



Synthesis and Characterization of Ni⁺², Cu⁺² and Zn⁺² complexes with Benzoxazole-2-thionate, Diphenyl Phosphinomethane and Iodine

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Abstract

The metal powder nickel, copper or zinc react with bis-benzoxazole disulfide (C₁₄H₈N₂S₂O₂) (L) in refluxing toluene to give the complexes of the type [M(L)₂], where M = Ni⁺², Cu⁺², Zn⁺² and L = benzoxazole-2-thionate (C₇H₄NSO) through an oxidative addition reaction. The complexes of type [M(L)₂Ph₂P(CH₂)PPh₂] were prepared by the reaction of [M(L)₂] with diphenylphosphinomethane in (1:1) and (2:2) molar ratio respectively. The reaction of some of the above complexes with iodine were also carried out. The complexes were characterized by IR, UV-Vis spectroscopy, metal content, elemental analysis, molar conductivity and magnetic measurements. Electronic and magnetic measurements indicate that some of the complexes have square planar geometry and the other contain tetrahedral geometry. Iodinated complexes behave as typical semi conductors and their conductivities were increases with temperature.

Key words: Complexes, benzoxazole-2-thionate, diphenyl phosphinomethane, iodine.

Introduction

Coordination chemistry of metallo-nitrogen or sulfur compounds are a source of stimulation to many research workers, due to the fact that it possesses unique stereochemical, magnetic and spectral properties metal complexes of ligands containing nitrogen and sulfur as donor atoms were reviewed by Yuan and Huynh¹⁻⁴.

Copper and nickel powder react directly with sodium dithiocarbamate in organic solvents and produce the corresponding metal complexes. The result showed that the copper powder react in chloroform more readily than any other system examined. This reaction has been successfully applied in the determination of copper content in brass and bronze powder⁵.

The powder is oxidized by Et₂P(S)SS(S)PEt₂ to tin(II) diethyldithiophosphate, the reaction involve the insertion of the metal in to the S-S bond⁶.

Tetramethylthiuram disulfide (DTS) an inhibitor or rephrotoxicity of Pt(II) drugs, an efficient agent in the treatment of chronic alcoholism and heavy metal toxicity. The reactions of tetramethylthiuram disulfide with K₂PtCl₄ in 1:1 or 1:2 molar ratio gave the compounds [PtCl₂(DTS)] and [Pt(S₂(NEt₂)₂)] respectively, were described by Cervantas⁷.

Indium metal react with (C₃H₄N₃S)₂ or (C₅H₁₄N₃S₂) in refluxing toluene give the compounds [In(L)₃] and [In(L₂)₃], L₁ = C₃H₄N₃S⁻, L₂ = C₅H₁₄N₃S⁻ through an oxidative addition reaction. Trinuclear complexes of the formula [In(L₁)₃(MCl₂)₂] and [In(L₂)₃(MCl₂)₂] were prepared by direct reaction of

MCl₂.6H₂O (M = Co, Ni) or CuCl₂.2H₂O and ZnCl₂.XH₂O with the above indium complexes. The prepared compounds and complexes were characterized by micro analysis, IR, UV-Vis spectra, metal content, conductivity and magnetic measurements⁸.

Palladium(II) and Platinum(II) complexes containing the mixed ligands Ph₂P(CH₂)_nPPh₂ (n=1-4) and benzo-1,3-imidazoline-2-thione, benz-1,3-oxazoline-2-thione or benzo-1,3-thiazoline-2-thione have been prepared and characterized by elemental analysis, spectral and magnetic studies as well as ³¹P, ¹H-NMR data⁹.

Homo binuclear complexes of the type [Cl₂MRC=CRMCl₂] [M= Ni(II), Pd(II) or Pt(II) and R = 5-Phenyl-1,3,4-oxadiazole-2-thiol, 4,5-diphenyl-1,2,4-triazole-3-thiol, or 2-mercapto-benzothiozole] have been prepared and characterized. Octahedral environment around Ni(II), while square planar geometry around Pd(II) or Pt(II) have been deduced on the basis magnetic and spectra measurements¹⁰.

Metal dithiolene complexes possess a delocalized electron system as a planar central core [M(C₂S₂)₂]. The conduction band is formed by the ligand π or orbital or mixed-metal-ligand orbital where the sulfur atoms play an important role¹¹.

