EXPERIMENT NUMBER	9
THE NAME OF THE EXPERIMENT	METAL ACETYLACETONATE COMPLEXES
FORMULA	$M(CH_3COCHCOCH_3)_n$

REACTION EQUATION

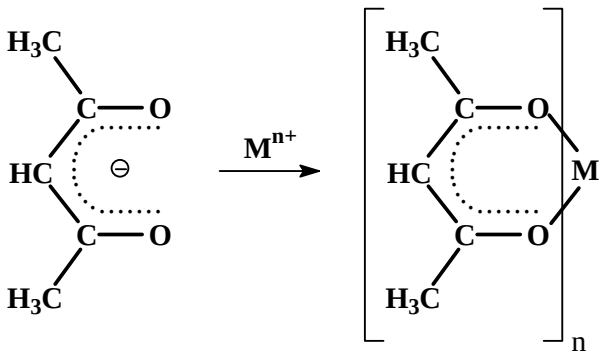
$$M^{n+} + n\ CH_3COCH_2COCH_3 \longrightarrow M(CH_3COCHCOCH_3)_n \quad (n=2 \text{ or } 3)$$

GENERAL INFORMATION

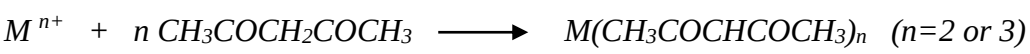
Acetylacetone (2,4-pentanedione, $CH_3COCH_2COCH_3$) is a typical β-diketone and ionizes as a weak acid in aqueous solution.

$$CH_3COCH_2COCH_3 \rightleftharpoons H^+ + CH_3COCHCOCH_3^-$$

The anion formed as a result of the ionization of acetylacetone in water acts as a ligand against metal ions, binds to a metal ion with both oxygen atoms and forms a 6-membered ring.

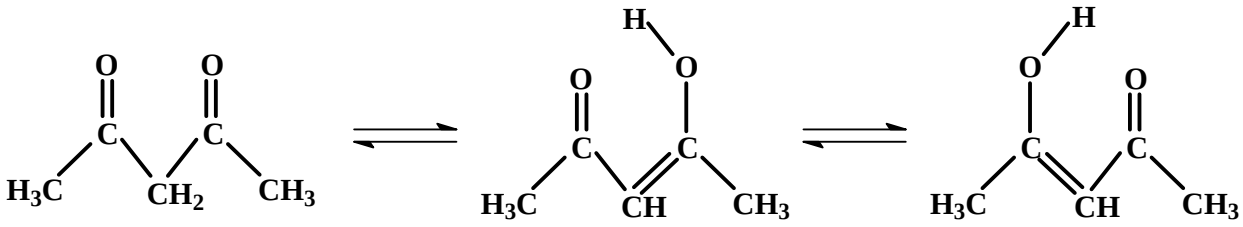


Metal acetylacetonate complexes, which are generally isolated as crystalline solids, are neutral. Therefore, a metal ion (M^{n+}) forms a complex, which has $M(CH_3COCHCOCH_3)_n$ stoichiometry, with acetylasetone ligand.



In complexes, MO_2C_3 rings are planar. In $M(CH_3COCHCOCH_3)_3$ complexes, MO_6 is in octahedral geometry, while in $Cu(CH_3COCHCOCH_3)_2$, MO_4 is in square planar geometry.

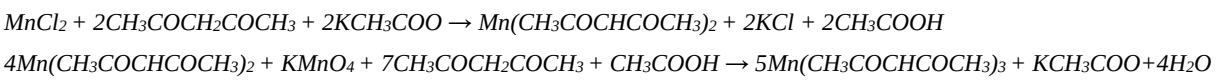
Acetylacetone has two tautomeric forms: Keto and enol.



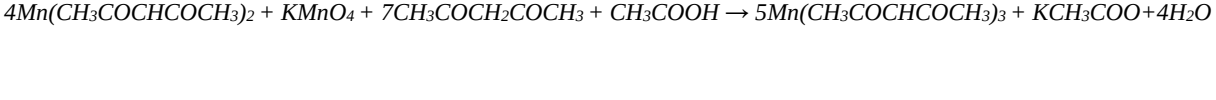
In this experiment, a metal complex of acetylacetone will be prepared and complex formation will be followed using thin layer chromatography.

