

Chemically bonded chelates as selective complexing sorbents for gas chromatography

II. Ketones, ethers and nitroalkanes

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ABSTRACT

Specific interactions of ketones, ethers and nitroalkanes with Cu(II) and Ni(II) acetylacetonates chemically bonded to silica surfaces were investigated. A number of relations between the structure of adsorbates and the retention parameters were discovered and described. The differences in specific interactions were sufficient to enable the separation of isomer-containing mixtures.

INTRODUCTION

In the last 20 years a significant number of papers on the application of β -diketonates of the *d*- and *f*-block elements in gas chromatography have been published. These complexes are actively added to liquid stationary phases (in particular, squalane and SE-30). Such systems have been studied by Schurig and co-workers [1–5], Picker and Sievers [6,7] and others [8–13].

A characteristic feature of the packings described in the above-mentioned papers is a proper metal β -diketonate dissolved in a non-polar or weakly polar liquid stationary phase.

Such packings are used in both classical analytical columns and capillary columns as well as in precolumns. In the last case the packings were used to retain strongly nucleophilic compounds (such as alcohols, amines, ketones and aldehydes). The utility of these sorbents was demonstrated by the analysis of cigarette smoke, volatile constituents of urine [7–9] and a cologne essence [6].

Another example of an application testifying to the high selectivity of metal β -diketonates dissolved in squalane is separation of the geometric isomers of butene and pentene [14].

Packings containing nickel(II) bis[3-(heptafluorobutanoyl)-(1*R*)-camphorate] are capable of separating enantiomers, which indicates their high enantioselectivity [5]. Columns containing lanthanide chelate sorbents are also effective in the analysis of volatile compounds of waste water [6]. It should be emphasized that this type of packing is characterized by high thermal stability, which permits their application at a temperature of 225°C, and in some cases even at 300°C [8].

As follows from a brief survey of the properties of packings containing metal β -diketonates, by setting appropriate parameters for the operation of the columns these packings may be used in two different ways. Firstly, as they are highly selective they may be employed in direct chromatographic analysis (including analysis of optically active compounds). Secondly, they may

be used as selective traps for a wide range of organic compounds. The latter application—because of the high selectivity of these packings—enables the analysis of complex mixtures, and to obtain a number of simpler chromatograms instead of one complex chromatogram. If particular compounds are of interest, it is possible to analyse only the trap-sorbent on which they are retained.

The sorbents studied by us [15] differ from those mentioned above in that appropriate metal β -diketonates [Cu(acac)₂ and Ni(acac)₂, where acac = acetylacetonate] were chemically bonded with the silica surface (Porasil C) via diphenylphosphine groups. Packings containing such bonds, despite having a considerably lower amount of active component (β -diketonate), proved to be able to interact specifically with unsaturated hydrocarbons. In the present paper their interactions with ethers, nitroalkanes and ketones are examined.

EXPERIMENTAL

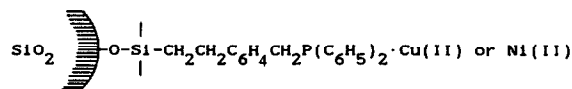
Apparatus

Chromatographic measurements were carried out on a GCHF 18.3 gas chromatograph manufactured by Chromatron (Berlin, Germany), equipped with a flame ionization detector and a digital thermometer (Slandi, Warsaw, Poland) for measuring the column temperature. Argon dried over a molecular sieve 4 Å was used as the carrier gas. The flow-rate of the carrier gas was measured using a digital flowmeter (J & W Scientific, Folsom, CA, USA).

Packings of columns

Copper(II) and nickel(II) acetylacetonates were bonded to the surface of silica (Porasil C, 80–100 mesh (177–149 μ m), Waters, Milford, MA, USA) via diphenylphosphine groups. Phosphinated silica was obtained as described previously [15]. The specific surface areas of the investigated packings were 85 and 83 m²/g for packings containing Cu(II) and Ni(II), respectively. The surface concentration of silanes was 4.01 μ mol/m². The method of preparing pack-

ings containing chemically bonded β -diketonate phases has been published previously (in Part I [15]). The investigated packings can be shown schematically as follows:



RESULTS AND DISCUSSION

From the literature, chemically bonded β -diketonates of transition metals are used in three different types of studies: (i) study of the structure of the chemically bonded β -diketonates and of the adducts formed with additional ligands (CO, pyridine) [16], (ii) application in gas chromatography and high-pressure liquid chromatography as a component of chemically bonded phases [15,17], (iii) application as trap-packings for a wide range of organic compounds [6–9].

