Tetrahedral Co-ordination of Nickel(II)

In a recent communication[1], Katzin has interpreted the appearance of blue colour in paramagnetic nickel(II) compounds as indicative of tetrahedral co-ordination. We have recently completed the determination of the crystal structure of $Ni(en)_2(NCS)_2$ (Brown, B. W., and Lingafelter, E. C., unpublished work). This compound is blue and paramagnetic, but the co-ordination of the nickel ion is transoctahedral, with Ni—N distances of 2·10 A. to the ethylenediamine and 2·15 A. to the *iso*thiocyanate. We are also investigating the crystal structure of $Ni(en)(H_2O)_4(NO_3)_2$, another blue paramagnetic compound. Although the study is still in the early stages and all atoms have not been located, the presence of a co-ordination octahedron about the nickel atom is already clear.

Thus these two compounds show that the blue colour cannot be taken as an indication of tetrahedral co-ordination of nickel(II).

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[1] Katzin, L. I., *Nature*, **182**, 1013 (1958).

A Method for improving the Solute Selectivity of Osmotic Membranes

An examination of the results obtained with a pair of 'Ultracella' filters (fein)—manufactured by the Membranfiltergesellschaft, Göttingen—which had been used for several months in benzene at 30° C. to determine the number-average molecular weights ($\overline{M}_n$) of polymer samples, showed that during this time the membranes had become markedly less permeable to solvent. A similar observation has been made by Philipp and Bjork[1] with a gel 'Cellophane' membrane, and they attributed the phenomenon to gradual ageing of the membranes. However, with the 'Ultracella' filters (fein) closer examination of the results indicated that the change in permeability had occurred in two distinct stages both of which could be associated with attempts to measure the $\overline{M}_n$ of a sample of poly(diallyl phthalate). Experiments were therefore carried out with three other pairs of 'Ultracella' filters (fein) in order to investigate this phenomenon further.

The membranes were assembled in standard Zimm–Myerson type osmometers and before and after treatment with solutions of poly(diallyl phthalate) were characterized by (*a*) the solvent permeability, measured by the rate of fall of the meniscus in the measuring capillary under a head of 10 cm. of benzene, and (*b*) the solute selectivity, measured by the maximum osmotic head developed with a 1 per cent (w/w) benzene solution of a commercial polystyrene which has a very wide distribution of molecular weights[2].

The results in Table 1 show that in each case after treatment with poly(diallyl phthalate) the membranes became less permeable and more selective (that is, gave higher osmotic heads). Furthermore, these experiments show that the magnitudes of these effects (*a*) increased with poly(diallyl phthalate) concentration (membranes UCF/F 457/*A*1 and UCF/F 1256/4) up to a maximum concentration of about 1·5 per cent (w/v) (membranes UCF/F 1256/5), (*b*) after 16 hr. were independent of the time the membranes were in contact with the poly(diallyl phthalate) solution (membranes UCF/F 1256/4), (*c*) in the molecular weight-range 13,000–22,000 were

Table 1. Measurements in Benzene at 30° C.; 'Ultracella' Filters (Fein) (UCF/F)

Treatment				Permeability		Selectivity	
Poly(diallyl phthalate) solution			Time left in osmometer (hr.)	Fall from 10 cm. head of benzene		Equilibrium osmotic pressure with 1 per cent (w/w) commercial polystyrene	
Sample	$\overline{M}_n$	Concentration (per cent) (w/v)		5 min. (cm.)	30 min. (cm.)	Pressure (cm.)	Time (hr.)
UCF/F 457/*A*1							
—	—	—	—	1·31	5·85	3·35	< 16
10·1	13,000	0·1	16	0·74	3·86	4·93	6
10·1	13,000	1·5	16	0·31	1·77	6·01	6
UCF/F 1256/4							
—	—	—	—	1·25	5·04	4·43	4
BSI	22,000	0·1	16	0·92	4·03	4·65	4½
BSI	22,000	0·1	64	0·68	3·35	4·97	< 18
BSI	22,000	1·5	16	0·33	1·91	5·94	< 21½
UCF/F 1256/5							
—	—	—	—	1·58	6·27	3·93	3
BSI	22,000	1·5	64	0·46	2·56	5·83	< 22½
10·1	13,000	10	16	0·51	2·62	5·72	8

Table 2. Measurements in Benzene at 30° C.; 'Ultrafein' Filters (UFF)

Treatment				Permeability		Selectivity	
Poly(diallyl phthalate) solution			Time left in osmometer (hr.)	Fall from 10 cm. head of benzene		Equilibrium osmotic pressure with 1 per cent (w/w) commercial polystyrene	
Sample	$\overline{M}_n$	Concentration (per cent) (w/v)		5 min. (cm.)	30 min. (cm.)	Pressure (cm.)	Time (hr.)
'Ultrafein' filter (gross) (UFF/G 1157/1)							
—	—	—	—	2·96	—	5·83	2½
BSI	22,000	1·5	66	0·74	—	7·99	~20
'Ultrafein' filter (fein) (UFF/F 457/2)							
—	—	—	—	1·20	4·89	4·94	22
BSI	22,000	1·5	16	0·99	4·30	5·72	21
'Ultrafein' filter (allerfeinst) (UFF/AF 457/*A*3)							
—	—	—	—	0·045	0·296	7·30	168
2*H*	25,400	0·4	352	0·050	0·305	8·31	166