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Short communication

Nickel(II) chelates of some tetradentate Schiff bases as stationary phases for gas chromatography

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Abstract

Nickel(II) chelates of four tetradentate Schiff bases, bis(acetylacetone)ethylenediimine (H_2AA_2en), bis(acetylacetone)propylenediimine (H_2AA_2pn), bis(acetylacetone)-*dl*-stilbenediimine (*dl*-H_2AA_2S) and bis(acetylacetone)-*meso*-stilbenediimine (*meso*-H_2AA_2S), were examined as stationary phases for gas chromatography. The complexes were coated with 3% OV-101 in the range 3–5%. The phases were packed in stainless-steel columns (3 m × 3 mm I.D.) and were examined for the separation of saturated aromatic hydrocarbons, heteroaromatic aldehydes, ketones, amines and alcohols. Kováts retention indices of alcohols, aldehydes and ketones increased with improvement in the separation when using mixed stationary phases, particularly 3% OV-101–5% *dl*-AA_2SNi compared with 3% OV-101.

1. Introduction

A number of attempts have been made to modify the stationary phases in gas chromatographic (GC) columns with inorganic electrolytes and metal chelate compounds. The copper, nickel, palladium and platinum chelates of N-dodecylsalicylaldimines, nickel, palladium and platinum chelates of *n*-octylglyoximes [1], beryllium, aluminium and nickel chelates of *n*-nonyl β-diketones [2], transition metal chelates of phthalocyanine [3], 1,10-phenanthroline and 2,2′-bipyridine [4], nickel chelates of bis[3-(trifluoroacetyl)-1R-camphorate] [5], 2,2′-biphenylenephosphoric acids [6], triphenylphosphine complexes of rhodium(I) and ruthenium(II) [7] and copper and nickel chelates of tetradentate Schiff bases [8–10] have been examined as stationary phases for GC individually or together with squalane or silicone oils. Wasiak [11] reported chemically bonded chelates as selective complexing sorbents for GC. The stationary phases have been evaluated for the separation of different organic compounds including hydrocarbons, alcohols and amines. Their relative retention and thermodynamic functions have been calculated [8,9,12]. Nickel chelates have also been used in kinetic studies of enantiomerization [5], enantiomer separations [13,14] and temperature-dependent reversal of elution sequences in complexation GC on chiral phases [15]. Some useful separations have been reported using Schiff base metal chelates as stationary phases with squalane [10], but in this work four tetradentate Schiff bases, bis(acetylacetone)ethylenediimine (H_2AA_2en), bis(acetylacetone)propy-

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lenediimine (H_2AA_2pn), bis(acetylacetone)-*dl*-stilbenediimine (*dl*-H_2AA_2S) and bis(acetylacetone)-*meso*-stilbenediimine (*meso*-H_2AA_2S), were investigated separately and as mixed stationary phase with OV-101. Their resolution was compared with 3% OV-101 on Chromosorb G/NAW (60–80 mesh). The nickel chelates of the ligands *dl*-H_2AA_2S and *meso*-H_2AA_2S containing phenyl groups were considered promising because their higher thermal stability was more suited to GC [16].

2. Experimental

The reagents H_2AA_2en, H_2AA_2Pn, *dl*-H_2AA_2S and *meso*-H_2AA_2S and their nickel(II) chelates (Fig. 1) were prepared as reported [17,18], by heating acetylacetone with the appropriate 1,2-diamine in a 2:1 molar ratio in ethanol. An equimolar solution (0.01 *M*) of nickel acetate and the reagent was warmed together to obtain nickel chelates.

A Hitachi Model 163 gas chromatograph connected with a flame ionization detector and a Model 056 recorder was used.

An appropriate amount of the nickel chelates, individually or together with OV-101 (BDH), dissolved in chloroform, was added by thoroughly mixing with the appropriate amount of Chromosorb G/NAW (60–80 mesh) (Merck). The solvent was removed at reduced pressure on a Rotavapor (Buchi). For AA_2enNi and AA_2PnNi, ethanol was used as a solvent. The dried materials were packed in columns (3 m × 3 mm I.D.) using the usual procedure. Each of the columns was conditioned at 130°C for at least 24 h before use. Injections (10–15) of different compounds were made on each of the columns, before measuring the analytical responses.