The ability to form adducts with additional ligands showing nucleophilic properties was used in the analysis of alkenes [15]. As can be seen in chromatograms shown in Figs. 1–3, these packings may also be used in the analysis of ketones, ethers and nitroalkanes.

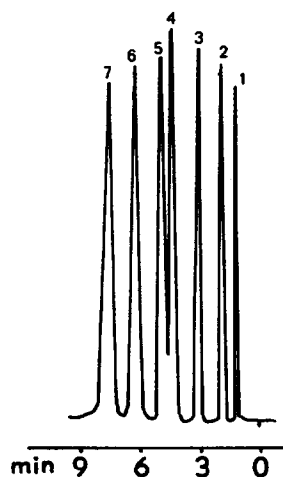


Fig. 1. Separation of a mixture of ketones on a Ni(acac)₂ packing. Column temperature, 155°C; carrier gas flow-rate, 20.2 ml/min. Peaks: 1 = propanone; 2 = 2-butanone; 3 = 3-pentanone; 4 = 3-methyl-2-butanone; 5 = 2-pentanone; 6 = 4-methyl-2-hexanone; 7 = 2-hexanone.

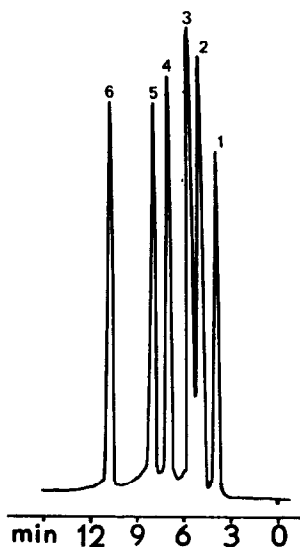


Fig. 2. Analysis of nitroalkanes on a $\text{Cu}(\text{acac})_2$ packing. Column temperature, 118.1°C ; carrier gas flow-rate, 20 ml/min. Peaks: 1 = nitromethane; 2 = nitroethane; 3 = 2-nitropropane; 4 = 1-nitropropane; 5 = 2-nitrobutane; 6 = 1-nitrobutane.

Ketones

Owing to free electron pairs at the oxygen atom, the carbonyl group in ketone molecules is able to interact specifically with the electron-acceptor centre on the surface of packings. These interactions are affected by at least three factors: location of a carbonyl group in the molecule, the presence of additional electron-donor centres (e.g. unsaturated bonds) and substituents in the hydrocarbon chain. The more the carbonyl group is shifted towards the centre of the molecule, the weaker are the interactions. This can be deduced from a comparison of k' , I , ΔM_e and V_g for such pairs of ketones as 2- and 3-pentanone, 2- and 3-hexanone and 2- and 3-heptanone. This effect is particularly pronounced for the first two pairs. On the other hand, in the case of linear C_7 ketones, the difference in ΔM_e values for 2-heptanone-2 and 3-heptanone is significantly smaller than that for C_6 ketones and is similar to that for C_5 ketones. This leads to the conclusion that chains longer than C_6 causes a considerable steric hindrance (Table I).

Solutes are listed in Table I by increasing boiling point. However, comparing V_g , k' or I

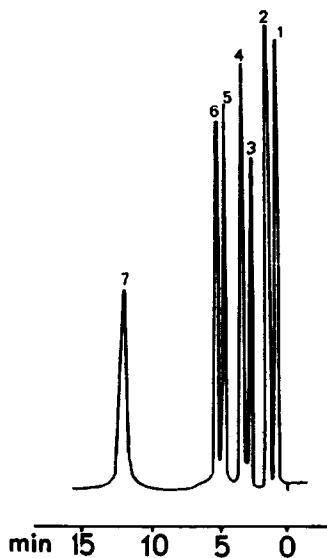


Fig. 3. Separation of mixture of cyclic and aliphatic ethers. Packing as in Fig. 1. Column temperature, 156.7°C ; carrier gas flow-rate, 18.8 ml/min. Peaks: 1 = furan; 2 = thiophene; 3 = diethyl ether; 4 = 3,4-dihydro-2H-pirane; 5 = methyl butyl ether; 6 = dipropyl ether; 7 = tetrahydrofuran.

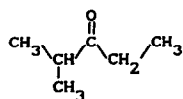
values of both packings studied results in a different sequence that depends on solute structure and electron-donor properties. For this reason compounds with lower boiling points are frequently eluted after compounds with higher boiling points.

