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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF METAL–TETRAPHENYLPORPHYRIN CHELATES ON A C_{18}-BONDED STATIONARY PHASE*

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SUMMARY

The retention behaviour of meso-tetraphenylporphyrin (H_2TPP) and its metal chelates with Mg(II), V(IV), Mn(III), Fe(III), Ni(II), Cu(II), Zn(II), Pd(II) and Cd(II) has been investigated on a C_{18}-bonded stationary phase. The retention of the chelate depends on its central metal ion, increasing in the order Zn(II) < V(IV) < Fe(III) < Mg(II) ≈ Cd(II) ≈ (H_2TPP) < Ni(II) ≈ Pd(II) < Cu(II) < Mn(III), although some irregularities are found when using different solvents used. This retention sequence is approximately the reverse of those observed on silica gel and cellulose. The chelates of Mg(II), V(IV), Ni(II), Cu(II), Zn(II) and Pd(II) have been separated in *ca.* 8 min using a LiChrosorb RP-18 column (250 × 4 mm I.D.) with acetone–acetonitrile (40:60) as the mobile phase at a flow-rate of 1 ml/min.

INTRODUCTION

Although many data on the high-performance liquid chromatography (HPLC) of a wide variety of compounds have been reported, metal chelates have rarely been dealt with. HPLC studies of metal chelates have commonly employed chelating ligands, such as β-diketones[1,2], dithizone[3] and diethyldithiocarbamate[4]. The chromatographic behaviour of a metal chelate generally depends on the properties of both the ligand and the metal ion, in addition to the properties of the stationary and mobile phases. Systematic studies should involve (1) the chelates of various types of chelating ligand with a given metal ion and also (2) the chelates of one of a series of ligands with different metal ions. A series of β-diketones and their metal(II, III) chelates were investigated by adsorption[5] and gel permeation[6–9] chromatography to determine the effects of ligand, metal ion, stationary support and mobile phase solvent.

Metalloporphyrins were adopted as the metal chelates of interest in our study, because of (1) their characteristic structure, including a planar N,N,N,N-tetradentate

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ligand, (2) their remarkably high stability and (3) the lack of published data obtained by modern chromatographic methods such as HPLC.

In recent years HPLC has been applied effectively to the analysis of free base carboxylic porphyrins[10–12] and their methyl esters[13–15]. HPLC data are available for several kinds of metalloporphyrins, such as copper chelates of porphyrin methyl esters[15], zinc protophorphyrin[16], nickel and vanadyl chelates of petroporphyrins[17] and haeme a, acetyl haeme a and their methyl esters (ferroporphyrins)[18] and also chlorophylls (magnesium chelates of chlorins)[19].

In previous work[20], free base meso-tetraphenylporphyrin (H_2TPP) and several metal TPP chelates were investigated by high-performance thin-layer chromatography (HPTLC) with different stationary phases, such as silica gel, cellulose and alkyl (C_8 or C_{18}) bonded silica. This paper describes the HPLC behaviour of H_2TPP and its metal chelates with nine metal ions on a C_{18}-bonded stationary phase.

EXPERIMENTAL

Materials

The free base form of the porphyrin (H_2TPP; see Fig. 1a) was prepared by the method of Adler *et al.*[21] and purified according to the method of Barnett *et al.*[22]. The TPP chelates of Mg(II), V(IV), Mn(III), Fe(III), Ni(II), Cu(II), Zn(II), Pd(II) and Cd(II) were prepared by the reaction of H_2TPP and the chloride of corresponding metal [vanadyl dichloride in the case of V(IV) chelate] in refluxing N,N-dimethylformamide and were then purified by column chromatography on alumina with chloroform[23]. Identification of the products was carried out by C, H, N and Cl analysis and also by comparing their visible spectra with those of pure compounds[24–26]. The chelates of divalent metals, such as Mg(II), Ni(II), Cu(II), Zn(II), Pd(II) and Cd(II), were identified as the compounds in the form of 1:1 complexes of metal ion and TPP, as illustrated in Fig. 1b [abbreviated to Mg(TPP), Ni(TPP), Cu(TPP), Zn(TPP), Pd(TPP) and Cd(TPP), respectively]. The chelates of Mn(III) and Fe(III) correspond to the 1:1:1 complexes of metal ion, TPP and axially ligated chloro anion[25] [abbreviated to Mn(TPP)Cl and Fe(TPP)Cl, respectively]. The V(IV) chelate was identified as a 1:1 complex of oxovanadium ion and TPP [abbreviated to VO(TPP)][26].

