

## The Mass Spectral Fragmentation of Copper(II) Complexes of Cyclic $\beta$ -Diketones

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**Summary.** Electron impact mass spectra of several bis(2-trifluoroacetylcycloalkanonato) copper(II) and bis(2-acetylcycloalkanonato) copper(II) chelates, in which the cyclic  $\beta$ -diketonate moiety comprises five-, six-, seven-, and eight-membered ring systems, have been recorded. Compared with other copper(II) chelates of acyclic  $\beta$ -diketonates, the present series of copper(II) cyclic  $\beta$ -diketonates exhibited more pronounced intramolecular reduction reactions accompanied by a remarkably facile hydrogen migration resulting in the formation of the  $[LCu^{(I)}-H]^+$  ion as the base peak in all complexes investigated. The proposed fragmentation pathways leading to the formation of a number of important copper-containing daughter ions have been confirmed by metastable scanning of the corresponding parent ion spectra using the defocusing technique.

**Keywords.** Mass Spectra; Bis(2-trifluoroacetylcycloalkanonato) copper(II); Bis(2-acetylcycloalkanonato) copper(II).

### Massenspektroskopische Fragmentierung von Kupfer(II)-Komplexen cyclischer $\beta$ -Diketone

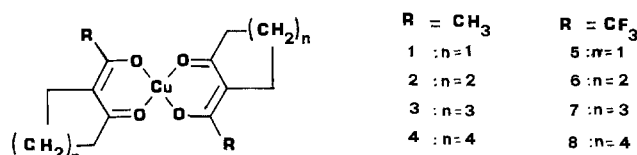
**Zusammenfassung.** Es wurden die EI-Massenspektren einiger Bis(2-trifluoracetylcycloalkanato)kupfer(II)- und Bis(2-acetylcycloalkanato)kupfer(II)-Chelate mit fünf-, sechs-, sieben- und achtgliedrigen cyclischen  $\beta$ -Diketonat-Liganden gemessen. Im Vergleich zu anderen Kupfer(II)-Chelaten mit offenkettigen  $\beta$ -Diketonaten zeigen die cyclischen Komplexe eine ausgeprägte Neigung zu intramolekularen Reduktionsreaktionen, die von einer bemerkenswert leicht erfolgenden Wasserstoffwanderung begleitet sind; dies führt zur Bildung von  $[LCu^{(I)}-H]^+$  als Basispeak für alle untersuchten Komplexe. Die vorgeschlagenen Fragmentierungswege, die zur Bildung einer Reihe wichtiger kupferhaltiger Tochterionen führen, wurden durch Untersuchung der entsprechenden metastabilen Mutterionen mittels der Defokussierungsmethode überprüft.

### Introduction

The electron impact induced mass spectral fragmentations of volatile neutral copper(II)  $\beta$ -diketonates produce a variety of Cu(I) species and rearrangement ions [1]. Such gas phase reactions involving valency changes have been rationalized in terms of intramolecular redox reactions [2, 3]. The occurrence of rearrangement ions, particularly in the mass spectra of fluorinated and chlorinated metal  $\beta$ -diketonates [4, 5], has been interpreted by the Hard/Soft Acid/Base (HSAB) formalism [6].

Although the mass spectra of metal chelates derived from acyclic  $\beta$ -diketonates have been widely investigated [7], no report has appeared in the literature on the mass spectra of metal chelates derived from cyclic  $\beta$ -diketonates. Our recent work on the mass spectra of 2-trifluoroacetylcycloalkanones [8] and their non-fluorinated analogues [9] has focused on the effect of ring size on the mass spectral fragmentations of cyclic  $\beta$ -diketonates.

