 670 spectrophotometer. Melting point or decomposition temperature were determined on a Buchi 510 melting point apparatus and were uncorrected IR spectra were recorded on Bruker Tensor 27Co FTIR spectro photometer in the 4000-200 cm⁻¹ range using KBr or CsI disc. Electronic spectra were recorded on Shimadzu UV/160 spectrophotometer for 10⁻³ M solution of the complexes in dimethyl sulfoxide (DMSO) using 1cm quartz cell. Conductivity measurement were made on conductivity meter 4070 Jenway for 10⁻³M solution of the complexes using DMSO. The magnetic measurements were carried out at 25°C on the solid state by Faraday's method using Bruker BM6 instrument.

Synthesis of the ligand

Treatment of disodium cystienate (prepared from the reaction of an equivalent amount of NaOH (1.60 g, 0.04 mol) and (0.28 g, 0.02 mol) cystiene in ethanol (30 ml) with 1,2-dibromoethane (1.88 g , 0.01 ml) in (10 ml) ethanol and the mixture was stirred under reflux for five hours. The colorless solution was concentrated 1/3 of it volume the precipitate was formed, washed several times with ethanol in order to remove the NaBr formed and then diethylether , then dried under vacuum for several hours.

Preparation of [M(L)] complexes.

M=Mn(II), Co(II), Ni(II),Cu(II) or Zn(II)

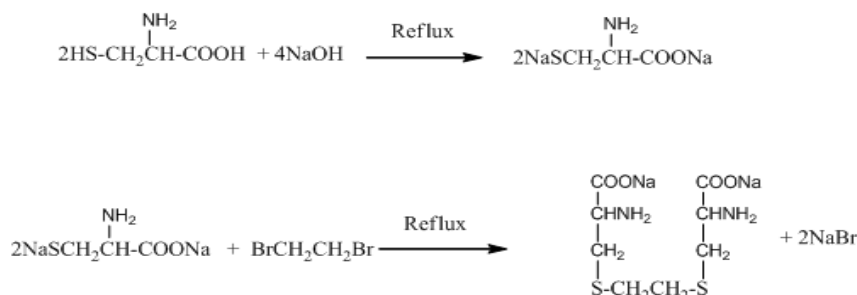
A clear solution of the ligand 1,2-bis(sodium cystienate) ethane (0.31g,1.0 mmol) in ethanol (20 ml) was added to a solution of MnCl₂.4H₂O; CoCl₂.6H₂O; NiCl₂.6H₂O; CuCl₂.2H₂O and ZnCl₂ (1.0 mmol) in (10ml) ethanol, the reaction mixture was refluxed for 2 hours. Then the mixture was left for 24h. at room temperature to give the precipitate which was filtered off, washed with ethanol and diethylether, then dried under vacuum for several hours.

Preparation of [M₂(L)Cl₂] complexes

A solution of (0.31g,1.0 mmol) of the ligand 1,2-bis (sodium cystienate) ethane in (20 ml) ethanol was added to a solution of MnCl₂.4H₂O,CoCl₂.6H₂O,NiCl₂.6H₂O, CuCl₂.2H₂O and ZnCl₂ (2.0 mmol) in ethanol (10ml). the reaction was refluxed for 2hours. The mixture was left at room temperature for 12 hours. A coloured precipitated formed in solution was filtered off, washed with ethanol in order to remove the formed NaBr then washed with ethanol and diethylether, then dried under vacuum for several hours.

Results and discussion

The new ligand (L) was prepared by the reaction of disodium cystienate salt with 1,2-dibromoethane to give 1,2-bis(sodium cystinate) ethane (L) in high yield (Scheme 1). The complexes were prepared through direct reaction of metal chlorides with the ligand (L) in (1:1) and (1:2) ligand to metal molar ratio gave the complexes of the general formula [M(L)] and [M₂(L)Cl₂].



Scheme 1: Synthesis of the ligand (L)

The analytical data of the ligand and its complexes are given in Table 1. These data were in a good agreement with the proposed formula. All the complexes are air stable at room temperature and insoluble in common organic solvent but they are soluble in dimethyl formamide (DMF) or dimethylsulfoxide (DMSO). Due to the fact that the molar conductance values are too low to account for any dissociation, all of these complexes are considered a non-electrolyte⁽¹⁴⁾.

