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Synthesis, Characterization of some Transition metal complexes of Piperidine dithiocarbamate and ethylenediamine

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ABSTRACT

Piperidine is heterocyclic amine used as starting material for preparation piperidine dithiocarbamate (pipdtc).add the some transition metal salt of this ligand with ethylinediamine gave complexes of the types:[M(pipdtc)$_2$en], [M(pipdtc)$_3$] when the ratio, (M: pipdtc:en,1:2:1), (M: pipdtc.1:3) respectively . The ligand dithiocarbamate (pipdtc) behaves as a bidentate and coordinated to the metal ion centers either through sulfur atoms and through nitrogen atoms of the ethylenediamine All the synthesized ligand and complexes are characterized by elemental analyses, conductivity, infrared, electronic spectra and susceptibility measurements and theoretical Calculations . From the obtained data octahedral geometry for the complexes have been suggested.

Keywords: piperidine, dithiocarbamate, complexes, ethylenediamine

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تحضير وتشخيص بعض معقدات العناصر الانتقالية مع بايبردين ثنائي الكبريت كاربميت و أثيلين ثنائي امين

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البايبردين هو امين ذو حلقة غير متجانسة أستخدم كمادة اولية في تحضير البايبردين ثنائي الكبريت كاربميت **(pipdtc)**. تم أضافة املاح الفلزات الانتقالية على الليكاند والاثيلين ثنائي الامين حيث أعطى معقدات من الانواع : $[M(pipdtc)_2en]$, $[M(pipdtc)_3]$ عندما تكون النسب (M: pipdtc:en,1:2:1)(M: pipdtc.1:3) على التوالي. يسلك ليكاند ثنائي الكبريت كاربميت كليكاند ثنائي السن عن طريق ذرتي الكبريت وعن طريق النايتروجين لاثيلين ثنائي الامين شخص الليكاند والمعقدات المحضرة بواسطة التحليل الدقيق للعناصر ، التوصيلية ، الاشعة تحت الحمراء ، الاطياف الالكترونية والحساسية المغناطيسية والحسابات النظرية بينت القياسات ان الليكاند يتناسق بشكل ثنائي السن من خلال ذرتي الكبريت لثنائي كبريت الكاربميت ومن خلال ذرات النتروجين للأثيلين ثنائي الامين وان الشكل الهندسي المقترح للمعقدات هو ثماني السطوح .

كلمات دالة: بايبردين ، ثنائي الكبريت كاربميت ، معقدات ، اثيلين ثنائي امين .

1. INTRODUCTION

The wide attention is paid to study of dithiocarbamate compounds present.[1] Because the application in the pharmaceutical and agrochemical industries.[2-3] Many dithiocarbamate used in agriculture as pesticides and in rubber industries as vulcanization accelerators and antioxidants. [4] dithiocarbamates have been found to act usually as bidentate ligands, coordinating through the both Sulphur atoms, and many bis- or tris (dithiocarbamato) complexes of transition metal ions have been studies [5] and able to stabilized transition metals in variety oxidation number [6,7].

2. Experimental

2.1 Materials and Methods

All reagents and solvents were commercially available high grade materials (Fluka A.G., Riedel-de Haën, BDH) and used as received, Infrared spectra were measured a using KBr discs with Nicolet 100 FTIR spectrophotometer in the 400-4000 cm^{-1}. NMR spectroscopy recored in avrin 300 MHz instrument. Conductivity measurements were carried out on 10^{-3} M solution of the complexes in DMSO using conductivity meter PCM3 Jenway at an ambient temperature. The electronic spectra were recorded on a PgT92+ UV-visible spectrophotometer for 10^{-3}M solutions of complexes in DMSO as solvent at 25°C using 1 cm quartz cell. Melting points were recorded on an Electrothermal 9300 apparatus. The magnetic measurements were carried out at 25°C on the solids by gouy method using Sherwood Scientific's instrument.

2.2 Syntheses of the ligand (sodium piperidine dithiocarbamate) Na(pipdtc) (1)

piperidine (0.85g, 0.01 mol) was dissolved in 30 ml of water containing sodium hydroxide (0.4 g, 0.01 mol) with constant stirring. The resulting solution was cooled in an ice bath, and carbon disulfide (0.76 g, 0.01 mol) was added dropwise with stirring. The mixture was stirred for 30 min. The yellow precipitate formed, was filtered off, washed with diethyl ether and dried in vacuum.

