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Analytical, Classical Mechanical and Semi Empirical Study of Transition Metal Complexes of (2E,2'E)-2,2'-(5,5-Dimethylcyclohexane-1,3-diylidene)dihydrazine Carboxamide

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Six new transition metal complexes of (2E,2'E)-2,2'-(5,5-dimethylcyclohexane-1,3-diylidene)dihydrazine carboxamide (dimedone *bis* semicarbazone = H_2DSC) have been synthesized. These complexes were characterized mainly by elemental analysis, molar conductance and magnetic susceptibility measurements, electronic and infrared spectral studies. The results obtained were analytically correlated with molecular mechanical and semi empirical calculations.

Key Words: Transition metal complexes, Dimedone, Semicarbazone, Molecular modeling.

INTRODUCTION

Basic limitations faced by the synthetic chemists are chiefly the complexity of abstract prediction carried out by the computational chemistry tools. This tool is basically derived from the classical, statistical and quantum mechanical methods. The fusion of information technology with computational chemistry created a big liberty for both synthetic and theoretical scientists. The use of information technology tools gives better result during the computational simulations. From the literature, it is obvious that the molecular modeling and computational studies are not many in the studies of coordination compounds. So the comparative study between the synthetical and computational results will be very much supportive in future research.

Key developments have been achieved in the research of coordination compounds with special emphasis on metal complexes of Schiff bases containing nitrogen and oxygen donors[1-5]. This may be due to their stability, biological activity[5,6] and potential applications in many fields[7,8]. Biological activity of complexes derived from semicarbazone has been widely studied[5] and contrasted for processes such as antitumor, antiviral, antimalarial and antituberculosis activities[5,6,9,10]. An attempt is made to synthesize a ligand, (2E,2'E)-2,2'-(5,5-dimethylcyclohexane-1,3-diylidene)-dihydrazine carboxamide [dimedone *bis*-semicarbazone, (H_2DSC)] and to explore its possibilities as active and potential biological agent. With the aim of further research, transition metal complexes of semicarbazone of dimedone were synthesized.

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Semicarbazone of dimedone can act as a tetradentate dianionic ligand containing the ONNO donor group. Besides two azomethine groups the ligand contains two-carbonyl oxygen which are enolizable and hence act as potential donor sites. Literature shows that studies about Schiff base complexes of dimedone are rare and those of semicarbazide are a few in number[11,12]. But complexes of H_2DSC are not reported so far. The computational studies will reveal the possible existence of the molecules (ligand and complexes) and the feasible out come of the heat of formation, binding energy *etc*. The other molecular parameters like bond length and bond angle were compared with standard crystallographic data of the fragment molecule-*dimedone*-. Electrostatic surfaces were plotted in accordance with molecular mechanics based MM+ calculations. So, it seems to be interesting to synthesize and characterize the transition metal complexes of dimedone *bis*-semicarbazide (H_2DSC) and to conduct detailed investigation about the structure, magnetic properties and thermal stabilities of these transition metal complexes.

EXPERIMENTAL

AnalaR grade chemicals (BDH, E.Merck and Glaxo) are used for the synthesis.

Molar conductance measurements of the complexes were carried out in nitrobenzene or DMSO solvent at 25 ± 2 ºC on Toshniwal conductivity bridge *ca*. 10^{-3} M solutions. Magnetic susceptibilities of the complexes were determined at room temperature by Gouy method. The infrared spectra of the ligand and metal complexes were recorded in the range 4000-400 cm^{-1} nm on a Shimadzu-IR 470 infrared spectrophotometer by KBr disc technique. The UV-Visible spectra of the ligands and complexes were carried out on a Shimadzu recording spectrophotometer using DMSO as solvent.

