

**SYNTHESIS AND
CHARACTERIZATION OF
BIS(DITHIOCARBAMATES) WITH
NICKEL(II) AND COPPER(II) METALS**

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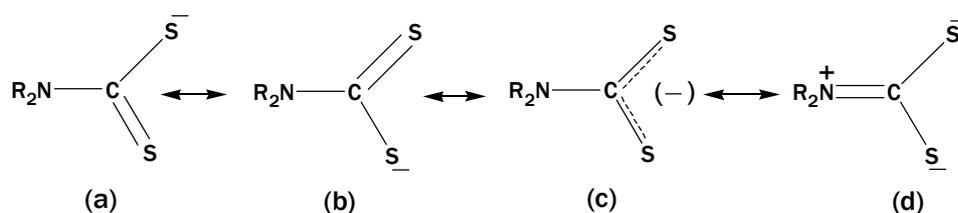
ABSTRACT

Nickel(II) and Copper(II) dithiocarbamate complexes of general formula $M(Rdtc)_2$. The present paper describes the synthesis and spectral properties of similar complexes of the following new dithiocarbamate ligands, cyclohexyldithiocarbamate (Chex Dtc), dicyclohexyldithiocarbamate (DchexDtc). The complexes have been characterized on the basis of analytical data, magneto-chemical, conductivity measurements, electronic and infrared spectroscopies as square planar Nickel(II), Copper(II) compounds. The results of the spectroscopic studies indicate that the dithiocarbamate ligands are always bidentate. All the complexes are non-conducting in DMF solution.

Key words: Nickel(II) and Copper(II),
Synthesis, dicyclohexyldithiocarbamate,
cyclohexyldithiocarbamate

INTRODUCTION

Metal complexes of dithiocarbamate have aroused considerable interest in view of their industrial and biological importance. It has been observed that introduction of metal ions considerably modifies the properties of dithiocarbamates, This has led to an increased interest in the chemistry of the complexes of these molecules. The dithiocarbamate group $R_2NCS_2^-$, usually coordinates in monovalent bidentate manner [1]. In fact the structure of dithioligands can be represented by the formalism:



The dithiocarbamate group can behave as monodentate ligand in the resonance forms (a) and (b), and as a bidentate S,S' donor ligand in forms (c) and (d), giving rise to complexes in which both the Sulphur atoms behave electron donors to the metal ion, thus forming a four-membered chelate ring. From the mentioned IR data we can conclude that structure (d) contributes more in the case of cyclohexyl, dicyclohexyldithiocarbamate as a contribution to the problem of the coordinating behaviour of the dithiocarbamate ligands and on the reactivity of their coordination compounds. We report in this study the preparation and characterization of new complexes of Ni(II),Cu(II) with cyclohexyl, dicyclohexyldithiocarbamate ligands.

1.THEORETICAL CALCULATION

Molecular mechanics uses an analytical $Y(R)$, differentiable and relatively simple potential energy Function, for describing the interactions between a set of atoms specified by their cartesian coordinates R .

Unlike first principles of quantum mechanical calculation molecular mechanics might be thought of as simply a fitting procedure , attempting to obtain as accurately as possible a representation of $Y(R)$ with of particular regard for theoretical foundations. However, it is found that the most successful fitting procedures , having generic utility, lead to Terms in the potential that can be ascribed to chemically meaningful interactions. For example, molecular mechanics potentials typically have simple analytic terms that provide an energetic penalty for deviation from standard bond lengths, bond angles and dihedral angles, together with simple analytic terms for long range coulombic and vander waals interactions. [2].

Table 1 contains a comparison of the calculated structural parameters with corresponding quantities from the crystallographically detertminded structures. See figure (1) [3]

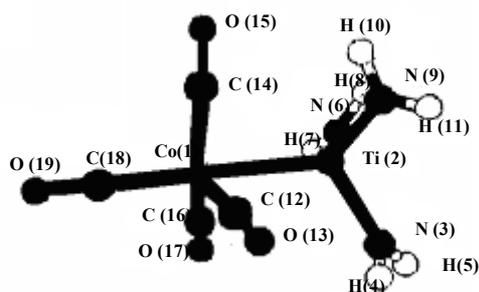


Figure 1: Views the structure of $[(H_2N)_3Ti-Co(Co)_4]$ complex optimized by Calculated methods.

The inspection of the data presented in table 1 suggests that the correspondence between experimental and modeled structural data is very satisfactory.

Table 1: calculated structural and experimental parameters for $[(H_2N)_3Ti-Co(Co)_4]$ complex.