Matsubayashi et al. reviewed donor abilities of the diimiredithiolene complexes. The complexes provide cation salts with various anions including I₃⁻, Br₃⁻.

In view of there interesting results and in continuation of our comprehensive studies on transition and non transition metals complexes with sulfur containing¹²⁻¹³ and other various donating ligands¹⁴⁻¹⁵, we reported here the preparation of some Ni(II),

Cu(II) and Zn(II) complexes with hybrid ligands of benzimidazole-2-thionate and diphosphine.

Material and Methods

All the chemical used were of high purity according to the supplier (Fluka). Analysis of ligand and complexes were carried out using CHNS elemental analyzer model 2400 Perkin Elmer. The metal content was estimated spectrophotometrically using Shimadza AA670 spectrophotometer. Melting point or decomposition temperature were determined on a Buchi melting point apparatus and were uncorrected, infrared spectra were recorded on a FTIR Bruker Tensor 27 Co. spectrophotometer in the 250-4000 cm^{-1} range using CsI disc. Electronic spectra were obtained with a Shimadzu UV-Vis recording UV1600 spectrophotometer at room temperature. The measurements were recording using a concentration of 10^{-3} M of the complexes in DMSO. The magnetic moments were carried out at 25°C on the solid state by Faradays method using Bruker BM6 instruments, conductivities were measured using Conductivity meter model PCM3- Jenway. These measurements were obtain using DMSO over the 10^{-3} M at 25°C.

The solid state electrical conductivities of compact samples were measured as a function of temperature (308-328 °K), on a Hewlett-Pukard LCR meter by the conventional two probe method. The pellets were prepared at load of (5-7 tor/cm^2) and the contact on the pellet surface was made with the help of silver paste.

Benzoxazolesulfide was synthesized by a standard method¹⁶.

Synthesis of the complexes: Preparation of $[\text{M}(\text{L})_2]$ complexes, $\text{M} = \text{Ni}^{+2}, \text{Cu}^{+2}$ or Zn^{+2} , $\text{L} = (\text{C}_7\text{H}_4\text{NSO})$: A clear solution of Benzoxazolesulfide (0.3g, 0.001 mol) in tetrahydrofuran (20 cm^3) was added to the metal powder ($\text{M} = \text{Ni}, \text{Cu}$ or zn) (0.001 mol) in (30 cm^3) ethanol-toluene. The reaction mixture was stirred under reflux for 12 h, by which time the metal was completely dissolved, refluxing was stopped at this stage and the stirred mixture was cooled to ambient temperature. The formed precipitate was filtered off washed with ethanol and diethylether and dried under vacuum.

Preparation of $[\text{M}(\text{L})_2(\text{Dppm})]$ complexes: A solution of $[\text{Ni}(\text{L})_2]$ complexes (0.36 g, 0.001mol) in (10 cm^3) toluene was added to a solution of (0.38 g, 0.001mol) of Dppm in (5 cm^3) toluene. The reaction mixture was stirred under reflux for 4 h. The formed precipitate was filtered off, washed with toluene and diethylether then dried under vacuum for severd hours. The rest of the complexes were prepared using the above procedure.

Preparation of $[\text{M}(\text{L})(\text{Dppm})]_2, \text{M} = \text{Ni}^{+2}, \text{Cu}^{+2}, \text{Zn}^{+2}$: A solution of $[\text{Ni}(\text{L})_2]$ (0.72 g, 0.002 mol) in (20 cm^3) toluene was added to a solution of (0.77 g, 0.002 mol) of Dppm in (10 cm^3) ethanol-toluene. The mixture was stirred under reflux for 6 h.

The mixture was left at room temperature for 12 h. A coloured precipitate formed in solution was filtered off, washed with ethanol and diethylether, then dried under vacuum for several hours.

Preparation of $[\text{M}(\text{L})_2]\text{I}$ complexes, $\text{M} = \text{Ni}^{+2}, \text{Cu}^{+2}$: A solution of $[\text{M}(\text{L})_2]$ (1 mmol) in ethanol-toluene (20 cm^3) was added to iodine (0.25 g, 0.002 mol) in (20 cm^3) of toluene. The mixture was refluxed for 10 h with continuous stirring. The precipitate was obtained after evaporation of the residue solution to about 1/3 of its volume, which was filtered off, washed with ethanol and diethylether, then dried under vacuum.

