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Werner complexes as stationary phases in gas chromatography

Werner complexes of the type MP_4X_2 , where M is a transitional metal ion, P is a pyridine derivative and X, in most cases, is NCS, were shown by SCHAEFFER *et al.*¹ to have the capacity to clathrate selectively many aromatic molecules depending on their shape. Recently DE RADZITZKY and co-workers²⁻⁴, have discovered clathration with new Werner complexes of the type $Ni(NCS)_2(1\text{-arylalkylamine})_4$. The purpose of this communication is to demonstrate the interesting possibilities offered by such complexes as selective phases for the gas chromatographic separation of crucial isomeric pairs, *e.g.* *m*- and *p*-xylene, and to present some evidence based on retention times for the nature of the clathration process with these two classes of coordination complexes.

In this preliminary study two coordinating complexes, $Ni(NCS)_2(4\text{-methylpyridine})_4$ and $Ni(NCS)_2(1\text{-phenylethylamine})_4$, were chosen to represent the two types of Werner complexes mentioned above. In all cases columns were made from 180-cm stainless steel tubes (4 mm I.D.) and were packed with Chromosorb P (-60 to +80 mesh) coated with 30% complex. A Perkin-Elmer 810 GC with F.I.D. and

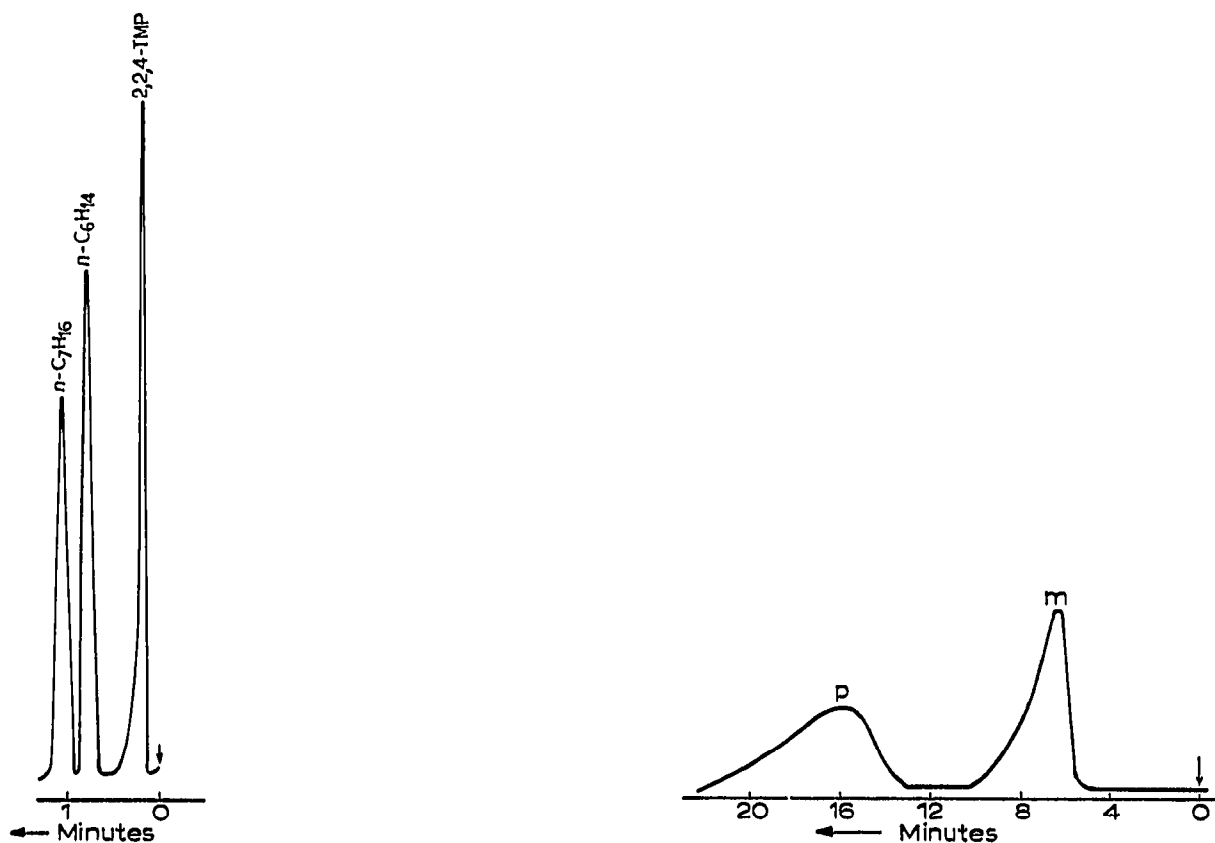


Fig. 1. Gas chromatographic separation of *m*- and *p*-xylenes on 30% $Ni(NCS)_2(4\text{-methylpyridine})_4$. N_2 flow, 90 ml/min; column temperature, 80° . The column was kept at 90° under N_2 flow for several hours before analysis.

Fig. 2. Order of elution of some aliphatic hydrocarbons; the column was the same as in Fig. 1.

a 1-mV Honeywell recorder were used. Base-line compensation was achieved through dual column operation.

