The Metal Complexes of Heterocyclic \( \beta \)-Diketones and their Derivatives, Part VIII

Synthesis, Structure, Proton NMR and Infrared Spectral Studies of the Complexes of Al(III), Fe(III), Co(III), Rh(III), In(III), and Zr(IV) with 1-Phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5 (HPMTFP)

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Metal Complexes, PMR Spectra, IR Spectra

New complexes of Al(III), Fe(III), Co(III), Rh(III), In(III) and Zr(IV) with 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5 (HPMTFP), have been synthesized and characterized by means of elemental analyses, conductivity and magnetic moment measurements, proton NMR and infrared spectroscopy. It is concluded that the ligand, HPMTFP, reacts as a bidentate enol forming neutral metal chelates. The PMR spectra of chelates sufficiently soluble in deuterated NMR solvents were recorded and studied. The IR spectra are measured between 4000–200 cm\(^{-1}\) and assignments are proposed for the observed frequencies. The M–O stretching frequency follows the order: Al > Rh > Fe = Co = Zr > In.

Introduction

In the course of our studies of the chemistry of metal complexes of heterocyclic \( \beta \)-diketones and their derivatives a considerable number of chelates of phenyl-substituted pyrazole-derived \( \beta \)-diketones have been prepared and characterised [1, 2]. Some of the general preparative procedures used in making metal(II) chelates of \( \beta \)-diketones [3] do not always apply to metal(III) chelates. In continuation of our serial study, the present work describes the various synthetic procedures for making the chelates of zirconium(IV) and a variety of trivalent metals with 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5 (HPMTFP). Some physical properties and infrared spectral studies of these complexes are also reported.

Experimental

Reagents

All reagents used were either Merck extra pure or B. D. H. (A. R.).

Preparation of ligand

1-Phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5 was synthesised in our laboratories by the method described in an earlier publication [4].

Preparation of complexes

The yields, colours, and melting points of the complexes are recorded in Table I.

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Al(HPMTFP)\(_3\)

HPMTFP (8.1021 g, 0.03 mole) was added to a solution of aluminium isopropoxide (2.0423 g, 0.01 mole) in 180 ml benzene. The resulting solution was allowed to stand overnight after which the benzene and the 2-propanol which was produced were removed by vacuum distillation at room temperature. A cream crystalline product was recovered.

Fe(HPMTFP)\(_3\)

Iron(III) chloride hexahydrate (2.7 g, 0.01 mole) dissolved in distilled water (75 ml) was added with stirring to a solution which was prepared by mixing HPMTFP (8.1021 g, 0.03 mole, in 100 ml 95\% ethanol) and sodium acetate (5 g in 40 ml distilled water). The wine red fine crystals which were deposited after the resulting reddish solution was refrigerated overnight were filtered off, washed several times with aqueous ethanol (1/1), and air-dried before storing in a dessicator over \( \text{P}_2\text{O}_5 \).

Co(HPMTFP)\(_3\)

To a solution of 8.1051 g (0.03 mole) of HPMTFP in 120 ml of 95\% ethanol were added 3.62 g (0.01 mole) of \( \text{Na}_2\text{Co(CO}_3\text{)}_\text{2} \cdot \text{3 H}_2\text{O} \) [5] and 5 ml of \( N\text{HNO}_3 \). The mixture was allowed to reflux for one hr. and the resulting yellowish precipitate was collected, washed with aqueous ethanol (1/1), air-dried and stored in a dessicator over \( \text{P}_2\text{O}_5 \).

