

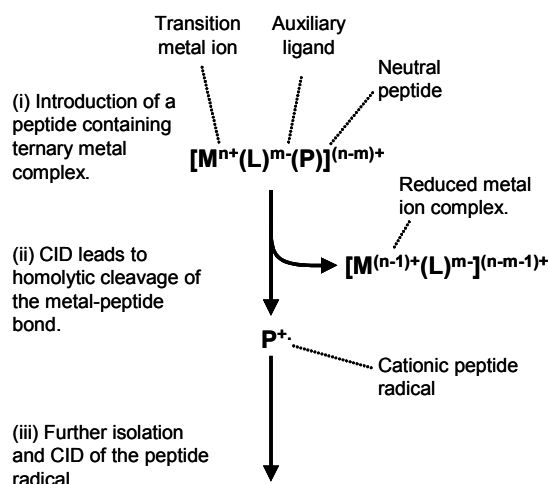
STUDENT 1

CATIONIC PEPTIDE RADICALS IN THE GAS PHASE FORMED BY OXIDATIVE DISSOCIATION FROM TRANSITION METAL COMPLEXES.

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Siu and co-workers demonstrated that collision induced dissociation (CID) of the $[\text{Cu}^{\text{II}}(\text{dien})(\text{YGGFLR})]^{2+}$ complex produces the complementary $\text{YGGFLR}^{\cdot+}$ and $[\text{Cu}^{\text{I}}(\text{dien})]^+$ ions.¹ This observation has led to a general methodology, outlined below, by which cationic peptide radical ions might be produced in the gas phase.



The CID of a series of gas phase complexes, $[\text{M}^{\text{III}}(\text{salen})(\text{P})]^+$ where; M = Cr, Mn, Fe and Co; P are the hexapeptides YGGFLR, WGGFLR and GGGFLR; and salen = N,N'-ethylenebis(salicylideneaminato); have been examined with respect to their ability to form the corresponding cationic peptide radical, $\text{P}^{\cdot+}$. This is the first application of the above methodology utilizing a metal ion other than copper(II). The fragmentation reactions competing with radical formation are highly dependent on the metal ion used. In addition, examination of complexes in which the periphery of the salen was substituted with electron donating or withdrawing groups allowed evaluation of electronic effects. These substitutions demonstrate that the ligand can be used to tune the dissociative chemistry to favour radical formation and suppress unwanted further fragmentation of the peptide radical immediately following its dissociation from the complex. Typically, only peptides which contain basic residues, tyrosine or tryptophan appear to form the corresponding cationic radical. As a first step in understanding the origins of this selectivity we have examined a number of ternary complexes with the common amino acids, AA. We find selective formation of the arginine radical cation from a series of $[\text{Fe}^{\text{III}}(\text{salen})(\text{AA})]^+$ complexes and the histidine and tryptophan radical cations from a series of $[\text{Cu}^{\text{II}}(\text{terpy})(\text{AA})]^{2+}$ complexes, terpy = 2,2':6',2''-terpyridine.

(1) Chu, I. K.; Rodriquez, C. F.; Lau, T. C.; Hopkinson, A. C.; Siu, K. W. M. *Journal of Physical Chemistry B* **2000**, *104*, 3393-3397.