Bond (A°)	Calc.	Exp.	Angle	Calc.	Exp.
Co(1)-Ti(2)	2.592	2.554	Co(1)-Ti(2)-N(3)	111.4	113.9
Ti(2)-N(3)	1.889	1.922	Co(1)-C(12)-O(13)	176.9	173.4
Co(1)-C(12)	1.790	1.763	N(3)-Ti(2)-N(6)	107.5	104.6
C (12)-O(13)	1.148	1.150	Ti(2)-Co(1)-C(12)	79.7	82.2
Co(1)-C(18)	1.812	1.784	C (12)-Co(1)-C(14)	116.9	118.2
C (18)-O(19)	1.141	1.156	C (12)-Co(1)-C(18)	100.3	97.8

2. EXPERIMENTAL

Preparation of the ligands:

Sodium salt of the ligands were prepared by reaction of cyclohexyldicyclohexylamine in dry Et₂O with CS₂ and adding NaOH under vigorous stirring over a 5h period . Molar ratio (amine : CS₂ : NaOH = 1:1:1) , the crude products were recrystallized from i-prOH .

Synthesis of the complexes:

The complexes were obtained from Nickel(II) and Coper(II) Chloride by reaction with the corresponding sodium dithiocarbamate in (1:2 molar ratio respectively) MeOH or EtOH[4]. The compounds which precipitated immediately were washed several times with water and dried in ear [1,5,6]. Found C,41.20;H,6.01;N, 6.93; S, 31.35; Ni, 14.40 % Calc. for

C₁₄H₂₄N₂NiS₄ [Ni(ChexDtc)₂] C,41.28;H,5.94;N, 6.88; S, 31.49; Ni, 14.41% . Found : C, 54.54;H, 7.73;N, 4.90; S, 22.35; Ni, 10.27 % Calc. for C₂₆H₄₄N₂NiS₄ [Ni(DchexDtc)₂] C,54.63; H, 7.76;N, 4.90; S, 22.44; Ni,10.27% . Found C, 40.25; H, 5.70; N, 6.63; S, 31.00; Cu, 15.32% ,Calc. for C₁₄H₂₄N₂CuS₄ [Cu(ChexDtc)₂] C, 40.80; H, 5.87; N, 6.80; S, 31.12; Cu, 15.42%, Found : C, 54.10; H, 7.60; N, 4.72; S, 22.11; Cu, 9.95 % Calc. for C₂₆H₄₄N₂CuS₄ [Cu (DchexDtc)₂] C, 54.17; H, 7.69; N, 4.86; S, 22.25; Cu, 11.02% .

3.MATERIALS AND METHOD

All the chemicals used were of p.a purity and were supplied sigma Aldrich Co. or Fluka Co. The carbon, hydrogen and sulphur analyses were determined on an Elements Analyser model 1106 (Carlo Erba Strametazion).

IR spectra were measured on a perkin Elemer 580 Infraed spectro photometer using KBr discs within the region (4000-200) Cm⁻¹. Electronic spectra in the liquied state were recorded on a shimadzu UV. Vis. Recording UV.-160 spectrophotometer. Magnetic susceptibilities were measured using a Bruker B.M.6 at room temperature. Conductivities were measured on a Conductivity meter Model PCM3 (JENWAY) at 25⁰C in DMF. Room temperature magnetic susceptibility measurements on solid complexes showed them to be diamagnetic indicating the well established square- planar geometry of the Nickel(II), Coper(II) dithiocarbamato complexes.

4. RESULT AND DISCUSSION

The complex obtained with their analytical date and the physical properties in the above reported. The complexes are soluble in carbon tetra chloride and N,N dimethy formamide

(DMF). Conductance measurement in DMF solution indicate the absence of ionic species in solution and magnetic susceptibility hence the covalent nature of the complexes. The most important IR peaks of the free ligand sodium salts and of the complexes are related in table 2 . The band in the 1445 - 1505 cm^{-1} is indicative of considerable double bond character in the carbon nitrogen bond , which,as a consequence, is shifted to higher energies In the metal dithiocarbamates here reported the band assigned to $\text{V}(\text{C}\cdots\text{N})$ in the above reported range lie between the stretching frequencies of $\text{V}(\text{C}=\text{N})$ and $\text{V}(\text{C}-\text{N})$, in the range 1350-1250 and 1690-1640 cm^{-1} respectively the shift of the $\text{V}(\text{C}\cdots\text{N})$ depends on the nature of the ligand As regards the influence of ligand type [7-9], the $\text{V}(\text{C}\cdots\text{N})$ values in the order dicyclohexyldithiocarbamate < cycloheptyldithiocarbamate [10-12]. The band observed at 939 - 990 Cm^{-1} had been associated with the stretching vibration of the carbon – sulphur bond and indicates that the dithioligands act a bidentate way. In the far – IR region the bands of the ligands are unchanged in the spectra of the complexes in addition, new bands, absent in the spectra of the starting materials, are observed in the (348 -390 Cm^{-1}) for there complexes. The band is due largely to M-S bond [13-15].

Electronic absorption spectra of the complexes are similar. The absorbance at 15870 and 15500 Cm^{-1} can be related to the $^1\text{Ag} \rightarrow ^1\text{B}_1\text{g}$ transition, while the observed in the 20200 and 20830 Cm^{-1} region are probably connected with $1\text{Ag} \rightarrow 1\text{B}_3\text{g}$. the absorbance maximum at 25230 and 25840 Cm^{-1} are probably caused by the charge transfer or $\pi \rightarrow \pi^*$ transition[16,17]. The electronic spectra of Cu(II) c0mplexes may be explained by assuming a dimeric structure (see figure 3) , in C_{2v} symmetry , containing penta coordinate Cu(II) ions resulting from very weak

axial Cu-S interaction between two square planar Cu-S4 units . The lowest energy , medium intensity band at (14800-16650 Cm^{-1}) are assigned (${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_g$) transition, the highest energy bands at (18000-18500 Cm^{-1}) due to (d-d) transition and the band at (22350-22720 Cm^{-1}) due to charge transfer(CT) [18-19].