The main aim of the present work was to examine the effect of ring size on the mass spectral behaviour of some neutral copper(II) complexes derived from 2-trifluoroacetylcycloalkanones and 2-acetylcycloalkanones comprising five-, six-, seven-, and eight-membered ring systems. These unsymmetrical copper(II)  $\beta$ -diketonate complexes may exist in either the *cis*- or *trans*-configuration. However, X-ray diffraction studies [7] on other unsymmetrical copper(II)  $\beta$ -diketonate complexes with bulky substituents such as bis(benzoylacetato) copper(II) have established the *trans*-configuration. Thus, it seemed reasonable to assume that the present series of copper(II) chelates exist in the *trans*-configuration as depicted in Scheme 1.



Scheme 1

## Experimental Part

The compounds examined have been described previously [10]. The mass spectra were determined with a Varian SM-1B double focusing mass spectrometer of attach-Herzog geometry operated at 70 eV ionizing voltage. The ion source temperature was maintained at 220°C. The direct inlet system was used for all the samples at 70–130°C depending upon the volatility of the chelates. Parent ion spectra were recorded using the defocusing technique [11, 12] by scanning the ion accelerating voltage (initially at 3 kV) at fixed setting of the electric and magnetic sectors.

## Results and Discussion

Important features in the mass spectra of bis(2-acetylcycloalkanonato) copper(II) ( $R = CH_3$ ) (compounds 1–4) and bis(2-trifluoroacetylcycloalkanonato) copper(II) ( $R = CF_3$ , compounds 5–8) chelates are summarized in Tables 1 and 2.

A large number of copper-containing fragment ions are produced. These are unambiguously identified by their  $^{63}Cu$  and  $^{65}Cu$  isotopes whose natural abundances are at nearly 2 : 1 ratio.

The results presented in Tables 1 and 2 clearly demonstrated the tendency of copper(II) to undergo intramolecular reduction. As a result, the mass spectra of the present series of copper(II)  $\beta$ -diketonates 1–8 exhibited peaks rationalized as containing both Cu(II) and Cu(I) species. The assignment of a given copper-containing ion to a particular oxidation state of the metal is based on the electron count in the ligand portion of the complex assuming that McLafferty's rule [13] is strictly obeyed. Thus, the loss of an odd-electron radical such as  $CF_3 \cdot$  (69 amu) from the molecular ion  $[CuL_2]^+ \cdot$  produces the even-electron  $[CuL_2-CF_3]^+$  ion in which the copper is in the +2 state. On the other hand, the loss of an even-

**Table 1.** Important ions in the mass spectra of bis(2-acetylcycloalkanonato) copper(II) chelates **1–4**; only ions containing  $^{63}\text{Cu}$  are listed

Ions	Cu oxidation state	Compounds							
		<b>1</b>		<b>2</b>		<b>3</b>		<b>4</b>	
		<i>m/z</i>	%	<i>m/z</i>	%	<i>m/z</i>	%	<i>m/z</i>	%
$[P]^{+\bullet}$ : $[\text{CuL}_2]^{+\bullet}$	+2	313	25	341	18	369	27	397	25
$[P-15]^+$ : $[\text{CuL}_2\text{-CH}_3]^+$	+2	298	3	326	2	354	2	382	1
$[P-28]^{+\bullet}$ : $[\text{CuL}_2\text{-CO}]^+$	+1	—	—	—	—	2	—	—	369
$[P-30]^{+\bullet}$ : $[\text{CuL}_2\text{-2CH}_3]^+$	+1	—	—	311	2	339	1	—	—
$[P-L]^+$ : $[\text{CuL}]^+$	+2	188	23	202	17	216	14	230	16
$[P\text{-HL}]^{+\bullet}$ : $[\text{CuL-H}]^+$	+1	187	100	201	100	215	100	229	100
$[P-L-15]^{+\bullet}$ : $[\text{CuL-CH}_3]^+$	+1	173	6	187	3	201	1	215	1
$[P-L-43]^{+\bullet}$ : $[\text{CuL-CH}_3\text{CO}]^+$	+1	145	12	159	6	173	4	187	13
$[P-L-71]^{+\bullet}$ : $[\text{CuL-CH}_3\text{CO-C}_2\text{H}_4]^+$	+1	—	—	—	—	145	2	159	4
$[P-L-85]^{+\bullet}$ : $[\text{CuL-CH}_3\text{CO-C}_3\text{H}_6]^+$	+1	—	—	—	—	—	—	145	3
$[P-2L]^{+\bullet}$ : $[\text{Cu}]^+$	+1	63	3	63	4	63	3	63	4
$[\text{HL}]^{+\bullet}$	—	126	33	140	61	154	46	168	5
$[\text{L}]^+$	—	125	8	139	8	153	4	167	1
$[\text{HL-CH}_3]^+$	—	111	43	125	38	139	30	153	28
$[\text{HL-CH}_3\text{CO}]^+$	—	83	12	97	12	111	10	125	7
$[\text{C}_4\text{H}_7]^+$ and $[\text{C}_3\text{H}_3\text{O}]^+$	—	55	15	55	14	55	13	55	10
$[\text{C}_2\text{H}_3\text{O}]^+$	—	43	38	43	50	43	35	43	39

