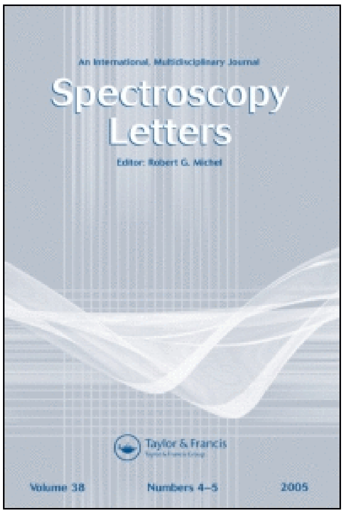

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# Spectral Assignments of New Symmetric Cobalt(III) Complexes with Macrocyclic and β-Diketonato Ligands

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## ABSTRACT

Three new cobalt(III) complexes of the general formula [Co(Rac)-cyclam]$(ClO_4)_2$, where *cyclam* and *Rac*$^-$ refer to 1,4,8,11-tetraaza cyclotetradecane and β-diketonato ligand, i.e., 1,3-diphenyl-1,3-propanedionato (*dibzac*), 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (*hfac*) and 2,2,6,6-tetramethyl-3,5-heptanedionato (*tmhd*) ions, respectively, have been prepared. Elemental analysis, conductometric measurements, UV/VIS, IR, $^1$H and $^{13}$C NMR as well as mass spectroscopy have been used to characterize them. In the complexes, cobalt is hexa-coordinated in an

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octahedral geometry of a folded macrocyclic ligand, and β-diketonates are bound as O,O′-bidentates. The spectroscopic data are influenced by the different R-groups depending on their steric and electronic effects. Finally, a mechanism of mass fragmentation is proposed.

*Key Words:* Cobalt(III); Cyclam; β-Diketones; Spectroscopic studies.

## INTRODUCTION

Investigation of complexes with macrocyclic molecules, especially in the presence of amine quadridentate ligands, is of great theoretical and practical interest.[1] The [14]ane$N_4$ *cyclam* (1,4,8,11-tetraazacyclotetradecane) a macrocyclic flexible ring, has its remarkable complexing properties extended by introducing four asymmetric amine nitrogen's and five isomeric forms realized by *trans* or *cis* configurations.[2,3] Nevertheless, it can be forced into a folded form that can be favored by additional bidentate exocyclic ligands.[4–9] Various interesting aspects of *cyclam* include not only physical[1,2] and structural[3] studies, but also the complex's activity both as a catalyst for $CO_2$ reduction[5] and for electrochemistry.[9,10]

Although β-diketones have been the subject of detailed investigation, there are still many obscurities in the structure and characteristics of their mixed-ligand complexes. Especially their structures have drawn attention, because of the ability to enolize, and a few different ways of coordination.[11] The chelating ''pseudoaromatic'' ring of β-diketones has found extensive application in inquiries related to the understanding of the formation of various transition-metal complexes.[12–14] They have been shown to impart appreciable stability and volatility to their metal-complexed products.[15] In addition, acetylacetone, perhaps the best known β-diketone, and derived β-diketonates with different R-groups have been studied extensively[16] not only in terms of their ability to complex many metal ions[11–17] but, in their applications in biomedicine,[18] in the production of homogeneous and heterogeneous catalysts,[19,20] in the petroleum industry for fuel additives,[21] and in superconducting thin film manufacturing.[22]

In our previous paper[7] we reported the synthesis of the complex $[Co(acac)cyclam](ClO_4)_2$ (H–*acac*=2,4-pentanedione) in which the *acac* anion acts as an O,O′-bidentate ligand and the macrocycle *cyclam* adopts a folded conformation. In continuation of our studies of cobalt(III) complexes with oxygen-based bidentate ligands,[5,7] our attention now has been put on the preparation and physicochemical properties of three mixed-ligand cobalt(III) complexes with *cyclam* and β-diketonato ligands ($Rac^-$), i.e., 1,3-diphenyl-1,3-propanedionato (*dibzac*), 1,1,1,5,5,5-hexafluoro-2,4-

pentanedionato (*hfac*) and 2,2,6,6-tetramethyl-3,5-heptanedionato (*tmhd*) ions. In order to gain new information concerning the electronic structure of the complexes, as well as to make a contribution to the problem of the coordination behavior of β-diketones, their mode of coordination was determined, and the spectrochemical properties of these compounds are discussed here.

