M.Sc Inorganic Chemistry
(Special-III) Elective Paper-1
Semester-IV

Course Title: Spectral Techniques in Inorganic Chemistry

Paper Code: 4101-A

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Application of mass spectrometry to inorganic compounds

Suppose, we have an unknown compound, and we wish to identify it using mass spectrometry. First, we can obtain an accurate mass, which for our unknown compound is measured at 243.982337 Da.

Knowing the mass to this number of significant figures allows us to suggest a possible empirical formula of $C_{10}H_8CrO_4$, which has a theoretical mass of 243.98222 Da. Knowing this, an EI mass

spectrum will be useful, as the resulting fragmentation pattern (Figure: 1) will allow us to connect the atoms into likely functional groups that have fragmented from the parent molecule. The resulting spectrum is complex, but we do not need to assign all the peaks to postulate a likely structure. For instance, the cluster of very intense peaks centered on m/z 51.9 corresponds to what we would expect to see for the Cr isotope series, which lends weight to our postulated empirical formula.

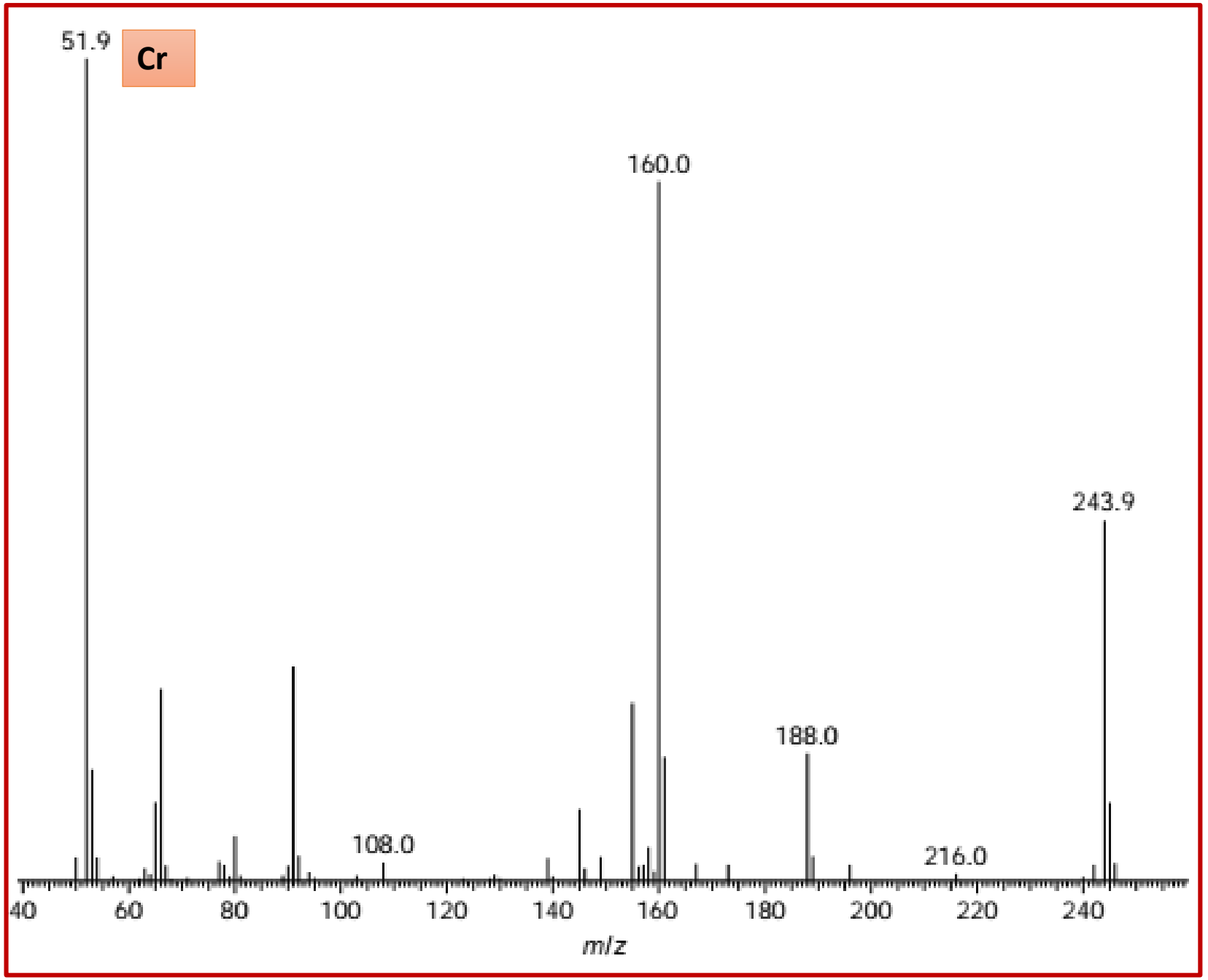


Figure 1: An EI-MS spectrum of $C_{10}H_8CrO_4$

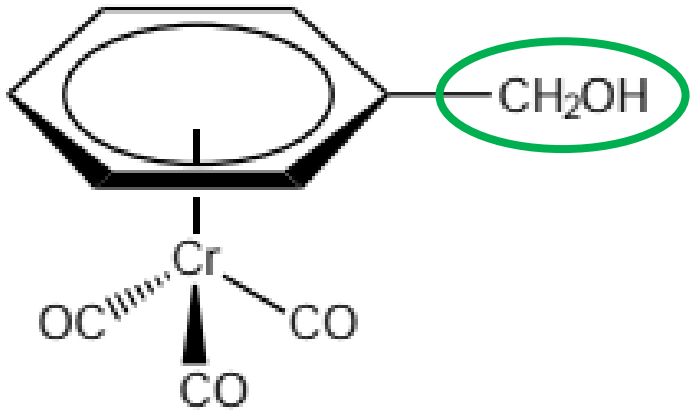
Now we need to look for patterns within the spectrum: peaks are recorded at 244.0, 216.0, 188.0 and 160.0 m/z. The differences between these peaks are 28 Da which, as we saw above, suggests the successive loss of carbonyl (CO) ligands, and our unknown compound must have started with three of them. Note that we cannot detect the CO ligand directly, as our spectrometer cannot detect any fragments with m/z below 40.0. Subtracting these atoms from our empirical formula leaves C_7H_8O.

This has a theoretical mass of 108 m/z, which accounts for another peak in the spectrum. And if we add the mass of Cr to the mass of C_7H_8O we are back to our peak at m/z 160.0. Our unknown compound is beginning to take shape: it is likely to be $[(C_7H_8O)Cr(CO)_3]$. Now all we need to do is determine the connectivity of the C_7H_8O ligand. The low ratio of hydrogen to carbon is highly suggestive of an aromatic system (which can be easily verified by infrared or ^1H NMR spectroscopy), for which $C_6H_5CH_2OH$ or $C_6H_5OCH_3$ are the only candidates.

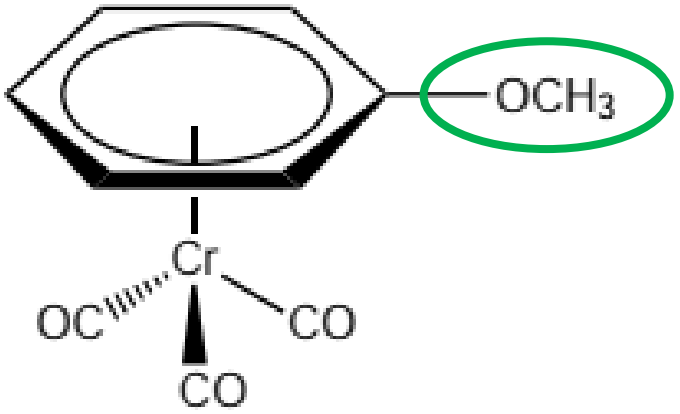
The identity of the complex is therefore either

[η6-($C_6H_5CH_2OH$)]$Cr(CO)_3$] (A) or

[η6($C_6H_5OCH_3$)$Cr(CO)_3$] (B).



A



B

We could confirm which one we had very quickly using vibrational spectroscopy to identify the presence (or absence) of the O–H stretching vibration. Our conclusions could be further substantiated by ^{1}H or ^{13}C NMR spectroscopy.