

Synthesis and Characterization of Some Metal (II) Complexes of Dithiocarbamate

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Abstract:

The synthesis of dithiocarbamate ligand (AIDTC) produce from reaction of $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ with CS_2 , CH_2I_2 , as well as its coordination compounds with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Hg(II) are reported. The synthesized compounds were characterized by elemental analysis for metals, magnetic, molar conductance measurements, electronic and IR spectral studies. From the analytical data the following general formula was suggested $[\text{M}(\text{L})_2\text{Cl}_2]$ where $\text{M} = \text{Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Hg(II)}$, $\text{L} = \text{N}_2\text{HCH}_2\text{CH}_2\text{NHCS}_2\text{CH}_2\text{I}$ (AIDTC).

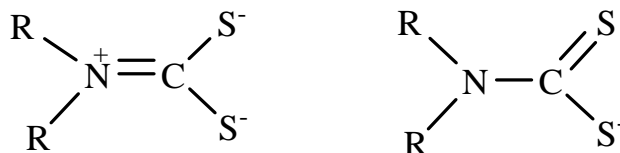
Magnetic susceptibility and electronic spectral studies suggest an octahedral structure for Mn(II), Co(II), Ni(II), Cu(II) complexes and tetrahedral structure for Zn(II), Hg(II) complexes.

Keywords: Metal(II), Dithiocarbamate, complexes

Introduction :

Dithiocarbamates form a large number of complexes with transition metals and give rise to neutral complexes⁽¹⁾. Dithiocarbamates complexes have been investigated extensively⁽²⁾. The interaction of metal dithiocarbamates with Lewis bases leads to the formation of the corresponding base adducts^(3,4).

Although the sulphur atoms of dithiocarbamate ligands possess donor and n-back donation character of the same order of magnitude, these ligands have a special feature, there is an additional n-electron flow from nitrogen to sulphur via a planar delocalized π -orbital system, as shown below:



This effect results in a strong electron donation and a high electron density on the metal leading to its next higher oxidation state⁽⁵⁾.

In coordination chemistry, dithiocarbamates act as ligands due to their selectivity and sensitivity to the reaction with transition and non transition metal ions. They are also important from biological point of view since they were found to affect many biological processes⁽⁶⁻⁸⁾. Moreover, metal dithiocarbamates have diversified applications in the field of rubber chemistry as vulcanization accelerator and antioxidants⁽⁹⁾.

In the present work we report the preparation and characterization of some new complexes obtained by the reactions of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) salts with 2-aminoethyldithiocarbamate-iodomethane.

Experimental:

1- Material and Measurements:

All chemicals were of reagent grade used as supplied without further purification. Infrared absorption spectra were recorded on FTIR spectrophotometer Tensor27, Brucker2003 in the $400\text{--}4000\text{cm}^{-1}$ range using KBr discs. Electronic spectra, were recorded by using a Shimadzu UV-Vis-Spectrophotometer UV-1650 for 10^{-3} M solution of the compounds in dimethyl formamide (DMF) at 25°C using 1cm quartz cell. Conductivity measurements were made

on 10^{-3} M solutions of the complexes in DMF at 25°C using conductivity measuring apparatus model PCM₃ Jenway. The magnetic susceptibility measurements were made at 25°C by the Faraday method on the solid in a Pyrex tube using Bruker BM6 instrument.

2- Preparation of the ligand: 2-aminoethyldithiocarbamateiodo- methane⁽¹⁰⁾:

The ligand was prepared by the addition of (0.1mol, 6.68ml) of ethylenediamine drop wise to a mixture of carbon disulfide (0.1 mol, 6.06ml) and diiodomethane (0.1 mol, 8.056ml) in ethanol (15 cm^3). The mixture was stirred for about 1 h, keeping the temperature at 0°C . The white solid product so obtained was filter off, washed with ethanol and dried in vacuum.