2.3 Synthesis of the complexes [M(pipdtc)$_2$ en] M= Fe(II), Co(II), Ni(II), Cu(II) (2a-d)

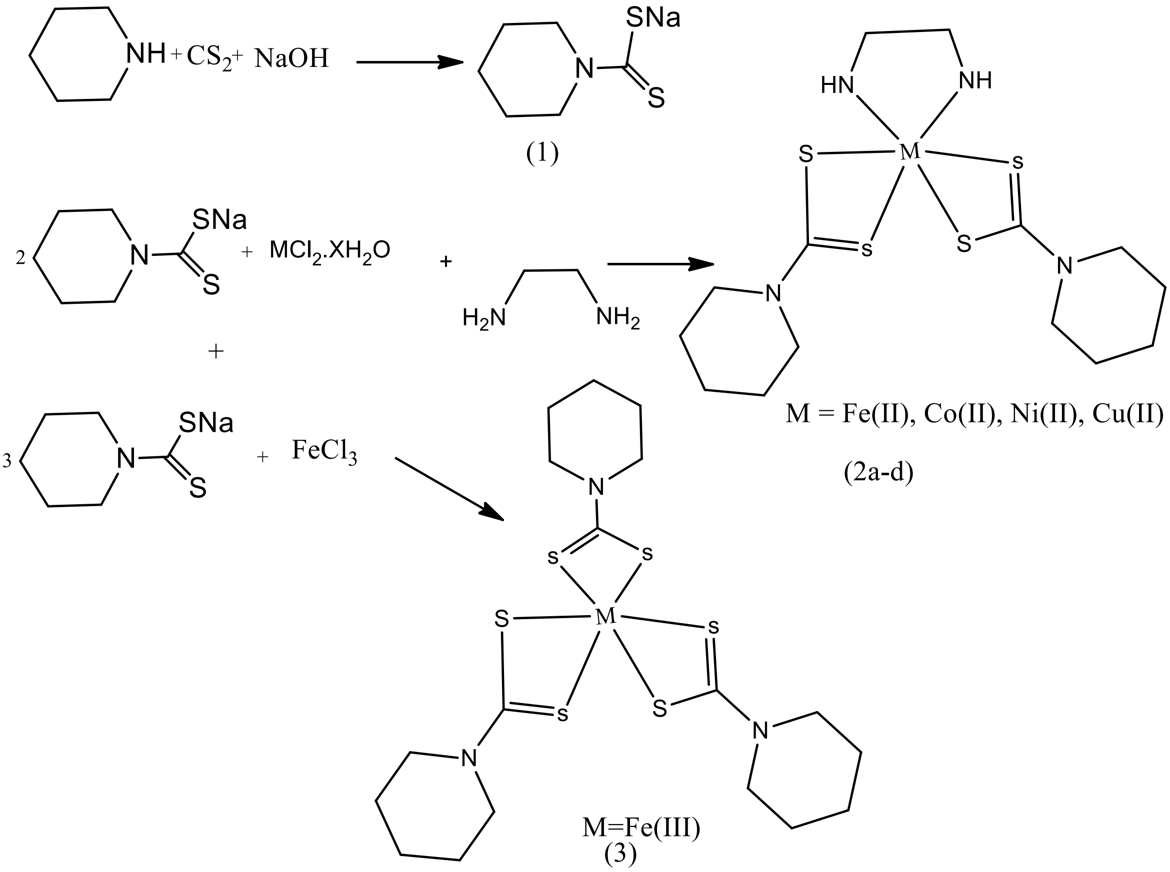
A solution of sodium piperidine dithiocarbamate (1.83 g, 0.01 mol) in 25 ml of water was added to aqueous solution of $FeCl_2.4H_2O$.(0.99 g, 0.005 mol) or $CoCl_2.6H_2O$, (1.15g, 0.005 mol) or $NiCl_2.6H_2O$ (1.18 g, 0.005 mol) or $CuCl_2.2H_2O$ (0.845 g, 0.005 mol) dropwise with a constant stirring at a room temperature and add (0.005 mol) of (ethylinediamine). After 30 min, the precipitate formed was filtered off, washed with 10ml of water dried under vacuum.