Preparations of ligand dimedone *bis* semicarbazone: A hot ethanolic solution of dimedone (1.40 g, 0.01 mol) was added drop wise to stirred solution (2.2 g, 0.02 mol) of semicarbazone dissolved in 20 water and 20 mL of ethanol. The mixture was refluxed for *ca*. 15 min and then cooled. The pale yellow precipitate formed was filtered, washed with alcohol and dried. To obtain dimedone *bis*-semicarbazone, a hot saturated solution of it was neutralized with dilute solution of sodium hydroxide. As the solution was cooled pale yellow crystals of dimedone *bis*-semicarbazone separated. Melting point of the ligand was found to be 211 ºC.

Synthesis of complexes of dimedone *bis*-semicarbazone: The metal complexes were prepared by adding slowly a hot aqueous solution of the corresponding metal acetate to a refluxing ethanolic solution of the ligand containing sodium acetate (0.5 g) until the metal ligand ratio reached 1:1. The reaction mixture was refluxed for 10-30 min and the complexes precipitated were separated. It was washed with water followed by ethanol and dried over anhydrous $CaCl_2$.

Complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were prepared by the above method.

RESULTS AND DISCUSSION

TLC established the purity and homogeneity of the ligand. Elemental analysis and IR data given in the Table-1 showed the close agreement with empirical formula for dimedone *bis*-semicarbazone (Fig. 1). All the complexes are coloured, stable and non-hygroscopic. They are moderately soluble in DMF and DMSO. The electrical conductivity data of these complexes in DMSO showed that they are non-electrolytic compounds. The complexes were analyzed for metal, estimated by using atomic absorption spectroscopy and carbon, hydrogen and nitrogen estimated by standard micro analytical methods. The analytical data of the complexes corresponds to the formula $ML(H_2O)_2$ where M = Mn(II), Co(II), Ni(II), Cu(II) and ML where M = Zn(II) and Cd(II).

TABLE-1
MICRO ANALYTICAL, MAGNETIC AND CONDUCTANCE DATA

Compound / m.f.	Conductance ohm^{-1} cm^2 mol	μ_{eff} (BM)	Elemental analysis %: Found (Calcd.)			
			M	C	H	N
H_2DSC $[C_{10}H_{18}O_2N_6]$	–	–	–	46.7 (47.2)	7.8 (7.1)	32.3 (33.1)
$[MnL(H_2O)_2]$ $[MnC_{10}H_{16}O_2N_6(H_2O)_2]$	43	5.85	16.01 (16.02)	34.1 (34.99)	5.77 (5.83)	24.00 (24.49)
$[CoL(H_2O)_2]$ $[Co\ _{10}H_{16}O_2N_6(H_2O)_2]$	23	4.89	17.02 (16.97)	34.01 (34.59)	5.18 (5.76)	23.2 (24.21)
$[NiL(H_2O)_2]$ $[NiC_{10}H_{16}O_2N_6(H_2O)_2]$	34	3.10	16.5 (16.93)	34.6 (34.61)	5.3 (5.76)	23.9 (24.22)
$[CuL(H_2O)_2]$ $[CuC_{10}H_{16}O_2N_6(H_2O)_2]$	16	1.77	18.04 (18.07)	33.2 (34.13)	5.12 (5.68)	23.1 (23.89)
[ZnL] $[ZnC_{10}H_{16}O_2N_6]$	23	Diamag.	21.00 (20.58)	36.3 (37.8)	5.01 (5.04)	25.9 (26.47)
[CdL] $[CdC_{10}H_{16}O_2N_6]$	14	Diamag.	29.06 (30.84)	32.88 (32.93)	4.27 (4.39)	24.56 (23.05)

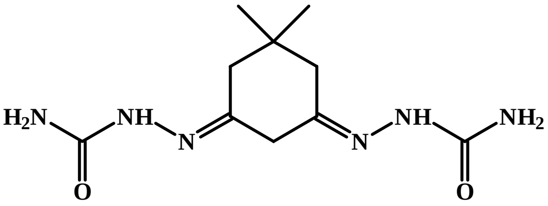


Fig. 1. Structure of (2E,2'E)-2,2'-(5,5-dimethylcyclohexane-1,3-diylidene)-dihydrazine carboxamide (H_2DSC)

