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Synthesis and Characterization of Polynuclear Complexes of Chromium (III) ions using β – diketonate Ligand and Oxalic, Succinic and Nitrite as Bridging Ligands

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Abstract
Polynuclear complexes of chromium (III) ions using β –diketone and either oxalic, succinic, or nitrite as bridging ligand have been synthesized successfully. The complexes formed binuclear compounds linked through the bridging ligand (nitrite, succinate or oxalate) andthey were insoluble in all the tested solvents,with high decomposition temperature(>250 ^{o}C). The elemental analysis was conducted and the observed values were in agreement with theoretical values.

Keywords: Metal complexes, dinulear, structures

Introduction

Multi – dimensional organic-inorganic hybrid open framework materials have recently attracted attention of inorganic chemist, owing to the compounds growing importance and relevance in the context of designing specialty materials (Drumel *et al.*,1996), harnessing their interesting magnetic (Inoue and Kubo, 1976; Kondo*et.al.*, 1995), electrical (Kobel and hanack, 1986), shape-specific and catalytic properties (Robson *et.al.*,1992). These compounds are very important because of their application as bioactive molecules, new high spin molecules and as single molecule magnets. They are also useful in the area of molecular electronics, medicine and sensing (Katerina *et. al.*, 2008). Inorganic chemists face difficulties with these compounds in characterization, despite the molecules' wide application in the areas mentioned above (Winpenny *et. al.*, 1999).

Transition metal chemist have made little progress in discovering general approaches to preparing compounds containing large or infinite number of metals centers due to the fact that these molecules were difficult to characterize until recently(Fujita *et. al.*, 1994).

Newer classes of dinuclear metal complexes through the usage of suitable bridging ligands lead to the formation of stable mixed valence states, these newer compounds attract the attention of synthetic inorganic chemist. The design approach of these compounds has been successful in producing series of many intriguing metal-organic clusters (Baxter 1994).The structures produced are to some extent predictable, as the coordination geometry of the metal ion used is known and the pre-

organized ligand donor sites and its flexibility is also known (Winpenny 1999). Various interesting framework systems have been reported using dicarboxylate ligands, in which their results showed different structural diversities (Lu *et. al.,* 1999; Pan *et.al.,* 2001;Jiang *et al.,* 2004).Similarly, Pan *et al.*,2000, reported a compound that differ from the conventional compounds in the literature,in their work, one of the carboxylate functions is coordinated as anion, while the other –COOH function remain neutral and totally uncoordinated.

Succinates ligands are one class of dicarboxylate system which exhibit interesting structural diversities. Previously an investigation have shown that versatile α,ω-dicarboxylate anions are effective and flexible bridging ligands which can interlink metal atoms into supra-molecular architectures with specific structure (Zheng*et.al.,* 2000; Kim *et.al.,* 2000).

This study is aimed at synthesizing chromium complex compound of acetylacetonate and further crosslink the molecule with bridging ligands*viz*. nitrite, oxalate and succinicate.

Materials

All reagents and chemicals purchased from Aldrich sigma were of analytical/spectroscopic grade and used without further purification. Melting points were measured using a digital melting point apparatus 1A 9000. The IR spectra were recorded on FT-IR -8400 Fourier transform infrared. UV-Vis Spectra were recorded using UV-vis T-60u Spectrophotometer, PG instrument Ltd. Microanalysis was conducted at Cairo University Egypt.

Methods

Synthesis of $[(Cr(acac)_2)_2(NO_2)]$

To an ethanol(50 mL) solution 1.046g of β-diketone were added three drops of ethanolic solution of NaOH. 0.792g of chromium (III) chloride was then added to the mixture which immediately yielded blueprecipitate. 0.173g of sodium nitrite was added to the precipitate and the suspension was refluxed for 1 hour. The resultant brown precipitate was cooled washed twice with 10 mL ethanol and dried in a desiccator for 3 days. The yield was 68%. Calculated for $CrC_{10}H_{16}O_6N$: C, 40;27 H, 5.41; N, 4.70; Found: C, 40.18; H, 5.63; N, 3.47 (Mustapha and Musa, 2014)

Synthesis of $[Cr(acac)_2(Oxal)_2]$

Synthesis of chromium (III) complex with bridging oxalic acid ligand by weighing 1.046g of acetylacetone and transferred into round-bottom flask in which 50 cm^3 of ethanol was added into it, followed by adding 0.792g of chromium (III) chloride which immediately turns to blue color. About 0.305g oxalic acid was also added into the content, after which the color changed to dark green. Few drops of sodium hydroxide was added and then refluxed for about 2 hours which was finally transferred into test tubes so as to allow ethanol to evaporate slowly. A dark green powder with 87 % yield was obtained. Calculated for $CrC_{14}H_{20}O_{12}$: C, 38;90 H, 4.66; O, 44.41; Found: C, 40.11; H, 5.01; O, 43.99.(Mustapha and Musa, 2014)

