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SYNTHESIS, CHARACTERIZATION OF SOME METAL COMPLEXES OF DIETHANOLAMINEDITHIOCARBAMATE AND (1,10-PHENATHROLINE)

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ABSTRACT

A dithiocarbamate ligand; sodiumdiethanolaminedithiocarbamte Na(deadtc) is synthesized from the reaction of diethanolamine with cabondisulfide and sodium hydroxide.(phen)= 1,10-phenathroline . Addition of metal salts, gave complexes of the types: [M(deadtc)$_2$ phen], where M = Fe(II), Co(II), Ni(II) and Cu(II). [M(deadtc)$_3$] where M= Fe(III). The ligand (deadtc) behaves as a bidentate and coordinated to the metal ion centers either through the sulfur atom of its dithiocarbamate and or through the nitrogen atoms of the phenathroline. All the synthesized ligands and complexes are characterized by elemental analyses, conductivity, infrared, electronic spectra and susceptibility measurements. From the obtained data octahedral geometry for the complexes have been suggested.

Keywords: diethanolamine , dithiocarbamte, 1,10-phenathroline, Transition metal complexes.

تحضير و تشخيص بعض معقدات ثنائي ايثانول امين ثنائي الكبريت كاربميت مع (١,١٠) فيناثرولين .

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الملخص:

ان الليكاند ثنائي الكبريت كاربميت : ثنائي ايثانول امين ثنائي الكبريت كاربميت (*deadtc*) والمحضر من ثنائي ايثانول امين مع كبريتيد الكاربون وهيدروكسيد الصوديوم. اضافة املاح الفلزات تعطي معقدات ذات الصيغ $[M(deadtc)_2 phen]$ حيث M = Fe(II)، Co(II)، Ni(II) و Cu(II) ، (phen) =١,١٠- فيناثرولين ، $[M(deadtc)_3]$ حيث M =Fe(III) تم تشخيص الليكاند والمعقدات المحضرة بواسطة التحليل

الدقيق للعناصر ، التوصيلية ، الاشعة تحت الحمراء ،الاطياف الالكترونية والحساسية المغناطيسية بينت القياسات ان الليكاند يناسق بشكل ثنائي السن من خلال ذرتي الكبريت لثنائي كبريت الكاربميت ومن خلال ذرات النتروجين للفينوثرولين وان الشكل الهندسي المقترح للمعقدات هو ثماني السطوح

الكلمات المفتاحية: ثنائي ايثانول امين، ثنائي الكبريت كاربميت ،١٠,١- فيناثرولين ، املاح الفلزات.

1. INTRODUCTION

Metal complexes of dithiocarbamates have been widely studied in recent years [1–5], because of their wide range of applications in agriculture as pesticides, in medicines, in industry as vulcanization accelerators, Besides that, nitrogen donor adducts of dithiocarbamate complexes are also widely used in the preparation of thin semiconductor [6–8]. Recently, 1,1-dithiolate ligands have attracted much attention, mainly because of interesting photophysical properties derived from their extensive electron delocalization over all of the ligand atoms [9]. Understanding bonding in these complexes will allow the design of new effective complexes used is biological systems [10]. Dithiocarbamate ligands display a strong propensity of binding to metal atoms such as nickel [11].

2. Experimental

2.1 Materials and Methods

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

2.2 Syntheses of the ligand (sodium diethanolamine dithiocarbamate) Na(deadtc)

Diethanolamine (1.05g, 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(deadtc)$_2$ phen] M= Fe(II), Co(II), Ni(II), Cu(II)