Table:2 Electronic spectra(Cm^{-1}) and IR data (Cm^{-1})

Compound	Electronic spectra(Cm^{-1})	IR data (Cm^{-1})		
		ν C-O	ν C-S	ν M-S
[Ni(ChexDtc) ₂]	15870 20200 25230	1445	939	348
[Ni(Dch.Dtc) ₂]	15500 20830 25840	1455	956	361
[Cu (ChexDtc) ₂]	14800 18000 22720	1505	967	390
[Cu (Dch.Dtc) ₂]	16650 18500 22320	1490	990	380

Geometry optimization of the complexes were made by the molecular mechanics MM+ and MM2 methods using the Hyperchem and chemoffice molecular modeling program package [20-22]. All calculations confirmed the square planar arrangement around the Nickel (II) atom, see figure (2). The calculations were stopped when the RMS- gradient was <0.001 kcal / mol. Selected inter atomic parameters are listed in table : 4 All experimental measurements.

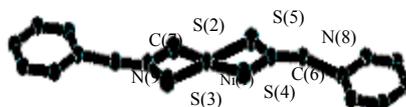
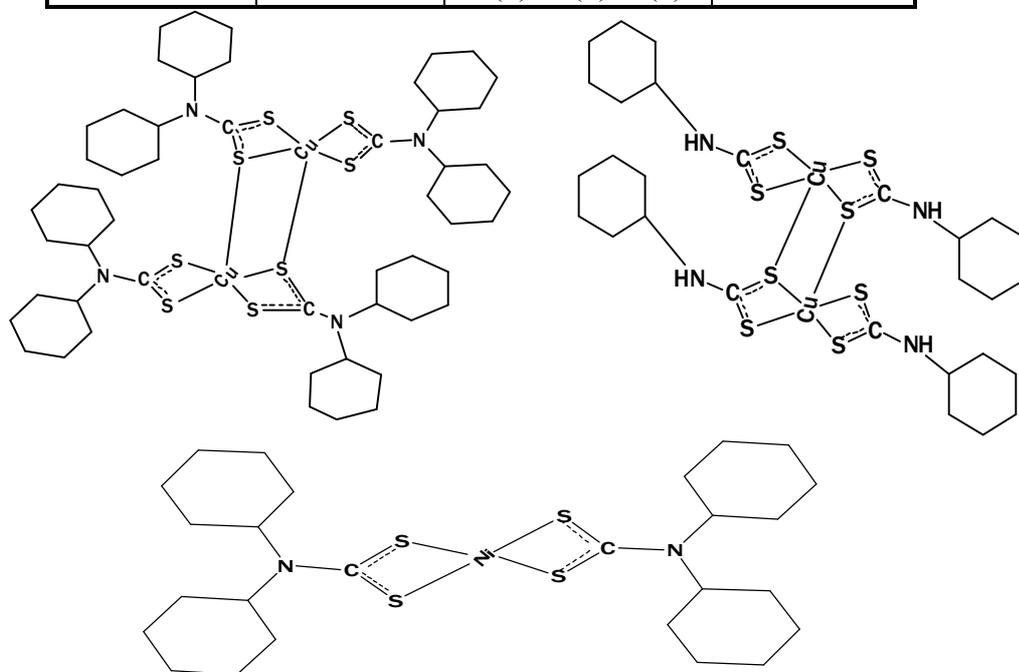


figure (2): predicted geometries of complexes optimized by

the MM+ method : Ni(ChexDtc)₂] complex .

Table3: Important Interatomic distances (Å⁰) and angels(deg) for Ni(ChexDtc)₂] by the MM2 method.

Selected bonds	Bond length (Å ⁰)	Selected angels	Angel value (deg)
N(8)- C (6)	1.365	N(8)- C (6)- S(4)	129.055
S(4)-Ni(1)	2.237	N(8)- C (6)- S(5)	128.213
S(5)-Ni(1)	2.242	C (6)- S(4)- Ni(1)	94.476
N(9)- C (7)	1.350	C (6)- S(5)- Ni(1)	95.851
C (7)-S(2)	1.630	S(2)- C (7)- S(3)	100.128
C (7)-S(3)	1.568	C (7)- S(2)- Ni(1)	94.893
S(2)-Ni(1)	2.239	S(4)-Ni(1)- S(3)	82.113
S(3)-Ni(1)	2.239	S(4)-Ni(1)- S(2)	100.257
		S(5)-Ni(1)- S(2)	85.752
		S(5)-Ni(1)- S(3)	100.171



Figure(3): Molecular structure for complexes

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