## EXPERIMENTAL

*Caution*. The perchlorate salts of compounds containing organic ligands, as prepared in this work, are potentially explosive and must be handled with care.

### Synthesis

High-purity grade commercial *cyclam* from Aldrich Chemical Co. and β-diketones, i.e., H−*dibzac*, H−*hfac* and H−*tmhd* respectively, from Merck Chemical Co. were used without further purification.

To a solution of the *cyclam* (200 mg, 1 mmol) in 15 mL of acetone was added $Co(ClO_4)_2 \cdot 6H_2O$ (366 mg, 1 mmol). The reaction mixture was stirred at room temperature and air bubbled through it for 30 minutes. Then 1 mmol of the β-diketones in different solvents (15 mL) were added dropwise, i.e., 224 mg H−*dibzac* in benzene, 0.14 mL H−*hfac* in acetonitrile, 0.21 mL H−*tmhd* in *n*-hexane. The reaction was continued with stirring on a water bath at 60°C for 3 hours. The filtrate was concentrated by slow evaporation to 10 mL. Upon cooling the mixture to room temperature an intensely colored crystalline product of the corresponding complexes was filtered and dried over $CaCl_2$. (1) *cis*-$[Co(dibzac)cyclam](ClO_4)_2$, orange, yield: 272 mg (40%), M*w*=681.5, Anal. Calcd. for $C_{25}H_{35}N_4O_{10}Cl_2Co$ (%): C, 44.06; H, 5.18; N, 8.22; Found: C, 43.75; H, 5.25; N, 7.97; (2) *cis*-$[Co(hfac)cyclam](ClO_4)_2$, purple, yield: 252 mg (38%), M*w*=665.2, Anal. Calcd. for $C_{15}H_{25}N_4O_{10}Cl_2F_6Co$(%): C, 27.08; H, 3.79; N, 8.42; Found: C, 27.33; H, 3.93; N, 8.82; (3) *cis*-$[Co(tmhd)cyclam](ClO_4)_2$, violet, yield: 284 mg (44%), M*w*=641.5, Anal.Calcd. for $C_{21}H_{43}N_4O_{10}Cl_2Co$ (%): C, 39.32; H, 6.76; N, 8.73; Found: C, 39.36; H, 6.89; N, 8.95.

### Measurements

Elemental analyses (C, H, N) were performed by standard micromethods at the Department of Instrumental Analysis of the Faculty of Chemistry, Belgrade. Electronic spectra of aqueous solutions of the complexes ($10^{-3}$ M) were recorded on a GBC UV/VIS 911 A spectrophotometer. Molar conductivities in acetone solution of the complexes ($10^{-3}$ M) were measured at 20°C with a Jenway-4009 conductivity meter. IR spectra in the 4000–400 $cm^{-1}$ range were measured on a Perkin Elmer 317 25 × FTIR spectrophotometer, using KBr discs. $^1H$ and $^{13}C$ NMR were run on a Gemini YH 200 spectrometer in $(CD_3)_2CO$ (1), DMSO–$d_6$ (2) and $D_2O$ (3) at room temperature. The chemical shifts were determined relative to TMS. Mass spectra were recorded on a gaseous ''ion-trap'' (VARIAN 3400) auto-sampler VARIAN 8100 spectrometer with mass-selected detector VARIAN SATURN II and capillary column (J&W Scientific DB-5MS, 60 m × 0.25 mm). The mass range was at 40–650 *m/z* at source temperature 260°C, in acetone solutions. The spectra were recorded at 70 eV electron energy for deeper penetration under an atmosphere of flowing helium gas.