2.4 Synthesis of the complexes [Fe(pipdtc)$_3$] (3)

A solution of sodium piperdine dithiocarbamate (1.83 g, 0.01 mol) in 25 ml of water was added to aqueous solution of $FeCl_3.4H_2O$.(0.6984 g, 0.003 mol) dropwise with a constant stirring at a room temperature . After 30 min, the precipitate formed was filtered off, washed with 10 ml of water dried under vacuum.

3 Results and Discussion

The ligand was prepared by the reaction of carbon disulfide with secondary amine piperidine in the presence of sodium hydroxide and the complexes were prepared by direct addition of the aqueous solution of the corresponding metal chloride to the ligand solution in aqueous media , using 1:2:1 (metal: ligand: adduct) and 1:3(metal: ligand) molar ratio. (Scheme 1).



Scheme (1) preparation of piperidine dithiocarbamate ligand and their complexes

The composition and analytical data for piperidine dithiocarbamate ligand and their complexes are given in Table 1. The low values of molar conductivities of the complexes in DMF (٥.3 –9.4 $ohm^{-1}.cm^{2}.mol^{-1}$) indicate that all the prepared complexes are non - electrolytes. [8]

Table 1: analytical and some physical properties of piperidine dithiocarbamate ligand and their complexes.

Comp.no.	Chemical formula	color	m.p °C	Λ ohm^{-1}.cm^{2}.mol^{-1}	Yield %
1	Na(pipdtc)	white	160-161	4.5	85
2a	$[Fe(pipdtc)_2\ en]$	red	240-242	9.4	80
2b	$[Co(pipdtc)_2\ en]$	orange	227-228	6.7	75
2c	$[Ni(pipdtc)_2\ en]$	Light green	230-231	5.3	60
2d	$[Cu(pipdtc)_2\ en]$	Brown	270-272	5.8	78
3	$[Fe(pipdtc)_3]$	Brown	244-246	6.6	90

3.1 Electronic spectra

The UV spectra of the free ligand (pipdtc) and complexes table 2. The band at about 32412 cm^{-1}due

to (π □□π$^{□}$□$^{□}$absorption of (NCS,SCS) group for free ligand [9].The electronic spectra of the prepared iron (II) complexes display bands at (10972 -12566 cm^{-1}) referring to (^{5}T2g→^{5}Eg) and other charge transfer bands at (31135-34531) which confirms the octahedral geometry around Fe(II). The cobalt(II) complexes display bands at (11280 cm^{-1}) ,(14932 cm^{-1}) and (28551 cm^{-1}) referring to $^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$, $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$, $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$ respectively and other charge transfer bands at (31227-35126 cm^{-1}) which confirms the octahedral geometry around Co(II). The nickel(II) complexes display bands at (11943 cm^{-1}) ,(15123 cm^{-1}) and (24471cm^{-1}) referring to ($^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$),($^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$), ($^3A_{2g}(F)\rightarrow{}^3T_{1g}$) respectively and other charge transfer bands at (33987cm^{-1}- 35911cm^{-1}) which confirms the octahedral geometry around Ni(II).The electronic spectrum of Cu(II) complex show bands at (15075 cm^{-1}), referring to (^{2}Eg→ ^{2}T$_2$g) and other charge transfer bands at (29931 cm^{-1}) which confirms the octahedral geometry around Cu (II). [10] For high spin d^5 Iron (III) configuration ($t_{2g}^{3}e_{g}^{2}$), all possible (d-d) electronic transitions were spin forbidden and orbital forbidden due to the presences of five unpaired electrons .The degree of forbidden decreases the absorption intensities by a factor of about 100 compared to the usual (d-d) absorption band, thus, the spectra are usually not observed in the visible region[11-12] The band at (33272-36219 cm^{-1}) due to charge transfer.

Table 2: The electronic data for sodium piperidine dithiocarbamate Na(pipdtc) and its metal complexes.