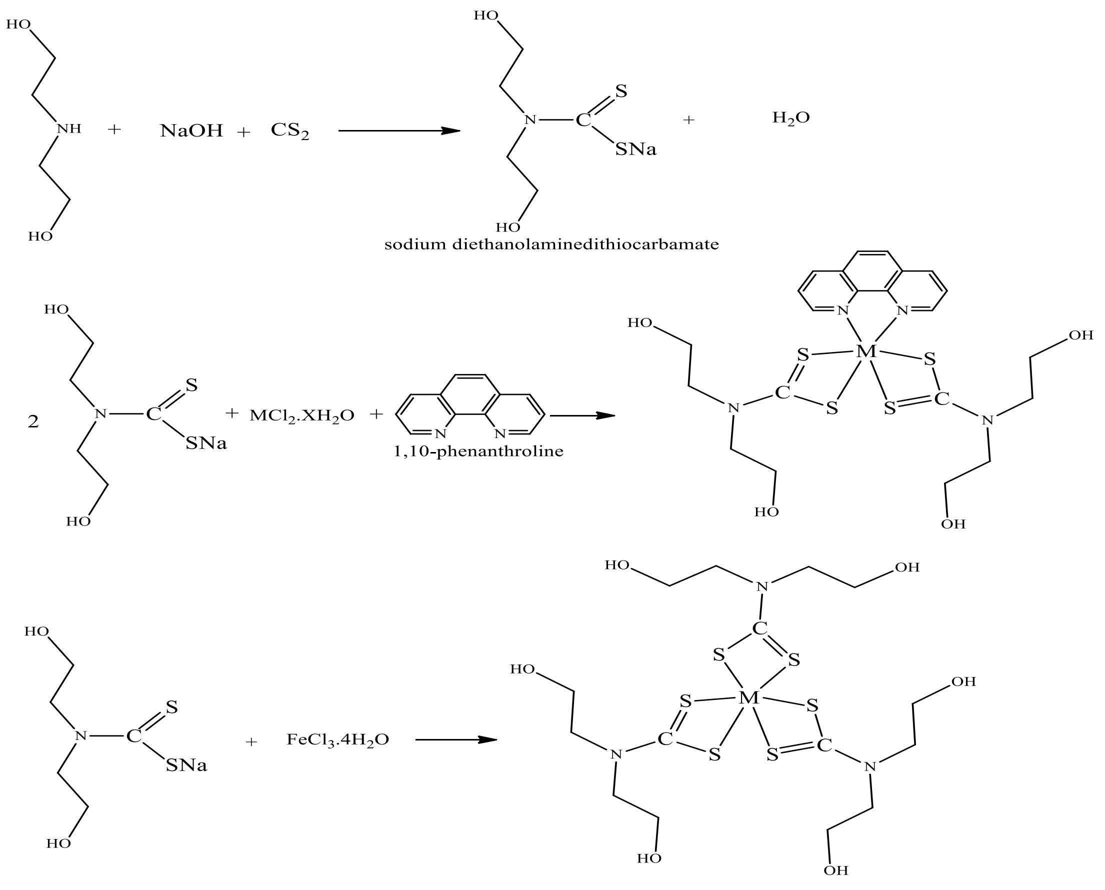
A solution of sodium diethanolaminedithiocarbamate (2.03 g, 0.01 mol) in 25 ml of water was added dropwise to each aqueous solution of $FeCl_2.4H_2O$ (0.99 g, 0.005 mol) and $CoCl_2.6H_2O$ (1.15g, 0.005 mol) and $NiCl_2.6H_2O$ (1.18 g, 0.005 mol) and $CuCl_2.2H_2O$ (0.845 g, 0.005 mol) with a constant stirring at a room temperature followed by addition of (0.005 mol) of (1,10 - phenathroline). After 30 min, the precipitate formed was filtered off, washed with 10ml of water and dried under vacuum.

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

A solution of sodium diethanolaminedithiocarbamate (2.03 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 and dried under vacuum.

3 Results and Discussion

The ligand was prepared by the reaction of carbon disulfide with the secondary amine diethanolamine, in the presence of sodium hydroxide and the complexes were prepared by direct addition of the aqueous solution of the chloride salats of the studied metals 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 ligand and dithiocarbamate complexes

The composition and analytical data for all complexes are given in Table 1. The low values of molar conductivities of the complexes in DMF (٥.٧ –1٥.3 $ohm^{-1}.cm^{2}.mol^{-1}$) indicate that all the prepared complexes are non-electrolytes. [13]

Table 1: Analytical and some physical properties of the prepared complexes.