Synthesis of $[(Cr(acac)_2)_2(NO_2)]$

To an ethanol(50 mL) solution 1.046g of β-diketone were added three drops of ethanolic solution of NaOH. 0.792g of chromium (III) chloride was then added to the mixture.0.345g of sodium nitrite was added to the mixturewhich immediately yielded brown precipitate and the suspension was refluxed for 1 hour. The resultant brown precipitate was allowed to cool and filtered, washed twice with 10 mL ethanol and dried in a desiccator for 3 days. The yield was 68%. Calculated for $CrC_{10}H_{16}O_6N$: C, 40.27; H, 5.41; N, 4.70; Found: C, 40.11; H, 4.79; O, 4.32.(Mustapha and Musa, 2014)

Synthesis of $[(Cr(acac)_2)_2(suc)]$

To an ethanol (50 mL) solution 1.046g of β-diketone were added three drops of ethanolic solution of NaOH. 0.792g of chromium (III) chloride was then added to the mixture. 0.590g of succinic acid was added to the precipitate which immediately turns to red precipitate and the suspension was refluxed for 1 hour. The resultant red precipitate was allowed to cool, filtered and washed twice with 10 ml ethanol and dried in a desiccator for 3 days. The yield was 58%. Calculated for $CrC_{18}H_{28}O_{12}$: C, 44.27;

H, 5.78; O, 39.31; Found: C, 44.71; H, 5.53; O, 39.63.(Mustapha and Musa, 2014)

Results and Discussion

The results obtained fromthe synthesis of the three complexes are shown in Tables 1 and 2.Table 1 indicates physical properties such as color, decomposition temperature and melting points of the chromium complex compounds. The crystalline powder was found to have relatively high melting/decomposition temperatures (melting point of between 210 – 301^{o}C and decomposition temperature of 290 – 320^{o}C).These high temperatures are indication of the complexes resistance to heat.

The solubility test for all the complexes was carried out, and the results in Table 2 indicate that the synthesizedcompounds are all soluble in water, this could be as a result of the complexes being ionic or that the water is associating with the complex. The complexes were insoluble in n- hexane. Nitrite and oxalic bridgedchromium complexes were found to be soluble in both benzene and chloroform while succinicate complex is sparingly soluble in both benzene and chloroform solvents.

The IR-Spectra Spectra of the synthesized complexes showed little difference when compared with that of known chromium (III) acetylacetonate complex. The IR – Spectra of the synthesized complexes were mostly dominated by absorption bands between 1350 cm^{-3} to 1470 cm^{-3} which correspond to C – C and C – H stretching vibration bands of the β – diketoneligand. Other absorption bands that are commonly found in all synthesized chromium complexes spectra are peaks within the range of 1620 cm^{-3} to 1680 cm^{-3} which corresponds to coordinated C = O groups in the β–diketone and also at 1500 cm^{-3} to 1590 cm^{-3} for C = C stretching in the β -diketone ligand. However, the synthesized chromium complexes posses a characteristic absorption bands at 3487.42 cm^{-1} , 3424.73 cm^{-1} and 3448.84 cm^{-1} which are assigned to Cr – O bond indicating chromium succinate, nitrite, and oxalate bond. coordination in$[(Cr(acac)_2)_2(succ)]$, $[((Cr(acac)_2)_2(NO_2)]$ and $[(Cr(acac)_2)_2(oxal)_2]$ respectively (Yadar, 2005).

Table 1: Physical Parameters, Colour, Melting Point and Decomposition Temperature.

Complexes	Colour	Melting Point (^{o}C)	Decomposition Point (^{o}C)
Chromium (III) Acetylacetone	Dull purple	210	290
$[Cr(acac)_2(NO_2)_2]$	Brown	298	305
$[Cr(acac)_2(Oxal)_2]$	Dark green	285	309
$[Cr(acac)_2(Succ)_2]$	Dark red	301	311

Table 2: The Solubility Tests on Various Solvents

	$[Cr(acac)_2(NO_2)_2]n$	$[Cr(acac)_2(Oxal)_2]n$	$[Cr(acac)_2(Succ)_2]n$
Water	S	SS	
n- Hexane	IS	ISIS	
Benzene	IS	ISIS	
Chloroform	IS	I S	IS

S = Soluble IS = Insoluble.

The shift in the absorption band of the chromium complexes produced could be due to mesomeric and inductive effects which cause shielding and deshielding of absorption bands in the spectrum obtained. Other reasons for the shift in the value of absorption bands could be associated with resonance of delocalized electrons in the nitro group and that of the β – diketone ligand. The elemental analysis is in agreement with the theoretical values, the values obtained were as a result of series of recrystallization of the synthesized complexes.

Conclusion

We have successfully synthesized the chromium (III) complexes with acetylacetonate and crosslinked the molecule with either succinicate, nitrite or oxalate. The complexes were proposed to be a polymer crosslinked via these molecules. The complexes are very stable with respect to heat and on exposure to open atmosphere.

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