The solvents used as the mobile phases were distilled prior to use.

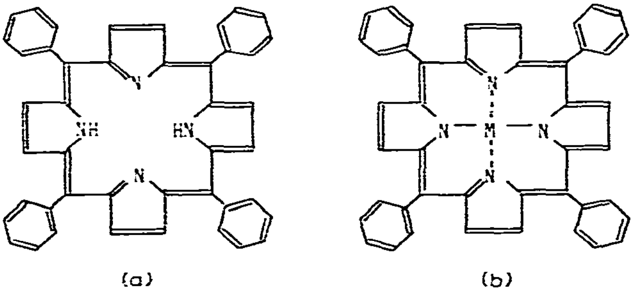

Fig. 1. Structures of (a) H_2TPP and (b) its metal(II) chelates.

HPTLC plates

Three kinds of pre-coated HPTLC plates were purchased from Merck (Darmstadt, G.F.R.): RP-18 F_{254s} (Merck product No. 13724), silica gel 60 (No. 5631) and cellulose (No. 5787). Each plate had a chromatographic layer 10 × 10 cm wide and 200 μm thick. The silica gel plate was activated prior to use by heating at 110°C for 1 h, and then cooling in a silica gel desiccator for 2 h. The other plates were not pre-treated.

HPLC system

A JASCO Model FLC-350 high-performance liquid chromatograph (Japan Spectroscopic, Tokyo, Japan) was used with a Merck LiChrosorb RP-18 Hibar column (Merck product No. 50394; particle size 7 μm; 250 × 4 mm I.D.). A Hitachi Model EPU-2 spectrophotometer (Hitachi, Tokyo, Japan) was used as a detector with a micro-flow-through cell (volume 8-μl; path length 10 mm).

Procedure

HPTLC was carried out in a thermostatically controlled room at 25°C. The sample solution of H_2TPP or metal TPP chelate was prepared in chloroform at a concentration of *ca.* 1 mg/ml, except for Ni(TPP), which was prepared at a concentration below 0.5 mg/ml because of its low solubility. A 0.5-μl portion of each sample solution was spotted on to an HPTLC plate. The chromatogram was developed in a sandwich chamber until the solvent front had run 75 mm from the starting point. Every spot on the chromatogram was easily detected owing to the characteristic intense colour of each compound in daylight.

HPLC experiments were carried out at room temperature (24–27°C). The sample solution of H_2TPP or its metal chelate was prepared in benzene. The TPP compounds other than Mn(TPP)Cl show characteristic sharp absorptions in the region between *ca.* 416 (Ni chelate in benzene) and 434 nm (Cd chelate) with molar absorptivities larger than 10^5 l mol^{-1} cm^{-1}, which is called the Soret band[24–26]. A wavelength of 420 nm was selected conveniently for the detection of the TPP compounds, except for Mn(TPP)Cl (477 nm) (the Soret absorption maximum wavelength[25]), with a spectral bandpass of 2 nm in the detection system. The chromatograms were obtained with a sample injection volume of 10 μl and a mobile phase flow-rate of 1 ml/min, unless specified otherwise.

RESULTS AND DISCUSSION

Chromatography of metal–TPP chelates by HPTLC —comparison of C_{18}-bonded phase with silica gel and cellulose

HPTLC data were available for the TPP compounds other than Pd(TPP) and VO(TPP) on different stationary phases[20]. The mobilities of these two compounds were measured in the present work.