Comp.no.	Chemical formula	color	m.p °C	Λ $ohm^{-1}.cm^{2}.mol^{-1}$	Yield %	μ_{eff} B.M
1.	Na(deadtc)	yellow	157	٥.٧	٨٧	-----
2.	$[Fe(deadtc)_2 phen]$	red	192-193	١٢.٥	٧٠	٤.٩٠
3.	$[Co(deadtc)_2 phen]$	orange	181-182	١٤.٧	٨٢	٤.٧٨
4.	$[Ni(deadtc)_2 phen]$	Light green	215-216	٩.٢	٩٠	٢.٩٥
5.	$[Cu(deadtc)_2 phen]$	Brown	245-246	١١.٨	٨٤	١.٩٢
6.	$[Fe(deadtc)_3]$	Brown	212-113	١٥.٣	٧٧	٥.٩

3.1 Electronic spectra

The band at 37313 cm^{-1} is assigned to (π □□π$^{□}$□$^{□}$absorption for ligand [14].The electronic spectra of the prepared iron (II) complex displays bands at (10365 cm^{-1}) refer to (^{5}T2g→^{5}Eg) and other charge transfer bands at (30894-35460).The cobalt(II) complex displays bands at (10728 cm^{-1}) ,(15635 cm^{-1}) and (27821 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 (30120-34965 cm^{-1}). The nickel(II) complex displays bands at (11532 cm^{-1}) ,(15013 cm^{-1}) and (23342 cm^{-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 (34873cm^{-1}- 35258cm^{-1}).The electronic spectrum of Cu(II) complex shows a band at (11247 cm^{-1}), referring to (^{2}Eg→ $^2T_2$g) and anther charge transfer band at (28472 cm^{-1}). [15] the electronic spectrum of Fe(III) shows a band at (31737cm^{-1}), which is assigned to charge transfer.

3.2 Magnetic susceptibility

The magnetic moments (μeff) for Fe (II), Co (II), Ni(II) and Cu(II) complexes are (4.90,4.78,2.95,1.95 B.M) respectively suggest an octahedral geometry.[16- 17]. The higher magnetic moment values than spin only moment of Fe(II) and Co(II) complexes are due to orbital contribution. The magnetic moment of the Fe (III) complex (5.9 B.M) Suggests a high spin octahedral geometry [18].

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

No.	Compounds	Band absorption	Assignment
		cm^{-1}	
1.	Na(deadtc)	37313	π □□π□
2.	[Fe(deadtc)$_2$ phen]	10365	${}^5T2g \rightarrow {}^5Eg$
		35460	Charge transfer
3.	[Co(deadtc)$_2$ phen]	10728,15635,27821	${}^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)$, ${}^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)$, ${}^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)$
		30120	Charge transfer
4.	[Ni(deadtc)$_2$ phen]	11532 ,15013,23342	${}^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)),({}^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)),$ $({}^3A_{2g}(F)\rightarrow{}^3T_{1g}$
		34873	Charge transfer
5.	[Cu(deadtc)$_2$ phen]	11247	${}^2Eg\rightarrow {}^2T_{2}g$
		28472	Charge transfer
6.	[Fe(deadtc)$_3$]	31737	Charge transfer

3.3 Infra-Red Spectroscopy

The most important bands in the FT-IR spectra of the prepared ligand and the complexes are recorded in Table 2. For dithiocarbamate compounds, three important regions of IR spectra are of interest. These are associated with the stretching vibration of ν (N–C), ν (–C=S) and ν (M–S) and the single absorption band in the second region suggests a bidentate behavior [19,20]. The ligand show a strong absorption at (1480) cm-1, which is assigned with the C-N stretching frequency, while the complexes showed absorption at (1484 -1509 cm-1). They are assigned to ν (C-N) stretching frequency. Compared with the ligand, the complex to shift to a higher frequency by (8-46) cm-1. The presence of a single strong band (955-1074) cm-1 due to a ν (CSS) mode in the spectra of the complex is strongly indicative of the bidentate behavior of the dithio ligand in the complexes. [21] the absorption bands at (410-486) cm-1 are assigned to ν (M-S) and ν (M-N).the absorption broad bands at (3383) cm-1 suggests (O-H) stretching frequency in the ligand and complexes. This band is unchanged or slightly shifted to higher frequency in the spectra of the complexes indicating that the OH group is not involved in coordination but engaged in intramolecular hydrogen bonding. [22]