Results and Discussion

The complexes of the type $[\text{M}(\text{L})_2]$ were prepared through an oxidative addition reaction. The mechanism of oxidative addition reactions involving the initial cleavage of the S-S bond of the ligand to form the thiolate ion and the oxidation of the metal from M to M^{+2} ¹⁶. Treatment of the prepared complexes $[\text{M}(\text{L})_2]$ with the diphosphine in (1:1) molar ratio gave new hybrid ligand complexes of the type $[\text{M}(\text{L})_2\text{Ph}_2\text{PCH}_2\text{PPh}_2]$, where as the dinuclear complexes were obtained from the reaction of the mononuclear complexes $[\text{M}(\text{L})_2]$ with diphosphine in (2:2) molar ratio.

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 these complexes are air stable at room temperature and insoluble in common organic solvents but they are soluble in dimethylformamide (DMF) or dimethylsulfoxide (DMSO).

The molar conductivity of 10^{-3} M solution of the complexes indicate that they are non-electrolyte in DMSO¹⁷, also it was found that they are insulator in solid state, while the complexes of the type $[\text{M}(\text{L})_2]\text{I}$ are (1:1) electrolyte. This is consistent with the stoichiometry for the complexes on the basis of analytical data.

The most important diagnostic feature of IR spectra of the complexes were listed in table 2. The IR spectra of the ligand showed a bands due to $\nu(\text{C}=\text{N})$ appear at 1618 cm^{-1} and $\nu(\text{C}-\text{S})$ 842 cm^{-1} , $\nu(\text{C}-\text{O}-\text{C})$ band at 1290 cm^{-1} and the $\nu(\text{S}-\text{S})$ band appeared at 473 cm^{-1} ¹⁰. In the complexes the band $\nu(\text{C}-\text{O}-\text{C})$ appear at the same position indicating that this band was not shared in coordination, while the $\nu(\text{S}-\text{S})$ band disappeared due to the cleavage of this bond as discussed before. The $\nu(\text{C}-\text{S})$ band observed at lower frequency which indicate it was shared in coordination with the metal ions. Further support of this coordination is provided by the appearance of new band 370-400 cm^{-1} which tentatively attributed to the $\nu(\text{M}-\text{S})$ ¹⁸. The $\nu(\text{C}=\text{N})$ band of the ligand was shifted to a lower wavelength number and appeared in the region 1590-1665 cm^{-1} in the spectra of metal complexes indicating coordination through the azomethine nitrogen atom to the metal atom. Formation of a metal nitrogen band was further supported by the present of the band at about 430-490 cm^{-1} for $\nu(\text{M}-\text{N})$ ¹⁹⁻²⁰.

The IR spectra of diphosphine ligand show a medium to strong band at $1050-110\text{ cm}^{-1}$, which may be a signal to vibration of $\nu(\text{C-P})$ group, the IR spectra of complexes showed new bands at $515-560\text{ cm}^{-1}$ assigned to $\nu(\text{M-P})$ ^{21,22}.

In order to obtain some information about the coordination properties of the metal ions, the electronic spectra has been recorded as 10^{-3} M solution in DMSO and the results were presented in table 2.

The bands observed at $36300-31100\text{ cm}^{-1}$ table 2, due to disulfide ligand which may assigned $n-\pi^*$ or to $\pi-\pi^*$ transition respectively.

The magnetic moments of Ni(II) complexes (No. 1,4,7 and 10) are diamagnetic which suggest a square planer geometry around the nickel atom.

The electronic spectra of mono and dinuclear Ni(II) complexes (No. 1,4,7 and 10) show two band at $15000-16000\text{ cm}^{-1}$ and $25510-26455\text{ cm}^{-1}$ table 2. These bands were assigned $^1A_{1g} \longrightarrow ^1A_{2g}$ and $^1A_{1g} \longrightarrow ^1E_g$ transition. These results suggested a square planer geometry around the nickel ion²³⁻²⁴.

