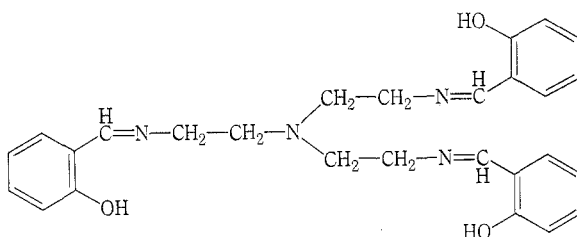# A POTENTIAL SEPTADENTATE LIGAND*

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Ligands with a septadentate function are rare and it was therefore of interest to examine the complexing ability of the Schiff base derived from 2,2′,2″-triamino-triethylamine (tren) and salicylaldehyde. The ligand tren is well known to afford octahedral complexes of the type [MX₂ tren] in which the amine behaves as a quadridentate and X is a unidentate ligand.[1] Likewise the related ligand 1,3-diamino-2-aminomethylpropane forms a tris-salicylidene derivative which has been shown to behave as a sexadentate ligand towards iron(III) and cobalt(III).[2]

We have found that condensation of tren with three molecules of salicylaldehyde gives the yellow Schiff base 2,2′,2″-(salicylideneimino)triethylamine (trensal) which readily forms a complex with iron(III).

Experimental

Triaminotriethylamine trihydrochloride was prepared by the literature method[3] (Found C, 28·1; H, 8·4; Cl, 42·1; N, 21·5. Calc. for $C_6H_{21}ClN_4$: C, 28·2; H, 8·3; Cl, 41·6; N, 22·0%).

Tris(salicylideneimino)triethylamine

2,2′,2″-Triaminotriethylamine trihydrochloride (3 g) and sodium acetate trihydrate (5 g) were dissolved in the minimum volume of hot water and a solution of salicylaldehyde (4·32 g) in ethanol (20 ml) was added. A yellow colour was immediately produced. The reaction mixture was heated at the boil for 3 min. Sufficient water was then added to just dissolve any solid which precipitated and the solution was cooled in an ice-bath. The yellow crystalline product was filtered off and recrystallized from hot ethanol. The yield was 0·7 g, m.p. 89–90° (Found: C, 70·4; H, 6·7; N, 12·2. Calc. for $C_{27}H_{30}N_4O_3$: C, 70·7; H, 6·6; N, 12·2%). The yellow Schiff base was very soluble in acetone and chloroform.

[1] Hall, D., and Woolfe, M. D., *Proc. chem. Soc.*, 1958, 346.

[2] Dwyer, F. P., Gill, N. S., Gyarfas, E. C., and Lions, F., *J. Am. chem. Soc.*, 1957, **79**, 1269.

[3] Jaeger, F., and Koets, P., *Z. anorg. allg. Chem.*, 1928, **170**, 347.

Tris(salicylideneimino)triethylamineiron(III) Hemihydrate

Tris(salicylideneimino)triethylamine (0·17 g) was dissolved in hot methanol (50 ml) and a solution of anhydrous iron(III) chloride (0·07 g) in methanol (10 ml) was added. A red-violet colour was immediately obtained. Aqueous sodium acetate (0·2 g) in water (22 ml) was added, the solution evaporated on a steam-bath to a volume of 20 ml, and the mixture cooled in ice. A finely crystalline purple solid was filtered off and washed with water and then acetone. The yield was 0·12 g (Found: C, 62·2; H, 5·5; Fe, 10·6; N, 10·8. Calc. for $C_{27}H_{28}FeN_4O_{3.5}$: C, 62·3; H, 5·4; Fe, 10·7; N, 10·8%). A $10^{-3}M$ solution in nitrobenzene gave a conductance of 0·44 $ohm^{-1} cm^2 mole^{-1}$.

The presence of water of crystallization was indicated by a weak broad infrared band about 3500 cm^{-1}. A mass spectrometric determination of the molecular weight gave 511 in agreement with the predicted value of 511·6 for the anhydrous complex.