EXPERIMENTAL PROCEDURE

Acetylacetonatomanganese (III) Complex [$Mn(CH_3COCHCOCH_3)_3$]



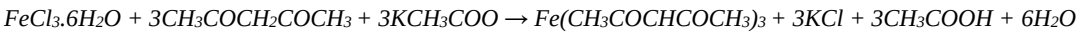
$$MnCl_2 + 2CH_3COCH_2COCH_3 + 2KCH_3COO \rightarrow Mn(CH_3COCHCOCH_3)_2 + 2KCl + 2CH_3COOH$$



$$4Mn(CH_3COCHCOCH_3)_2 + KMnO_4 + 7CH_3COCH_2COCH_3 + CH_3COOH \rightarrow 5Mn(CH_3COCHCOCH_3)_3 + KCH_3COO + 4H_2O$$

5.2 g (0.0026 mole) of manganese (II) chloride and 9.8 g (0.1 mole) of potassium acetate are dissolved in 200 mL of water. To this solution, 20.5 mL of acetylacetone is added slowly with stirring. To the solution obtained, 1.04 g (0.0066 mole) of potassium permanganate dissolved in 50 mL of water are added in portions at room temperature. After stirring for a few minutes, 13.6 g (0.1 mole) of potassium acetate dissolved in 50 mL of water are again added to the solution. The mixture is heated for 10 minutes and cooled to room temperature. The green-black crystals formed are filtered and washed several times with water.

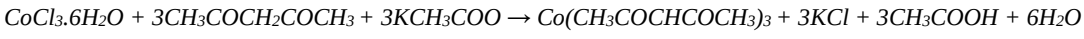
Acetylacetonatoiron (III) Complex [$Fe(CH_3COCHCOCH_3)_3$]



$$FeCl_3.6H_2O + 3CH_3COCH_2COCH_3 + 3KCH_3COO \rightarrow Fe(CH_3COCHCOCH_3)_3 + 3KCl + 3CH_3COOH + 6H_2O$$

1.17 g (0.012 mole) of potassium acetate is dissolved in 15 mL of water. 1.3 mL (0.012 mole) of acetylacetone is added slowly with stirring. 1 g (0.004 mole) of iron (III) chloride hexahydrate solution in 15 mL of water is added to the light yellow solution formed, and it is heated and left to crystallize for a few minutes. The crystals obtained are washed with water and dried in the air.

Acetylacetonatocobalt (III) Complex [$Co(CH_3COCHCOCH_3)_3$]



$$CoCl_3.6H_2O + 3CH_3COCH_2COCH_3 + 3KCH_3COO \rightarrow Co(CH_3COCHCOCH_3)_3 + 3KCl + 3CH_3COOH + 6H_2O$$

1.17 g (0.012 mole) of potassium acetate is dissolved in 15 mL of water. 1.3 mL (0.012 mole) of acetylacetone is added slowly with stirring. A solution of 1 g (0.004 mole) of cobalt (III) chloride hexahydrate in 15 mL of water is added to the light yellow solution formed, and it is heated and allowed to crystallize for a few minutes. The crystals obtained are washed with water and dried in the air.

Acetylacetonatoaluminum (III) Complex [$Al(CH_3COCHCOCH_3)_3$]

$Al_2(SO_4)_3.17H_2O + 6CH_3COCH_2COCH_3 + 6NH_3 \rightarrow 2Al(CH_3COCHCOCH_3)_3 + 3(NH_4)_2SO_4 + 17H_2O$

6 g (about 5 mL) of acetylacetone is placed in 40 mL of water. Ammonia is added dropwise until the resulting suspension disappears. 6 g (0.009 mole) aluminum (III) sulfate heptadecahydrate solution in 60 mL of water is added to this solution. The solution mixture should be neutral against litmus paper. For this purpose, a small piece of litmus paper is thrown into the mixture and if the color of litmus paper is red, ammonia is added dropwise until the red color of the litmus is blue. The solution is cooled. The colorless crystals formed are separated by filtration through the Bucher funnel.

Acetylacetonatocopper (II) Complex [$Cu(CH_3COCHCOCH_3)_2$]

$CuCl_2 + 2CH_3COCH_2COCH_3 + 2KCH_3COO \rightarrow Cu(CH_3COCHCOCH_3)_2 + 2KCl + 2CH_3COOH$

0.8 g (0.008 mole) of potassium acetate is dissolved in 15 mL of water. 0.85 mL (0.008 mole) of acetylacetone is added slowly with stirring. 0.5 g (0.004 mole) of copper (II) chloride solution in 15 mL of water is added to the solution. The blue-gray crystals formed immediately by the addition of the copper salt are filtered and washed with water several times and dried in the air.