No.	Compounds	Band absorption cm^{-1}	Assignment	µeff (B.M) Geometry
1	Na(pipdtc)	32412	π □□π□	
2a	[Fe(pipdtc)$_2$ en]	10972 - 12566	$^5T2g\rightarrow{}^5Eg$	4.9
		31125-34531	Charge transfer	
٢b	[Co(pipdtc)$_2$ en]	11280-14932 -28551	$^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$, $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$, $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$	4.78
		31227-35126	Charge transfer	
2c	[Ni(pipdtc)$_2$ en]	11943 - 15123 - 24471	($^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$),($^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$), ($^3A_{2g}(F)\rightarrow{}^3T_{1g}$)	2.95
		33987 - 35911	Charge transfer	
2d	[Cu(pipdtc)$_2$ en]	15075	$^2Eg\rightarrow{}^2T_2g$	1.95
		29931	Charge transfer	
3	[Fe(pipdtc)$_3$]	33272-36219	Charge transfer	5.9

3.2 Magnetic susceptibility

The magnetic moments of the complexes table ١. The magnetic moments for Fe (II), Co (II), Ni(II) and Cu(II) complexes are (4.90,4.78,2.95,1.95 B.M) respectively.

From compare these data with spin only value. Suggest the high values of magnetic moments for Fe(II) and Co(II) complexes are due to orbital contribution an octahedral geometry of complexes and their hybridization is (sp^3d^2).The magnetic moments values of hexacoordinate Fe(III) complex is (5.9 B.M). Suggest a high spin. [13- 15].

3.3 Infra-Red Spectroscopy

The most important bands in the FT-IR spectra of the prepareed ligand and their complexes are listed in Table 2. The ligands shows a strong absorption at (1475) cm^{-1}, which is assigned to the C-N stretching frequency, while the complexes showed an absorption at (1492 -1512 cm^{-1}). Which is assigned to the ν (C-N) stretching frequency. Compared with the ligand the complex to shift to a higher frequency by (17-37) cm^{-1}. The presence of a single strong band at (952-1067) cm^{-1} due to a ν (C=S) mode in the spectra of the ligand and their complexes. The strong single absorption this region assigned to bidentate behavior of the dithio ligand and their complexes. [16-18]. the absorption bands at (412-482) cm^{-1} which assigned to ν (M-S) and ν (M-N)[19].

Table (3): Selected IR bands of the sodium piperidine dithiocarbamate Na (pipdtc) and its metal complexes (cm^{-1}).

No.	Compounds	υ(C=S)cm^{-1}	υ(C-N)	υ (M-N)	υ(M-S)
1	Na(pipdtc)	962	1475	-	-
2a	[Fe(pipdtc)$_2$ en]	952	1489	482	425
٢b	[Co(pipdtc)$_2$ en]	993	1512	454	429
2c	[Ni(pipdtc)$_2$ en]	986	1490	423	416
2d	[Cu(pipdtc)$_2$ en]	1054	1498	435	412
3	[Fe(pipdtc)$_3$]	1005	1480		431

