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Mechanism of Mass Spectral Fragmentation of Mixed-Ligand Cobalt(III) Complexes with Heterocyclic Dithiocarbamates and Tetraazamacrocyclic Ligand

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The mass spectral fragmentation of three mixed-ligand Co(III) complexes of the general formula [Co(Rdtc)cyclam]$(ClO_4)_2$ **(1)**–**(3)**, where *cyclam* and *Rdtc* refer to 1,4,8,11-tetraazacyclotetradecane and 2-methylpiperidine-(2-*Mepipdtc*), 3-methylpiperidine-(3-*Mepipdtc*) and 4-methylpiperidine-(4-*Mepipdtc*) dithiocarbamates, respectively, have been investigated. It is shown to be of mechanistic significance, clarifying the major products of their fragmentation. A possible mechanism entails a multi-step decomposition process, which can also be well separated into individual steps. Every step is determined to know the nature of the intermediates.

Key words: Mass spectra, Cobalt(III) complexes, Tetraazamacrocycle, Tetraazacyclotetradecane, Dithiocarbamates

INTRODUCTION

Dithiocarbamato ligands have high tendency of MS_4 and MS_6 coordination and act as almost uninegative bidentate ligands coordinating through both the sulfur atoms[1]. Both four- and hexa-coordinated complexes of many transition metal ions have been isolated[2, 3], but being very stable towards substitution, they rarely form mixed-ligand complexes. To achieve stable mixed-ligand heterocyclic dithiocarbamato complexes they must be combined with other ligands of comparable coordinating ability. In this respect the macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane (*cyclam*) is especially suitable to form and stabilize the complex of MN_4S_2 chromophore[4–6].

This paper is an extension of the study on the synthesis, characterization and structure of cobalt(III) complexes with tetraazamacrocyclic ligand *cyclam* and heterocyclic dithiocarbamato ligands[5], *i.e.*, 2-methylpiperidine-(2-*Mepipdtc*), 3-methylpiperidine-(3-*Mepipdtc*) and 4-methylpiperidine-(4-*Mepipdtc*) dithiocarbamates (*Rdtc*$^-$), respectively (Fig. 1) which prompted us to undertake a detailed mechanism of their mass spectral behaviour. The aim of these investigations is the ability to predict and hence interpret the principal modes of mass spectral fragmentation of fairly complicated complexes[7] and, hopefully, developing a parallel route to analogues.

EXPERIMENTAL

The complexes [Co(Rdtc)cyclam]$(ClO_4)_2$ **(1)**–**(3)** were obtained by mixing the $Co(ClO_4)_2 \cdot 6H_2O$, *cyclam* and $RdtcNa \cdot 2H_2O$ in molar ratio 1 : 1 : 1 in ethanol/-water solution as previously described[5]. Mass spectra were recorded on a double focusing reverse geometry Finnigan-MAT 8230 mass spectrometer at a resolution of 1000 using a combined EI-CI source at 200°C. The sample was introduced with tungsten wire (diameter 0.08 mm) using a DCI probe. The current through the wire was programmed linearly at the rate of 40 mAs^{-1}. This technique is known as the *ln*-beam technique[8]. The reagent gas for chemical ionization was 1 m torr of isobutane. CI spectra were recorded at 150 eV electron energy for deeper penetration through the reagent gas and 0.2 mA collector current.

RESULTS AND DISCUSSION

Mass spectral data exhibit the presence of basic intact ion $[Co(cyclam)]^{3+}$ at m/z 86 founded for the observed complexes. Concerning the suggested structure presented in Fig. 1 the appearance of this ion and the presence of peaks containing the chelate ligand moiety indicates that the dithicarbamato ligands (*Rdtc*$^-$) leaving the coordination sphere first, are expected, weaker ligands than the macrocyclic *cyclam* ligand. This behaviour reflects the fact that stepwise removal of a cyclic ligand from the coordination sphere of a metal tends to be more difficult than for open-chain chelate ligands[9]. Besides, mass spectra of all the complexes show the presence of monocation $[Co(Rdtc)cyclam](ClO_4)^+$ (m/z 532) and dication $[Co(Rdtc)cyclam]^{2+}$ (m/z 217). The pertinent m/z data were collected in Table-1.