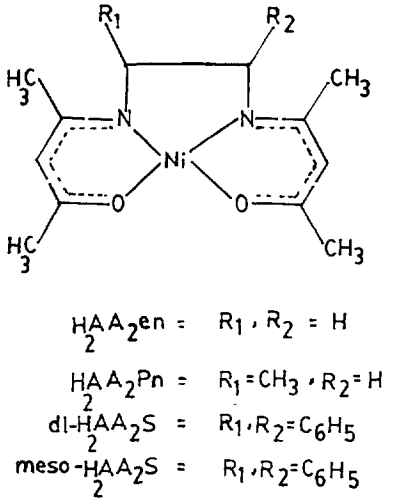

Fig. 1. Structure of metal chelates.

Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out on a Shimadzu TG30 thermal analyser in the temperature range from room temperature to 500°C at a heating rate of 10°C/min and with a nitrogen flow-rate 45 cm^3/min. Sample amounts of 7–15 mg were used.

3. Results and discussion

The nickel complex *meso*-AA_2SNi, having the highest thermal stability [10], was selected for coating at 3%, 5% and 10% on Chromosorb G/NAW (60–80 mesh size). However, difficulties were encountered in coating 10% uniformly on the solid support, some crystals of metal chelates being visible in the coated material. When DTA and TG were applied to each of the materials, a decrease in mass started at 220°C and losses of 3% and 5% occurred up to 300°C. However, with the material with 10% coating, a loss of 8% was observed within the same temperature range.

Each of the phases after packing and conditioning was examined for elution and GC separation of saturated and aromatic hydrocarbons, heteroaromatic aldehydes, ketones and alcohols. Their chromatographic characteristics were compared with those for an uncoated Chromosorb G/NAW (60–80 mesh) solid support packed in the same column. It was observed that the retention times of alcohols and heteroaromatics increased and tailing of the peaks decreased in the order (1) Chromosorb G/NAW (60–80 mesh size) (2) 3%, (3) 5% and (4) 10% *meso*-AA_2SNi on Chromosorb G/NAW

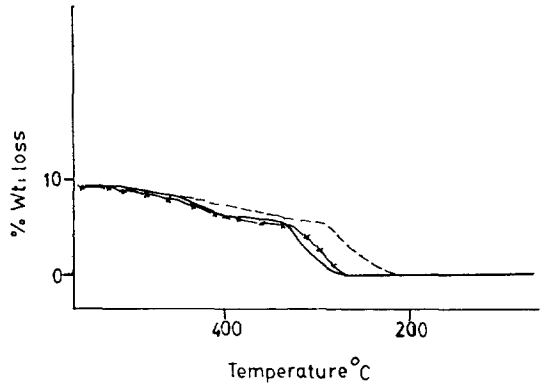

Fig. 2. TG of (– – –) 3% OV-101–5% AA_2PnNi (×) *dl*-AA_2SNi and (———) 3% OV-101–5% *meso*-AA_2SNi on Chromosorb G/NAW (60–80 mesh). Heating rate, 10°C/min; nitrogen flow-rate, 45 ml/min.

(60–80 mesh). The retention times of *n*-pentanol on columns 1, 2, 3 and 4 were 2.28, 3.0, 3.36 and 3.48 min, respectively. However, the columns did not seem to serve a useful purpose for the separation of organic compounds. Mixed stationary phases were therefore considered.

The thermoanalytical studies of mixed phases of 5% nickel chelates plus 3% OV-101 on Chromosorb indicated that the decrease in mass for AA_2PnNi, AA_2enNi, *dl*-AA_2SNi and *meso*-AA_2SNi started from 215, 220, 265 and 270°C, respectively, and losses of ca. 5%, corresponding to nickel chelates occurred, up to 270, 285, 325 and 335°C, respectively. This was followed by a secondary loss of 3% in the temperature range 380–500°C, corresponding to OV-101 (Fig. 2).