The magnetic moments of mono and binuclear Cu(II) complexes (No. 2,5,8 and 11) has been found to be (2.00,1.70,2.01 and 1.89 B.M) which indicate the presence of one unpaired electron. The Cu(II) complexes No. (2 and 5) showed a band at 10162 cm^{-1} and 13204 cm^{-1} which are assigned to $^2T_2 \longrightarrow ^2E$ transition in tetrahedral environment²⁵.

The magnetic susceptibility measurements showed that all Zn(II) complexes (3,6 and 9) were diamagnetic, and the electronic spectra of these complexes do not show any d-d band.

In the complexes of the formula $[\text{M}(\text{L})_2]\text{I}$, similar observation was found in the IR and UV/Vis spectra expected to have a dark coloured complexes.

The electrical conductivities of the compact sample of the complexes were nonconducting the conductivities values in solid state are $1.3-9.61 \times 10^{-12}\text{ }\Omega^{-1}\text{cm}^{-1}$, while the complexes of the type $[\text{M}(\text{L})_2]\text{I}$ and $[\text{M}(\text{L})_2\text{Ph}_2\text{PCH}_2\text{PPh}_2]\text{I}$ recorded in the temperature range $30-55\text{ }^\circ\text{C}$ ($303-328\text{ }^\circ\text{K}$) showed that the complexes exhibit typical semi conducting behavior. The conductivities of present complexes are well in the range of $3.10-3.39 \times 10^{-8}\text{ }\Omega^{-1}\text{cm}^{-1}$ which similar to a number of transition metal containing polymers such as $[\text{M}(\text{C}_4\text{S}_4)]_n$, $\text{M} = \text{Ni(II)}$ ions²⁶.

The temperature dependent measurements of electrical conductivities of some of the complexes over the range $303-328\text{ }^\circ\text{K}$, figures 1 and 2 indicate thermally activated conductivity.

The plot of $\log \sigma$ verse $1/T$ almost linear over this temperature range and the activation energy is low, table 3. The increasing in electrical conductivities of these complexes with increasing of temperature shows the semi conducting properties of the complexes.

The band gaps evaluated from these plots and by using equation 1, were found to be low 2.9 and 6.12 KJ mol^{-1} which is also indicative semi conducting behavior.

$$\sigma = \sigma_0 e^{-\Delta E / KT} \quad (1)$$

The thiolate ligand used in this study, coordinated to metal ions in mono or bidentate fashion from thiolate sulfur atoms and azomethine group for mono nuclear complexes or from thiolate sulfur atom, where is the diphosphine coordinated in bidentate fashion in mono nuclear and dinuclear complexes as shown in figure 3.