The most diagnostic features of the recorded infrared spectra of the ligand and the synthesized complexes are listed in Table 2. Assignments of the observed vibrational modes as shown in Table 2, are based on the literature sources (Rakhi and Shelly, 2011). The infrared spectrum of the ligand exhibits a sharp bands at 3323, 2927, 1597, 1417 and 850 cm^{-1} , which are assigned to $\nu(\text{NH}_2)$, $\nu(\text{CH})$, $\nu_{\text{asy}}(\text{COO})$, $\nu_{\text{sy}}(\text{COO})$ and $\nu(\text{C-S})$ respectively⁽¹⁵⁾. There are a clear differences between the infrared spectra of the functional group of ligand and their complexes. The most significant information on the geometry of the complexes No.(1-6) were came from the analysis of carboxylate group and thioether absorption region. Stretching frequencies of these functional groups are closely related to the way in which they are coordinated to the metal atom. The IR spectra of the complexes showed broad and intense bands ranging between 1593-1618 and 1358-1417 cm^{-1} assigned for $\nu_{\text{asy}}(\text{COO})$ and for $\nu_{\text{sy}}(\text{COO})$ respectively. (Table 2) the magnitude of $\Delta\nu$ ($\Delta\nu = \nu_{\text{asy}}(\text{COO}) - \nu_{\text{sy}}(\text{COO})$) were in the range of 184-199 cm^{-1} suggesting bidentate bonding of the carboxylate group to the metal ion. Further support for this argument came from the IR of the complexes which showed a new bands at 534-588 cm^{-1} , attributable to $\nu(\text{M-O})$ ⁽¹⁶⁾.

The $\nu(\text{C-S})$ band of the free ligand was observed at 850 cm^{-1} upon coordination with metal ion with complex No. (1-5), remains almost constant upon coordination indicating the O-bonding with the metal ions.

In the dinuclear complexes (No.6-10) the carboxylate group bonding to the metal ions in bidentate fashion that was clear from the magnitude of $\Delta\nu$, which are in the range of 187-232 cm^{-1} , as well as the $\nu(\text{C-S})$ was observed at lower frequency values Table 2. Further support for this coordination has been provided by the appearance of new bands in the range 360-385 cm^{-1} ranges which are tentatively attributed to $\nu(\text{M-S})$. These complexes also show a band in the region 290-320 cm^{-1} which may be due to $\nu(\text{M-Cl})$ vibrational frequency⁽¹²⁾.

The magnetic moment values of the Mn(II) complexes (1,6) are 5.4 and 5.6 B.M (Table 1). These values of magnetic moments reveal the presence of five unpaired electrons there by showing the complexes are of high spin type.

The manganese complexes (1,5) shows maximum absorption at 269-276 and 360-380 nm indicating that Mn(II) complexes are tetrahedral. In tetrahedral fields the transition are still spin forbidden but no longer pairy for bidden⁽¹⁷⁾.

The magnetic moment of cobalt complex (2) was (2.31 B.M) this suggested the presence of one unpaired electron which revealed the low spin nature of the complex while complex (7) was (4.56 B.M) which suggested the presence of three unpaired electrons. The electronic spectrum of the complex (2) show a band at 414 and 712 nm assign to ${}^2A_{2g} \rightarrow {}^2E_g$ transition these values suggest to a square planer geometry for the complex, while complex (7) show a band at 678 nm these bands is assigned to

${}^4A_{2g} \rightarrow {}^4T_{1g}$ (p) transition and the other bands at 280 and 338 nm are assigned for charge transfer these bands suggest that Co(II) complex (6) have tetrahedral geometry⁽¹⁸⁾.

The magnetic measurement, indicates that Ni(II) complex (3) is diamagnetic, while the magnetic moment of the Ni(II) complex (8) is (3.12 B.M), which suggest a square planar for (3) and tetrahedral geometry for (8) respectively. The electronic spectra of Ni(II) complex (3) showed to have two band at 694 and 418. The bands were assigned to ${}^1A_{1g} \rightarrow {}^1A_{2g}$ (ν_1) and ${}^1A_{1g} \rightarrow {}^1B_{1g}$ (ν_2) transition is a square planar environment around nickel ion⁽⁹⁾.

The Ni(II) complex (8) show the presence of one characteristic absorption band at 748 nm which may be assigned to ${}^3T_1 \rightarrow {}^3T_1$ (p) transition suggesting the tetrahedral geometry around Ni(II) as compared to reported values⁽¹⁹⁾. The magnetic moments of Cu(II) complexes (4,9) has been found to be (1.92 and 2.01) B.M, suggested the presence of one unpaired electron.

The electronic spectra of the complexes showed a band at 751 and 588 nm assigned to ${}^2T_2 \rightarrow {}^2E$ transition, suggesting tetrahedral geometry around Cu(II) ion⁽²⁰⁾.

The magnetic susceptibility showed that all Zn(II) complexes (5 and 10) were diamagnetic, and the electronic spectra of these complexes do not show any d-d band.

The ligand used was coordinated to different metal ions in bidentate or tridentate fashion through the oxygen atoms or the sulphur atoms forming mononuclear or dinuclear complexes as shown in fig1.