On silica gel, the TPP compounds can be classified with respect to mobility into the following three groups: (1) Cu(TPP), Pd(TPP) and Ni(TPP)· (2) Mg(TPP), Cd(TPP), VO(TPP), Zn(TPP) and H_2TPP; and (3) Mn(TPP)Cl and Fe(TPP)Cl. The compounds assigned to the first group showed high mobility on silica gel even with weak solvents, such as carbon tetrachloride and carbon disulphide. In contrast, the latter two metal(III)–TPP chelates showed very low mobilities even with a strong solvent, such as dichloromethane, with which other compounds migrated up to the points of R_F *ca.* 0.9 or more. The migration sequence, in order of increasing R_F values, observed for the TPP compounds on silica gel is Mn(TPP)Cl $\approx$ Fe(TPP)Cl $<$ Zn(TPP) $\approx$ VO(TPP) $\approx$ H_2TPP $\approx$ Cd(TPP) $\approx$ Mg(TPP) $<$ Pd(TPP) $\approx$ Ni(TPP) $\approx$ Cu(TPP).

The HPTLC separation of these three groups of compounds was easily achieved with an appropriate developing solvent, *e.g.*, *m*-xylene. However, intra-group separation of the compounds was unsuccessful even with a variety of developers.

On cellulose the migration sequence observed for the TPP compounds with non-polar solvents, such as cyclohexane and carbon tetrachloride, is Mg(TPP) $\approx$ Mn(TPP)Cl $<$ Zn(TPP) $\approx$ VO(TPP) $\approx$ Fe(TPP)Cl $<$ H_2TPP $\approx$ Cd(TPP) $\approx$ Pd(TPP) $<$ Ni(TPP) $\approx$ Cu(TPP). Every compound gave such diffuse, tailing spots on the chromatograms that successful separation could not be achieved despite the considerable differences in the R_F values.

On a C_{18}-bonded stationary phase the migration sequence observed for the TPP compounds other than the Fe(III) and Mn(III) chelates is almost independent of the developing solvent used, as follows: Cu(TPP) $<$ Pd(TPP) $\approx$ Ni(TPP) $<$ Mg(TPP) $\approx$ Cd(TPP) $\approx$ H_2TPP $<$ VO(TPP) $<$ Zn(TPP). The mobility of Fe(TPP)Cl and Mn(TPP)Cl depended considerably on the solvent used, compared with the other compounds. With alcohols and also acetonitrile these two metal(III) chelates showed high mobilities relative to others, with the following order of R_F values: H_2TPP $<$ Fe(TPP)Cl $<$ Mn(TPP)Cl. With acetone Fe(TPP)Cl showed a higher R_F value than H_2TPP, whereas Mn(TPP)Cl showed a lower R_F value than Ni(TPP). With N,N-dimethylformamide both metal(III) chelates showed low mobilities, with the order as Mn(TPP)Cl $\leqslant$ Cu(TPP) $\sim$ Fe(TPP)Cl $<$ Ni(TPP). With alcohols both Fe(III) and Mn(III) chelates migrated with slight tailing, and most other compounds showed considerable tailing. In contrast, with acetone all TPP compounds gave tail-free spots.

Fig. 2 shows an example of the relationship between the mobility (R_F) of TPP

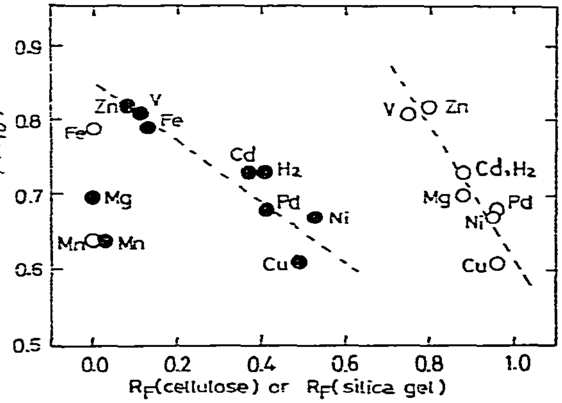

Fig. 2. HPTLC R_F values for metal–TPP chelate in the C_{18}-bonded phase–acetone system plotted against those in the cellulose–cyclohexane (●) and the silica gel–benzene (○) systems. The R_F data for the compounds other than the Pd and VO chelates are taken from ref. 20.

compounds on a C_{18}-bonded phase and that on silica gel or cellulose. It is clear that the order of R_F values on the C_{18}-bonded phase is approximately the reverse of that on silica gel or cellulose, although there are a few exceptions.

HPLC behaviour of metal–TPP chelates with single-component mobile phases

The HPLC behaviour of the compounds was investigated with five single-component mobile phases, *viz.*, methanol, ethanol, acetone, acetonitrile and N,N-dimethylformamide.

The compounds other than Fe(TPP)Cl and Mn(TPP)Cl gave sharp elution peaks. In contrast, these two metal(III)–TPP chelates showed wide peaks relative to others; the manganese chelate in particular gave such a wide and tailing peak that no chromatographic data could be evaluated with high precision.

Typical chromatograms for the separation of metal–TPP chelates are shown in Fig. 3. The peak tailing observed for Mn(TPP)Cl was somewhat suppressed by using alcohol as a mobile phase. No additional investigation was carried out to find a mobile phase that suppressed the peak tailing. The considerable peak tailing and long retention time observed for Mn(TPP)Cl with acetone (see Fig. 3b) is in conflict with the HPTLC behaviour of this compound observed with the same mobile phase solvent. [It is clearly shown in Fig. 2 that Mn(TPP)Cl does not give such a small R_F value on the C_{18}-bonded phase as the other compounds.] When HPTLC experiments were tried with C_{18}-bonded plates that had been preliminarily heated at 110°C for 1 h, the manganese chelate, in particular, showed a depressed mobility and also a considerably tailing spot; for example, the spot observed with acetone diffused from *ca.* 0.3 to 0 on the R_F scale. Taking account of the strong adsorption of Mn(TPP)Cl on to a

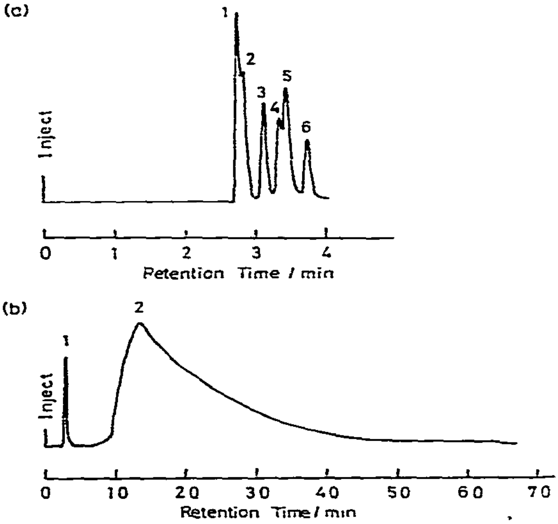

Fig. 3. HPLC separation of metal–TPP chelates. (a) Separation of (1) 6 ng of Zn(TPP), (2) 7 ng of VO(TPP), (3) 15 ng of Mg(TPP), (4) 25 ng of Ni(TPP), (5) 31 ng of Pd(TPP) and (6) 24 ng of Cu(TPP). (b) Separation of (1) 0.1 μg of Fe(TPP)Cl and (2) 25 μg of Mn(TPP)Cl. Column, LiChrosorb RP-18 (7 μm) (250 × 4 mm I.D.); mobile phase, acetone at 1 ml/min; detection at 420 nm, except for Mn(TPP)Cl at 475 nm; 0.5 a.u.f.s.