Acetylacetonatonickel (II) Complex [$Ni(CH_3COCHCOCH_3)_2$]

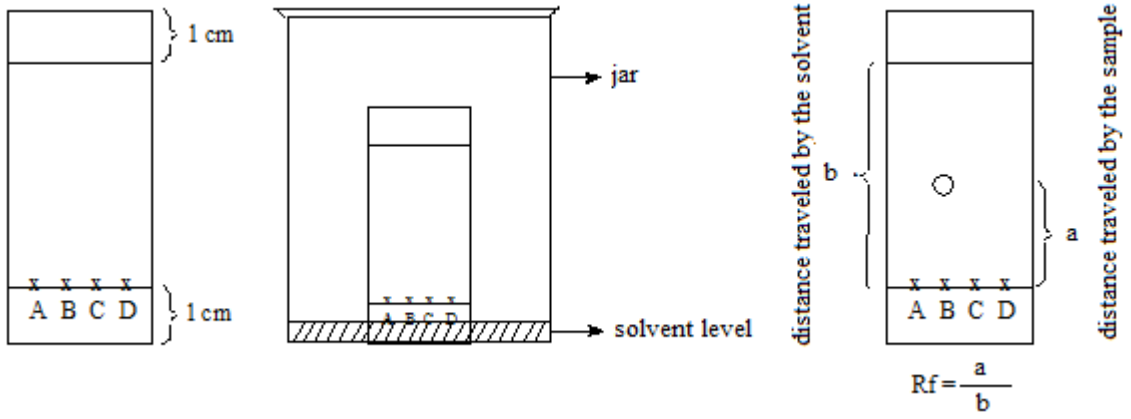
$NiCl_2.6H_2O + 2CH_3COCH_2COCH_3 + 2KCH_3COO \rightarrow Ni(CH_3COCHCOCH_3)_2 + 2KCl + 2CH_3COOH + 6H_2O$

0.8 g (0.008 mole) of potassium acetate is dissolved in 15 mL of water. 0.85 mL (0.008 mole) of acetylacetone is added slowly with stirring. To the solution obtained, 1 g (0.004 mole) of nickel (II) chloride hexahydrate solution is added in 15 mL of water. The green crystals formed by the addition of the nickel salt are filtered and washed with water several times and dried in the air.

THIN LAYER CHROMATOGRAPHY OF METAL ACETILACETONATE COMPLEXES

Thin layer chromatography is one of the most used procedures for the separation, purification and identification of the compounds synthesized in chemistry laboratories. Chromatography can be defined as the separation of the compounds that make up the mixture by the action of a mobile solvent in a porous environment, as a result of different movements. In thin layer chromatography, adsorbance (usually silica or alumina etc.) is spread on the glass or aluminum layer in the form of a thin film. The sample where the chromatography will be applied must be in solution or solids must be dissolved in a suitable solvent. After selecting the thin layer to be used;

1. *A line parallel to the edge is drawn with a pencil about 1 cm high from the bottom of the thin layer and a cross mark is placed on this line as much as the number of samples to be determined with a pencil.*
2. *A parallel line is drawn to determine the distance the solvent travels about 1 cm below from the top of the thin layer.*
3. *The sample to be determined is dropped with a thin capillary on the crosses of the thin layer.*
4. *The prepared thin layer is immersed in a glass jar with a suitable solvent of 1 cm height. However, while doing this process, it should be noted that the samples dropped on the thin layer do not touch the solution. The mouth of the jar is tightly closed. When the solution reaches the level drawn at the top of the thin layer, the layer is removed from the jar.*
5. *Distances, where the solvent and the sample travel, are measured separately, and Rf values are determined using these measurements. The Rf value is different for each compound, depending on the solvent used and the adsorbance in the layer.*



Note the Rf values of the $M(CH_3COCHCOCH_3)_n$ complexes by obtaining them on the silica thin layer in CH_2Cl_2 / CH_3OH (2/1) solvent mixture.