Magnetic behaviour: Mn(II) complex shows a magnetic moment of 5.85 BM indicating d^5 octahedral geometry[13]. The Co(II) complex of H_2DSC shows magnetic moment of 4.89 BM indicating octahedral geometry and is further supported by electronic spectral data[13,14]. The Ni(II) complex of H_2DSC shows a magnetic moment of 3.1 BM, which indicates an octahedral geometry[13,14], which is further supported by electronic spectral data. In regular octahedral Cu(II) complexes ground term is ^2Eg and hence no orbital contribution is expected. The spin only magnetic moment value corresponding to one unpaired electron is 1.73 BM, but the observed values fall in the range 1.80-2.10 BM. The slightly higher value is due to the spin orbit coupling. The observed magnetic moment values of Cu(II) complexes of H_2DSC are 1.77 BM which indicates octahedral geometry[15,16]. The Zn(II) complexes and Cd(II) complexes were found to be diamagnetic as expected for the d^{10} configurations.

IR spectra: IR spectra of H_2DSC shows bands at 1671 and 1613 cm^{-1} which are due to C=N stretching and C=O stretching, respectively[17]. The band at 3350 cm^{-1} is probably due to NH stretching and 3450 cm^{-1} is possibly due to stretching of NH_2 groups[17]. The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation. The band at 1613 cm^{-1} is the characteristic of the azomethine group present in the free ligand. The lowering in this frequency region (1599-1543 cm^{-1}) observed in all the complexes, indicates the involvement of the azomethine nitrogen atom in coordination[18,19]. The band at 1671 cm^{-1} is characteristic of the C=O in the free ligand. In all the complexes this band disappears and new band appears around 1000 cm^{-1} due to ν(C-O). This may be due to enolization and subsequent coordination of this carbonyl group[21]. The band at 3350 is assigned to the >NH stretching, this band disappears in all the complexes, supporting enolization. Ligand shows absorption at the frequency 3450 cm^{-1} which may be assigned to the NH_2 stretching[17]. The bands at 521-517 and 424-418 cm^{-1} are due to the formation of M-N and M-O bonds, respectively[17,21]. Presence of a broad band around 3447 cm^{-1} (except in Zn(II), Cd(II) complexes) may be due to the OH stretching of coordinated water. But in some of the complexes this bands are not obvious due to the overlapping of some other bands[17,21]. In addition to that a medium band approximately at 966-944 suggests that the water molecules are coordinated. The characteristic frequency of free acetate ion[11,17] at 1560, 1415 are absent in all the complexes. However, the non-conducting nature and stoichiometry of this complex indicate that acetate ion is not present in them.

Electronic spectra: A high spin Mn(II) complex in octahedral field gives spin forbidden as well as parity forbidden transitions. Hence octahedral Mn(II) complexes are usually pale in colour and the absorptions are very weak. The tale of CT bands overlap with weak transition thus obscuring them. In tetrahedral environments the transitions are still spin forbidden but no longer parity forbidden. These transitions are therefore about 100 times stronger and complexes have noticeable light yellow green colour[22,23]. Here Mn(II) complex of H_2DSC shows a number of weak bands which may be assigned to charge transfer or *d-d* transition in octahedral field.