TABLE I

RETENTION DATA FOR METAL–TETRAPHENYLPORPHYRIN CHELATES ON A C_{18}-BONDED STATIONARY PHASE WITH VARIOUS SINGLE-COMPONENT MOBILE PHASES

Column: LiChrosorb RP-18 (7 µm) (250 × 4 mm I.D., Merck 50394 Hibar).

Compound	*Ethanol*		*Acetone*		*Methanol*		*Acetonitrile*		*N,N-Dimethylformamide*	
	V_R *(ml)*	*k'*	V_R *(ml)*	*k'*	V_R *(ml)*	*k'*	V_R *(ml)*	*k'*	V_R *(ml)*	*k'*
Mg(TPP)	5.82	1.33	3.22	0.287	22.53	8.01	32.03	11.8	3.03	0.213
Ni(TPP)	8.18	2.27	3.42	0.367	45.30	17.1	50.02	19.0	3.10	0.240
Cu(TPP)	9.37	2.75	3.82	0.527	55.83	20.5	67.83	26.1	3.37	0.347
Zn(TPP)	3.30	0.320	2.85	0.140	6.97	1.79	12.48	3.99	2.77	0.107
Pd(TPP)	7.80	2.12	3.52	0.407	43.30	16.3	54.13	20.7	3.20	0.280
Cd(TPP)	5.90	1.36	3.22	0.287	22.00	7.80	31.55	11.6	3.07	0.227
Fe(TPP)Cl	4.38	0.753	2.95	0.180	12.53	4.01	20.50	7.20	3.47	0.387
VO(TPP)	3.82	0.527	2.93	0.173	6.85	1.74	20.62	7.25	2.72	0.087
H_2TPP	5.87	1.35	3.20	0.280	22.10	7.84	31.50	11.6	3.03	0.213

silica gel thin layer, such a depression in the mobility on a preliminarily treated C_{18}-bonded plate is considered to result from adsorptive interaction between the chelate and the activated silianol groups remaining in the C_{18}-bonded material. The long retention time and peak tailing of the manganese chelate shown in Fig. 3b is probably due to adsorption of the chelate on to the silanol residue of C_{18}-bonded phase which has been activated by conditioning with a large amount of dry mobile phase.

The retention volumes, V_R, and the capacity factors, k', were measured for the compounds other than Mn(TPP)Cl and the results are summarized in Table I. The k' values were calculated from the equation

$$k' = (V_R - V_0)/V_0 \qquad (1)$$

where V_0 is the column hold-up volume. V_0 was assumed to be equal to the V_R value observed for water with acetone as the mobile phase (water was detected as a negative peak on the chromatogram monitored at 340 nm); thus V_0 = 2.50 ml.

The retention sequence, in increasing order of k', observed for the TPP compounds with a C_{18}-bonded column is Zn(TPP) < VO(TPP) < Fe(TPP)Cl < Mg(TPP) ≈ Cd(TPP) ≈ H_2TPP < Ni(TPP) ≈ Pd(TPP) < Cu(TPP); however, some irregularities were found when using different solvents. It can be predicted that the separation of Mg(TPP), Cd(TPP) and H_2TPP is practically impossible with any of the solvents specified in Table I.

When the retention data for the TPP compounds obtained by HPLC are compared with those obtained by HPTLC, the log k' *versus* log k' plots for the compounds with different mobile phases are as shown in Fig. 4. The retention behaviour in HPLC correlates well with that in HPTLC with every solvent system.

HPLC separation of metal TPP chelates

A common mobile phase used in reversed-phase HPLC is methanol–water. From the retention data for the TPP compounds shown in Table I, it was con-