## RESULTS AND DISCUSSION

The complexes were obtained by direct synthesis with Co(II) to Co(III) oxidation by air, in a molar ratio 1:1:1, starting from $Co(ClO_4)_2 \cdot 6H_2O$, *cyclam* and H–*dibzac* (benzene/acetone), H–*hfac* (acetonitrile/acetone) or H–*tmhd* (hexane/acetone) solutions (1:1, *v*/*v*). The analytical data are in good agreement with the proposed stoichiometry of the complexes. The compounds are colored and appear to be microcrystalline, stable in atmospheric conditions and soluble in water and in common organic solvents. The molar conductivity values of $10^{-3}$ M solutions fall into the range anticipated for a 1:2 electrolyte[23] (Table 1).

***Table 1.*** Molar conductivity's values ($\lambda_M/\Omega^{-1}cm^2mol^{-1}$) as well as positions of $\lambda_{max}$ (nm) and molar absorption coefficients ($\varepsilon/M^{-1}cm^{-1}$) for the complexes (**1**)–(**3**).

| Complex | | $\lambda_M$ | $\lambda_{max}$ (ε) *d–d* | $\lambda_{max}$ (ε) of the *Rac*$^-$ |
|---|---|---|---|---|
| **1** | [*Co*(*dibzac*)*cyclam*](*ClO*$_4$)$_2$ | 153 | 513 (200)<br>377 (1851) | 305 (2958)<br>269 (6690)<br>231 (4338) |
| **2** | [*Co*(*hfac*)*cyclam*](*ClO*$_4$)$_2$ | 163 | 530 (61)<br>$380_{sh}^{a}$ (1260) | 233 (7492) |
| **3** | [*Co*(*tmhd*)*cyclam*](*ClO*$_4$)$_2$ | 173 | 527 (196)<br>332 (2876) | 237 (6993) |

[a] *sh*, shoulder.

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## Electronic Absorption Spectra

The complexes obtained, with chromophore $\mathrm{CoN_4O_2}$, have similar electron absorption spectra, which indicates that the central ion and ligands are coordinated in a similar mode. In the visible region they exhibit two maxima which correspond to the spin-allowed *d–d* transitions, $^1\mathrm{A}_{1g}\rightarrow{}^1\mathrm{T}_{1g}$ and $^1\mathrm{A}_{1g}\rightarrow{}^1\mathrm{T}_{2g}$ (Table 1). The third very intense band (230–240 nm) appearing in the near ultraviolet region is thought to be an $n\rightarrow\pi^*$ transition in the enolate ring[24] with some degree of ''benzenoid'' resonance in addition to the enolate type resonance in which the principal $\pi$-delocalization occurs. In the case of the complex (1) bands at 305 and 269 nm correspond to $\pi\rightarrow\pi$ and $\pi\rightarrow\pi^*$ transitions, respectively, upon introduction of the phenyl group, which is consistent with the possibility for enhanced delocalization of $\pi$ electrons in the benzoylacetonates. Since the metal and ligand $\pi$ levels are mixed, these bands may have some charge transfer character. The large value of molar absorption coefficients supports the resonance form of the *Rac*$^-$ structure, indicating its symmetric coordination. Generally, the $\beta$-diketone on chelation to cobalt causes a bathochromic shift in the wavelength of maximum absorption.[25]

## IR Spectra

The most informative bands for *cyclam* and *Rac*$^-$ coordination are collected in Table 2. The appearance of three $\rho$(N–H) and two $\rho(\mathrm{CH_2})$ bands in the 800–910 cm$^{-1}$ range clearly indicates a *cis* configuration of *cyclam*.[4–9] In contrary, the presence of three bands in this region indicates a *trans* configuration.[4] The $\nu$(NH) vibration consists of two peaks that suggest coordination of the folded macrocycle, whereas bands of ionic perchlorate are located at about 1110 cm$^{-1}$ [$\nu(\mathrm{ClO_4})$] and 625 cm$^{-1}$ [$\delta(\mathrm{ClO_4})$].