X-ray diffractometer measurements for the Fe trensal complex made with a Phillips Pw1049 recording counter diffractometer using a nickel-filtered copper Kα radiation are tabulated below since they are useful for characterization purposes. The intensities are given in Table 1 relative to the strongest reflection.

TABLE 1

INTENSITY DATA

$\sin^2\theta$*	Intensity	$\sin^2\theta$*	Intensity	$\sin^2\theta$*	Intensity
0·0037	0·63	0·0125	1·00	0·0209	0·31
0·0052	0·44	0·0144	0·19	0·0247	0·42
0·0079	0·11	0·0159	0·16	0·0272	0·15
0·0109	0·23	0·0173	0·13	0·0344	0·22

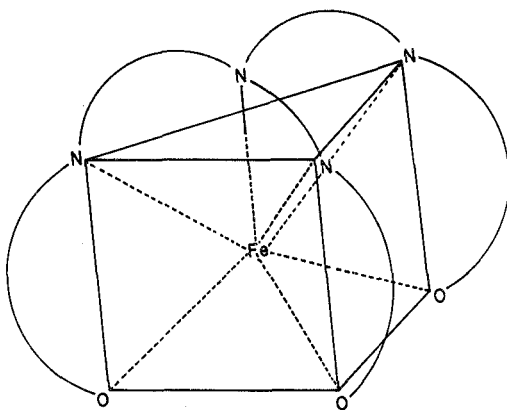* The estimated accuracy is $\pm$ 0·0002.

Discussion

The new iron(III) complex is an intense purple-red finely crystalline solid insoluble in water and ethanol, but slightly soluble in nitromethane, acetonitrile, chloroform, nitrobenzene, or sulpholane to give claret-red solutions. The absorption spectrum in acetonitrile consists of two main bands each showing evidence of splitting. Absorption maxima (mμ) and extinction coefficients (cm^{-1} l. $mole^{-1}$ in parentheses) are as follows: 515 (5880), 435sh (3830), 325 (14600), 295sh (13700).

Magnetic susceptibility measurements by the Gouy method give a value of 5·9 B.M., thus showing the iron to be in the high-spin state. Though this is consistent with other examples of iron(III) in complexes of higher coordination number, lower coordination numbers could also produce the moment observed here. It is interesting that the X-ray work of Hoard et al.[4] has confirmed seven-coordination in the [Fe(OH₂)Y] anion (Y = ethylenediaminetetraacetate) in which the iron is high spin (sextet). Chemical evidence concerning septacoordination for the trensal-iron(III) complex is equivocal. The intense colour of the iron complex is quickly destroyed in dilute sulphuric acid. Red chloroform solutions are likewise immediately decolorized by shaking with dilute hydrochloric acid, and the hexaaquoiron(III) species is extracted into the acid. These observations indicate ready acid-catalysed decomposition. Protonation most probably would occur at the phenolic oxygens or

[4] Lind, M. D., Hamor, M. J., Hamour, T. A., and Hoard, J. L., *Inorg. Chem.*, 1964, **3**, 34.

at the tertiary nitrogen provided that the last mentioned was not coordinated to the metal. A Stuart–Briegleb model may be constructed for trensal and suggests that positioning of all four nitrogens and three oxygen donors about a metal is subject to no special steric hindrance. It seems likely from the structure of this ligand that the tertiary nitrogen will be held at bonding distances to the metal, so that the remaining centres for protonation are the phenolic oxygens. The fact that the complex is a non-electrolyte tends to support the view that all three of these oxygen atoms are coordinated.

The analytical data suggest that one-half a molecule of water is present which could not be removed by drying at 150°/20 mmHg for 2 hr. This water is thought to be held in the lattice (and so readily lost) rather than coordinated since there were no peaks above 511 in the mass spectrum. Though it is not possible, in the absence of complete X-ray studies, to decide the stereochemistry of this complex, the use of Stuart–Briegleb models does indicate one way in which septacoordination might be achieved: