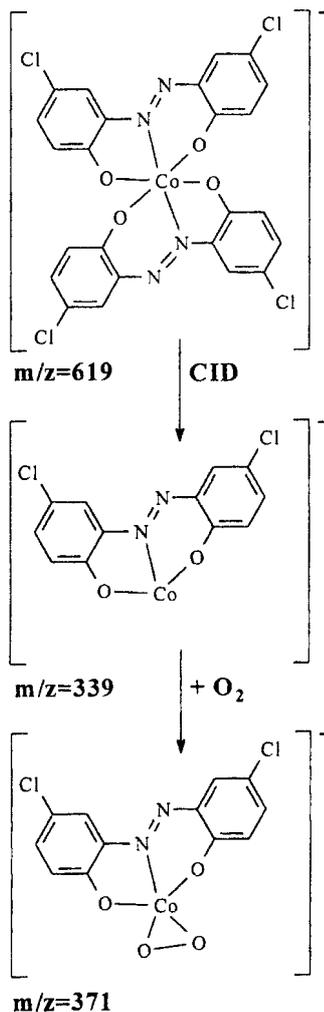


**RCM**  
**Letter to the Editor**

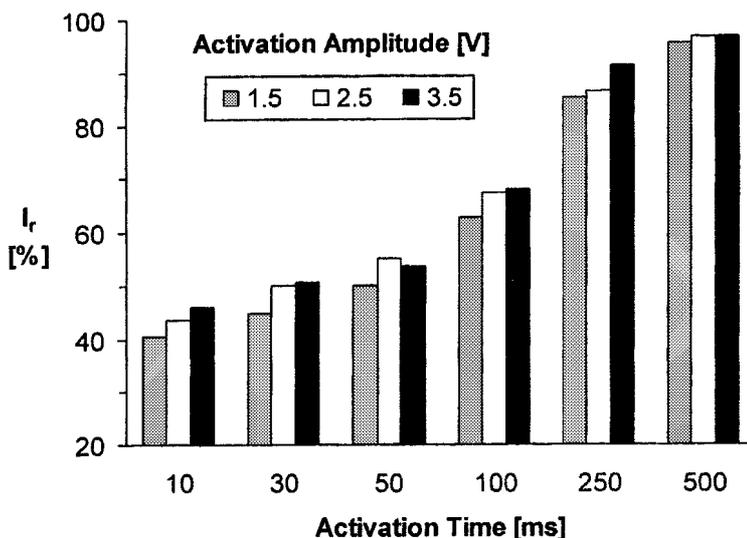
To the Editor-in-Chief  
 Sir,

**Oxygen attachment to metal complex ions during their collision induced dissociation in ion trap**

In our study of collision induced dissociation (CID) of some ions of cobalt(III) and aluminium(III) complexes with azo dyes,<sup>1</sup> we observed the appearance of unusual adducts



**Figure 1.** Structure of cobalt(III) complex with the fragmentation scheme leading to the adduct with oxygen molecule.

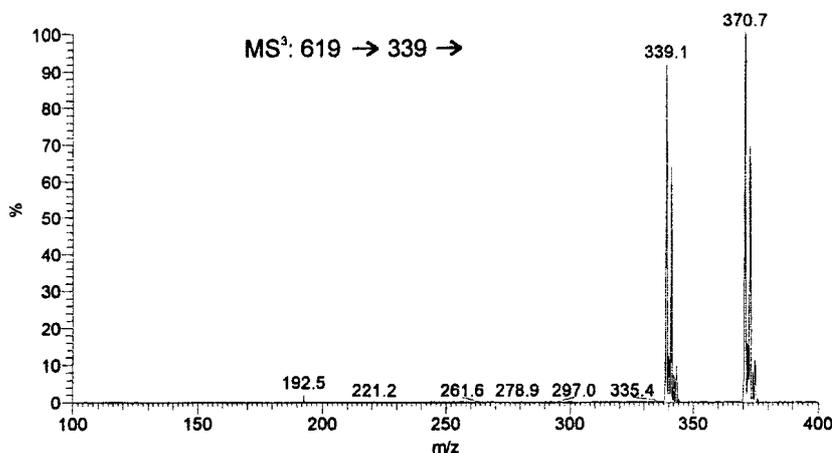


**Figure 2.** Dependencies of the relative intensity ratio for ion  $m/z$  371 ( $I_r$ , defined in the text) on the activation time and activation amplitudes (1.5, 2.5 and 3.5).

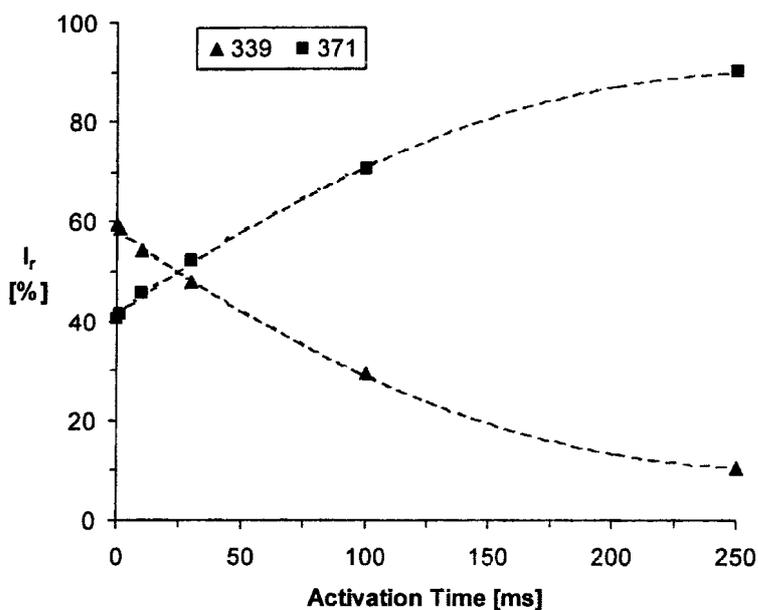
( $m/z = \text{fragment ion} + 32$ ) in the negative-ion electrospray mode. Our original measurements were conducted using an LCQ ion trap instrument (Finnigan MAT, San Jose, CA, USA), and were confirmed by using an Esquire ion trap (Bruker Daltonics, Bremen, Germany) although the relative abundances of the oxygen adduct ions were different (about one order of magnitude less pronounced in the latter instrument). We eliminated the possibility of adduct formation with methanol by changing the solvent from methanol to acetonitrile. As the adduct abundance remained unchanged the influence of methanol was reasonably excluded. The attachment of sulphur was also excluded by the intensity ratios of corresponding isotopic peaks. The only remaining possibility

was the ion-molecule reaction of the fragment ions with residual oxygen molecules present in the ion trap. In contrast to the results obtained using the ion traps, such adducts were not observed in the results from in-source CID measurements using a linear quadrupole analyser (Platform, Micromass, Manchester, UK). Moreover the relative abundances of all other ions (except for the adducts in question) were similar, regardless of whether the collision dissociation occurred directly in the ion source or in two different ion trap analysers.

Trivalent metal ions form six-coordinate complexes with *o,o'*-dihydroxyazobenzenes and related compounds.<sup>2</sup> These complexes themselves carry a negative charge<sup>1,3</sup> and, in negative electrospray ionisation form  $[M - H]^-$  ions where M here denotes



**Figure 3.** MS<sup>3</sup> spectrum for  $m/z$  619 → 339 → ?; activation time 30 ms for both steps; activation amplitude 2 V for  $m/z$  619, and zero for  $m/z$  339.



**Figure 4.** Dependencies of  $I_r$  (after isolation of the ion  $m/z$  339 in the trap) on the activation time without applying collisional activation.

the overall-neutral complex with a proton as the counterion. In the case of two cobalt complexes we have studied elsewhere,<sup>1</sup> the peak corresponding to the adduct is surprisingly either the base peak in the spectrum or one of the most intense peaks. The oxygen molecule appears to react with fragment ions produced after a cleavage of two metal–oxygen bonds. One can assume that the molecule of oxygen occupies vacancies thus created in the coordination sphere of the central metal atom. We have investigated dissociation of a fragment ion at  $m/z$  339, a product of the  $[M - H]^-$  ion of one of our azobenzene cobalt complexes (see Fig. 1), under different conditions in the ion trap. The appearance of an adduct at  $m/z$  371 was obvious. The influence of various activation times and activation amplitudes (collision energies) on the relative abundance of this adduct with the oxygen molecule is shown in Fig. 2. The change of activation amplitude at constant activation times does not lead to a significant change in the relative

ratios of intensities,  $I_{r339} = 100 \cdot [I_{339} / (I_{339} + I_{371})]$  and/or  $I_{r371} = 100 \cdot [I_{371} / (I_{339} + I_{371})]$ , where  $I_{339}$  and  $I_{371}$  correspond to the absolute intensities of ions at  $m/z$  339 and 371, respectively. In contrast, an increasing activation time resulted in a significant increase in the intensity ratio  $I_{r371}$ .

Having induced the fragmentation of the  $[M - H]^-$  ion, we isolated the ion at  $m/z$  339 in the ion trap. We observed that the increase in adduct abundance ( $m/z$  371) depends on time spent in the trap, and that the adduct is formed even without applying any collisional activation (activation amplitude was set to 0 V, see Fig. 3), as confirmed using the Esquire instrument. The effect on the  $I_r$  values of the activation time, without applying collisional activation, is illustrated in Fig. 4. The parent ion at  $m/z$  339 has a higher abundance than the corresponding adduct ion at  $m/z$  371 for reaction times less than 10 ms only. At longer times a strong increase in the adduct abundance is observed. The results demonstrate significant

affinity of fragment ions with vacancies in the coordination sphere towards oxygen. This effect is stronger, i.e. higher abundances of adduct ions were observed, for cobalt(III) complexes than for aluminium(III) ones.

This observation demonstrates unexpected ion-molecule reactions which can occur in an ion trap. Product ions at  $m/z$  values higher than that of the parent ions may be observed. The potential of such reactions for the recognition of different central atoms might be interesting. Metal-azo dye complexes are well suited for this purpose, but further investigation of the influence of various parameters on the extent of ion-molecule reactions in the trap is needed.

### Acknowledgements

We thank Dr. Andrea Kiehne (Bruker Daltonics, Bremen, Germany) for measurements on the Esquire ion trap, and Prof. Antonín Lyčka (Research Institute for Organic Synthesis, Pardubice, Czech Republic) for providing the compounds studied. M.H. acknowledges the support of project No. 203/00/P024 sponsored by Grant Agency of Czech Republic. K.L. acknowledges the support of projects VS-96021 and MSM 153100013 sponsored by the Ministry of Education of Czech Republic.

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Received 4 August 2000  
Accepted 8 August 2000