electron fragment such as CO (28 amu) from the molecular ion produces the odd-electron  $[\text{CuL}_2\text{-CO}]^{+\bullet}$  ion which may be interpreted as containing Cu(I). In a similar manner, the consecutive loss of two odd-electron fragments from the molecular ion also produces an ion containing Cu(I).

The most remarkable feature of the mass spectra of the present series of copper(II)  $\beta$ -diketonates **1–8** is the presence of abundant  $[\text{HL}]^{+\bullet}$  and  $[\text{CuL}_2\text{-HL}]^{+\bullet}$  ions. The latter ion which may be rationalized as  $[\text{LCu}^{(I)}\text{-H}]^+$  is the base peak (100% intensity) for all chelates investigated. Metastable scanning of the parent ion spectra for the  $[\text{HL}]^{+\bullet}$  and  $[\text{LCu}^{(I)}\text{-H}]^+$  daughter ions (Table 3) clearly established that both ions were formed directly from the molecular ions. The formation of the  $[\text{LCu}^{(I)}\text{-H}]^+$  ion involves migration of a hydrogen atom from one  $\beta$ -diketonate moiety to another, followed by subsequent fragmentations of the resulting rearrangement ion to form the  $[\text{HL}]^{+\bullet}$  and  $[\text{LCu}^{(I)}\text{-H}]^+$  ions as shown in Scheme 2. It is interesting that the mass spectra of copper(II)  $\beta$ -diketonates containing aromatic substituents were also found [14–16] to afford  $[\text{LCuH}]^+$  and  $[\text{LCu-H}]^+$  ions resulting from hydrogen atom migrations, but with lower abundances. In the case of bis(acetylacetonato) copper(II), these ions were observed [17] at much lower abundances (< 5%) that their presence was overlooked by early investigators [18–20].

Elimination of CO (28 amu) was observed for some of the chelates (see Tables 1

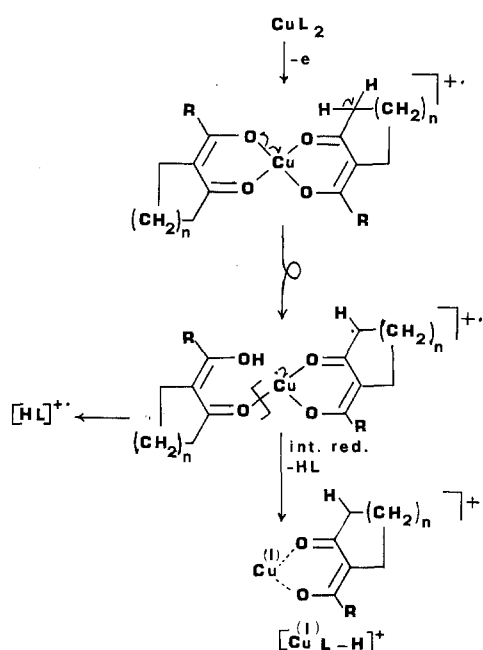
**Table 2.** Important ions in the mass spectra of bis(2-trifluoroacetylcycloalkanonato)copper(II) chelates **5–8**; only ions containing  $^{63}\text{Cu}$  are listed