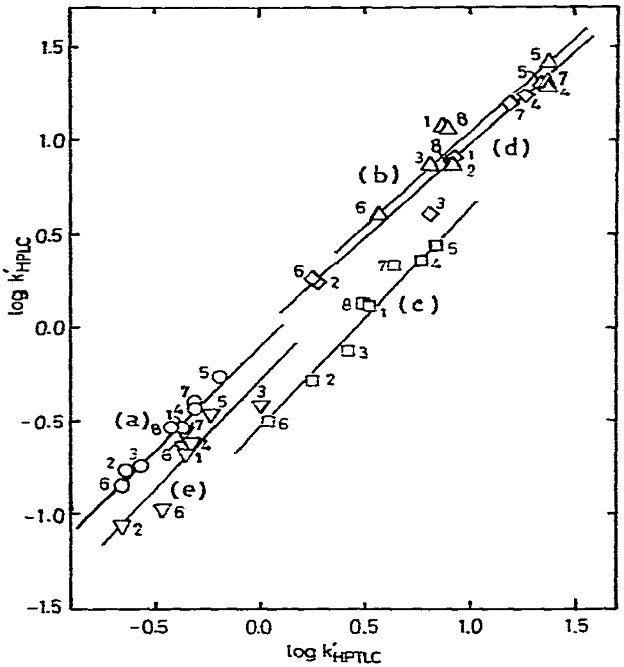

Fig. 4. Relationship between k' values of metal–TPP chelates in HPLC (k'_{HPLC}) and in HPTLC (k'_{HPTLC}) with the same solvent. HPLC column as in Fig. 3. HPTLC plate, RP-18 F_{254}, (Merck). Solvents: (a) acetone; (b) acetonitrile; (c) ethanol; (d) methanol; (e) N,N-dimethylformamide. Compounds: (1) Mg(TPP); (2) VO(TPP); (3) Fe(TPP)Cl; (4) Ni(TPP); (5) Cu(TPP); (6) Zn(TPP); (7) Pd(TPP); (8) Cd(TPP).

cluded that methanol was not suitable for their rapid HPLC separation because of the considerable retention. It could be predicted that much larger retention volumes would be observed with methanol–water than with methanol alone. Acetonitrile was not useful for similar reasons, if it was used alone. Ethanol, acetone and N,N-dimethylformamide gave relatively small retention volumes for the TPP compounds. Taking account of the solubility of the TPP compounds, the viscosity and the cost, acetone was considered to be the most convenient solvent. Most of the metal–TPP chelates of interest showed much lower solubilities in ethanol than in acetone. The high viscosity of N,N-dimethylformamide caused a high pressure drop along the column when using a high flow-rate of the mobile phase.

An example of the separation of metal–TPP chelates with acetone is shown in Fig. 3a. With this solvent the separation of four compounds, *viz.*, Zn(TPP), Mg(TPP), Pd(TPP) and Cu(TPP), was achieved within *ca.* 4 min. It was difficult to separate Zn(TPP) from VO(TPP) and Ni(TPP) from Pd(TPP) with acetone alone. In order to improve the resolution of these pairs of compounds, acetone–acetonitrile was examined. Log k' of a metal–TPP chelate increased linearly with increase in the volume fraction of acetonitrile in the acetone–acetonitrile mixture. Such relationships observed for different metal chelates were almost parallel to each other, indicating that the separation factor, α, defined by eqn. 2, for all pairs of compounds varied little with the composition of the mobile phase.

$$\alpha = (k'_2/k'_1) \tag{2}$$

where subscripts 1 and 2 represent compounds 1 and 2.

The resolution R_s, defined by eqn. 3, for each pair of metal–TPP chelates showed a strong dependence on the solvent, as shown in Fig. 5.

$$R_s = 2(V_{R,2} - V_{R,1})/(W_1 + W_2) \tag{3}$$

where W is the peak width at the base, and subscripts 1 and 2 refer to the compounds of interest. This equation is related to α, k' and the number of theoretical plates in the column, N, by the equation[27]

$$R_s = \frac{1}{4}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k'_2}{1 + k'_2}\right)(N_2)^{1/2} \tag{4}$$

It has already been mentioned that (1) α for a pair of metal–TPP chelates varies little with the composition of an acetone–acetonitrile mixture and (2) the k' value of each chelate increases with increase in the acetonitrile content of the mixture. Taking account of eqn. 4, it is reasonable to conclude that the increase in N with the composition of the mobile phase contributes predominantly to the improvement in R_s with increase in the acetonitrile content of the binary mixture of acetone and acetonitrile, as shown in Fig. 5.