Octahedral geometries are commonly found in Co(II) complexes and such complexes are pink in colour. The expected *d-d* transitions are[24-27]:

$^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$	1250-1000 nm
$^4T_{1g}(F) \longrightarrow {}^2E_g(F)$	880 nm
$^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$	700-500 nm
$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$	500-400 nm

Co(II) complex shows absorptions which can be assigned to the *d-d* transitions of octahedral geometry as given in the Table-3. Low intensity of bands and purple colour support octahedral geometry. Ni(II) complex of H_2DSC shows 3 absorption bands which are assigned as given in the Table-3 and these data support the octahedral geometry. The ratio of wave numbers of transitions:

$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$	929 nm
$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$	512 nm

is in the range[12] 1.6 to 1.8 which confirms the octahedral geometry. For octahedral Cu(II) complexes only a single band due to the transition ^2E_g-$^2T_{2g}$ would result. But the observed band is very broad and clearly contains several components which are the result of tetragonal distortions due to Jahn-Teller effect[22]. In the case of the Cu(II) H_2DSC complex an absorption band present 674 nm is assigned to the *d-d* transition in octahedral complexes[28,29].

Molecular mechanical calculations: All the molecular mechanics calculations were carried on Pentium IV 2.46 GHz with the MM+ force field. The search of the lowest energy conformations are performed by Monte Carlo methods. This method generated new conformations with randomly varied torsion angle. Monte Carlo search used the temperature T = 300 to 400 K. The molecule obtained is minimized by using Polak-Ribiere optimizer. Energy minimization was terminated when the gradient root mean square was below 0.01 k cal /mol. After the minimization acceptance was determined by the following criteria (i) execution of a conformational search by the simulated annealing method heat time - 0.1 ps, run time- 0.5 ps, cool time-0.1 ps starting temperature 100 k simulation temperature 300 k with a temperature step 30 k which is described by Choe *et al.*[30] (ii) the structure obtained was minimized with a semi-empirical method (PM3) and we verified that there were no negative frequencies in the vibration spectrum.

The ligand H_2DSC drawn in Macro model (Maestero-Schrodinger) graphical user inter phase. The molecule is minimized by using MM+, Polak Ribiere optimizer. Better conformations produced by molecular dynamics and Monte Carlo simulations methods. Selected conformations with least energy are represented in Figs. 4-6. The calculated out put of the ligand molecule is summarized in the Tables 6-8 The electrostatic potential and charge density of the molecule can visualize by using the various contour and isosurface Fig. 5.

TABLE-2
CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES (cm^{-1})

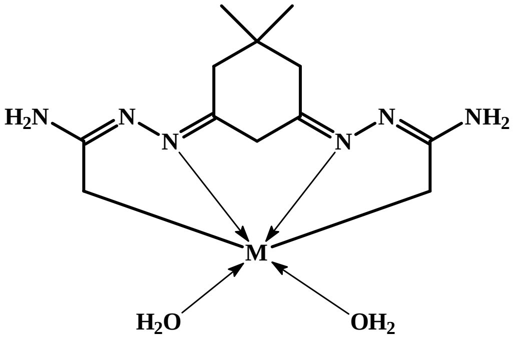
Compounds	ν(H_2O)	ν-(C=O)	ν-(C-O)	ν(>C=N-)	γ(OH)(H_2O)	ν(M-N)	ν(M-O)
H_2DSC	–	1671m	–	1613.s	–	–	–
$[MnDSC(H_2O)_2]$	3436m	–	989m	1597s	944w	520w	413m
$[CoDSC(H_2O)_2]$	3451br	–	979m	1599s	952w	517w	418w
$[CuDSC(H_2O)_2]$	3412br	–	988m	1543s	966w	517.8w	418m
$[NiDSC(H_2O)_2]$	3410br	–	964m	1578s	945w	521w	424m
[ZnDSC]	–	–	976m	1585s	–	517m	418m
[CdDSC]	–	–	934m	1543s	–	517m	418m

TABLE-3
CHARACTERISTIC UV FREQUENCIES

Complex	Band (nm)	Assignment	Geometry
$[MnDSC(H_2O)_2]$	412	CT	Octahedral
$[CoDSC (H_2O)_2]$	1075 666	$^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$	Octahedral
$[NiDSC (H_2O)_2]$	929 512	$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$ $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$	Octahedral
$[CuDSC (H_2O)_2]$	674	$^2E_g \longrightarrow {}^2T_{2g}$	Distorted octahedral
[ZnDSC]	395	CT	Tetrahedral
[CdDSC]	323	CT	Tetrahedral