3-Preparation of Complexes:

In appropriate molar ratio (1:2) a solution of metal salt of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01mol, 2.37g), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01mol, 2.37g), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.01mol, 1.70g), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.01mol, 1.97g), HgCl_2 (0.01mol, 2.71g), or ZnCl_2 (0.01mol, 1.36g), in ethanol (15 cm^3) was added to a solution of the ligand (0.02mol, 5.51g) in (15 cm^3) ethanol at a temperature of $15 - 20^\circ\text{C}$. The mixture was stirred for 2 h at 20°C , then cool to 0°C . The precipitated solid was filtered, washed with cold ethanol and dried in vacuum. Table-1 shows some physical properties of the ligand and its complexes.

Table – 1 : Analytical and some Physical Properties of the ligand and its complexes

Compound	Color	M.P (°C)	Λ_M (DMF) ($\Omega^{-1}\text{mol}^{-1}\text{cm}^{-2}$)	% yield	%M (Found) Calcu.
(AIDTC) ($\text{C}_4\text{H}_9\text{N}_2\text{S}_2\text{I}$)	White	79	--	90	--
$[\text{Co}(\text{L})_2\text{Cl}_2]$	Violet	170	17	70	(8.64) 8.04
$[\text{Ni}(\text{L})_2\text{Cl}_2]$	Green	267	10	73	(8.61) 9.24
$[\text{Cu}(\text{L})_2\text{Cl}_2]$	Blue	237	23	83	(9.25) 9.70
$[\text{Mn}(\text{L})_2\text{Cl}_2]$	Yellow	227	12	77	(8.10) 8.00
$[\text{Hg}(\text{L})_2\text{Cl}_2]$	White	106	19	60	(24.36) 25.09
$[\text{Zn}(\text{L})_2\text{Cl}_2]$	White	137	10	66	(9.50) 9.07

Table – 2 : selected infrared bands (cm^{-1}) of the ligand and its complexes

Compound	$\nu(\text{NH}_2)$	$\nu(\text{C}=\text{S})$	$\nu(\text{C}-\text{S})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{N})$
(AIDTC) ($\text{C}_4\text{H}_9\text{N}_2\text{S}_2\text{I}$)	3420m	975w	1047w	--	--
$[\text{Co}(\text{L})_2\text{Cl}_2]$	3320	870w	1047w	366w	460m
$[\text{Ni}(\text{L})_2\text{Cl}_2]$	3317	907w	1049s	370w	457w
$[\text{Cu}(\text{L})_2\text{Cl}_2]$	3370	933w	1047w	390w	466w
$[\text{Mn}(\text{L})_2\text{Cl}_2]$	3360	947w	1045m	377s	497w
$[\text{Hg}(\text{L})_2\text{Cl}_2]$	3417	890w	1047m	417m	--
$[\text{Zn}(\text{L})_2\text{Cl}_2]$	3420	879w	1047m	370m	--

w=weak, m=medium, s=strong

Table – 3:Magnetic moment and electronic Spectral data of the prepared complexes

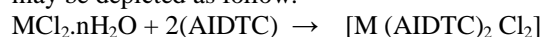
Compound	χ_{eff} (B.M)	$\nu_1(\text{cm}^{-1})$	$\nu_2(\text{cm}^{-1})$	$\nu_3(\text{cm}^{-1})$	C.T*(cm^{-1})
$[\text{Co}(\text{L})_2\text{Cl}_2]$	4.70	11070	16777	21700	
$[\text{Ni}(\text{L})_2\text{Cl}_2]$	2.87	10000	15970	23775	
$[\text{Cu}(\text{L})_2\text{Cl}_2]$	1.99	13077-14090			
$[\text{Mn}(\text{L})_2\text{Cl}_2]$	5.77				29470 - 30277
$[\text{Hg}(\text{L})_2\text{Cl}_2]$	Diam**				27397 - 40327
$[\text{Zn}(\text{L})_2\text{Cl}_2]$	Diam				2770 - 31600

*C.T = Charge Transfer

**Diam = Diamagnetic

Results and Discussion:

The reaction of the metal salts with the ligand (2-aminoethyldithio- carbamatiodomethane) (AIDTC) may be depicted as follow:



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

n= 0,2,4,6

All complexes were stable in air at room temperature but they decomposed without melting at elevated temperature (above 300 °C). The complexes are completely insoluble in water, ethanol, methanol but they are moderately soluble in dimethylformamide. The molar conductivities measured in DMF for 10^{-3}

M solutions at room temperature (Table – 1) suggested a non-electrolytic nature⁽⁶⁾.