After the necessary conditioning, each of the columns was injected with saturated long-chain hydrocarbons and the logarithm of adjusted retention time with *n*-hexane was plotted versus carbon number; a linear correlation was obtained (Fig. 3). This was followed by the injection of different aromatic hydrocarbons, alcohols, aldehydes, ketones and heteroaromatics. It was observed that the retention times, theoretical plate numbers and Kováts retention indices on mixed stationary phases increased in comparison with 3% OV-101 (Tables 1 and 2).

The utility of the mixed stationary phases for

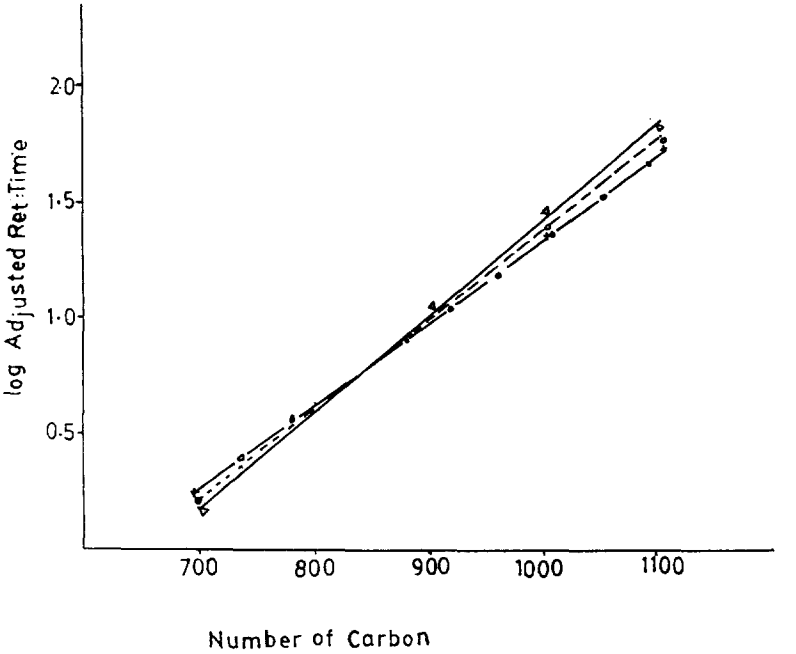

Fig. 3. Variation of log (adjusted retention time) with carbon number. ▽ = 3% OV-101, ○ = 3% OV-101–5% *meso*-AA_2SNi and × = 3% OV-101–5% *dl*-AA_2SNi on Chromosorb G/NAW (60–80 mesh). Column, 3 m × 3 mm I.D.; column temperature, 80°C; injection port temperature, 100°C; nitrogen flow-rate, 12 ml/min. X-axis shows number of carbon ×100.

Table 1
Total number of theoretical plates (n) on each phase packed in a 3 m × 3 mm I.D. column

Compound	3% OV-101	3% OV-101–5% AA_2PnNi	3% OV-101–5% AA_2enNi	3% OV-101–5% *meso*-AA_2SNi	3% OV-101–*dl*-AA_2SNi
Pyridine	417	429	529	576	981
2-Picoline	655	704	860	913	1216
3-Picoline	676	882	981	1239	1354
2,6-Dimethylpyridine	690	986	1244	1745	1897
Toluene	661	711	700	900	1337
Paraldehyde	601	892	952	1024	1273
Pentanol	437	1024	1273	1422	1554
Hexanol	601	2136	2885	3076	3317