Rh(HPMTFP)\(_3\)

To a solution of 2.0255 g (0.0075 mole) of HPMTFP in 5 ml of 95\% ethanol was added with stirring a solution of 0.6583 g (0.0025 mole) of rhodium chloride trihydrate in 20 ml of distilled
water. The resulting solution was heated with stirring on a hot plate until it became cloudy after which it was put away to cool. The deposited orange crystals were filtered, washed with aqueous ethanol (1/1), air-dried and stored in a dessicator over P₂O₅.

\[
\text{In}(\text{PMTFP})₃
\]

Indium(III) chloride (2.2119 g, 0.01 mole) dissolved in distilled water (75 ml) was added with stirring to a solution of HPMTFP (8.1021 g, 0.03 mole) in 95\% ethanol (100 ml). Conc. NH₄OH (3 ml) was added to the reaction mixture which was stored overnight. The whitish crystals which formed were filtered, washed clean with distilled water and air-dried. The product was purified by recrystallising from aqueous ethanol.

\[
\text{Zr}(\text{PMTFP})₄
\]

Anhydrous zirconium chloride (2.3322 g, 0.01 mole) was added to HPMTFP (10.8028 g, 0.04 mole) dissolved in carbon tetrachloride (100 ml) under reflux. The reaction mixture was refluxed until evolution of hydrogen chloride ceased when it was put aside to cool. The fine yellow solid which deposited was filtered, washed clean with acetone, dried and stored over P₂O₅ in a dessicator.

**Physical measurements**

IR spectra (400-200 cm⁻¹) were recorded on a Perkin-Elmer 577 spectrophotometer in pressed KBr discs and Nujol. The calibration of the instrument was checked against a polystyrene film in the 2850, 1600, and 900 cm⁻¹ regions. Reproducibility was ± 2 cm⁻¹.

Proton NMR spectra were obtained using a Varian Associates T-60 spectrometer at 60 Hz. Chemical shifts are reported as δ (ppm) relative to TMS as an internal standard.

Melting points were determined with a Fisher-Johns apparatus and were uncorrected.

**Table I. Physical and analytical data for 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5, (HPMTFP) and its Zr(IV) and some trivalent metal complexes.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Melting or decomp. Temp. [°C]</th>
<th>Yield [%]</th>
<th>Calcd [%]</th>
<th>Found [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₂H₂₀O₄N₂F₃ · H₂O</td>
<td>light pink</td>
<td>139-140</td>
<td>89</td>
<td>50.00</td>
<td>3.85</td>
</tr>
<tr>
<td>(C₁₂H₂₀O₄N₂F₃)₃Al</td>
<td>Cream</td>
<td>198-199</td>
<td>83</td>
<td>51.62</td>
<td>2.89</td>
</tr>
<tr>
<td>(C₁₂H₂₀O₄N₂F₃)₃Fe</td>
<td>Wine red</td>
<td>184-185</td>
<td>94</td>
<td>49.90</td>
<td>2.79</td>
</tr>
<tr>
<td>(C₁₂H₂₀O₄N₂F₃)₃Co</td>
<td>yellowish brown</td>
<td>209-210 dec.</td>
<td>87</td>
<td>49.72</td>
<td>2.78</td>
</tr>
<tr>
<td>(C₁₂H₂₀O₄N₂F₃)₃Rh</td>
<td>Orange</td>
<td>118 dec.</td>
<td>88</td>
<td>47.33</td>
<td>2.65</td>
</tr>
<tr>
<td>(C₁₂H₂₀O₄N₂F₃)₃In</td>
<td>bone white</td>
<td>84-85</td>
<td>91</td>
<td>46.72</td>
<td>2.61</td>
</tr>
<tr>
<td>(C₁₂H₂₀O₄N₂F₃)₄Zr</td>
<td>yellow</td>
<td>272-273</td>
<td>93</td>
<td>49.35</td>
<td>2.76</td>
</tr>
</tbody>
</table>

**Results and Discussion**

**Structure of ligand**

Even though the ligand, 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5 with its four donor atoms may exist in four tautomeric forms (I), (II), (III) and (IV) only a light-pink tautomer (m.p. 139-140) has been isolated and characterised as the enol form (IV) crystallising with one molecule of water of crystallisation [6].