The infrared spectra of free ligand and its complexes (5and6) are shown in Fig. 2,3 ,4 and its feature are given in (Table – 2). The ν (C – S) stretching frequency has been used to distinguish between a monodentate and a bidentate behavior of the dithiocarbamate group⁽¹¹⁾. In case of monodentate dithiocarbamate ligand a doublet arises around 1000 cm^{-1} separated by $\geq 20 \text{ cm}^{-1}$ due to non-equivalence of two(C – S) stretching vibrations. On the other hand in case of bidentate dithiocarbamate a strong singlet is observed at ca. ~

1000 cm^{-1} region, which is indicative of symmetrically, bound dithiocarbamate moiety. The infrared spectra of dithiocarbamate ligand showed a band at 975 cm^{-1} assigned to $\nu(\text{C}=\text{S})$ group shifted towards a lower frequency on coordination^(12,13). The other band observed at 1047 cm^{-1} due to $\nu(\text{C}-\text{S})$ band remained unaltered on complexation, which indicated that the ligand is monodentate⁽¹⁴⁾.

The appearance of a broad strong band in the IR spectrum of the ligand at (3420 cm^{-1}) is assigned to NH stretching vibration of the NH_2 group. In all spectra of complexes, this band is shifted to a lower frequency

(50 – 103 cm^{-1}) indicating that the ligand was coordinated to the metal ions through the nitrogen atom of the NH_2 group⁽¹⁵⁾. Except that of Zn(II) and Hg(II) which was remained almost at the same position (3420 cm^{-1}) that in the ligand.

The other band at (500 cm^{-1}) due to C – I group⁽¹⁶⁾ remained unaltered in the complexes indicating that there is no coordination through the C – I group. Moreover, the spectra of all complexes showed new bands (not observed in ligand spectra) at 457 – 497 cm^{-1} and 366 – 417 cm^{-1} due to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$ respectively^(16,17). The presence of these bands supported the formation of the complexes under investigation. The bands due to coordinate chloride ion in complexes fall below the limits of our infrared spectrophotometer and could not be observed.

The magnetic moment of Mn(II) complex was 5.77 BM which indicated a high spin octahedral geometry around the metal ion⁽¹⁸⁾. The electronic spectra of the manganese complex, the d – d transitions, doubly forbidden from the fundamental term ${}^6\text{A}_1\text{g}$ towards the quartet terms ${}^4\text{A}_1\text{g}(\text{G})$, ${}^4\text{E}_\text{g}(\text{G})$, ${}^4\text{T}_2\text{g}(\text{G})$, ${}^4\text{T}_1(\text{G})$ exhibit a very small intensity and are concealed by the intraligand transition. The absorption band at 29470 – 30277 cm^{-1} can be attributed to charge transfer of ligand to metal^(19,20).

The Co(II) complex exhibited three bands at 11070, 16777 and 21700 cm^{-1} , assigned to ${}^4\text{T}_1\text{g}(\text{F}) \rightarrow {}^4\text{T}_2\text{g}(\text{F})\nu_1$, ${}^4\text{T}_1\text{g}(\text{F}) \rightarrow {}^4\text{A}_2\text{g}(\text{F})\nu_2$, and ${}^4\text{T}_1\text{g}(\text{F}) \rightarrow$

${}^4\text{T}_1\text{g}(\text{P})$ transition respectively which predicted the high spin octahedral geometry of the complex that was confirmed by observed magnetic moment value 4.70 BM. This value of magnetic moment is higher than the spin-only for three unpaired electrons and may be ascribed to substantial orbital contribution to the moment^(21,22).