the separation of aromatic hydrocarbons, heteroaromatics and alcohols was examined. The separation of alcohols showed pronounced tailing on 3% OV-101, but using mixed-phase columns some improvement in peak shape was observed. The optimum separation was obtained using 3% OV-101–5% *dl*-AA_2SNi (Fig. 4). Similarly, when a mixture of pyridine, 2-picoline, 3-picoline and 2,6-dimethylpyridine was injected on to the column packed with 3% OV-101 and mixed stationary phases, better peak shapes were obtained on the latter and 3-picoline and 2,6-dimethylpyridine, which co-eluted on 3% OV-101, were separated on 3% OV-101–5% *dl*-AA_2SNi (Fig. 5). The resolution factors (R_s) calculated for the separation of 1,2-xylene and 1,3-xylene on columns (5) 3% OV-101; 3% OV-101–5% (6) AA_2PnNi, (7) AA_2enNi, (8) *meso*-AA_2SNi and (9) *dl*-AA_2SNi were 1.52, 1.62, 1.63, 1.64 and 1.71, respectively, using the same operating conditions. The improvement in resolution may be due to adsorption on planar nickel chelates due to electron donor–acceptor complexation [8–10].

4. Conclusion

Four nickel chelates, AA_2PnNi, AA_2enNi, *meso*-AA_2SNi and *dl*-AA_2SNi, were examined as stationary phases individually and as mixed phases with 3% OV-101 on Chromosorb G/NAW (60–80 mesh). The mixed stationary phases showed some promise for the separation of aromatic hydrocarbons, alcohols and heteroaromatics compared with 3% OV-101. The

Table 2
Comparison of Kováts retention indices on different stationary phases packed in a 3 m × 3 mm I.D. column

Compound	3% OV-101	3% OV-101–5% AA_2PnNi	3% OV-101–5% AA_2enNi	3% OV-101–5% *meso*-AA_2SNi	3% OV-101–*dl*-AA_2SNi
1-Pentanol	770	790	814	805	820
1-Hexanol	875	880	890	900	910
1-Heptanol	970	980	986	990	1015
2-Octanol	995	1005	1008	1012	1030
Aniline	940	978	975	988	1012
Toulene	745	760	770	775	790
p-Xylene	844	876	870	880	890
Benzaldehyde	926	950	948	955	976
Methyl isobutyl ketone	710	720	720	730	742
Cyclohexanone	870	890	885	893	912