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

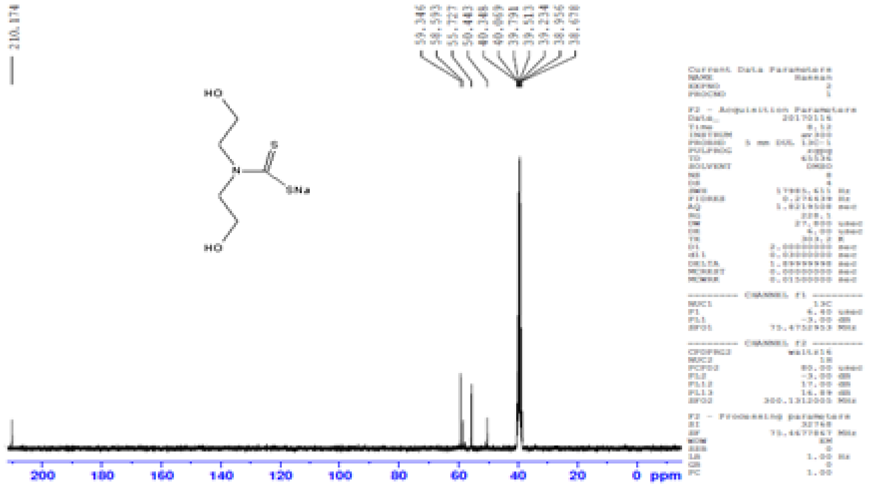
No.	Compounds	υ(O-H)	υ(C=S)	υ(C-N)	υ (M-N)	υ(M-S)
1.	Na(deadtc)	3338	982	1480		
2.	[Fe(deadtc)$_2$ phen]	3386	1006	1490	568	468
3.	[Co(deadtc)$_2$ phen]	3342	995	1492	572	466
4.	[Ni(deadtc)$_2$ phen]	3347	991	1511	586	484
5.	[Cu(deadtc)$_2$ phen]	3280	993	1489	548	468
6.	[Fe(deadtc)$_3$]	3343	987	1508		495

3.4 NMR Spectroscopy

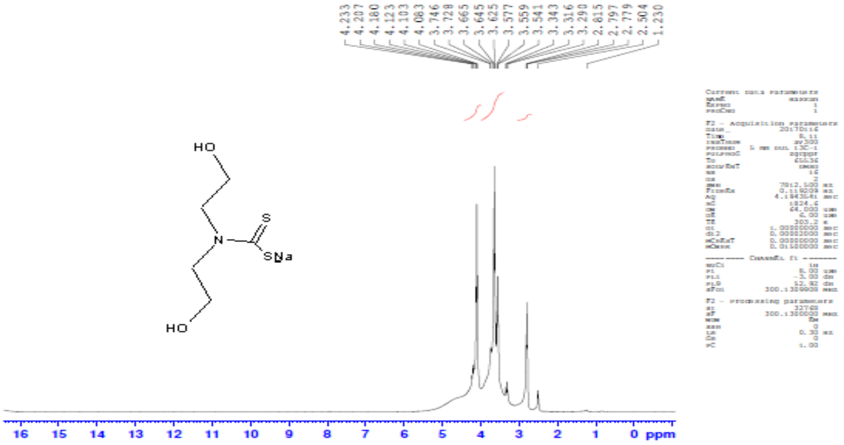
The NMR spectra for the ligand and [Cu(deadtc)2 phen] complex recorded in Av 300 spectrometer . The 1HNMR spectra for the ligand and complex show signals at δ (4.08 , 3.54 , 2.7) and (9.02 , 8.50 , 8.00 ,7.7 , 4.9 , 3.7, 3.4) respectively. The signals at δ (8- 9.02) are assigned to (1,10-phenathroline). The 13CNMR spectra show signals at δ (210 , 204) assigned to CS2 in the ligand and complex as in Table (4).