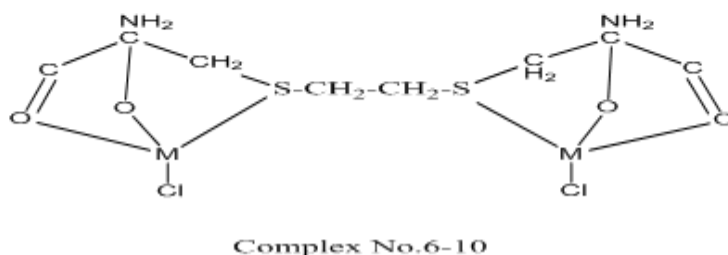
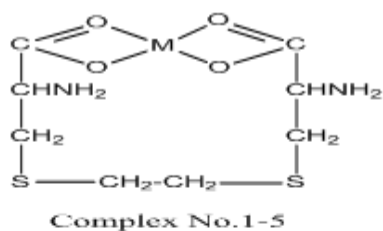


Fig 1: Suggested structures of the complexes

Table 1: Physical properties of the ligand and its complexes

d= decomposition temperature

Seq.	Compound	m.p (°C)	color	Analysis found (calc.)%					Molar conductivity Λ cm ² .ohm ⁻¹ . mol ⁻¹	μ_{eff}
				C	H	N	S	M		
L	$\text{C}_8\text{H}_{14}\text{N}_2\text{O}_4\text{S}_2\text{Na}_2$	190-192	White	30.70 (30.77)	4.41 (4.48)	8.95 (8.97)	20.47 (20.51)	---	---	---
1	[Mn(L)]	250 ^d	White	29.93 (29.90)	4.31 (4.36)	8.70 (8.72)	19.85 (19.93)	17.09 (17.13)	25.1	5.4
2	[Co(L)]	230 ^d	Pink	29.50 (29.54)	4.28 (4.31)	8.59 (8.61)	19.65 (19.69)	18.09 (18.15)	9.5	2.31
3	[Ni(L)]	240 ^d	Bulish green	29.51 (29.56)	4.30 (4.31)	8.59 (8.61)	19.68 (19.71)	18.04 (18.08)	8	Dia
4	[Cu(L)]	220 ^d	Green	29.08 (29.13)	4.20 (4.25)	8.45 (8.49)	19.39 (19.42)	19.30 (19.28)	5	1.93
5	[Zn(L)]	240	White	28.66 (28.97)	4.01 (4.22)	8.24 (8.44)	19.08 (19.13)	19.64 (19.73)	19	Dia
6	[Mn ₂ (L)Cl ₂]	250 ^d	White	21.-5 (21.44)	3.04 (3.13)	6.12 (6.25)	14.13 (14.29)	24.41 (24.54)	10	5.6
7	[Co ₂ (L)Cl ₂]	240	Pink	21.03 (21.11)	3.00 (3.07)	6.07 (6.15)	14.03 (14.07)	25.85 (25.91)	12	4.56
8	[Ni ₂ (L)Cl ₂]	140	Green	21.11 (21.13)	3.01 (3.08)	6.03 (6.16)	14.01 (14.08)	25.73 (25.84)	20	3.48
9	[Cu ₂ (L)Cl ₂]	180-182	Pale green	20.50 (20.69)	2.98 (3.01)	6.00 (6.03)	13.65 (13.79)	27.25 (27.38)	25	2.01
10	[Zn ₂ (L)Cl ₂]	230 ^d	White	20.40 (20.52)	2.83 (2.99)	5.84 (5.98)	13.27 (13.68)	27.86 (27.95)	18	Dia

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

Comp.	Band maxima (λ_{max}) (nm)	$\nu_{as}(\text{COO})$	$\nu_{sy}(\text{COO})$	$\Delta\nu = (\nu_{as} - \nu_{sy})$	$\nu(\text{C-S})$	$\nu(\text{NH}_2)$	$\nu(\text{M-O})$	$\nu(\text{M-S})$	$\nu(\text{M-Cl})$
L	270	1597 _s	1417 _s	180	850 _m	3323 _s	---	---	302 _w
1	276,380	1601 _s	1417 _s	184	850 _m	3300 _s	534 _w	---	310 _w
2	418,694	1601 _s	1358 _s	243	850 _m	3344 _s	534 _w	---	300
3	344,418,751	1593 _s	1400 _s	193	850 _m	3350 _s	577 _w	---	320 _w
4	390,624	1593 _s	1406 _s	187	851 _m	3300 _s	546 _m	---	295
5	269,360	1597 _s	1406 _s	193	850 _m	3344 _s	569 _w	---	305
6	280,388,678	1618 _s	1419 _s	199	806 _m	3369 _s	570 _m	380 _w	300 _w
7	424,790	1593 _s	1406 _s	187	806 _m	3356 _s	588 _m	370 _w	292 _w
8	302,748	1604 _s	1415 _s	189	808 _w	3311 _s	573 _w	385 _w	310 _w
9	418,588	1608 _s	1415 _s	193	829 _m	3305 _s	571 _w	360 _w	320 _m
10	330	1626 _s	1388 _s	238	808 _m	3288 _s	538 _w	365 _w	325 _m

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