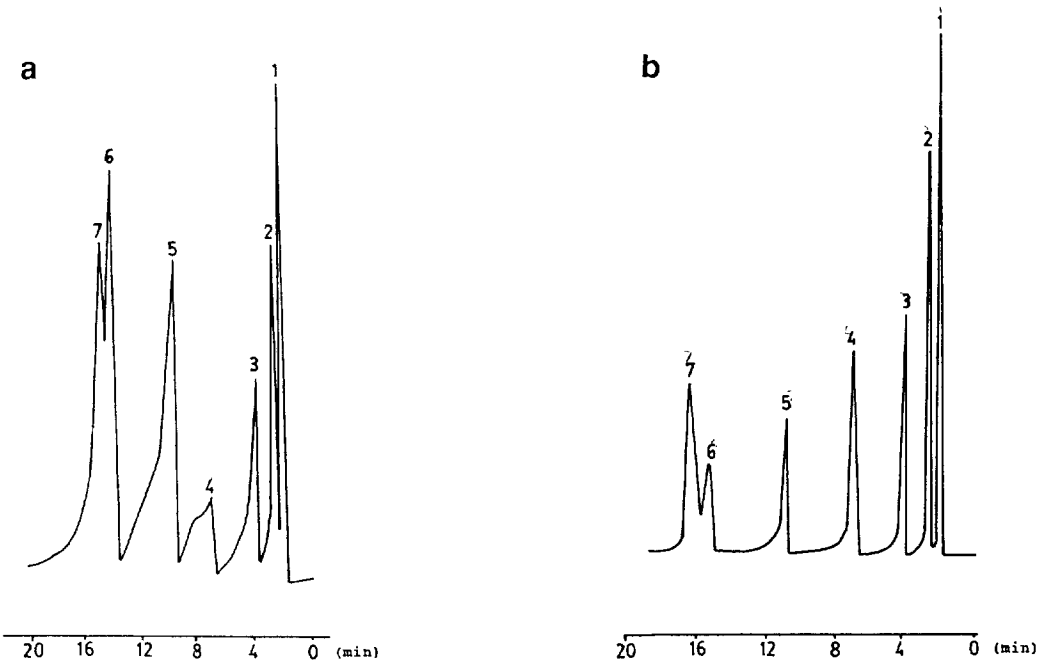

Fig. 4. Separation of (1) ethanol, (2) *n*-propanol, (3) *n*-butanol, (4) *n*-pentanol, (5) *n*-hexanol, (6) *n*-heptanol and (7) octan-2-ol. Column, 3 m × 3 mm I.D., packed with (a) 3% OV-101 and (b) 3% OV-101–5% *dl*-AA_2SNi, on Chromosorb G/NAW (60–80 mesh). Column temperature, 80°C for 4.40 min, then programmed at 4°C/min to 120°C; injection port temperature, 130°C; nitrogen flow-rate, 12 ml/min; flame ionization detection.

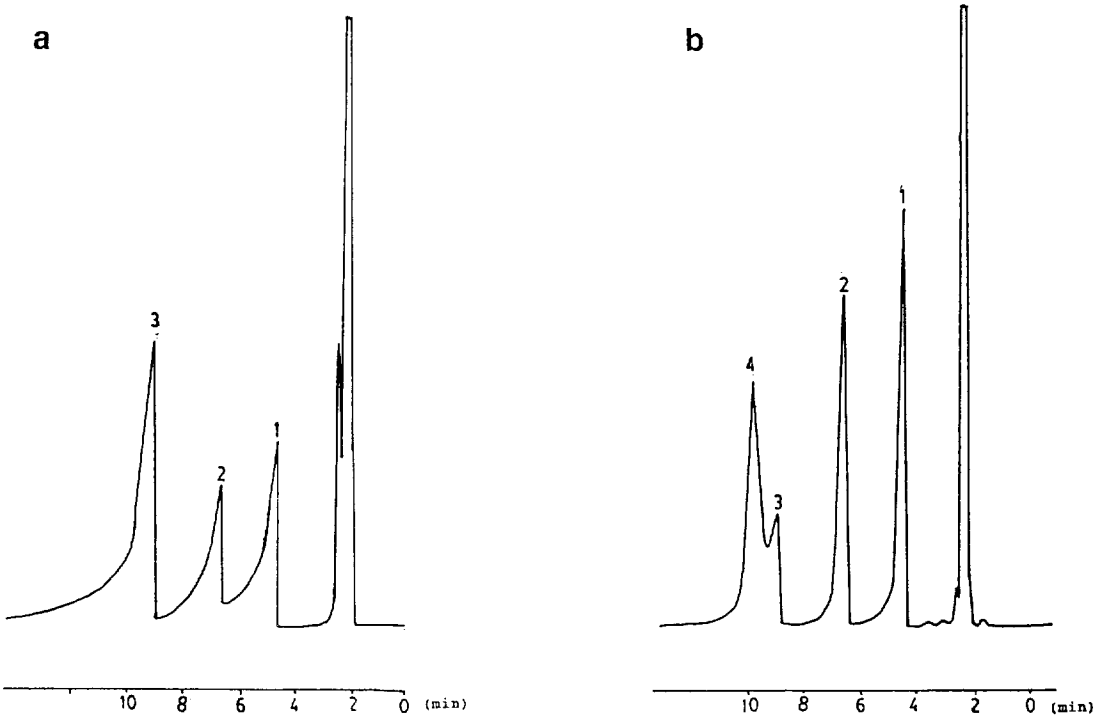

Fig. 5. Separation of (1) pyridine, (2) 2-picoline, (3) 3-picoline and (4) 2,6-dimethylpyridine. Columns as in Fig. 4. Column temperature, 80°C; injection port temperature, 100°C; nitrogen flow-rate, 12 ml/min; flame ionization detection. In (a) peaks 3 and 4 overlap.

mixed stationary phase 3% OV-101–5% *dl*-AA_2SNi on Chromosorb G/NAW (60–80) gave the best results.

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