This also holds true for branched ketones (e.g. 2-methyl-3-pentanone is eluted before 4-methyl-2-pentanone). Introducing methyl substituents into the hydrocarbon chain, because of the increased steric effect, reduces the degree of interaction between the carbonyl group and the metal. This is illustrated by a pair of ketones, 3-methyl-2-butanone and 3,3-dimethyl-2-butanone, for which the ΔM_e values are 30.7 and 20.1 for $\text{Cu}(\text{acac})_2$ and 80.9 and 61.1 for $\text{Ni}(\text{acac})_2$, respectively. Moreover, it was found out that the greater the distance between the substituent and the $>\text{C}=\text{O}$ group, the weaker its influence (e.g. 4-methyl-2-hexanone interacts more weakly with the packing than 5-methyl-2-hexanone). By comparing the values of ΔM_e for two isomers, 2-methyl-3-pentanone (a) and 4-methyl-2-pentanone (b):

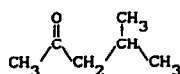
TABLE I

RETENTION PARAMETERS: SPECIFIC RETENTION VOLUMES (V_g), CAPACITY FACTOR (k'), RETENTION INDICES (I), MOLECULAR RETENTION INDICES (ΔM_e) AND MOLAR REFRACTION FOR LINEAR, BRANCHED AND UNSATURATED KETONES

	Packing								Molar refraction (R_M)
	Cu(acac) ₂				Ni(acac) ₂				
	V_g (cm ³ /g)	k'	I	ΔM_e	V_g (cm ³ /g)	k'	I	ΔM_e	
Propanone	3.30	1.92	753	49.5	9.24	4.49	1064	93.2	16.18
2-Butanone	4.39	2.56	815	44.2	11.20	5.44	1109	85.4	21.30
3-Buten-2-one	4.64	2.70	826	47.8	11.49	5.88	1115	88.2	20.69
3-Methyl-2-butanone	4.47	2.61	819	30.7	15.09	7.33	1177	80.9	25.24
3-Pentanone	4.83	2.82	835	33.0	10.47	5.08	1094	69.3	25.21
2-Pentanone	5.54	3.23	864	37.1	15.52	7.54	1183	81.8	25.33
3,3-Dimethyl-2-butanone	5.02	2.92	843	20.1	13.15	6.11	1135	61.1	30.07
2-Methyl-3-pentanone	5.62	3.27	867	23.4	12.58	6.39	1145	62.4	29.74
4-Methyl-2-pentanone	6.51	3.79	900	28.1	19.14	9.30	1269	79.8	30.08
3-Hexanone	6.68	3.89	905	28.8	15.31	7.41	1180	67.4	29.80
2-Hexanone	8.20	4.78	946	34.5	24.72	12.02	1349	91.1	30.01
4-Methyl-3-penten-2-one	6.38	3.72	895	29.4	31.79	11.45	1428	104.1	30.08
Cyclopentanone	11.58	6.75	1017	60.5	35.59	17.29	1482	125.7	23.12
4-Methyl-2-hexanone	10.19	5.94	981	26.8	21.13	10.27	1309	71.4	–
4-Heptanone	9.25	5.39	988	24.1	22.68	11.02	1327	73.9	34.40
5-Methyl-2-hexanone	11.72	6.82	1020	30.1	37.64	18.29	1506	99.1	31.60
3-Heptanone	10.05	5.86	1002	27.8	24.43	11.87	1346	76.6	34.47
2-Heptanone	10.71	6.24	1047	28.3	31.06	15.09	1417	86.3	34.18
Cyclohexanone	14.58	8.50	1066	53.4	51.64	25.09	1624	131.6	27.85
5-Methyl-3-heptanone	12.86	7.44	1039	19.5	32.13	15.66	1434	74.9	38.94
2-Methylcyclohexanone	16.11	9.39	1088	42.4	54.82	26.64	1648	120.9	32.48
3-Methyl-2-heptanone	15.34	8.94	1077	24.8	49.22	23.81	1605	98.9	39.24
2,6-Dimethyl-4-heptanone	15.19	9.85	1075	10.5	31.33	15.22	1421	59.1	41.85
3-Methylcyclohexanone	18.04	10.22	1111	46.6	58.05	28.21	1670	124.0	32.66
4-Methylcyclohexanone	18.89	11.02	1121	47.1	62.51	30.38	1699	128.1	32.69



(a)



(b)

one can see that they indeed reflect the abilities of particular adsorbates to interact with the packings. In the case of 2-methyl-3-pentanone (a) two factors contributed to the inhibition of the contact between the carbonyl group and metal. The carbonyl group is centrally located, while the methyl substituent is in the close vicinity. In the case of compound (B), the carbonyl group and the substituent take extreme

positions, which is reflected in the values of retention parameters.