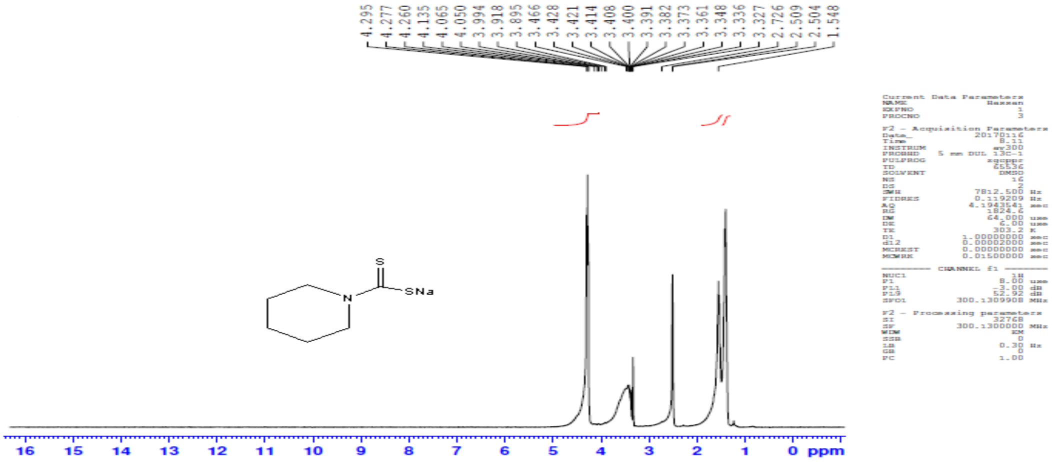
3.4 NMR Spectroscopy

The H^{1}NMR spectra of ligand and bis(piperidinedithiocarbamate)ethylenediamine nickel(II) show signals at δ (,1.54,1.9 ,4.05) , δ (1.40, 1.91, 2.2,2.9,3.9) respectively that meant environment of hydrogen. This is a good agreement result. ^{13}CNMR spectra of ligand show signals at δ(24.03, 25.36, 38.6, 50.27, 51.96 ,206.202 (NCS$_2$)).due to five carbon atoms and the last signal assigned to NCS$_2$ .table (4).

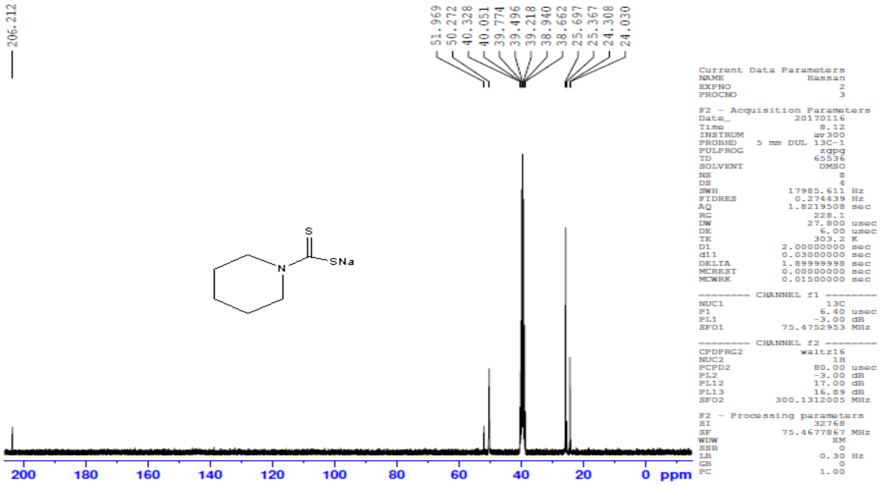
Table (4): most important signals ^{1}HNMR, ^{13}C NMR Spectra of the Ligand and Complex.

No.	Compound	NMR	ppm
1	Na(pipdtc)	^{1}HNMR	1.54 (2H), 1.9 (4H), 4.05(4H)

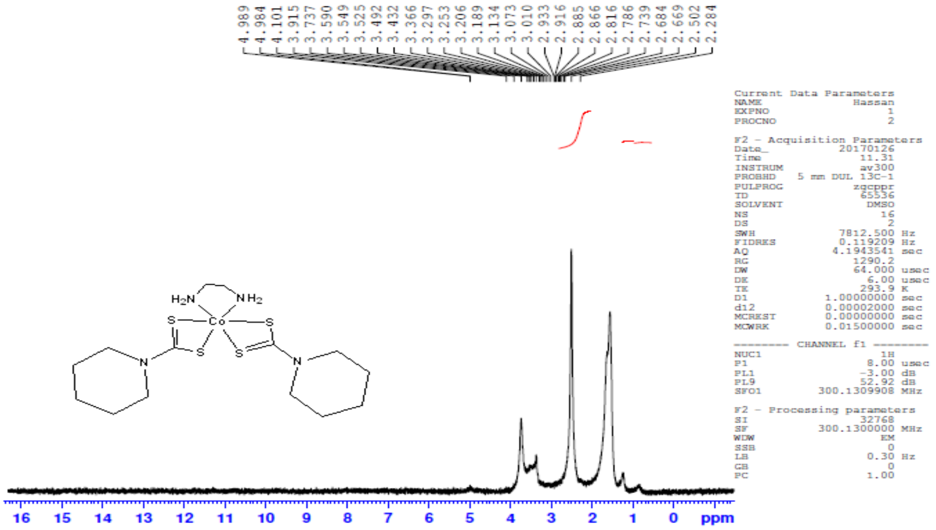
		^{13}CNMR	24.03, 25.36, 38.6, 50.27, 51.96 ,206.202 (NCS_2).
2c	[Ni(pipdtc)$_2$en]	^{1}HNMR	1.40(4H), 1.91(8H), 2.2(4H),2.9 (4H),3.9(8H),