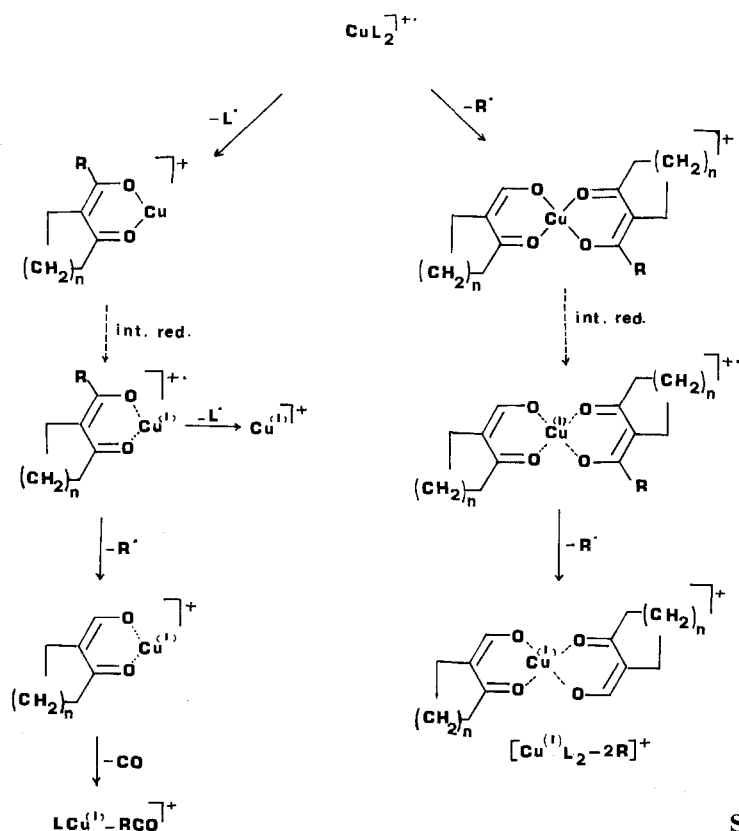
Ions	Cu oxidation state	Compounds								
		<b>5</b>		<b>6</b>		<b>7</b>		<b>8</b>		
		<i>m/z</i>	%	<i>m/z</i>	%	<i>m/z</i>	%	<i>m/z</i>	%	
$[P]^+$	: $[\text{CuL}_2]^+$	+2	421	47	449	31	477	20	505	29
$[P-19]^+$	: $[\text{CuL}_2\text{-F}]^+$	+2	402	2	430	2	458	1	486	3
$[P-28]^+$	: $[\text{CuL}_2\text{-CO}]^+$	+1	393	1	—	—	449	1	477	2
$[P-47]^+$	: $[\text{CuL}_2\text{-FCO}]^+$	+2	374	4	402	2	430	1	—	—
$[P-69]^+$	: $[\text{CuL}_2\text{-CF}_3]^+$	+2	352	24	380	8	378	3	—	—
$[P-97]^+$	: $[\text{CuL}_2\text{-CF}_3\text{CO}]^+$	+2	324	5	—	—	—	—	—	—
$[P-138]^+$	: $[\text{CuL}_2\text{-2CF}_3]^+$	+1	283	16	311	14	339	2	367	1
$[P-166]^+$	: $[\text{CuL}_2\text{-2CF}_3\text{-CO}]^+$ and $[\text{CuL}_2\text{-2CF}_3\text{-C}_2\text{H}_4]^+$	+1	255	6	283	1	311	3	—	—
$[P-L]^+$	: $[\text{CuL}]^+$	+2	242	24	256	17	270	15	284	22
$[P-HL]^+$	: $[\text{CuL-H}]^+$	+1	241	100	255	100	269	100	283	100
$[P-L-28]^+$	: $[\text{CuL-CO}]^+$	+2	214	2	228	4	242	4	256	2
$[P-L-56]^+$	: $[\text{CuL-CO-C}_2\text{H}_4]^+$	+2	186	4	200	4	—	—	228	3