M^{n+}	Mn^{3+}	Fe^{3+}	Co^{3+}	Cu^{2+}	Ni^{2+}
Rf					

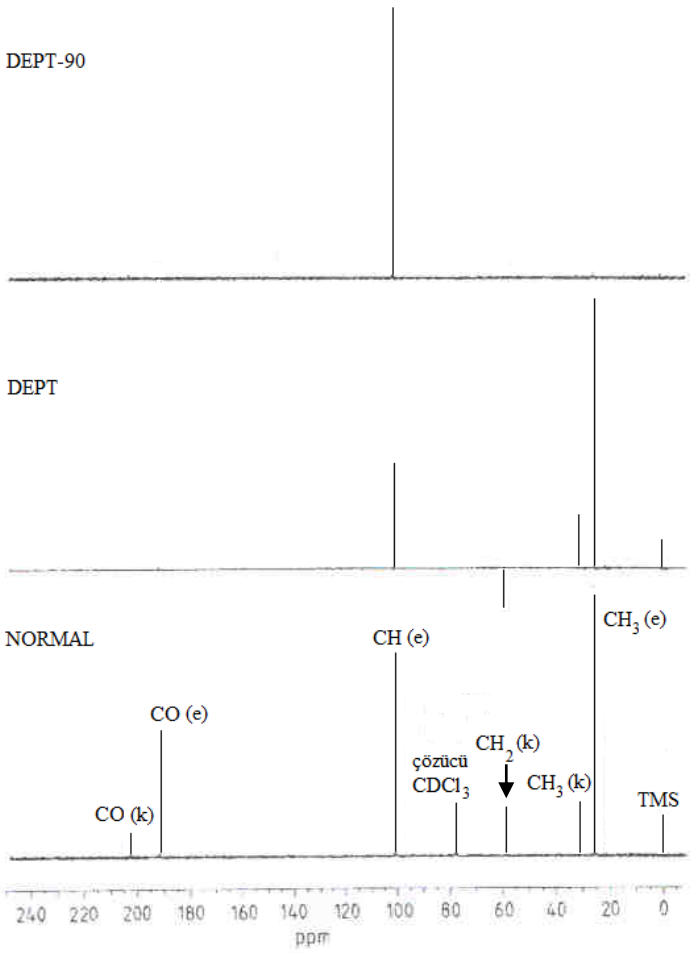
NMR SPECTRA OF ACETILACETONE AND THE COMPLEXES

^{1}H and ^{13}C NMR spectra of acetylacetone and $Al(CH_3COCHCOCH_3)_3$ complex will be described as examples. All carbon types (CH_3, CH_2, CH and tertiary C) can be seen on a ^{13}C NMR spectrum. In the DEPT spectrum, the signals of tertiary carbons are not visible and the signals of CH_2 carbons are reversed. In the DEPT-90 spectrum, the signals only appear for CH carbons. Thus, four different types of carbon can be easily identified in the ^{13}C NMR spectrum. As mentioned earlier, acetylasetone has both keto and enol forms, and acetylasetone bonds to metal ions via its enol form as a ligand. The signals of enol (e) and keto (k) forms were marked in both ^{1}H and ^{13}C NMR spectra of the compounds.

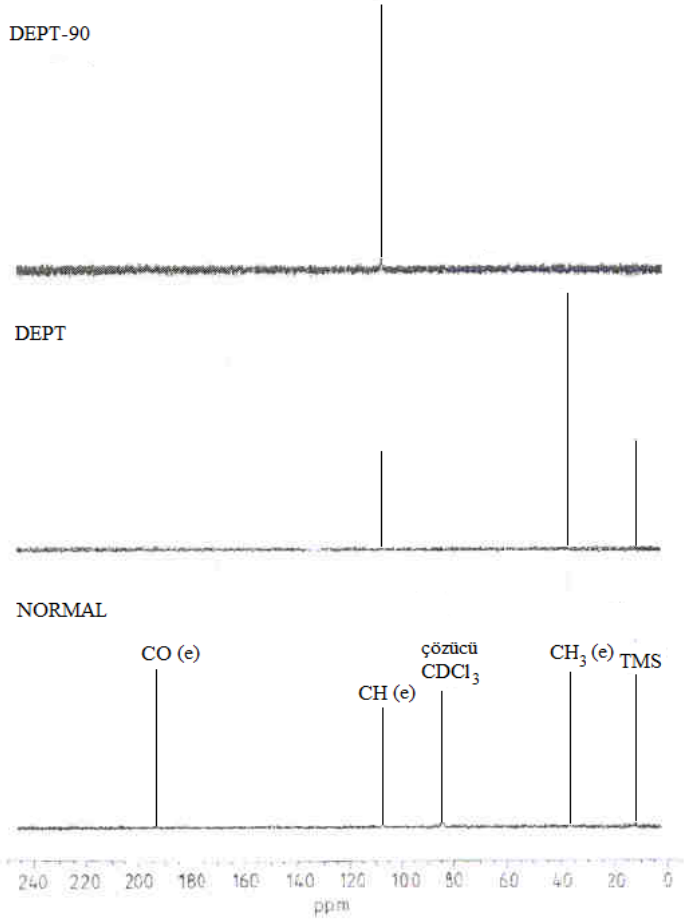
QUESTIONS

1. *What is thin layer chromatography? Define the Rf value.*
2. *Draw complex structures and explain whether the complexes are optically active.*
3. *Why should excessive use of ammonia be avoided during the preparation of the acetylacetonatoaluminum(III) complex?*
4. *What is its tautomer? Write the tautomers of the acetylacetone ligand. When acetylasetone forms a complex with metal ions, which is the tautomeric form used as a ligand and why the other form is not used?*