Scheme (2) The H^{1}NMR of sodium piperidine dithiocarbamate ligand



Scheme (2) The C^{13}NMR of sodium piperidine dithiocarbamate ligand



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DS                     2
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FIDRES          0.119209 Hz
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RG                1290.2
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DE                  6.00 usec
TE                 293.9 K
D1            1.00000000 sec
d12           0.00002000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

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PL1                -3.00 dB
PL9                52.92 dB
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WDW                   EM
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LB                  0.30 Hz
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PC                  1.00
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Scheme (3) The H^1NMR of Bis(piperidine dithiocarbamate)ethylenediamine cobalt(II)

3.5 theoretical Calculations.

Characterization and inferences of geometrical optimization for the prepared complex. We applied molecular mechanics MM+ Module in Hyper Chem. 6.0 and MM2 Module in the CS ChemOffice Molecular Modeling Program to calculate the angles and bond length for [Co(pipdtc)$_2$en]. Table (5) the structure adopted distorted octahedral figure (1). That agreement with literature [21]

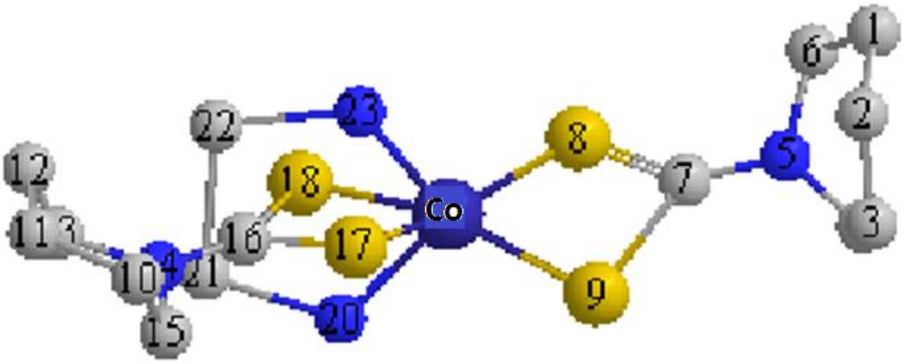

Figure (1) the Structure of [Co(pipdtc)$_2$en] Using MM2 CS ChemOffice Program

Table (5) the bond length and angles of [Co(pipdtc)$_2$en] complex.

No.	atoms	Acual A°
1.	Co(19)-N(20)	2.0197
2.	Co(19)-N(23)	1.9336
3.	S(18)-Co(19)	2.1792
4.	S(17)-Co(19)	2.1185
5.	S(9)-Co(19)	2.2859

6.	S(8)-Co(19)	2.1781
NO.	Angles	Acual
1.	N(20)-Co(19)-N(23)	96.3092
2.	N(20)-Co(19)-S(18)	55.6789
3.	N(20)-Co(19)-S(17)	64.2661
4.	N(20)-Co(19)-S(9)	108.9581
5.	N(20)-Co(19)-S(8)	146.5865
6.	N(23)-Co(19)-S(18)	56.9719
7.	N(23)-Co(19)-S(17)	60.5109
8.	N(23)-Co(19)-S(9)	142.8261
9.	N(23)-Co(19)-S(8)	106.7731
10.	S(18)-Co(19)-S(17)	79.8009
11.	S(18)-Co(19)-S(9)	159.8672
12.	S(18)-Co(19)-S(8)	118.9553
13.	S(17)-Co(19)-S(9)	106.2886
14.	S(17)-Co(19)-S(8)	148.7456
15.	S(9)-Co(19)-S(8)	65.3093

3- Conclusion

From above discussions we suggested the structure of hexcoordinated complexes are distorted octahedral except complex (6) is octahedral.

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