$[P-(L-H)-69]^+$	: $[\text{CuLH-CF}_3]^+$	+2	174	6	188	3	—	—	—	—
$[P-L-69]^+$	: $[\text{CuL-CF}_3]^+$	+1	173	38	187	22	201	9	215	5
$[P-L-97]^+$	: $[\text{CuL-CF}_3\text{CO}]^+$	+1	145	17	159	5	173	5	187	5
$[P-L-125]^+$	: $[\text{CuL-CF}_3\text{CO-C}_2\text{H}_4]^+$	+1	117	4	131	4	145	4	159	7
$[P-L-139]^+$	: $[\text{CuL-CF}_3\text{CO-C}_3\text{H}_6]^+$	+1	—	—	117	3	131	4	—	—
$[P-L-153]^+$	: $[\text{CuL-CF}_3\text{CO-C}_4\text{H}_8]^+$	+1	—	—	—	—	117	4	131	4
$[P-L-167]^+$	: $[\text{CuL-CF}_3\text{CO-C}_5\text{H}_{10}]^+$	+1	—	—	—	—	—	—	117	7
	$[\text{CuH}_2\text{O}]^+$	+1	81	5	81	2	81	9	81	8
$[P-2L]^+$	: $[\text{Cu}]^+$	+1	63	17	63	11	63	5	63	8
	$[\text{HL}]^+$	—	180	25	194	12	208	14	222	11
	$[\text{L}]^+$	—	179	2	193	2	207	1	221	6
	$[\text{HL-CF}_3]^+$	—	111	52	125	47	139	31	153	9
	$[\text{HL-CF}_3\text{CO}]^+$	—	83	3	97	4	111	1	125	4
	$[\text{C}_4\text{H}_3\text{OF}_3]^+$	—	124	19	124	1	124	2	124	2
	$[\text{C}_4\text{H}_7]^+$ and $[\text{C}_3\text{H}_3\text{O}]^+$	—	55	38	55	25	55	15	55	20
	$[\text{C}_2\text{H}_3\text{O}]^+$	—	43	8	43	8	43	14	43	23
	$[\text{C}_3\text{H}_5]^+$	—	41	10	41	28	41	16	41	21