The absorption spectra of nickel (II) complex display three d – d transition bands in the range 11025, 15970 and 23775 cm^{-1} . The transitions correspond to the ${}^3\text{A}_2\text{g}(\text{F}) \rightarrow {}^3\text{T}_2\text{g}(\text{F})\nu_1$, ${}^3\text{A}_2\text{g}(\text{F}) \rightarrow {}^3\text{T}_1\text{g}(\text{F})\nu_2$ and ${}^3\text{A}_2\text{g}(\text{F}) \rightarrow {}^3\text{T}_1\text{g}(\text{P})\nu_3$, respectively, these transitions are also supported by the value of magnetic moment of 2.97 BM for the complex confirmed the presence of two unpaired electrons and octahedral environment to it^(21,23).

The electronic spectrum of the Cu(II) complex showed one broad band at 13077 cm^{-1} due to two or three transition ${}^2\text{B}_1\text{g} \rightarrow {}^2\text{A}_1\text{g}$, ${}^2\text{B}_1\text{g} \rightarrow {}^2\text{B}_2\text{g}$ and ${}^2\text{B}_1\text{g} \rightarrow {}^2\text{E}_\text{g}$ ⁽²²⁾ suggesting a distorted octahedral geometry with D_{4h} symmetry in terms of Jahn-Teller effect for the complex. The observed magnetic moment value 1.99 BM also support the distorted octahedral geometry of the complex^(20,22).

The Zn(II) and Hg(II) complexes are diamagnetic properties and have no d – d transition. They are four coordinated, which could either be tetrahedral. However, tetrahedral geometry is the more preferred stereochemistry for Zn(II) and Hg(II)^(13,24) (Table – 3).

From the above results and the various physicochemical, spectral and analytical studies, it was concluded that the ligand acts as monobidentate coordinating through sulfur atom or sulfur and nitrogen atoms forming mononuclear complexes.

Thus hexacoordinated octahedral structure was suggested for Mn(II), Co(II), Ni(II), and Cu(II) complexes, and tetraordinated tetrahedral structure was suggested for Zn(II) and Hg(II) complexes. The proposed structures for the complexes are presented in Fig. 1.

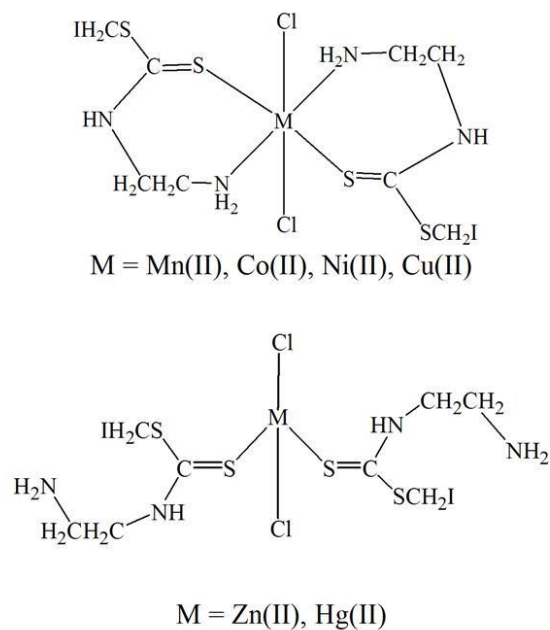


Fig. 1. The proposed structures of the complexes .

