## SHORT COMMUNICATION

## CHELATION AS A PROCESS FOLLOWING CHEMISORPTION UPON EMITTERS FOR FIELD DESORPTION AND FIELD IONIZATION MASS SPECTROMETRY

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Abstract—Acetylacetone (Hacac) admitted as a gas to an ion source containing  $CoCl_2$  adsorbed on a field ionization/field desorption emitter produces the ion  $[Co(acac)Cl]^+$ . Similar ions arising from interaction of adsorbed salt and a ligand admitted as a gas were found for  $CoCl_2$  and trifluoroacetylacetone, and for  $FeCl_2$  and acetylacetone. The chelation process represents a new kind of reaction of chemisorbed species in field ionization mass spectrometry.

SEVERAL processes may occur in field ionization mass spectrometry (FIMS) as a result of reactions following adsorption from the gaseous state.<sup>1.2</sup> The primary process is a proton transfer concerted with ionization.<sup>2</sup> Examples include protonation [Eqn. (1)], condensation and cluster formation [Eqn. (2)], and the shift of equilibria. There are also processes whose

$$2 \operatorname{ROH} \to \operatorname{ROH}_2^+ + \operatorname{RO} + e^- \tag{1}$$

$$3 \text{ ROH} \rightarrow (\text{ROH})_2 \text{H}^+ + \text{RO} + e^-$$
(2)

products resemble those of ordinary unimolecular mass spectral fragmentations, such as possible formation of McLafferty rearrangement products in the condensed phase.<sup>3</sup>

In addition to these reactions, which do not obviously require a chemisorptive process, reactions have been observed in FI which point to a chemical interaction of the adsorbate with the surface material. These include the formation of metal-hydride bonds in the course of the 'hydrogen promotion effect,'<sup>4</sup> the formation of CH<sub>3</sub>O radicals from alcohols on surfaces,<sup>5</sup> and the dissociative chemisorption of alkanes<sup>6,7</sup> and cycloalkanes<sup>8</sup> on surfaces.

We are engaged in a study of the applicability of field desorption mass spectrometry (FDMS) to chelated transition metal compounds, having shown its applicability to salts of quaternary ammonium ions.<sup>9</sup> In the course of examining several inorganic salts\* by FDMS, we had occasion to examine the behavior of hexaquocobalt(II) chloride deposited on the emitter by the usual FD emitter dipping technique,<sup>10</sup> using

<sup>\*</sup> Dr H.-R. Schulten has privately informed us of studies of simple inorganic salts at the University of Bonn.



FIG. 1. FD spectrum of  $[Co(H_2O)_6^{++} Cl^{-}_2]$  in the presence of acetylacetone; emitter current 30 mA.

an aqueous solution. This compound did not produce a measurable ion current with a filament current below 50 mA. However, the admission of acetylacetone vapor by the gas inlet system through a molecular leak to produce a source pressure of  $3 \times 10^{-5}$  Torr while hexaquocobalt(II) chloride was on the emitter produced the spectrum shown in Fig. 1 at an emitter current of 30 mA.

The peaks below m/e 102 are also found in the FI spectrum of acetylacetone with high emitter current: they are explained as  $[CH_2CO]^+$ , m/e 42;  $[CH_3CO]^+$ , m/e 43;  $[M - 15]^+$ , m/e 85;  $[M]^+$ , m/e 100;  $[M + H]^+$ , m/e 101. The m/e 101 peak presumably arises from a surface hydrogen abstraction reminiscent of Eqns. (1) and (2). The fragment peaks are more intense at higher emitter currents.

Remarkably, this spectrum also shows ions at m/e 193 and 195. These correspond to [Co(acac)Cl]<sup>+</sup> and are not found in the FI spectrum of acetylacetone alone. For this ion to be explained, it is necessary to invoke chemisorption of acetylacetone on the surface of the adsorbed cobalt chloride. A possible route to the formation of [Co(acac)Cl]<sup>+</sup> could be postulated as follows:

$$Co(H_2O)_6Cl_2 \xrightarrow{\Delta} CoCl_2 + 6H_2O$$
 (3)

$$CoCl_2 + Hacac \rightarrow Co^{II}(acac)Cl + HCl$$
 (4)

$$\mathrm{HCl} + \mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{H}_{3}\mathrm{O}^{+} + \mathrm{Cl} \cdot + e^{-}$$
(5)

$$Co^{II}(acac)Cl \rightarrow Co^{III}(acac)Cl^+ + e^-$$
 (6)

All of these are envisioned as occurring in the condensed phase. The dehydration step might be expected on the heated filament, and the final oxidation step [Eqn. (6)] is analogous to the internal oxidations postulated to explain the fragmentation of many compounds containing metals with adjacent oxidation states.<sup>11</sup>

Exposure of an emitter on which cobalt chloride had been absorbed to trifluoroacetylacetone in the source likewise produced ions at m/e 247 and 249, which correspond to the ion [Co(tfa)Cl]<sup>+</sup>. When FeCl<sub>2</sub> was used on the emitter with acetylacetone admitted, peaks corresponding once again to a similar process were observed.

The facilitation of ion formation by chelation after adsorption of a ligand may have applications in analysis of small quantities of metals; it resembles the facilitation of detection of sodium from adsorbed sodium chloride by admitting various ligands,<sup>12\*</sup> such as acetic acid, in which case m/e 105 [Na<sub>2</sub>OOCCH<sub>3</sub>]<sup>+</sup> is observed with no heating current.\* The method also seems useful for examining mechanisms of catalysis, by extension of previous observations.<sup>6–8</sup>

## EXPERIMENTAL

The spectra were taken on an AEI Ltd, MS-702 mass spectrometer which was modified in a manner similar to that described by Beynon.<sup>13</sup> The anode, a 10  $\mu$ m W wire activated at high temperature in benzonitrile,<sup>14,15</sup> was placed about 1 mm from the grounded cathode plate. The potential difference was 10 kV, giving a mass range of up to m/e 550. Typical pressures were in the range 3 to 5  $\times$  10<sup>-5</sup> Torr. The spectra were recorded using Ilford Q2 plates and standard techniques for development; a typical exposure was 0.3 nC. Relative intensities were determined by a modified Churchill two-line technique.<sup>16</sup>

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