TABLE-4
ENERGY COMPONENTS OF LIGAND BY USING (MM+)
FORCE FIELD LIGAND-ANALYTICAL

k cal/mol							
Energy	Gradient	Bond	Angle	Dihedral	Vdw	Stretch-	Electrostatic
-2.5470	0.0077	0.69	2.753	3.32	4.037	0.153	-13.51



where M = Mn(II), Co(II), Ni(II), Cu(II)
Fig. 2. Octahedral complexes of H_2DSC

TABLE-5
COMPARISON OF CRYSTALLOGRAPHIC DATA WITH COMPUTATIONAL DATA BY USING MM+

Bond	Bond distances (A) MM+	Crystallographic bond distance (Å)	Bonds	Bonds (°) MM+	Crystallographic bond angle
C3-O2	1.21000	1.246	O2-C3-C4	119.800	118.5
C3-C4	1.51900	1.500	O2-C3-C2	120.600	122.5
C3-C2	1.35600	1.418	C4-C3-C2	119.434	118.9
C2-C1	1.34200	1.351	C3-C2-C1	122.660	120.5
C2-H1	1.10300	0.960	H1-C2-C1	118.359	131.4
C1-O1	1.36000	1.326	H1-C2-C3	118.977	108.3
C1-C6	1.50800	1.491	O1-C1-C2	121.656	123.9
C6-C5	1.53700	1.524	O1-C1-C6	116.010	113.2
C6-H4	1.11500	1.000	C1-C6-C5	111.886	113.3
C6-H5	1.11400	0.970	C1-C6-H4	109.496	109.0
C5-C4	1.53800	1.527	C1-C6-H5	107.607	106.2
C5-C7	1.54400	1.526	C6-C5-C4	107.700	107.7
C5-C8	1.54200	1.526	C6-C5-C7	110.438	109.0
C4-H3	1.11500	0.960	C6-C5-C8	110.020	110.5
C4-H2	1.11500	1.000	C5-C4-C3	113.210	114.5
C7-H8	1.11380	0.990	H3-C4-C5	110.186	113.0
C7-H7	1.11380	0.970	H2-C4-C5	109.760	108.4
C7-H9	1.11310	1.011	H3-C4-H2	107.120	105.3
C8-H10	1.11380	0.960	H8-C7-C5	112.200	112.3
C8-H11	1.11390	0.990	H7-C7-C5	111.200	111.2
C8-H12	1.11385	0.990	H9-C7-C5	111.200	108.0
O1-H6	0.97180	0.870	H10-C8-C5	111.200	110.2
			H11-C8-C5	111.100	108.6
			H12-C8-C5	111.500	109.4
			C6-C1-C2	122.300	122.8
			C4-C5-C7	109.978	109.5
			C4-C5-C8	110.100	110.3
			C7-C5-C8	108.200	109.2

TABLE-6
COMPARISON THE STABILITY OF OCTAHEDRAL AND TETRAHEDRAL GEOMETRY OF THE COMPLEXES

	Cobalt(II)		Nickel(II)		Copper(II)		Manganese(II)	
	O	T	O	T	O	T	O	T
Energy	59.90	104.10	57.550	103.92	52.700	100.92	57.42	103.65
Bond	7.26	2.63	6.580	2.75	5.890	2.52	6.53	2.59
Angle	14.71	85.52	16.950	87.05	16.690	86.00	14.80	84.90
Dihedral	19.60	17.63	20.530	17.91	19.710	17.20	19.77	17.67
Vdw	22.90	3.29	22.100	5.66	19.210	3.80	21.06	3.19
Stretch bend-	0.05	0.09	0.092	0.18	0.078	0.17	0.03	0.09
Electrostatic	4.49	-4.71	8.530	9.61	8.678	-0.84	4.75	4.83
convergence	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

O = Octahedral; T = Tetrahedral.