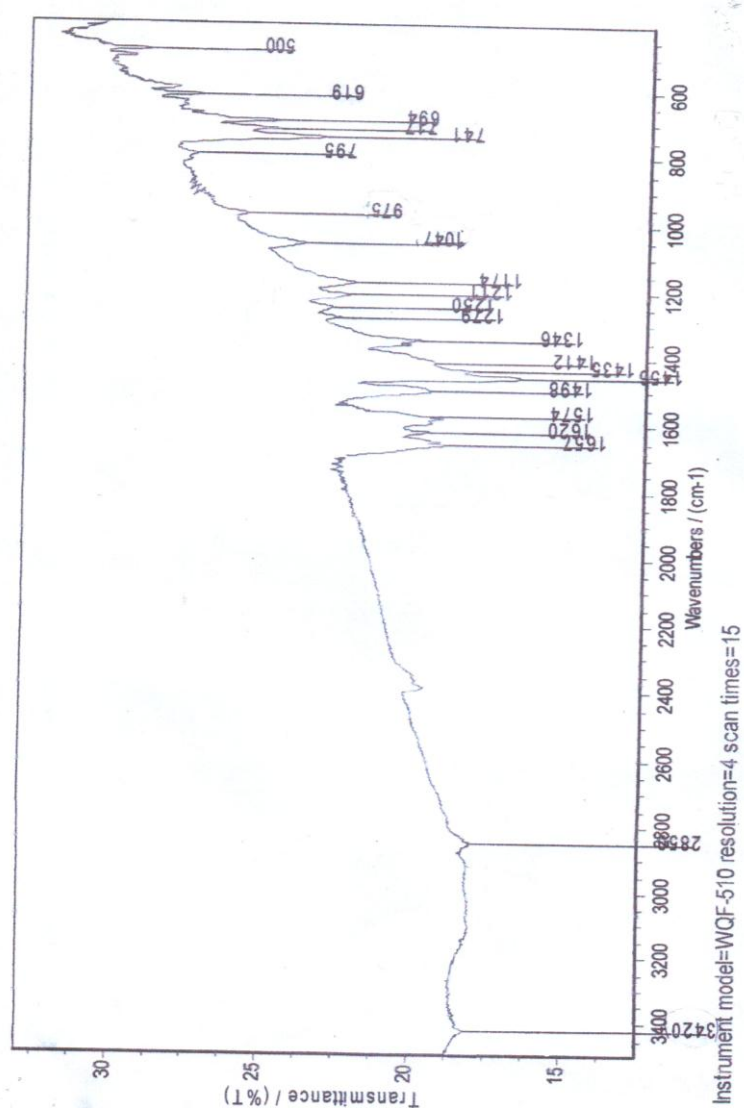
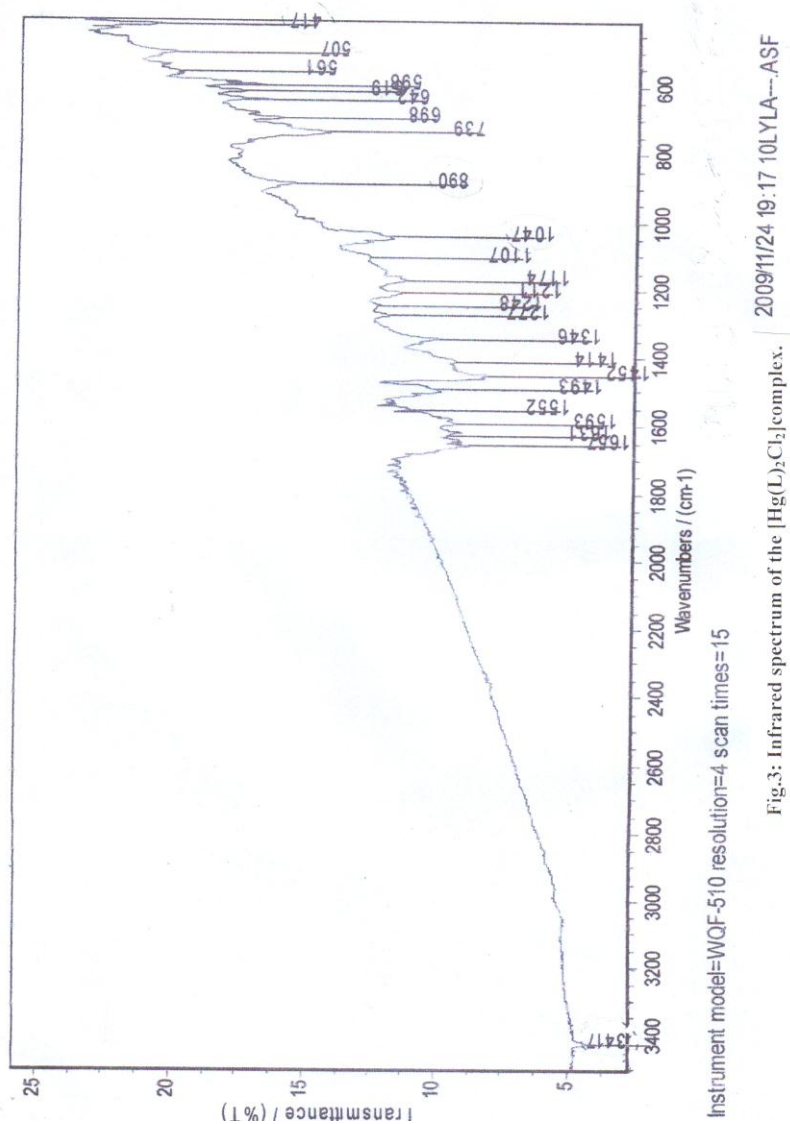


Fig.2: Infrared spectrum of the ligand (AIDTC).

