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Synthesis and characterization of the pseudohalide metal complexes

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ABSTRACT

This paper presents the synthesis and study of some new complexes containing DMG and NCS with some metals. The resulting products were found to be solid crystalline complexes which have been characterized by using (FT-IR, UV-Vis) spectra, melting point, elemental analysis (C.H.N). The proposed structure of the complexes using program, CS chem office 3D(2000).

The general formula have been given for the prepared complexes :

$[M(A)_2(B)_2]$

M(II): Pb(II), Fe(II), Cd(II).

A = DMG(dimethyl glyoxime) = $C_4H_8N_2O_2$

B = NCS(thiocyanate) for first 2 complexes (oac)₂(acetate) for third complex

Key words: DMG, Coordination chemistry, Pb(II), Fe(II), complex, Cd(II), spectra

INTRODUCTION

It is well known that the oximatogroup(=N-O⁻) can act as a bridge to find two metal ions through the imino nitrogen atoms and the deprotonated oxygen atoms, which can co-ordinate with metal ions in versatile ways. H₂dmg is a potential tetradentate ligand as well as a mono, bi and tridentate ligand. Framework molecular model shows that it is more likely to act as a bridge between two metal ions than as a terminal ligand[1-4] With the aim of investigating versatility of oximes in coordination chemistry and for further research on the supramolecular polymer chemistry, designed and synthesised some polymeric chain like complexes successfully with oximato groups as bridges[5-9]. In order to add other kinds of anion on complex, we synthesized short bridging ligand complexes, proposed structures and spectroscopic properties of the afore mentioned complexes were discussed.

MATERIALS AND METHODS

A: Reagents and instruments : DMG and NCS were purchased from BDH .

All solutions and metal chloride were purchased from merck and. Elemental analysis was obtained using a FLASH EA 1112 SERIES CHNS analyzer. Melting point were recorded by using stuart melting point apparatus . IR spectra were obtained with a Shimadzu FT-IR 8000 spectrometer .The proposed molecular structure of the complexes were determined by using chem office 2000, 3DX prog .

*B: General synthesis :**Synthesis of $Cd(dmgl)_2(NCS)_2$*

An methanolic (10 ml) solution of dimethylglyoxime (0.116g, 1.0 mmol) was added to an aqueous solution(10ml) of cadmium acetate (0.268g, 1.0 mmol) under stirring conditions and then aqueous solution of NCS (0.097 g, 1.0 mmol) was added which resulted into colourless solution with some turbidity. After constant stirring at room temperature for 30 minutes,The product was precipitated,filtered off and washed with methanol. The product is also obtained from the solution left for evaporation in the beaker in the form of crystalline precipitate. The compounds are soluble in methanol. Yield 0.185 g

Synthesis of $[Fe(dmgl)_2(NCS)_2]$

An methanolic (10 ml) solution of dimethylglyoxime (0.116g, 1.0 mmol) was added to an aqueous solution(10ml) of ferrous sulphate (0.260g, 1.0 mmol) under stirring conditions and then aqueous solution of NCS(0.097 g, 1.0 mmol) was added which resulted into colourless solution with some turbidity. After constant stirring at room temperature for 30 minutes,The product was precipitated,filtered off and washed with methanol. The product is also obtained from the solution left for evaporation in the beaker in the form of crystalline precipitate. The compounds are soluble in methanol. Yield 0.153 g

Synthesis of $[Pb(dmgl)_2(oac)_2]$

An methanolic (10 ml) solution of dimethylglyoxime (0.116g, 1.0 mmol) was added to an aqueous solution(10ml) of lead acetate (0.379g, 1 mmol) under stirring conditions and then aqueous solution of NCS(0.097 g, 1.0 mmol) was added which resulted into colourless solution with some turbidity. After constant stirring at room temperature for 30 minutes,The product was precipitated,filtered off and washed with methanol. The product is also obtained from the solution left for evaporation in the beaker in the form of crystalline precipitate. The compounds are soluble in methanol. Yield 0.240 g

RESULTS AND DISCUSSION

Physical properties and elemental analysis are presented in Table (1) . Formula $M(A)_2 (B)_2$ giving good agreement between the observed and the calculated values by elemental analysis . All complexes are dissolved in Methanol solvent .

The electronic spectra :

The electronic spectra of all complexes are listed inTable (2) . In the $[Pb(dmgl)_2(oac)_2]$ complexes the two bands at 233 and 223.50nm are characteristic. In the $[Fe(dmgl)_2(NCS)_2]$ complex the two bands at 236.50 and 227.50 nm are characteristic of this complex. In $[Cd(dmgl)_2(NCS)_2]$ two bands at 237 and 227.50 nm are characteristic of this complex.

Fourier-transform infrared spectra :

The assignment of some of the most characteristic FT-IR band of the complexes are shown in Table (3) together with that of dmgl recorded for comparative purposes and facilitate the spectral analysis .Absorption bands in the $2050-2070\text{ cm}^{-1}$ region are considered to be due to metal-nitrogen(of pseudohalide) vibrations [10,11] whilst those occurring around 1143 cm^{-1} are thought to arise from nitrogen-oxygen vibration in coordinated dmgl [12,13] the sharp bands at $(3325-3300)\text{ cm}^{-1}$ are attributed to the N-H stretching[14] .