If an additional function (such as an unsaturated bond) is introduced into the ketone molecule, estimation of the influence of particular parameters on retention becomes more difficult and complicated. As follows from Table I, the presence of an unsaturated bond causes an increase in specific interactions. The strongest interactions were observed for cyclic ketones, as shown by high values of molecular indices of retention. In the case of linear ketones, the interactions become weaker with increase in the length of carbon chain, the strongest being observed (taking into account ΔM_e) for 2-pro-

panone. On the basis of the data obtained for both studied packings, it was found that the packing modified with nickel(II) acetylacetonate interacts more strongly with nucleophilic adsorbates than the packing modified with $\text{Cu}(\text{acac})_2$. The dependence of $\log k'$ on molar refraction, R_M , shown in Fig. 4 (which is a function of the molecule polarizability), is linear, and the distance between the straight lines for both packings under study points to a relative increase in specific interactions when going from $\text{Cu}(\text{acac})_2$ to $\text{Ni}(\text{acac})_2$. For the sake of comparison, the series of straight lines for *n*-alkanes ($\text{C}_5\text{--C}_9$) is presented.

Nitroalkanes

A nitrogen atom in the nitric group has an sp^2 hybridization, yielding three co-planar σ bonds (one C–N and two N–O bonds). The remaining two p electrons at the nitrogen atom and individual electrons at two oxygen atoms form a π bond. Owing to such an electron distribution in the nitric group, the nitrogen atom is positively charged, while the oxygen atoms are negatively charged, according to the scheme given below:



Because of the polar character of the nitric group, nitroalkenes are characterized by high

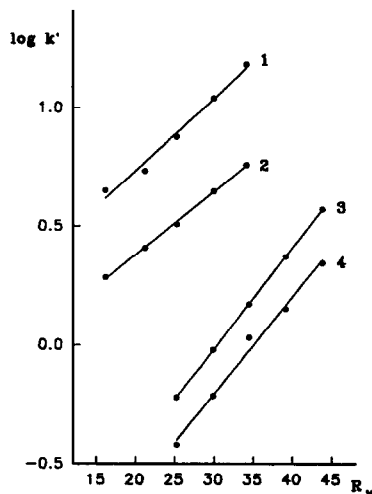


Fig. 4. The dependence of $\log k'$ on molar refraction for *n*-ketones $\text{C}_3\text{--C}_7$ (lines 1 and 2) and *n*-alkanes $\text{C}_5\text{--C}_9$ (lines 3 and 4). Lines 1 and 4 are for $\text{Ni}(\text{acac})_2$ packing, and lines 2 and 3 are for $\text{Cu}(\text{acac})_2$ packing.

dielectric constant ϵ (in the range 25–35) and high dipole moments of about 3.6 D, which is reflected by long retention times. The results obtained are presented in Table II.

The high electron density on the protruding part of the molecule provides favourable conditions for electron donor–acceptor interactions. This is shown by high values of retention parameters, and in particular in the values of the

TABLE II

RETENTION PARAMETERS AND DIELECTRIC CONSTANTS (ϵ) FOR NITROALKANES

Solute	ϵ	Packing							
		$\text{Cu}(\text{acac})_2$				$\text{Ni}(\text{acac})_2$			
		V_g (cm^3/g)	k'	I	ΔM_e	V_g (cm^3/g)	k'	I	ΔM_e
Nitromethane	35.87	9.31	1.99	781	50.5	23.72	10.4	1242	115.1
Nitroethane	28.06	10.45	2.24	806	39.9	29.15	12.77	1301	109.4
1-Nitropropane	23.24	12.97	2.78	852	32.4	36.15	15.84	1365	104.3
2-Nitropropane	25.52	10.48	2.25	807	26.1	31.32	13.72	1322	98.3
1-Nitrobutane	–	18.68	4.01	903	29.3	47.55	20.83	1452	102.5
2-Nitrobutane	–	14.73	3.16	880	22.3	39.37	17.25	1392	94.1
1-Nitropentane	–	24.19	5.15	984	22.8	63.43	27.80	1547	101.8
2-Nitropentane	–	19.54	4.16	938	16.4	48.12	21.09	1456	89.1

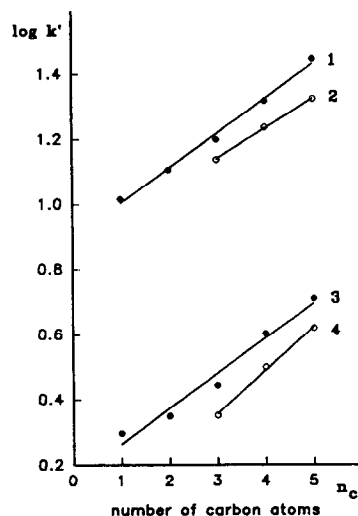


Fig. 5. Log k' of nitroalkanes vs. number of carbon atoms. Lines 1 and 2 are for $\text{Ni}(\text{acac})_2$, and lines 3 and 4 are for $\text{Cu}(\text{acac})_2$. ● = 1-Nitroalkanes (C_1 – C_5); ○ = 2-nitroalkanes (C_3 – C_5).