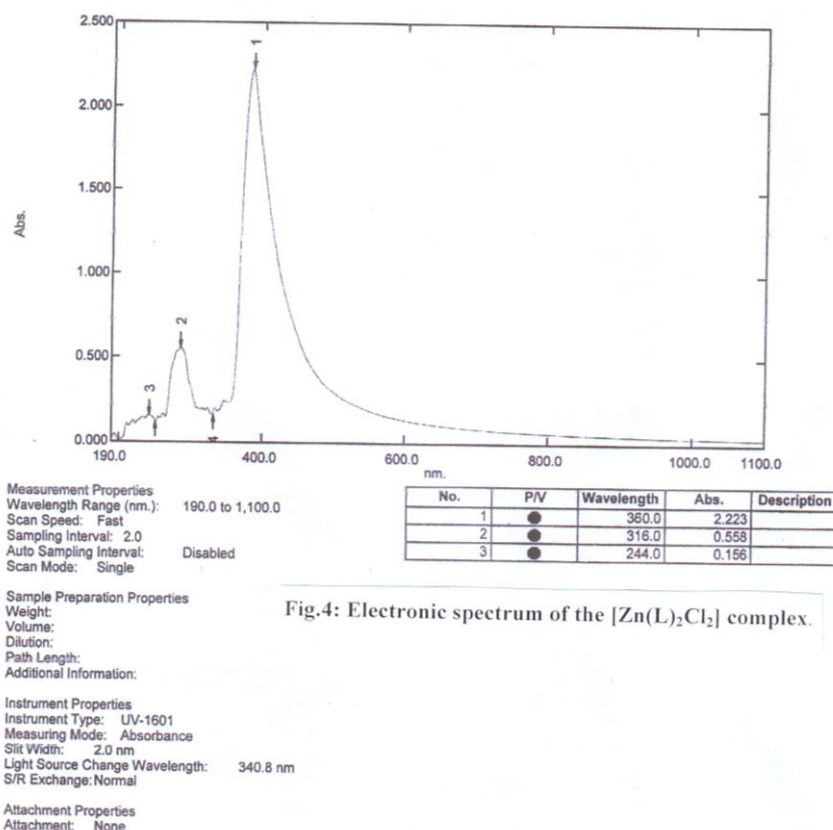


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Fig.4: Electronic spectrum of the $[Zn(L)_2Cl_2]$ complex.

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تحضير وتشخيص عدد من معقدات الفلزات (II) مع ليكاند ثنائي ثايوكارباميت

ليلي جمعة نجم ، ماهر عبد الرزاق محمد

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الملخص

حضرت معقدات جديدة للمنغنيز (II) والكوبلت (II) والنيكل (II) والنحاس (II) والخرصين (II) والزنك (II) مع ليكاند 2-امينوإثيل ثنائي ثايوكارباميت ايودوميثان المحضر من تفاعل الاثيلين ثنائي أمين مع ثنائي كبريتيد الكاربون وثنائي ايودوميثان (AIDTC) شخّصت المعقدات الناتجة باستخدام التحليل الدقيق للفلزات وقياس التوصيلية الكهربائية المولارية والاطياف الالكترونية والاشعة تحت الحمراء والقياسات المغناطيسية. أظهرت هذه القياسات أن المعقدات الناتجة ذات صيغة عامة هي:



أوضحت قياسات التوصيلية المولارية بان المعقدات غير الكتروليتية وتكون سداسية التناسق ذات شكل ثماني السطوح ما عدا معقدات الخرصين (II) والزنك (II) تكون رباعية التناسق ذات شكل رباعي السطوح.