IR spectra are characteristic for the *Rac*$^-$ anion bounded to the metal through both oxygens.[11] The $\nu(\mathrm{C}\overset{\text{-----}}{\text{—}}\mathrm{C})$ and $\nu(\mathrm{C}\overset{\text{-----}}{\text{—}}\mathrm{O})$ bands of the chelate $\beta$-diketones are in the range 1507–1627 cm$^{-1}$ and indicate charge delocalization in the major coordination mode with a resultant coordination via both oxygen atoms.[17] The high symmetry of the complexes (1)–(3), due to the presence of a $C_2$ axis of symmetry through both of the ligands, was reflected in the spectral assignments, which is remarkable in a view of the different R-group of the $\beta$-diketonato ligands. In the complex (1), presumably a combination of negative inductive and positive resonance effects of the R-phenyl group is presented. The $-\mathrm{CF_3}$ group in the complex (2) due to the electron-withdrawing effect, affects an electronic density decrease,[16] and consequently results in a shift of $\nu$(C–C) and $\nu$(C–O)

***Table 2.*** The most important IR bands ($\mathrm{cm}^{-1}$) for the (**1**)–(**3**) complexes.

| Complex | $\rho$(N–H) | $\rho(\mathrm{CH_2})$ | $\nu$(NH) | $\nu(\mathrm{C}\,\underline{\cdots}\,\mathrm{C})$ | $\nu(\mathrm{C}\,\underline{\cdots}\,\mathrm{O})$ | Vibrations of R-groups | $\nu(\mathrm{ClO_4})$<br>$\delta(\mathrm{ClO_4})$ |
|---|---|---|---|---|---|---|---|
| **1** | $910_{sh}$ | $821_{w}$ | $3226_{s}$ | $1589_{m}$ | $1527_{s}$ | $\nu_{ar}(\mathrm{CH})_{st}$ $3060_{w}$ | $1109_{vs}$ |
| | $877_{m}$ | $810_{w}$ | $2969_{m}$ | $1569_{m}$ | | $\nu_{ar}(\mathrm{CC})_{st}$ $1482_{s}$; $1451_{m}$ | $626_{m}$ |
| | $859_{m}$ | | | | | | |
| **2** | $906_{m}$ | $818_{w}$ | $3230_{s}$ | $1627_{m}$ | $1530_{w}$ | $\nu(\mathrm{CF_3})$ 669; 734; $788_{m}$ | $1110_{vs}$ |
| | $891_{m}$ | $806_{sh}$ | $3094_{m}$ | $1576_{s}$ | | $\gamma(\mathrm{CF_3})$ 1147s; $1257_{s}$ | $625_{m}$ |
| | $854_{m}$ | | | | | | |
| **3** | $902_{m}$ | $826_{m}$ | $3229_{s}$ | $1560_{s}$ | $1507_{m}$ | $\delta(\mathrm{CH_3})_{as}$ $1459_{m}$; $1428_{m}$ | $1110_{vs}$ |
| | $886_{m}$ | $815_{w}$ | $3117_{m}$ | $1549_{s}$ | | $\delta(\mathrm{CH_3})_{sy}$ $1364_{w}$ | $626_{m}$ |
| | $863_{m}$ | | | | | $\gamma(\mathrm{CH_3})$ $1270_{s}$ | |

Abbreviations: *sh*, shoulder; *w*, weak; *m*, medium; *s*, strong; *vs*, very strong.

bands toward higher frequencies. On the other hand, because of a positive inductive effect of the methyl group which increases the electron density, the complex (3) has a strong but opposite influence on the IR spectrum, moving these bands to lower wave numbers. It can be concluded that the differences in electronic effects of the R-substituents (from high negative to positive) are indicative and largely influence the shifting of frequencies of bands of the coordinated diketone, in the order of the complexes with *hfac*>*dibzac*>*tmhd* ligands. Characteristic IR absorption bands for the coordinated β-diketone R-groups are in expected regions and are also presented in the Table 2.

## NMR Spectra

The NMR spectral data for all the complexes are listed in Table 3. The degeneracy of the chemical shifts of the chemically equivalent nuclei of the macrocyclic as well as β-diketonato ligands are affected by the presence of a $C_2$ axis through both ligands (Table 3 and Figure 1).