Nomenclature of prepared complexes :

Complexes	Nomenclature
$Cd(dmgl)_2(NCS)_2$	Didimethylglyoximatodithiocyanato N-Cadmium(II)
$Fe(dmgl)_2(NCS)_2$	Didimethylglyoximatodithiocyanato N-Ferrate(II)
$Pb(dmgl)_2(oac)_2$	Didimethylglyoximatodiacetato Lead(II)

Proposed molecular structure :

Studying complexes on bases of the above analysis , the existence of tetracoordinated $[M(A)_2(B)_2]$, $M(II) = Cd , Fe , Pb$

A proposed models of the speciese were built with chem 3D (15) shows in Fig (1)(2)(3) .

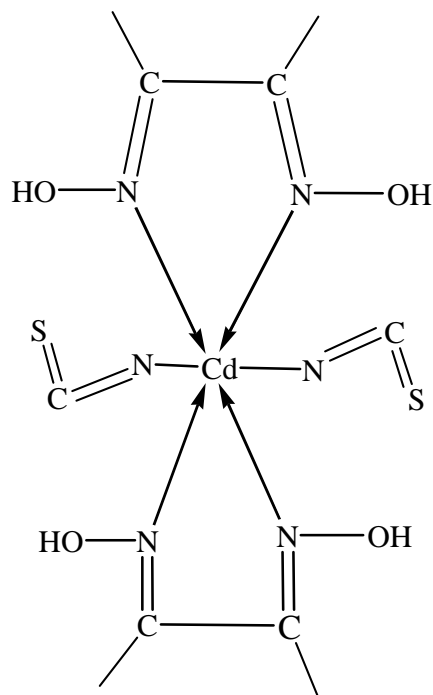
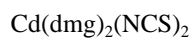


Fig (1) : The proposed structure of the complex 1

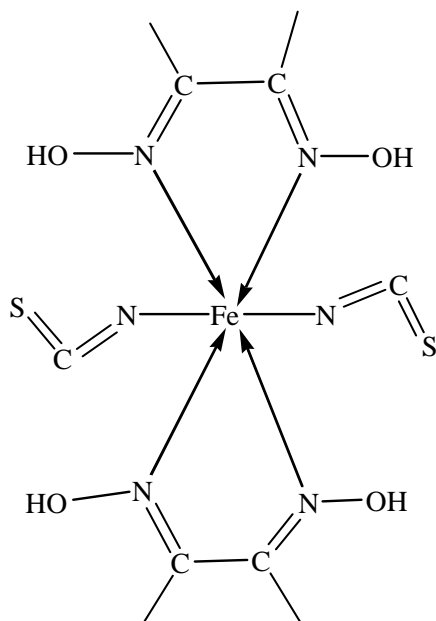
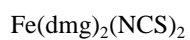


Fig (2) : The proposed structure of the complex 2

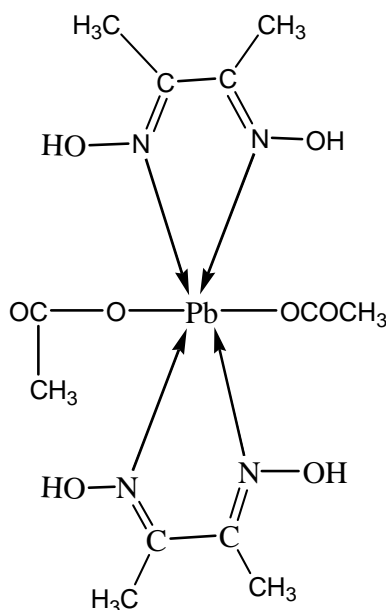
Pb(dm_g)₂(oac)₂

Fig (3) : The proposed structure of the complex 3

Table 1: The physical properties of the complexes Elemental Analysis

Compound	Colour	M.P. ^o c	%C		%H		%N	
			Calc	Found	Calc	Found	Calc	Found
DMG	White	240-241	-	-	-	-	-	-
NCS	White	173.2	-	-	-	-	-	-
Cd(dm _g) ₂ (NCS) ₂	White	Above 300	26.06	25.86	3.50	4.02	18.24	18.86
Fe(dm _g) ₂ (NCS) ₂	Grey	Above 300	29.71	29.02	3.99	4.32	20.79	21.44
Pb(dm _g) ₂ (oac) ₂	White	Above 300	25.85	24.98	3.98	4.19	10.05	10.76

M.P = Melting point

Table 2 :Electronic spectra of the studied complexes and two ligands

Compounds	Wavelength (nm)		Wavenumber (cm ⁻¹)	
DMG	229.99		43480	
NCS	266		37593.98	
Cd(dm _g) ₂ (NCS) ₂	246	237	40650.40	42194.09
	230	227.50	43478.26	43956.04
Fe(dm _g) ₂ (NCS) ₂	236.50		42283.29	
	227.50		43956.04	
Pb(dm _g) ₂ (oac) ₂	233		49218.45	
	223.50		44742.72	

Table 3 : FT-IR Spectrl Data of the Ligands and its Complexes

complex	v(OH)	v(NH)	v(C-H)	v(C=C)	v(N-O)	v(C=N-O)	v(M-N)	v(COO)
dmg	3205	2928	2850	1490	1143	760	-	-
1	3410	-	2926	1431	1143	761	2067	-
2	-	3246	2924	1437	1143	758	2056	-
3	3312	3236	2924	1440	1143	752	-	1363

Complex 1 = Cd(dm_g)₂(NCS)₂Complex 2 = Fe(dm_g)₂(NCS)₂Complex 3 = Pb(dm_g)₂(oac)₂

CONCLUSION

Metal complexes were synthesized by self-assembly method. All the proposed structures are showing Octahedral geometry and agreed with electronic data. The obtained results were characterized by using spectroscopy and physical methods.

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