**Structure of complexes**

1. The analytical data (Table I) show complexes of the general formulae:
   a) M(PMTFP)₄ (M = Zr(IV)).
   b) M(PMTFP)₃ (M = Al, In, Fe(III), Co(III), Rh(III)) where PMTFP is the anion of 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5.
Table II. Solubility data for 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5, (HPMTFP) and its Zirconium(IV) and trivalent metal complexes.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Ligand (HPMTFP)</th>
<th>Al (PMTFP)</th>
<th>Fe (PMTFP)</th>
<th>Co (PMTFP)</th>
<th>Rh (PMTFP)</th>
<th>In (PMTFP)</th>
<th>Zr (PMTFP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>i</td>
<td>i</td>
<td>i</td>
<td>i</td>
<td>i</td>
<td>i</td>
<td>i</td>
</tr>
<tr>
<td>Methanol</td>
<td>vs</td>
<td>sp</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>i</td>
</tr>
<tr>
<td>Ethanol</td>
<td>vs</td>
<td>sp</td>
<td>s</td>
<td>sp</td>
<td>vs</td>
<td>vs</td>
<td>i</td>
</tr>
<tr>
<td>Benzene</td>
<td>s</td>
<td>s</td>
<td>vs</td>
<td>sp</td>
<td>vs</td>
<td>vs</td>
<td>i</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>vs</td>
<td>sp</td>
<td>s</td>
<td>s</td>
<td>vs</td>
<td>vs</td>
<td>i</td>
</tr>
<tr>
<td>Acetone</td>
<td>vs</td>
<td>s</td>
<td>s</td>
<td>s</td>
<td>vs</td>
<td>vs</td>
<td>i</td>
</tr>
<tr>
<td>DMSO</td>
<td>vs</td>
<td>sp</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>sp</td>
</tr>
<tr>
<td>DMF</td>
<td>vs</td>
<td>sp</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>sp</td>
</tr>
<tr>
<td>Tetrahydrofuran</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>sp</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>sp</td>
<td>sp</td>
<td>vs</td>
<td>vs</td>
<td>i</td>
<td>i</td>
<td>i</td>
</tr>
<tr>
<td>Dioxane</td>
<td>vs</td>
<td>sp</td>
<td>vs</td>
<td>vs</td>
<td>s</td>
<td>vs</td>
<td>sp</td>
</tr>
<tr>
<td>Chloroform</td>
<td>vs</td>
<td>s</td>
<td>s</td>
<td>sp</td>
<td>s</td>
<td>vs</td>
<td>i</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>vs</td>
<td>s</td>
<td>vs</td>
<td>sp</td>
<td>sp</td>
<td>vs</td>
<td>sp</td>
</tr>
<tr>
<td>Pyridine</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>vs</td>
<td>sp</td>
</tr>
</tbody>
</table>

Abbreviations: i, insoluble; sp, sparingly; s, soluble; v, very.

2. The DMF solutions of the complexes (10⁻³ M) exhibit negligible molar conductance values indicating their non-ionic nature.

3. IR evidence.
   a) The shift of νC=O from 1680 cm⁻¹ in the ligand to νasC=O: 1607 cm⁻¹ (Rh) - 1640 cm⁻¹ (Co(III)) in the complexes suggests that the carbonyl group is involved in bonding.
   b) The strong broad O–H···O stretching band centered at 2700 cm⁻¹ in the IR spectrum of the ligand has disappeared in spectra of the complexes revealing the involvement of OH in bonding.
   c) The absence of any peak between 3100 and 3600 cm⁻¹ in the complexes indicates the absence of ν(–NH–) and this removes the possibilities of the amino-diketo tautomeric form (structure 1) coordinating either only through one or two of the carbonyl groups or forming a coordinate bond to metal ion through the nitrogen atom of its secondary amino group – a revelation that supports the view that the reacting specie is an enol.
   d) The presence of absorption peaks between 300 and 500 cm⁻¹ characteristic of metal β-diketonates suggests the presence of M–O bonds [7].

4. The proton magnetic resonance spectral data for the ligand and some of the complexes (Table III) reveal that the enolic proton signal which is present in the ligand spectrum has disappeared in the spectra of the complexes indicating that the enolic proton is lost during complexation.