The $^1$H NMR spectra of the complexes (1)–(3), show three main proton resonance bands belonging to coordinated *cyclam*. There are three types of hydrogen's:[4–9] 1) the four attached to the nitrogen atoms, 2) the sixteen attached to the α-carbon atoms, and 3) the four attached to the β-carbon atoms. The resultant signals for the α- and β-protons of the macrocycle ligand are typical and all the bands are split, as would be expected from the spin–spin interactions, while the resonances of the amine proton are broadened as a result of quadrupole coupling. The amine proton region could serve as a diagnostic feature for the *cis* or *trans* configuration. In the *trans* complexes all four amine protons in the amine proton region are equivalent and there is only one proton signal,[4] but in the *cis* complexes there are two pairs of non-equivalent protons.[4–9] The resonance at δ 5.93–5.31 ppm [for the complexes (1)–(3)] may be assigned to the two amine protons adjacent to the *Rac*$^-$ ligand ($N_e$ two equatorial hydrogen atoms) and the resonance between δ 6.82–5.93 ppm belongs to the two amine protons in the environment of the methylene groups ($N_a$ two axial hydrogen atoms). The *cis* conformation of *cyclam* is predicted on the basis of minimum-strain arguments[5] for *cyclam* taking into account the anisotropy of cobalt(III).[26]

In the region of the macrocyclic aliphatic protons, the resonance's at 2.01–1.96 and 1.89–1.85 ppm may be assigned, based on their chemical shifts, to the methylene groups of the β-carbon atoms remote from the nitrogen atoms (i.e., C4 hydrogen atoms). The remaining partial assignment, mostly based on characteristic coupling patterns, deals with the protons on the α-carbon atoms, of both –N–$(CH_2)_2$–N– groups (at the

***Table 3.*** $^{1}$H NMR and $^{13}$C NMR chemical shifts[a] (in ppm) of coordinated *cyclam* and $Rac^{-}$ ligands for the complexes (**1**)–(**3**).

| Complex | δ |
|---|---|
| **1** | 6.82, s, 2*H* (2-$\mathbf{N}_a$); 5.31, d, 2*H* (2-$\mathbf{N}_e$);<br>2.84, t, 2.39, d, 4*H* (2-**C1**);<br>3.01, d, 2.24, d, 4*H* (2-**C2**);<br>2.73, d, 2.04, d, 4*H* (2-**C3**);<br>1.97, d, 1.89, d, 4*H* (2-**C4**);<br>2.59, q, 2.15, d, 4*H* (2-**C5**);<br>6.50, d, *H* (**C6**); 7.21–8.07,<br>m, 6*H* (**C8–C11**)<br>**C1**, 54.49; **C2**, 49.51; **C3**, 46.12; **C4**, 24.44;<br>**C5**, 51.33; **C6**, 94.12; **C7**, 184.82;<br>**C8–C11** 128.32–136.52 |
| **2** | 6.63, s, 2*H* (2-$\mathbf{N}_a$); 5.52, s, 2*H* (2-$\mathbf{N}_e$);<br>3.01, d, 2.52, d, 4*H* (2-**C1**);<br>3.08, t, 2.68, t, 4*H* (2-**C2**);<br>2.89, d, 2.42, d, 4*H* (2-**C3**);<br>1.96, t, 1.85, d, 4*H* (2-**C4**);<br>2.77, d, 2.23, d, 4*H* (2-**C5**);<br>6.23, s, *H* (**C6**)<br>**C1**, 52.72; **C2**, 47.54; **C3**, 47.54; **C4**, 26.69;<br>**C5**, 52.72; **C6**, 108.53; **C7**, 165.26; **C8**, 114.31 |
| **3** | 5.93, d, 2*H* (2-$\mathbf{N}_a$); 5.93, d, 2*H* (2-$\mathbf{N}_e$);<br>2.93, d, 2.39, d, 4*H* (2-**C1**);<br>3.08, t, 2.63, m, 4*H* (2-**C2**);<br>2.83, d, 2.33, d, 4*H* (2-**C3**);<br>2.01, d, 1.89, d, 4*H* (2-**C4**);<br>2.73, d, 2.10, d, 4*H* (2-**C5**);<br>6.21, s, *H* (**C6**); 1.22, t, 18*H* (2-**C9**)<br>**C1**, 55.85; **C2**, 50.21; **C3**, 47.07; **C4**, 24.28;<br>**C5**, 50.53; **C6**, 94.70; **C7**, 203.79; **C8**, 44.18;<br>**C9**, 30.54 |

Abbreviations: *s*, singlet; *d*, doublet; *t*, triplet; *m*, multiplet.
[a] In ppm relative to TMS. For the assignment of the various atoms see Figure 1.