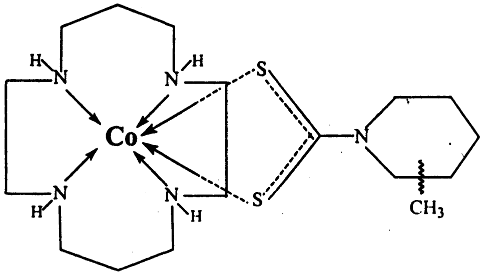


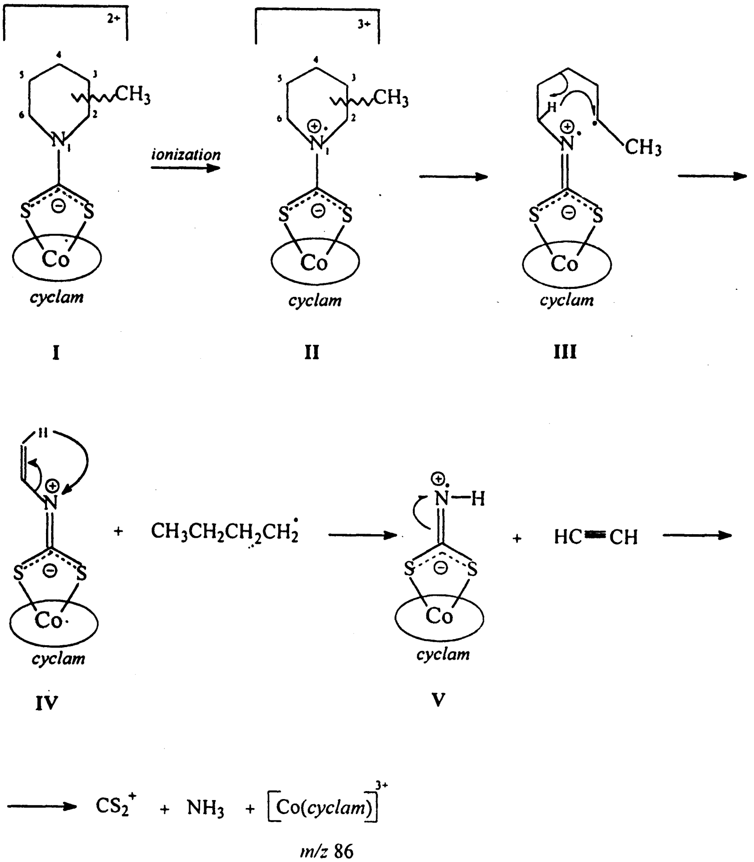
Fig. 1. Structure of the complex cation $[Co(Rdtc)cyclam]^{2+}$ with a methyl group on the piperidine ring in 2, 3 or 4 position for the **(1)**–**(3)** complexes

The further decomposition of the complexes can be presented by the most plausible mechanism that explains the general features of the fragmentation, as represented in **Scheme-1**. After the cation $[Co(Rdtc)cyclam]^{2+}$ **(I)** ionization the trication $[Co(Rdtc)cyclam]^{3+}$ **(II)** with a positive charge on the nitrogen atom is

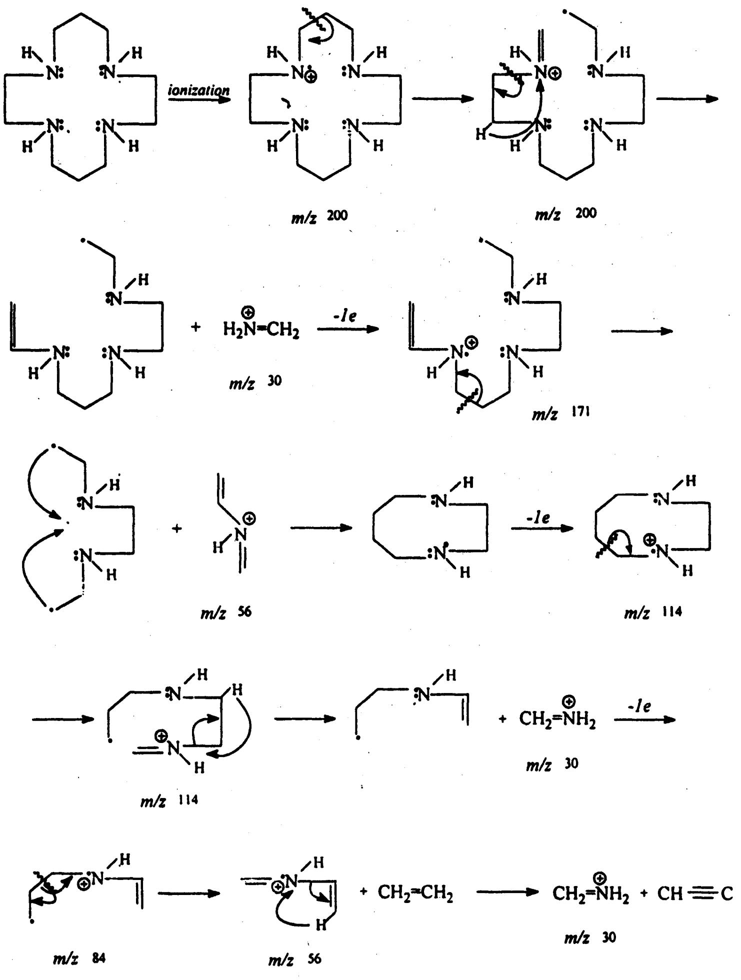
TABLE-1
FRAGMENTATION IONS OF THE OBTAINED COMPLEXES (1)–(3)
AND OF THE MACROCYCLIC LIGAND *Cyclam*