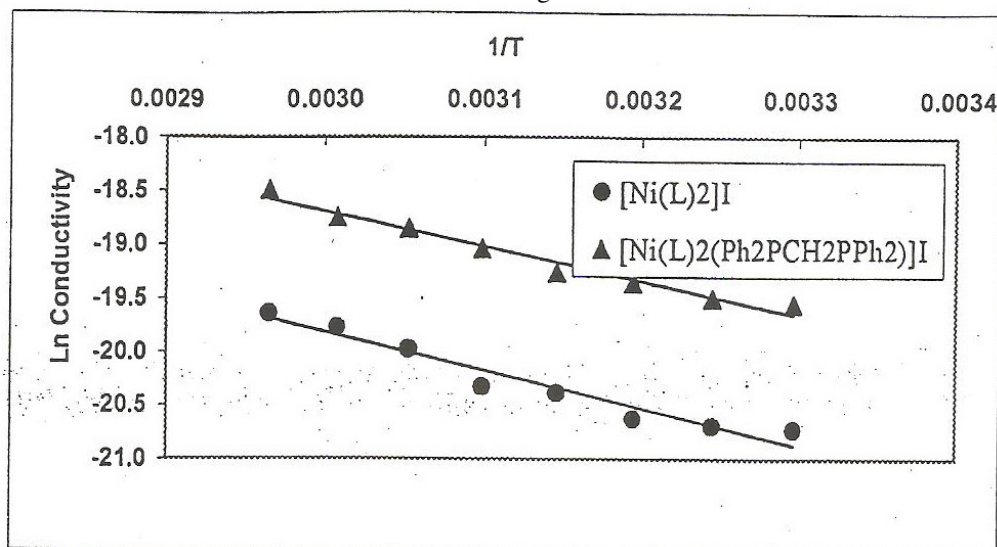


Figure-1
Correlation between Ln conductivity an 1/T

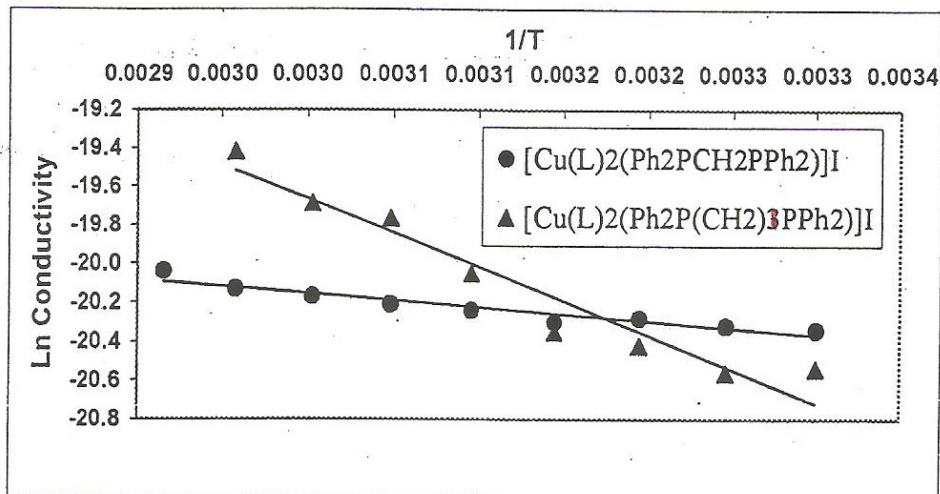


Figure-2
 Correlation between Ln conductivity an 1/T

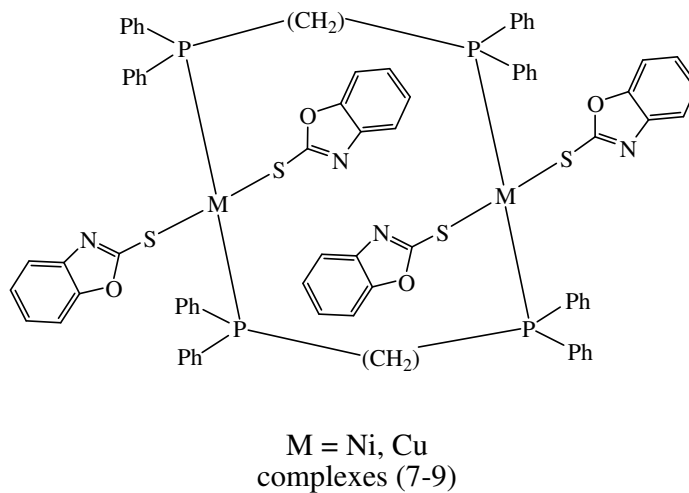
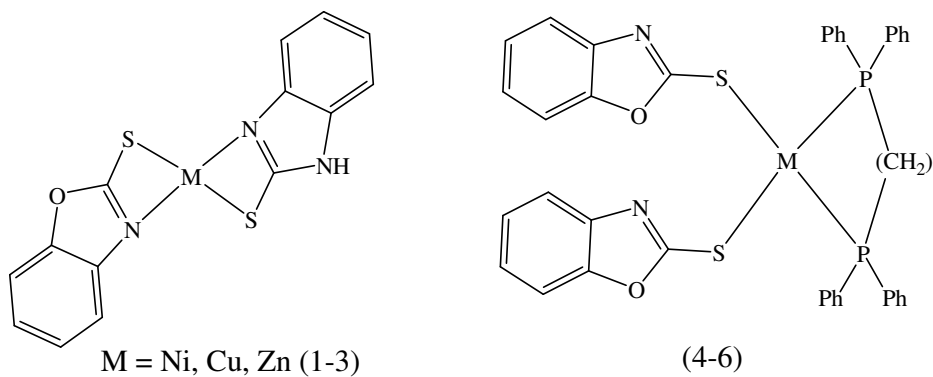