A combination of all the available data provide ample evidence that the ligand is reacting as a bidentate enol forming neutral metal chelates of the type:

Table III. Proton NMR spectral data of HPMTFP and chelates (chemical shifts in δ ppm relative to TMS).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Methyl protons</th>
<th>Water molecule protons</th>
<th>Phenyl protons</th>
<th>Hydroxyl proton</th>
<th>NMR Solvent</th>
<th>Remarks (if any)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁₂H₉F₃N₂O₂·H₂O, (HPMTFP)</td>
<td>2.40 (sp,s)</td>
<td>5.93 (sp,s, 2H)</td>
<td>7.30–8.0 (m)</td>
<td>5.93 (sp,s)</td>
<td>Acetone-d₆</td>
<td>–</td>
</tr>
<tr>
<td>Al(PMTFP)₃</td>
<td>2.33 (sp)</td>
<td>–</td>
<td>7.0–8.0 (m)</td>
<td>–</td>
<td>CDCl₃</td>
<td>–</td>
</tr>
<tr>
<td>In(PMTFP)₃</td>
<td>2.23, 2.27,</td>
<td>–</td>
<td>7.20–8.20 (m)</td>
<td>–</td>
<td>Acetone-d₆</td>
<td>Ratio of cis-trans isomers obtained from integration of methyl signals is 1:2</td>
</tr>
</tbody>
</table>

sp, sharp; br, broad; s, singlet; m, multiplet; d, doublet.
Proton magnetic resonance (PMR) spectra

Amongst the M(III) and M(IV) ions whose chelates were investigated, Al\(^{3+}\), In\(^{3+}\) and Zr\(^{4+}\) are diamagnetic, while Co\(^{3+}\) with four 3d unpaired electrons, Fe\(^{3+}\) with five 3d unpaired electrons and Rh\(^{3+}\) with four 4d unpaired electrons are all paramagnetic. As a result of the expected paramagnetism of some of the complexes under study and the accompanying isotropic shifts of the nuclear resonances the PMR spectra covered a range of ~30 ppm at 32 °C.

Tris-chelate complexes exist in enantiomeric configurations, \(A\) and \(A\), about the metal atom and, when the chelating ligand is unsymmetrical, that is when it has two different ends like in HPMTFP, there are also geometrical isomers, cis and trans [8-10]. Each geometrical isomer exists in enantiomeric forms. Here cis and trans refer to facial and meridional arrangements of like donor atoms in the octahedral coordination sphere. Cis isomers would have a threefold symmetry axis (C\(_3\)) relating corresponding nuclei on different ligands, and only one resonance signal for each kind of ligand nucleus would be expected. On the other hand, the trans isomers have no such symmetry and up to three resonance signals for each kind of ligand nucleus may occur. The PMR spectrum of this chelate suggests therefore that it is the paramagnetic complex that is formed with HPMTFP, and the observed magnetic moment of 5.42 Bohr magnetons confirms this.

4. With the Fe(III) chelate no signals were also observed at very high spectral amplitudes. Again, this observation is not surprising since Fe\(^{3+}\) with five unpaired 3d electrons is capable of forming at least theoretically, two types of chelates:

   a) a weakly paramagnetic low spin inner orbital complex with octahedral 3d\(^2\)4s4p\(^3\) bonds and

   b) a strongly paramagnetic high spin outer orbital complex with octahedral 4s4p\(^3\)4d\(^2\) bonds with a calculated magnetic moment \(\mu_s = \mu_{s+L}\) of 5.90 Bohr magnetons.

The PMR spectra of these complexes reveal the following:

1. Four methyl signals are obtained in the PMR spectrum of the indium chelate taken in acetone-d\(_6\) (Table III). Integration of the peaks reveals that the signals at \(\delta 2.23, 2.27, \) and 2.33 belong to the trans isomer of the chelate while the signal at \(\delta 2.40\) belongs to the cis isomer and the ratio of cis:trans is 1:2. It is obvious in this case that a mixture of both cis and trans forms is present, at least in acetone solution.