C1 and C2 hydrogen atoms) while the resonance's of the C3 and C5 hydrogen atoms can be attributed to the $-N-(CH_2)_3-N-$ moiety in the α position to the nitrogen atoms (Table 3).

The chemical shifts of the β-diketonate protons are alleged to be due to the ''aromatic'' nature of the ring[27] or to its magnetic anisotropy[28] and,

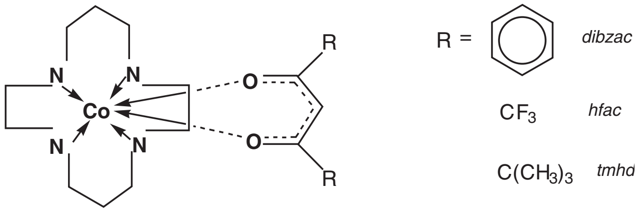


*Figure 1.* Suggested structure of the complex cation [Co(Rac)cyclam]$^{2+}$.

others to the nature of the central atom and the orbitals used in σ and π bonding to the ring.[27] With regards to the *Rac*$^-$ ligands, the $^1$H NMR spectroscopy can be analyzed as follows: let's assume that the coordinated *acac* shows only two signals (6:1) due to methyl and methinic protons as well is in the primary complex.[7] The chemical shift of the (C6) proton of –CH group in the *Rac*$^-$ ring depends mainly on the electrical symmetry of the complexes, and in the case of compounds (1)–(3) shifts to high field in 6.50–6.21 ppm range relative to the *enol* form of the free *Rac*$^-$ anion. This effect may be a function of the symmetric *Rac*$^-$ coordination, suggesting that strong cobalt–oxygen bonding occurs.[29]

The described $^1$H NMR spectra of the complexes (1)–(3) are in good agreement with similar *cis* complexes of known structure[4–9] and provide additional confirmation of their structure and of the present assignments, as represented in Figure 1.

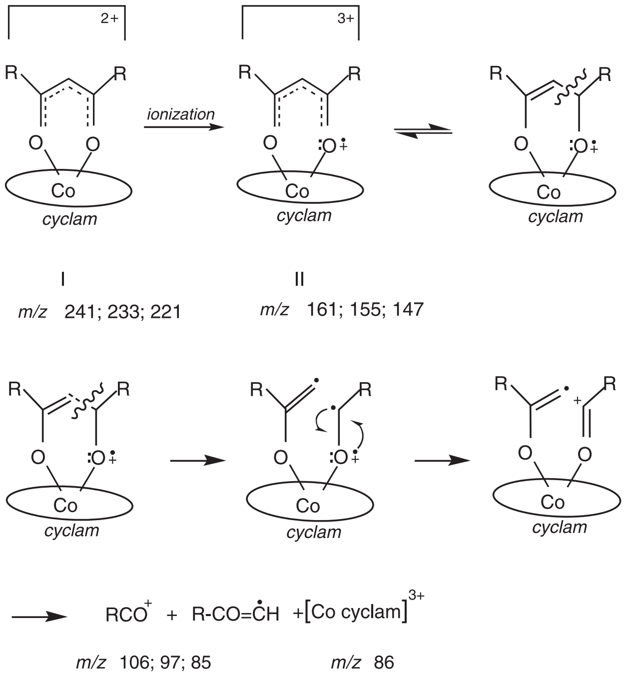
The high symmetry of the complexes is reflected in the $^{13}$C NMR spectra (Table 3 and Figure 1). The various types of carbons have been successfully assigned and notations of these resonance's are according to Figure 1. There are five lines that belong to the symmetric *cyclam* (these five-carbon atoms are non-equivalent) and the others belong to the *Rac*$^-$ ligands, depending on the chemically equivalent nuclei. The two carbons of the *Rac*$^-$ anion, i.e., α carbon (C6) and carbonyl (C7), from the complexes (1)–(3) are in expected regions, as well as the other carbons depending on changed R-groups of the ligands (Table 3). The influence of R-groups exhibits movement of these bands in different directions. The powerful efficacy of six fluor atoms, of the *hfac* ligand in the complex (2), moves the chemical shifts strongly downfield in comparison with hydrogencarbon remainders [complexes (1) and (3)] when their values are approximately equal. Carbonyl (C7) carbons are under the strong influence of electronic effects of R-groups, following from a positive to high negative inductive effect, with chemical shifts in the order of complexes with *tmhd*>*dibzac*>*hfac* ligands. A lower, but noticeable influence of R-groups affects the chemical shifts of the (C6) α carbon.