and 2), but only low intensity ions were produced. Compounds **5–8** showed no tendency to eliminate HF from their molecular ions.

An alternative pathway for the fragmentation of **1–8** involved the stepwise elimination of methyl/trifluoromethyl or ligand ( $L^*$ ) radicals.

The resulting fragment ions were more abundant in the fluorinated chelates **5–8** which exhibited a higher tendency for intramolecular reduction compared with the unfluorinated chelates **1–4**. This is evident from the observed consecutive loss of two  $\text{CF}_3^*$  radicals in all the fluorinated chelates **5–8** leading to the formation of the  $[\text{CuL}_2\text{-2CF}_3]^+$  ion. The latter ion was observed at 14–16% intensity in

**Table 3.** Representative parent ion spectra; only ions containing  $^{63}\text{Cu}$  are listed; intensity relative to daughter = 1 000**Bis(2-acetylcyclohexanonato) copper(II) (2):**Daughter ion  $m/z$  125 :  $[\text{HL}-\text{CH}_3]^+$  $m/z$  (I) 140 (6.04) 203 (17.9)Daughter ion  $m/z$  140 :  $[\text{HL}]^{+\cdot}$  $m/z$  (I) 203 (10.29) 341 (0.91)Daughter ion  $m/z$  201 :  $[\text{CuL}-\text{H}]^+$  $m/z$  (I) 341 (30.16)Daughter ion  $m/z$  202 :  $[\text{CuL}]^+$  $m/z$  (I) 298 (8.06) 326 (7.0) 341 (23.93)**Bis(2-trifluoroacetylcyclohexanonato) copper(II) (6):**Daughter ion  $m/z$  125 :  $[\text{HL}-\text{CF}_3]^+$  $m/z$  (I) 194 (17.28)Daughter ion  $m/z$  187 :  $[\text{CuL}-\text{CF}_3]^+$  $m/z$  (I) 256 (13.89) 311 (13.89)Daughter ion  $m/z$  255 :  $[\text{CuL}-\text{H}]^+$  $m/z$  (I) 449 (24.29)Daughter ion  $m/z$  256 :  $[\text{CuL}]^+$  $m/z$  (I) 449 (25.0)**Bis(2-trifluoroacetylcycloheptanonato) copper(II) (7):**Daughter ion  $m/z$  269 :  $[\text{CuL}-\text{H}]^+$  $m/z$  (I) 477 (29.23)**Scheme 2**



compounds **5** and **6**, but at much lower intensities ( $\sim 2\%$ ) in compounds **7** and **8**, indicating that ring fragmentation of the cyclic  $\beta$ -diketonate moiety in these chelates competes favourably with the elimination of alkyl radicals in the higher membered ring systems. This view is also supported by the fact that in the unfluorinated chelates ( $R = \text{CH}_3$ , **1–4**), the  $[\text{CuL}_2 - 2\text{CH}_3]^+$  ion was observed (Table 1) only in compounds **2** and **3** with 1–2% intensity.

The results presented in Tables 1 and 2 clearly showed that the  $[\text{CuL}]^+$  ion was the major precursor of several fragment ions in the spectra of compounds **1–8** as illustrated in Scheme 3. Elimination of the  $\text{RCO}^\bullet$  radical from the  $[\text{CuL}]^+$  ion was more pronounced than that from the molecular ion  $[\text{CuL}_2]^{2+}$  for all chelates investigated. Elimination of the  $\text{RCO}^\bullet$  radical from  $[\text{CuL}]^+$ , which involved a valency change to Cu(I), was followed by elimination of an alkene moiety from the  $\beta$ -diketonate ring. The latter process, which was more pronounced in the fluorinated chelates **5–8**, produced several ions of the composition  $[\text{CuL}-\text{RCO}-\text{C}_m\text{H}_{2m}]^+$  leading to the  $m/z$  117 ion having the composition  $[\text{CuOC}_3\text{H}_2]^+$ .

A further demonstration of the tendency of the present chelates to undergo intramolecular reduction was provided by the occurrence of the  $[\text{Cu}^0]^+$  ion which may be formed by successive loss of two ligand radicals from the molecular ion. The presence of an electron-withdrawing group such as  $\text{CF}_3$  is known [21] to decrease the strength of the Cu-O bond. As a result, the  $[\text{Cu}]^+$  ion was more abundant in copper(II) chelates derived from fluorinated  $\beta$ -diketonates ( $R = \text{CF}_3$ ) (see Tables 1 and 2). Moreover, within the fluorinated chelates **5–8**, the intensity of the  $[\text{Cu}]^+$  ion evidently reflected the influence of ring size of the cyclic  $\beta$ -

diketonate moiety on the stability of the chelates. Thus, on the basis of the validity of the correlation between the intensity of the  $[\text{Cu}]^+$  ion and the strength of the Cu-O bond, it would be possible to suggest that in the present series of copper(II)  $\beta$ -diketonate chelates, the Cu-O bond is weakest in the bis(2-trifluoroacetyl)cyclopentanonato) copper(II) chelate (5).

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