Bridging Intermediates in a Redistribution Reaction of Some Metal Chelates

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Summary Exchange of ligand between bis-(*N*-methylsalicylaldimino)nickel(II) and bis-(*N*-methylsalicylaldimino)zinc(II) is fast on an n.m.r. time scale at room temperature and above in $CDCl_3$ providing evidence for the intermediacy of paramagnetic mixed-metal oligomers in the exchange.

IN mixtures of bis-(*N*-methylsalicylaldimino)nickel(II) (abbreviated as Ni(msal)$_2$) and bis-(*N*-methylsalicylaldimino)zinc(II) [Zn(msal)$_2$] in $CDCl_3$ solution, dynamic equilibria are observed in which the ligand exchanges between nickel and zinc sites *via* intermediate paramagnetic oligomers containing nickel and zinc with the oxygens of the ligand bridging the two metals. Bridged species of this type are usually postulated as intermediates in redistribution reactions.[1,2] The paramagnetic oligomers are distinguished by their contact shifted n.m.r. spectra and they are further identified by near i.r. spectra.

A single wide n.m.r. line observed for NMe hydrogen in mixtures of Ni(msal)$_2$ and Zn(msal)$_2$ with various Ni:Zn ratios at 328K, is downfield of either parent signal and thus cannot represent an averaged signal for the two parent species; at least one more species, containing paramagnetic nickel, is implied. A maximum downfield shift of this signal appears at the nickel:zinc ratio of 2:1. At lower temperatures the single line separates into several signals, including those of the parent compounds. This effect is maximised at 290K and for the 2:1 mixture when the largest signal area is for a species (or species) other than the parent compounds. These species are not uniquely defined even at and below this temperature since the downfield signal is very broad and may correspond to an averaged signal. At even lower temperatures further broadening is observed and it is inferred that mixed-metal octahedral species are present and that exchange with octahedral species still occurs.

A complementary analysis of the nickel chromophores in the system was made by visible–near i.r. spectroscopy, comparing the spectra observed with the known spectra of nickel salicylaldimines in various geometries: this showed the presence of new species changing in concentration with change in the Ni:Zn ratio and steadily increasing in concentration as the temperature is lowered. The unresolved band at *ca.* 9000 cm^{-1} corresponds to these species and cannot be attributed to either of the monomer nickel chromophores.[3]

Oligomer intermediate(s) are thus shown to lie on the reaction co-ordinate for the redistribution of ligand between Ni(msal)$_2$ and Zn(msal)$_2$, and are probably implicated in other similar systems.[1]

One of us (S.K.) thanks the University of Ceylon (Sri-Lanka), Colombo for study leave and support. We also thank the S.R.C. for support, and Drs. J. R. Blackborow, C. M. Wheeler, and B. P. Straughan for helpful discussion.

(*Received*, 10*th November* 1972; *Com.* 1887.)

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