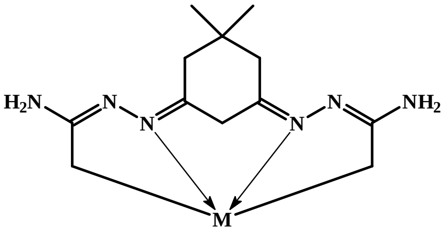
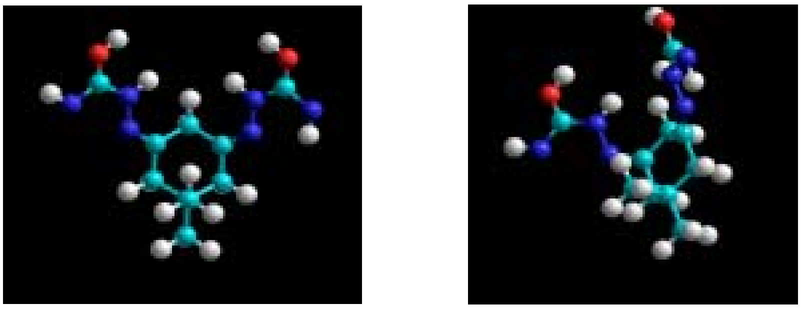


Fig. 3. Tetrahedral complexes of H_2DSC where M = Zn(II), Cd(II)



Front view

Side view

Fig. 4

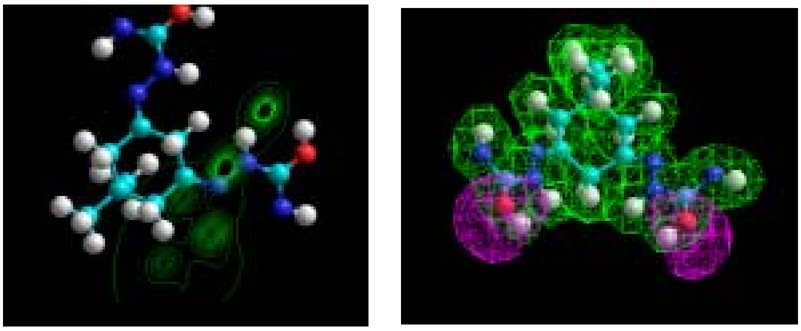
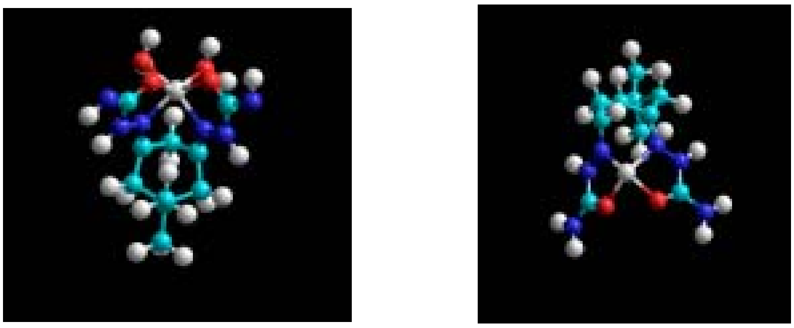


Fig. 5. 3d iso surface of the ligand molecule



Structure Mn Complex molecule

Structure Cd Complex molecule

Fig. 6. 3d view after energy optimization (MM+)

TABLE-7
COMPARISON THE STABILITY THE COMPLEXES kcal/mol

Name of the complexes	Zn(II) complexes		Cd(II) complexes	
	Octahedral	Tetrahedral	Octahedral	Tetrahedral
Energy	44.040	100.3500	144.050	95.540
Bond	4.097	2.3430	11.790	1.790
Angle	15.560	85.3070	99.516	84.640
Dihedral	19.450	17.6300	47.441	16.290
Vdw	16.130	5.4031	10.600	10.500
Stretch bend-	-0.010	0.0147	-6.352	0.110
Electrostatic	-9.349	-10.5020	19.043	-7.616
Convergence	No	Yes	Yes	Yes