$\text{Ni}(\text{NCS})_2(4\text{-methylpyridine})_4$ selectively clathrates *p*-disubstituted benzenes¹. Fig. 1 shows an extremely efficient separation ($\alpha = 2.5$) of *m*- and *p*-xylenes. With this column it was found that 4-methylanisole is eluted later than the 3-isomer; toluene, *o*-, and *m*-xylenes are eluted simultaneously; 1,3,5-trimethyl benzene (b.p. 164.7°) has a shorter retention time than *p*-xylene (b.p. 138.4°); 2,2,4-trimethylpentane is eluted earlier than *n*-hexane and *n*-heptane (Fig. 2).

$\text{Ni}(\text{NCS})_2(1\text{-phenylethylamine})_4$ has been shown to be *o*-selective from competitive clathration studies². Elution orders of some compounds studied on this column are as follows:

(A) Cyclohexane < cyclohexene < benzene.

(B) Methylcyclohexane < toluene.

(C) Benzene < toluene < chlorobenzene < (*m*- + *p*-)xylenes < *o*-xylene < 1,3,5-trimethylbenzene < 1,2,3-trimethylbenzene.

(D) *n*-Hexane < *n*-heptane < 2,2,4-trimethylpentane.

The column temperature for series A, B and D was 30° and for series C, 60°; N_2 flow was 30 cc/min in all cases.

It will be observed that the elution characteristics of the guest molecules are different in the two cases. In the case of the methylpyridine complex and its *p*-xylene clathrate, HART AND SMITH⁵ did not observe any remarkable change in the infrared spectra, thus precluding the formation of any chemical bond. On the other hand, LEYSEN AND VAN RYSELBERGE⁶ observed the appearance of new clathrate bands at 12.63 μ , 12.56 μ and 12.49 μ in the spectra of the clathrates formed from 1-phenylethylamine complex with *o*-, *m*- and *p*-xylenes, respectively. This band shifts from higher to lower wavelengths according to the order of selectivity for the guest (*o* > *m* > *p*). The same phenomenon can be observed with the xylene clathrates of $\text{Ni}(\text{NCS})_2(1\text{-phenylbutylamine})_4$ ⁷. Thus the spectra of such complexes are definitely not due to superposition of the spectra of the host and the guest. Under comparable steric conditions the clathration selectivity was shown to depend primarily on charge-transfer interactions between the aromatic nuclei of the components of the clathrates^{7,8}. In the present work the elution orders of various compounds as shown in series A to C also agree with this explanation. The greater the electron density in the aromatic ring of the guest, the greater is the interaction with the aromatic nucleus of 1-phenylethylamine (which behaves as an electron acceptor⁸), and hence the longer is the retention of the guest. No such explanation is valid, however, for the methylpyridine complex. In this case retention times seem to be governed primarily by the cross-sectional area of the guest molecule rather than by electronic factors. X-ray diffraction patterns (powder) of the complexes of 4-methylpyridine and 1-phenylbutylamine as well as their *p*-xylene clathrates have been reported to indicate a change in the crystal lattice of the host following clathration^{5,7}. The methylpyridine complex has a smaller molar volume than its *p*-xylene clathrate⁵, indicating lattice expansion. However, in contrast with the phenylethylamine complex studies in this work, the methylpyridine complex is well known for its ready ability to form clathrates by simple contact. This difference in behaviour does not appear to be general because coordination complexes with 1-phenylbutylamine and 1-phenylpropylamine are also known to form clathrates by solid-liquid contact^{4,7}. Aliphatic

hydrocarbons are known not to be clathrated by either of these two classes of Werner complexes. In this context the fact that 2,2,4-trimethylpentane is eluted from the two columns in the opposite order (see Fig. 2 and series D above) becomes significant and may be explained by the presence of some permanent clathration holes in the $\text{Ni}(\text{NCS})_2(4\text{-methylpyridine})_4$ crystal. This would also explain the fact that 1,3,5-trimethylbenzene has a shorter retention time than *p*-xylene.

Finally Werner complexes, although very selective as GC phases, decompose rapidly even at a column temperature of 90° , resulting in a linear fall in resolution with time. This is a serious practical limitation which prevented us from examining the retention characteristics of other high-boiling, difficult to separate isomers like 1-, and 2-methylnaphthalenes, phenanthrene and anthracene. One way to obviate this difficulty would be to enrich the carrier gas with the vapour of the coordinating amine. Further work on this aspect is in progress.

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Gas-chromatographische Untersuchung von Isothiocyanaten

In einer vorangegangenen Publikation beschreibt BINDER¹ die mit Schwierigkeiten verbundene quantitative Bestimmung von Isothiocyanaten, die als Folgeprodukt einer thermischen Spaltung substituierter Thioharnstoffe im Einspritzblock eines Gas-Chromatographen auftreten. Doch auch bei einer direkten Einspritzung organischer Isothiocyanate treten Störungen in der gas-chromatographischen Analyse auf. So finden WAHLROSS UND SAARIVIRTA² an gealterten Polyester-Trennsäulen eine

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