molecular retention index. The order of elution is affected by the position of the nitro group in the adsorbate molecule; thus the isomer with the functional group located inside the molecule is eluted first, *i.e.* 2-nitropropane before 1-nitropropane, or 2-nitrobutane before 1-nitrobutane, etc.

As for ketones, the strongest interactions were observed for small adsorbate molecules, and

they tended to decrease from nitromethane to nitropropane or, in other words, with increasing length of carbon chain.

The k' values increased in the direction from $\text{Cu}(\text{acac})_2$ to $\text{Ni}(\text{acac})_2$, on average five-fold, while the values of the retention indices changed by 400–500 retention index units. Examples of chromatograms presented in Fig. 2, obtained for mixtures of nitropropane and nitrobutane isomers, show that the selectivity of acetylacetonate-containing packing is high enough to obtain a complete separation of isomers in a very short period of time. The separation is better than that obtained on packings containing SE-30, polyethylene glycol adipate (PEGA) or Porapak R [18]. The dependence of log k' on the amount of carbon atoms for particular nitroalkanes is shown in Fig. 5.

Ethers

Aliphatic and cyclic ethers belong to a class of monodentate ligands, owing to the basic nature of oxygen, with two electron pairs. There are known stable complexes of ethers (ethyl ether, furan) with boron(III) and aluminium(III) fluorides as well as magnesium(II), tin(II) and titanium(IV) halides [19]. Examples of ethers used in the present paper as adsorbates are listed in Table III.

The results obtained enabled us to establish a

TABLE III
RETENTION PARAMETERS FOR LINEAR AND CYCLIC ETHERS

Solute	Packing							
	$\text{Cu}(\text{acac})_2$				$\text{Ni}(\text{acac})_2$			
	V_g (cm^3/g)	k'	I	ΔM_c	V_g (cm^3/g)	k'	I	ΔM_c
Diethyl ether	3.75	0.80	588	10.36	10.90	8.73	1011	69.79
Butyl methyl ether	6.35	1.35	702	12.32	18.80	15.06	1119	70.83
Dipropyl ether	7.52	1.60	735	2.92	2.92	22.36	1153	61.56
Dibutyl ether	18.69	3.98	929	2.12	28.77	8.38	1079	51.27
Diisoamyl ether	34.52	7.36	1058	-7.86	31.58	25.30	1212	13.72
Diamyl ether	46.97	10.01	1123	1.24	45.08	36.12	1274	22.41
Furan	3.26	0.69	557	12.06	1.29	1.03	585	15.98
Tetrahydrofuran	47.50	10.13	1125	87.69	45.45	36.41	1280	103.50
3,4-Dihydro-2H-pirane	6.30	1.28	690	14.67	9.30	7.45	980	55.36

few relationships between the retention parameters and the structure of ethers. Because the angle C–O–C in aliphatic ethers is 110°, free access to a lone electron pair will be the more difficult the longer are the carbon chains connected to oxygen. This will undoubtedly affect the value of specific interactions, which will decrease with increasing (or branching) of the hydrocarbon chains. As can be seen in Table III, the ΔM_e values for isoamyl ether are negative for $\text{Cu}(\text{acac})_2$ and low (13.7) for $\text{Ni}(\text{acac})_2$. This testifies to a significant influence of the steric effect on specific interactions between ethers and a metal complex chemically bonded to SiO_2 .

The strength of the influence of electron pairs at the oxygen atom on specific interactions can be seen by comparing the values of retention parameters for furan and tetrahydrofuran. In the case of the former, oxygen, by assuming the sp^2 hybridization, becomes a donor of two electrons to the aromatic sextet. The presence of these electrons in this sextet implies that they will be partly distributed all over the ring, as a result of which the ring will have a negative charge, while the oxygen will assume a partial positive charge. Therefore, specific interactions with a planar ring of aromatic compounds will be much more dependent on the steric effects than it is in the case of tetrahydrofuran, in which electron pairs are located on oxygen. The chromatogram of a mixture of linear and cyclic ethers, shown in Fig. 3, is characterized by sharp and symmetric peaks, which is indicative of a large degree of homogeneity of the packing surface.

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