TABLE-8
COMPARISON OF BINDING ENERGY AND HEAT OF FORMATION
(kj/mol) SEMI EMPIRICAL RESULT (PM3)

Name of the molecule	Geometry	Binding energy	Heat of formation
Mn(II) complexes	Octahedral	-4077	-238
	Tetrahedral	-3628	-116
Co(II) complexes	Octahedral	-4290	-416
	Tetrahedral	-3788	-242
Ni(II) complexes	Octahedral	-4246	-372
	Tetrahedral	-3770	-223
Cu(II) complexes	Octahedral	-4030	-87.12
	Tetrahedral	-3585	-60
Zn(II) complexes	Octahedral	Not converged	Not converged
	Tetrahedral	-3865	-62
Cd(II) complexes	Octahedral	Not converged	Not converged
	Tetrahedral	3397.	72.67

Bond length and bond angle: Bond length and bond angles of the common fragment of the dimedone part in the ligand are compared with crystallographic data[31]. The result is summarized in the Table-5. The comparison of the bond distance from the crystallographic data are in quiet agreement with the data calculated by MM+ of dimedone part in the ligand molecule. It should be noted that the differences between the calculated and experimental values for the bond lengths are all generally less than 0.1 Å, the difference then reaches 0.15 Å. In the same way, the differences between the calculated and experimental values for the bond angles generally do not exceed 3°. The difference then reaches 10.8°. By considering this similarity with crystallographic data, we can conclude that the calculated parameters show good agreement with experimental crystallographic data.

Stability of complexes: The relative stabilities of the various complexes are compared by using the results obtained from the molecular mechanics (MM+) calculations. We compared both tetrahedral and octahedral possibilities by the same method adopted earlier[30]. The result is summarized in the Tables 4-6 From this, the following conclusion has been made.

(1) Octahedral (distorted) geometry energetically favourable for the Mn(II), Co(II), Ni(II), Cu(II) complexes, which supports analytical findings. (2) The major difference in energy between tetrahedral and octahedral compounds is in angle energy and Vander waals energy. (3) In the case of Zn(II) complexes and Cd(II) complexes the convergence is not occurring for an octahedral geometry.

Semi-empirical methods: The molecule obtained by the MM+ force field and Polak-Ribiere optimizer is reoptimized by using the PM3 semi empirical methods[32]. The PM3 methods can provide valuable data like heat of formation, binding energy and dipole moment. The result obtained is given in the Table-8. The following conclusion can be made (1) The results show clearly that enthalpy of formation and binding energy is satisfactorily negative for the formation of ligand from their component molecules. We further used the same technique to estimate the thermodynamic feasibility of the complexes derived from this ligand. (2) From the Table-8 it is obvious that the octahedral geometry is preferred by the 4 complexes *i.e.*, Cu(II) Mn(II), Co(II) and Ni(II). This result strongly supports the experimental data and also result obtained by the MM+ calculations. Surprisingly here also cadmium and zinc complexes are giving an abnormal result. The converged molecule is far away from the really expected molecule. The octahedral shape is completely distorted. We failed to establish that the molecule is existing in tetrahedral geometry, but we could clearly establish that the molecule cannot exist in octahedral environment and the molecule is very close to the tetrahedral geometry.

Conclusion

The coordinate compounds of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with dimedone *bis* semicarbazone (H_2DSC) were synthesized. The physico-chemical properties of all the complexes were studied. The complexes have the general formula $[M(DSC)(H_2O)_2]$ where M = Cu(II), Ni(II), Co(II), Mn(II).

The comparison between computational study and crystallographic data also reveals that analytically obtained structure is feasible either by molecular mechanics or semi-empirical methods.

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