Fast Intramolecular Exchange of Metal Ions in Complexes with Ninhydrin and Alloxan Radicals: a New Type of Ligand, forming Fluxional Complexes

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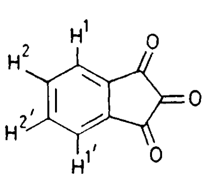
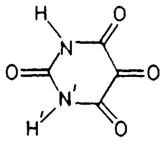
Summary The radical anions of ninhydrin and alloxan form complexes with closed shell metal ions undergoing rapid intramolecular exchange between two equivalent co-ordination sites, as observed by line-width effects in their e.s.r. spectra.

COMPLEXES of free radical ligands with diamagnetic metal ions show highly resolved e.s.r. spectra, yielding detailed structural information about such species in solution.[1] We describe here complexes of two rigid radicals, each having two identical co-ordination sites. These are the radical anions of ninhydrin (**1**) and of alloxan (**2**).



(1) nin



(2) all

Upon electrolytic reduction in the e.s.r. cavity in dimethylformamide (DMF), the spectra of the radicals nin$^-$ and all$^-$ can be easily observed. The coupling constants, given in the Table, correspond to a symmetric electron spin distribution with respect to the C_2-axes of the molecules. After addition of a solution containing metal ions (generally, perchlorates were used), complexes M(nin$^-$) and M(all$^-$) are formed. With M = Ca^{2+}, Cd^{2+}, and La^{3+}, e.s.r. spectra are observed, in which the apparent symmetry is still C_{2v}, *i.e.* the pairwise equivalence of H^1, $H^{1'}$; H^2, $H^{2'}$ in nin$^-$ and N, N′; H, H′ in all$^-$ is preserved (Table). On the other hand, Mg^{2+}, Zn^{2+}, and Y^{3+} form complexes having either different coupling constants for the two nuclei in a pair, or showing pronounced alternating line width effects.[2]

TABLE. E.s.r. parameters. Coupling constants are given in μT.

	a_H	$a_H{}'$	a_N	$a_N{}'$	a_M
all$^-$	33	33	48	48	—
Zn(all$^-$)$^+$ (25 °C)	81	41	41	0	135^a
Zn(all$^-$)$^+$ (120 °C)	62	62	17	17	135^a
	$a_H{}^1$	$a_H{}^{1'}$	$a_H{}^2$	$a_H{}^{2'}$	a_M
nin$^-$	104	104	92	92	—
Cd(nin$^-$)$^+$	96	96	70	70	956/1000

^{a} $T_{coal.}$ 78 °C.

This behaviour can be interpreted in each case by assuming rapid exchange between the two equivalent co-ordination sites on an e.s.r. time scale for Ca^{2+}, Cd^{2+}, and La^{3+}, and slow or intermediate exchange for Mg^{2+}, Zn^{2+}, and Y^{3+}. For the complexes Mg(all$^-$), Zn(all$^-$), Y(all$^-$), and Zn(nin$^-$), the transition from slow to fast exchange has been observed by changing the temperature.

The observation of the metal hyperfine structure (^{111,113}Cd, ^{139}La, ^{67}Zn, ^{89}Y) proves the intramolecular mechanism for the exchange reactions. The exchange rate constant at the coalescence temperature, k_{ex}, is *ca.* 10^5 s^{-1}, and the sequence of the metals seems to correspond to the general trend observed in ligand substitution reactions. Model calculations are in progress to test the hypothesis that the path of the exchanging metal ion lies in the plane of the radical ligand, corresponding to a transition state of C_{2v} symmetry.

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[1] S. Richter, C. Daul, and A. von Zelewsky, *Inorg. Chem.*, 1976, **15**, 943.
[2] E. de Boer and E. L. Mackor, *J. Amer. Chem. Soc.*, 1964, **86**, 1513.