These findings lead to the inference that the 'cryoscopic effect constant', like the dispersion ratio, can be expected to be characteristic of the solute. A comparative investigation of the constant for various categories of solutes and for various solvents, as well as their correlation with other constants of the solute, will perhaps throw more light on the properties of matter.

I wish to thank Mrs. Parvathy Rangappa and Mr. R. N. Sood for assistance in these experiments.

K. S. Rangappa

Central Water and Power Commission,
New Delhi, India.

---

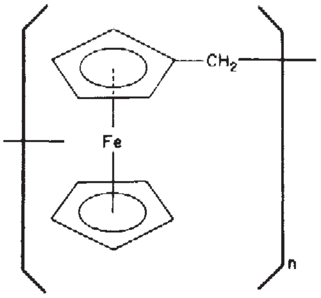
[1] Rangappa, K. S., *Nature*, **198**, 682 (1963).

[2] Kaye, G. W. C., and Laby, T. H., *Tables of Physical and Chemical Constants*, 157 (Longmans Green and Co., London, 1956).

Ferrocene-containing Polymers: Intermediary Complex Formation in the Polycondensation of *N*,*N*-Dimethylaminomethylferrocene

In an earlier paper[1] discussing the $ZnCl_2$-HCl-catalysed polycondensation of *N*,*N*-dimethylaminomethylferrocene I to give polymer II, the formation of intermediates III and IV was postulated on the basis of the stoichiometry of the starting materials required and the composition of by-product V ($C_{10}H_9Fe$ = ferrocenyl). While III could indeed be isolated, no interception of IV was possible.

$$C_{10}H_9Fe—CH_2—N(CH_3)_2 . HN(CH_3)_2 . ZnCl_2 . 2HCl \rightleftharpoons$$
$$[C_{10}H_9Fe—CH_2—HN(CH_3)_2]^+ + [H_2N(CH_3)_2]^+ + [ZnCl_4]^{2-} \quad (I)$$



(II)

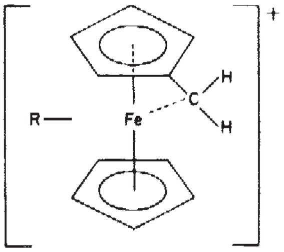
$$2C_{10}H_9Fe—CH_2—N(CH_3)_2 . ZnCl_2 . 2HCl \quad (III)$$

$$C_{10}H_9Fe—CH_2—N(CH_3)_2 . HN(CH_3)_2 . ZnCl_2 . 2HCl \quad (IV)$$

$$2HN(CH_3)_2 . ZnCl_2 . 2HCl \quad (V)$$

The isolation of IV has now been accomplished from polycondensation reactions interrupted prior to completion. For example, from experiments (20–40 min, 160°) conducted by the conventional procedure[1], using I, $ZnCl_2$ and HCl in a 2 : 1 : 2 ratio, IV was separated in 5–9 per cent yield besides III and V by fractional crystallization from the isopropanol extract of the reaction mixture. Similarly, equimolar amounts of I, $ZnCl_2$ and H_2O (HCl generated by hydrolysis) at 160° (4 h) gave IV in 8·7 per cent yield. The water-soluble complex forms yellow plates, m.p. 140°–142° (calc.: C, 36·22; H, 5·27; Cl, 28·51; Fe, 11·23; N, 5·63; found: C, 36·56; H, 5·35; Cl, 28·31; Fe, 11·52; N, 5·94); in aqueous or alcoholic solution it dissociates (further dissociation of the tetrachlorozincate ion in the equilibrium $ZnCl_4^{2-} \rightleftharpoons Zn^{2+} + 4Cl^-$ may be neglected here) according to equation I, as indicated by chemical reactions and molecular weight determinations[1].

The 3·30μ band (CH_3 on N^+) in the infra-red spectrum (potassium bromide pellet) of IV was almost as strong as in V, whereas the stretching band near 2·85μ, strong in III, showed considerable attenuation. Decreased intensity was also observed with the NH_2^+ bands near 4·2, 6·4 and 11·35μ (stretching, bending, rocking). No NH^+ absorption in the 3·8–4·1μ region (as exhibited by the hydrochloride of I) was noticed. These findings suggest protonation of the dimethylamine nitrogen, while the Mannich base nitrogen appears to exist essentially in a non-protonated form as analogously suggested[1] for III, and, hence, may involve co-ordinate covalent N → Zn bonding.



VI*a*, *R* = H
VI*b*, *R* = residual polymer chain

The isolation of IV in addition to III during intermediate stages of the polycondensation of I corroborates the reaction course proposed earlier. (IV was also directly obtained by fusing a 1 : 1 mixture of III and V. This reaction, well in accord with the evidenced double-salt character of the compound, is expected and not contradictory to the reaction path postulated.) The primary complex III is formed from I, $ZnCl_2$ and HCl (equation (3*a*), *loc. cit.*[1]). Aided by N → Zn co-ordination, III dissociates at one of the two C_α—N bonds, and the resulting IV undergoes further ionization at the remaining C_α—N bond, thus leading to V. The metallocarbocations VI*a* produced in these two ionization steps (and, similarly, VI*b* arising from polymeric analogues of III and IV in advanced stages of propagation) may now undergo the earlier proposed propagation and termination steps leading to II.

E. W. Neuse
E. Quo

Polymer Laboratory,
Missile and Space Systems Division,
Douglas Aircraft Co., Inc.,
Santa Monica, California.

---

[1] Neuse, E. W., and Quo, E., *J. Polymer Sci.* (in the press).

Stereochemistry of Copper in *Bis*(*N*-t-butylsalicylaldiminato)copper(II)

It has been established that copper(II) will adopt an approximately tetrahedral environment under certain circumstances but evidence on the exact geometry of this configuration is still meagre. That which is available, with two possible exceptions[1,2], shows a stereochemistry which is more nearly planar than tetrahedral[3]. For instance, in 2,2′-biphenyl*bis*-(2-iminomethylenephenolato) copper(II), where copper is complexed by a tetradentate molecule with donor atoms which are naturally tetrahedrally disposed, the ligand is considerably distorted and the expected 90° angle between the two planes containing the salicylaldimine groups is reduced to 43°.

A recent investigation of *bis*(*N*-isopropylsalicylaldiminato)copper(II) (ref. 1) has shown the crystals to be nearly, but not perfectly, isomorphous with those of the analogous nickel complex, which in its turn has been shown by X-ray analysis[4] to adopt a configuration which is only slightly distorted from tetrahedral. The angle between the salicylaldimine planes is 81° and the six bond angles about the nickel atom range from 94° to 125°. It is deduced that the copper atom has a similar configuration. Steric arguments, together with spectral data and dipole moment