2. It is clear from these PMR spectra that the hydroxyl proton has been lost in the complexes and that the OH of the enolic form of the ligand was involved in chelation.

3. With the cobalt(III) chelate no signals were observed even at very high spectral amplitudes. This may be due to either huge paramagnetic shifts or extensive broadening of the signals or a combination of both. This is hardly surprising since Co\(^{3+}\) with four unpaired 3d electrons is capable of forming at least theoretically, two types of chelates:

   a) a diamagnetic inner orbital complex with octahedral 3d\(^2\)4s4p\(^3\) bonds and

   b) a paramagnetic outer orbital complex with octahedral 4s4p\(^3\)4d\(^2\) bonds with calculated magnetic moment, \(\mu_s\), of 4.90 and \(\mu_{s+L}\) of 5.48. The PMR spectrum of this chelate suggests therefore that it is the paramagnetic complex that is formed with HPMTFP, and the observed magnetic moment of 5.42 Bohr magnetons confirms this.

5. a) Aluminium(III) forms only one type of complex – a diamagnetic outer orbital complex with octahedral 3s3p\(^3\)3d\(^2\) bonds.

   b) Indium(III) forms only a diamagnetic outer orbital complex with octahedral 5s5p\(^3\)5d\(^2\) bonds. Their PMR spectra with sharp signals and no paramagnetic shifts are expected (Table III).
Infrared spectral study

The observed frequencies have been assigned by comparison with the spectra of acetylacetonates, trifluoroacetylacetonates, benzoylacetonates, trifluorobenzoylacetonates [7, 11, 12] and pyrazole [13]. The IR spectra are divided into two main absorption regions and will be discussed accordingly.

3500-1100 cm\(^{-1}\)

The spectra are devoid of absorption bands in the 3500-3100 cm\(^{-1}\) region indicating the absence of OH stretchings of water molecules. This shows that the chelates are anhydrous.

Of interest are the C\(_{\wedge}\)O and C\(_{\wedge}\)C stretching bands (\(v_{as}\)C\(_{\wedge}\)O and \(v_{as}\)C\(_{\wedge}\)C) of the chelate ring. These are known to be sensitive to substitution in 1,3-diketonates [7]. The intense band observed between 1607 (Rh) and 1640 (Co(III)) cm\(^{-1}\) and the strong peak between 1502 (Rh) and 1520 (Co(III)) cm\(^{-1}\) in the spectra of these M(PMTFP)\(_3\) chelates have been attributed to \(v_{as}\)C\(_{\wedge}\)O and \(v_{as}\)C\(_{\wedge}\)C modes respectively. This agrees well with similar assignments in acetyl-acetonates [14, 15] and the chelates of 1-phenyl-3-methyl-4-acetyl-pyrazolone-5 [16]. Similarly, symmetric C=O and C=C stretches (\(v_s\)C=O and \(v_s\)C=C) are assigned to absorptions near 1370 and 1250 cm\(^{-1}\) respectively. The order of the carbonyl stretching frequency (\(v_{as}\)C=O) for these M(III) chelates is:

$$\text{Co} > \text{In} > \text{Al} > \text{Fe} > \text{Rh}.$$  

Of interest also are the prominent strong bands located at about 1150 and 1200 cm\(^{-1}\) characteristic of CF\(_3\) stretching vibrations [17].

1100-200 cm\(^{-1}\)

The metal-ligand vibrations expected below 700 cm\(^{-1}\) are important since they provide information on the strength of the M–O bonds and hence the stability of the chelates.

In the IR spectra of these chelates of HPMTFP, the peak at 430 (Al), 397 (Fe), 397 (Co), 397 (Zr), 407 (Rh), and 395 (In) has been assigned to the M–O stretching mode, the spectrum of HPMTFP being taken as reference. The M–O stretching frequency follows the order:

$$\text{Al} > \text{Rh} > \text{Fe} = \text{Co} = \text{Zr} > \text{In}.$$  

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