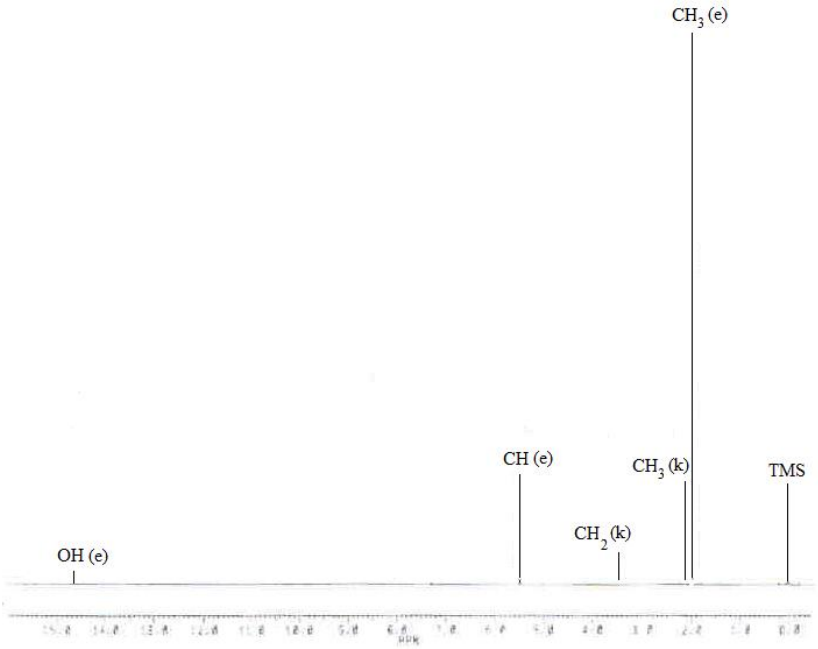
Working rate: 1/2



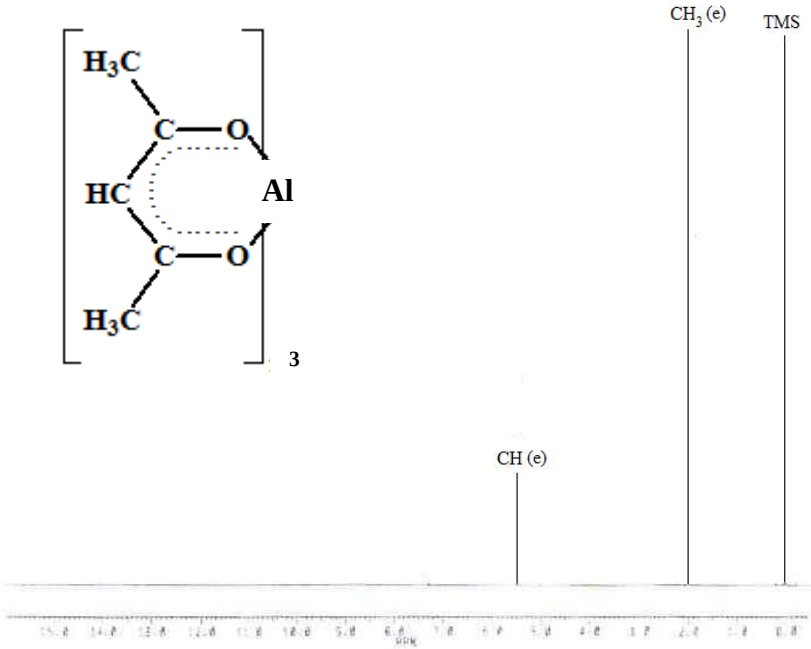
^{13}C NMR spectrum of $CH_3COCH_2COCH_3$



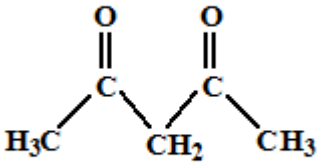
^{13}C NMR spectrum of $Al(CH_3COCHCOCH_3)_3$ complex



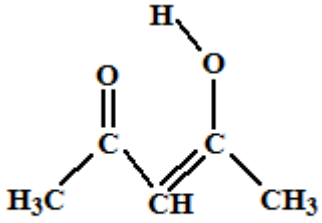
^{1}H NMR spectrum of $CH_3COCH_2COCH_3$



^{1}H NMR spectrum of $Al(CH_3COCHCOCH_3)_3$ complex



Keto



Enol