Fig. 5 indicates that a resolution between Ni(TPP) and Pd(TPP) of greater than unity can be obtained when the mixture contains more than 40% (v/v) of acetonitrile, and also that a satisfactory resolution ($R_s > 1.5$) between these compounds is achieved by use of a mixture containing more than 60% (v/v) of acetonitrile.

The effect of amount of sample on the height equivalent to a theoretical plate (HETP) was investigated with acetone–acetonitrile (60:40) at a flow-rate of 1 ml/min.

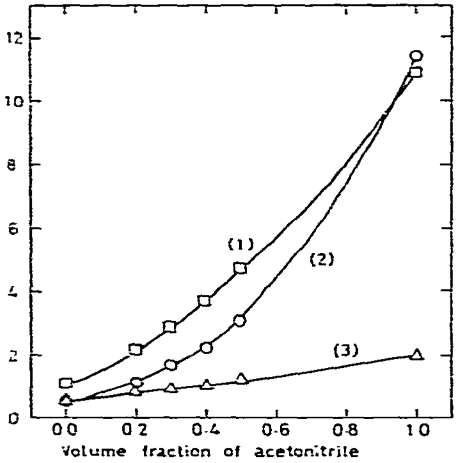

Fig. 5. Relationship between the resolution, R_s, and the composition of the acetone–acetonitrile mobile phase. Compound pairs: (1) Mg(TPP) and Ni(TPP); (2) Zn(TPP) and VO(TPP); (3) Ni(TPP) and Pd(TPP). Column as in Fig. 3; flow-rate, 1 ml/min.

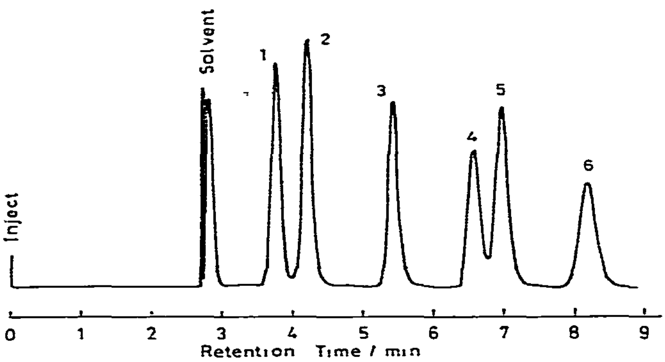

Fig. 6. Separation of metal-TPP chelates. Compounds: (1) Zn(TPP), 31 ng; (2) VO(TPP), 38 ng; (3) Mg(TPP), 77 ng; (4) Ni(TPP), 120 ng; (5) Pd(TPP), 150 ng; (6) Cu(TPP), 120 ng. Column, LiChrosorb RP-18 (7 μm) (250 × 4 mm I.D.); mobile phase, acetone-acetonitrile (60:40) at 1 ml/min. Detection at 420 nm; sensitivity, 0.5 a.u.f.s.

When less than $3 \cdot 10^{-7}$–$4 \cdot 10^{-7}$ g of solute was injected, the HETP varied little. Above this amount, Zn(TPP) and VO(TPP) tended to broaden more than the other compounds.

In conclusion, the separation of Zn(TPP), VO(TPP), Mg(TPP), Ni(TPP), Pd(TPP) and Cu(TPP) has been achieved, by using the following conditions: mobile phase, acetone-acetonitrile (60:40); flow-rate, 1 ml/min; detection at 420 nm. Acceptable separation was achieved within *ca.* 8 min, as shown in Fig. 6. This exemplifies the succesful HPLC separation of metal cations as their porphyrin chelates and indicates that reversed-phase HPLC is a promising method for the separation of various metal chelates of a particular porphyrin.

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