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

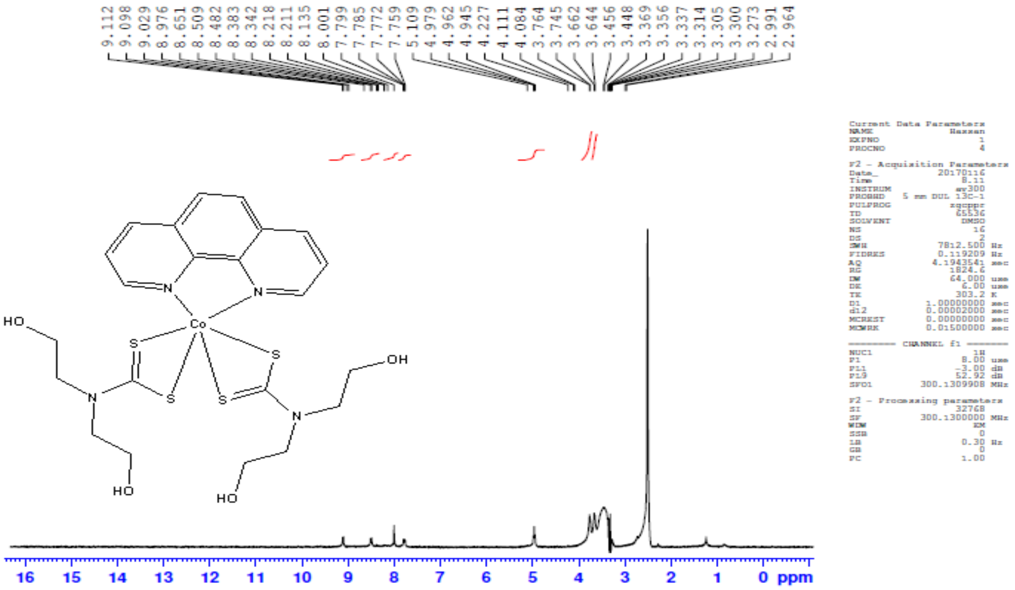
No.	Compound	NMR	δ ppm
1.	Na(deadtc)	^{1}HNMR	4.08(2H), 3.54(4H), 3.62(4H),2.7(4H)
		^{13}CNMR	39.2 ,55.4 , 55.7 ,59.7 , 210 (NCS_2).
2.	[Cu(deadtc)$_2$phen]	^{1}HNMR	3.4 (8H), 3.7 (8H), 4.9(4H),7.7(2H), 8.0(2H), 8.5(2H), 9.02(2H).
		^{13}CNMR	39.8 ,41.7 ,51.6 ,58.1, 105 , 138.9, 158.3 ,204.9(NCS_2).



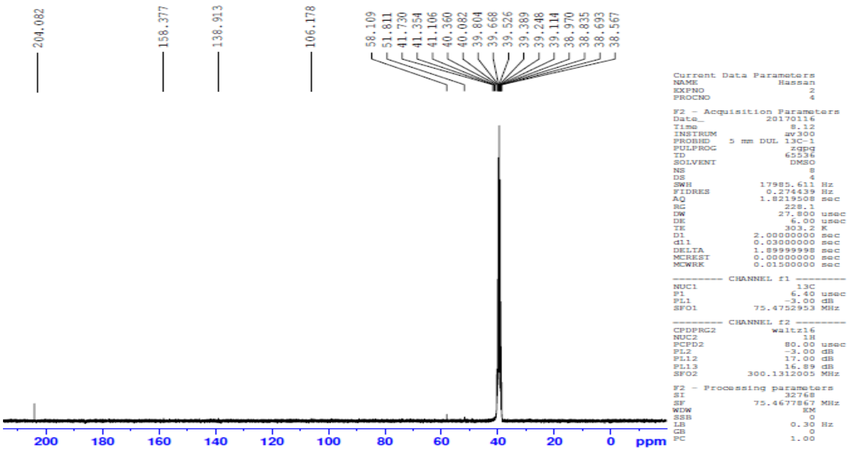
Scheme (2) The^{13} C NMR of sodium diethanolamine dithiocarbamate ligand



Scheme (2) The ^{1}HNMR of sodium diethanolamine dithiocarbamate ligand



Scheme (2) The ^{1}HNMR of [Cu(deadtc)$_2$ phen] complex



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PROCNO                   4

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PULPROG               zgpg
TD                   65536
SOLVENT               DMSO
NS                       8
DS                       4
SWH              17985.611 Hz
FIDRES            0.274439 Hz
AQ               1.8219508 sec
RG                   228.1
DW                  27.800 usec
DE                    6.00 usec
TE                   303.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST          0.00000000 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                    6.40 usec
PL1                  -3.00 dB
SFO1            75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -3.00 dB
PL12                 17.00 dB
PL13                 16.89 dB
SFO2           300.1312005 MHz

F2 - Processing parameters
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WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
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Scheme (2) The ^{1}HNMR of [Cu(deadtc)$_2$ phen] complex

3 Conclusion

From the above discussion we suggested that the structure of (2,3,4,5) complexes are distorted octahedral except Fe (III) complex is octahedral. The mixed ligands effect to convert the symmetry of complex O_h to D_{4h} .

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