Complex		Macrocyclic ligand	
$[Co(Rdtc)cyclam](ClO_4)^+$	532	$C_{10}H_{24}N_4^+$	200
$[Co(Rdtc)cyclam]^{2+}$ (I)*	217	$C_9H_{21}N_3^+$	170
II	144	$C_6H_{14}N_2^+$	114
III	144	$C_5H_{10}N^+$	84
IV	125	$C_3H_6N^+$	56
V	117	$CH_3—^+HN=CH_2$	44
$[Co(cyclam)]^{3+}$	86	$CH_2=NH_2^+$	30

*Ions according to the **Schemes 1 and 2**



Scheme-1. Probable mechanism of the fragmentation according to mass spectral data for the (1)–(3) complexes



Scheme-2. Proposed mechanism of the mass spectral fragmentation of the macrocyclic ligand *cyclam*

formed. The cation **II** fragmentation starts with cleavage of α-bond, moving of electronic density and forming of double bond between this nitrogen and the carbon atom of dithiocarbamato group. In such a way the obtained cation **III** as well as the cation **II** have the same relation of m/z 144 for **(1)–(3)** (Table-1) but different structures. The cation **IV** at m/z 125 for the **(1)–(3)** complexes is a result of intermolecular rearrangement prior to fragmentation[10] involving migration of α-hydrogen atom across the six-member cyclic ring followed by simultaneous cleavage of 4–5 bond. In addition to cation **IV**, the butyl radical $CH_3CH_2CH_2CH_2^{\bullet}$ is formed, too. In the next steps the movement of β-hydrogen atom to its nitrogen atom of cation **V** (m/z 117) with cleavage of 1–6 bond occurs.. This is facilitated by stabilization of the resulting ion **V** that represents the basic ion of these complexes. Besides ion **V**, the molecule of ethyne is also produced. In the last step of fragmentation the molecule of NH_3, ion CS_2^+ and ion $[Co(cyclam)]^{3+}$ are formed.

The macrocyclic ligand *cyclam* undergoes further fragmentation into the $C_{10}H_{24}N_4^+$, $C_9H_{21}N_3^+$, $C_6H_{14}N_2^+$, $C_5H_{10}N^+$ and $C_3H_6N^+$ ions at m/z values of 200, 170, 114, 84 and 56, respectively (Table-1) and the postulated mechanism is represented in **Scheme-2**. After the *cyclam* ionization molecular ion with a positive charge on one of four nitrogen atoms at m/z 200 is formed. Then, the breaking of β-bond happens followed by replacing of electronic density to the nitrogen atom forming of double bond and moving of β-hydrogen atom to this nitrogen with cleavage of α-bond. A few available sequences lead to the ring opening and characteristic peaks for the secondary amine are obtained [10]. Several cleavages, which are of secondary importance for the *cyclam*, are especially significant for the lower molecular weight fragments. Basic ion $CH_2{=}NH_2^+$ at m/z 30 and radical with a nitrogen atom less than in the starting macrocycle *cyclam* are produced. Further fragmentation with cleavages of the same nature of this radical appears to be formed by a similar process to that shown in the first step. The latter event is followed by elimination of ethylene and ethyne to give $CH_2{-}CH{-}^+NH{=}CH_2$ (m/z 56) and $CH_3{-}NH^+{=}CH_2$ (m/z 44).

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