Figure-3
 Suggested structure for the complexes

Table-1
Physical properties of the ligands and its complexes

No	Complexes	Colour	m.p °C	Analysis found (Calc)					Λ .ohm ⁻¹ . cm ² mol ⁻¹	μ_{eff} (B.M)
				C%	H%	N%	S%	M%		
L1	(C ₇ H ₄ N ₂ O ₂ S ₂)	Pale yellow	190	56.10 (56.00)	2.53 (2.66)	9.30 (9.33)	21.29 (21.33)	---	10	---
1	[Ni(L) ₂]	Green	230	46.96 (46.83)	2.18 (2.07)	7.73 (7.81)	17.91 (17.80)	16.39 (16.36)	4	Dia
2	[Cu(L) ₂]	Dark Brown	360	46.42 (46.22)	2.44 (2.20)	7.43 (7.70)	17.69 (17.60)	17.54 (17.47)	16	2.00
3	[Zn(L) ₂]	Pale grey	220 ^d	46.00 (45.97)	2.03 (2.19)	7.80 (7.66)	17.54 (17.51)	17.91 (17.89)	12	Dia
4	[Ni(L) ₂ (Dppm)]	Dark green	260 ^d	67.00 (66.79)	4.50 (4.28)	3.87 (3.94)	9.00 (9.13)	8.25 (8.30)	4.9	Dia
5	[Cu(L) ₂ (Dppm)]	Brown	250 ^d	66.39 (66.33)	4.67 (4.25)	3.73 (3.96)	9.00 (9.07)	9.10 (9.00)	9	1.70
6	[Zn(L) ₂ (Dppm)]	Pale grey	340	66.75 (66.15)	4.03 (4.24)	3.12 (3.96)	9.16 (9.04)	9.94 (9.24)	8	Dia
7	[Ni(L)(Dppm)] ₂	Olive	300 ^d	64.98 (64.78)	4.30 (4.38)	2.52 (2.36)	5.21 (5.39)	9.92 (9.90)	20	Dia
8	[Cu(L)(Dppm)] ₂	Pale brown	270 ^d	64.72 (64.07)	4.56 (4.34)	2.14 (2.34)	5.41 (5.34)	10.71 (10.90)	5	2.01
9	[Zn(L)(Dppm)] ₂	yellow	344	64.01 (63.96)	4.47 (4.33)	2.14 (2.33)	5.95 (5.33)	10.80 (10.88)	15	Dia
10	[Ni(L) ₂]I	Dark brown	280 ^d	34.96 (34.59)	1.53 (1.65)	5.67 (5.64)	13.77 (13.17)	12.31 (12.08)	40	Dia
11	[Cu(L) ₂]I	Black	230	34.65 (34.15)	1.42 (1.63)	5.52 (5.63)	13.60 (13.17)	12.50 (12.94)	42	1.89

Table-2
Electronic and infrared spectra data of the ligand and their complexes

No	Band maximum (cm ⁻¹) λ_{max}	IR band assignment (cm ⁻¹)					
		$\nu(\text{C-S})$	$\nu(\text{C=N})$	$\nu(\text{C-P})$	$\nu(\text{M-S})$	$\nu(\text{M-N})$	$\nu(\text{M-P})$
L	36300, 31100	840 _s	1618 _s	---	---	---	---
1	1500,26200	830 _s	1605 _s	---	380 _m	430 _m	---
2	10162	824 _s	1600 _s	1050 _m	370 _m	480 _m	---
3	32000,30000	820 _s	1590 _s	1070 _m	400 _m	450 _m	---
4	16000,26000	829 _s	1603 _s	1100 _w	390 _w	460 _m	525 _w
5	13204	822 _s	1595 _s	1090 _w	375 _m	490 _m	540 _m
6	33000	819 _s	1598 _s	1095 _m	395 _m	470 _m	560 _m
7	15980,26453	820 _s	1615 _s	1100 _s	400 _w	---	550 _m
8	15974	815 _s	1620 _s	1090 _s	390 _w	---	540 _s
9	32000	810 _s	1618 _s	1080 _w	400 _m	---	550 _s
10	15900,26000	815 _s	1600 _s	---	390 _w	460 _w	---
11	16286	820 _s	1590 _s	---	380 _w	470 _m	---

Conclusion

In this research we reported synthesis and characterization a bidentate and monodentate ligands and its nickel, copper and zinc complexes. The complexes were characterized by physical, spectral data, conductivity and magnetic measurements. According spectral and magnetic measurements square planar and tetrahedral environment were suggested for the complexes.

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