From the results presented above it could be concluded, the β-diketone moiety includes the two carbonyl groups and one more carbon fixed in the α position, while donating oxygen atoms and the rigidity of the end-group of the ligand are responsible for the molecular design.[12] Spectroscopic behavior of the complexes (1)–(3), which are generally differentiated only in view of the R-groups, are a consequence of their steric, resonance and inductive effects along with conjugation of double bonds through to the whole molecule, not just the oxygen atoms bonded to the cobalt ion.

## Mass Spectra

Observations of mass spectra were also utilized for prediction and characterization of the molecular structure of the complexes obtained. At a working temperature of 260°C ionization is followed by thermal decomposition of the molecules. Under these circumstances, affected by the presence of the counter perchlorate ions, the β-diketonato ligand leaves the coordination sphere first. It is supported by two fragments in the mass spectra, i.e., $[Co(Rac)cyclam]^{2+}$ (cation I) appearing at *m/z* 241, 233 and 221 [for (1)–(3)], respectively and basic $[Cocyclam]^{3+}$ cation at *m/z* 86. After the cation I ionization, the cation II $[Co(Rac)cyclam]^{3+}$ with positive charge on the carbonyl oxygen atom is formed.

The further decomposition of the complexes can be presented by the most plausible mechanism, which explains the general features of fragmentation, as represented in Scheme 1. The base peaks at *m/z* 161, 155, 147 for (1)–(3), respectively, result from bond cleavage α to the carbonyl group and the charge remaining with the oxygenated fragment. Further fragmentation involving charge migration through the ‘‘pseudoaromatic’’ ring of the β-diketones followed by simultaneous formation of a double carbon–oxygen bond is especially noticeable. The presence of these peaks is evidence for oxygen coordination and seems to be a convincing approach to understanding the molecular structure. The next step is cleavage of the cobalt–oxygen bond which leaves the charge on the fragments $R(CO)^+$ and gives rise to peaks at *m/z* 106 (1), 97 (2) or 85 (3). The most intense peaks are the basic R-groups of the diketones with at *m/z* 78 (1), 69 (2) or 57 (3). In the stable cation $[Cocyclam]^{3+}$ with *m/z* 86, which is an elementary ion of the complexes (1)–(3), the macrocyclic ligand *cyclam* undergoes further fragmentation into the $C_{10}H_{24}N_4^+$, $C_9H_{21}N_3^+$, $C_8H_{19}N_3^+$, $C_7H_{15}N_2^+$ and $C_4H_8N^+$ ions at *m/z* values at 200, 171, 157, 127 and 70, respectively. The most intense ion in the mass spectra of the complexes is the peak at *m/z* 127, which corresponds to the coordinated *cyclam* and primary cleavage



***Scheme 1.*** The probable mechanism of the fragmentation's according to mass spectral data for (**1**)–(**3**) complexes.

bonds next to the two symmetric nitrogen atoms, accompanied by the rearrangement of the hydrogen atom and opening of the ring. Several available sequences follow the ring opening to characteristic peaks for the secondary amine. Several cleavages, which are of secondary importance for the *cyclam*, are especially significant for the lower molecular weight fragments. The latter event is followed by elimination of ethylene to give $CH_3{-}CH_2{-}^{+}NH{=}CH_2$ (*m/z* 58), thence by loss of a methylene group to give $CH_3{-}^{+}NH{=}CH_2$ (*m/z* 44).

It could be concluded that the presence of peaks containing the chelate ligand moiety in mass spectra of the complexes (1)–(3) is characteristic, indicating that the β-diketones, as expected, are weaker coordinating agents than the macrocyclic *cyclam* ligand. This behavior 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.[30]

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