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Note

Behaviour of tri- and tetranuclear iron and nickel clusters in high-performance liquid chromatography

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High-performance liquid chromatography (HPLC) can be successfully applied to the chemistry of transition metal clusters[1] with the aim of monitoring the reaction pathways and separating the final products. Previous studies on di-, tri- and tetrametallic clusters[2–6] have shown that the nuclearity and the shape of the clusters and the nature of the metals and of the substituent ligands determine the separations of chemically and/or structurally related species.

Here we report a study on the HPLC behaviour of some tri- and tetranuclear carbonyl clusters based on iron and iron-nickel metal cores. They are listed in Table I together with their electronic absorption maxima, structures and literature references[7–14].

Most of these complexes are products of the reactions of $(cp)_2Ni_2(PPh_2C{\equiv}CR)$ or $(cp)_2Ni_2(RC{\equiv}CR')$ with $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$ and belong to the same series of cluster expansion and contraction reactions[12]. Moreover, it is generally accepted that tetrahedral (6 M–M), butterfly (5 M–M), square-planar and spiked triangular (4 M–M) cluster cores are correlated by successive additions of two electrons[15]. Clusters 1–5 show triangular cores, clusters 6–9 quasi-planar square core, clusters 10 and 11 spiked triangular cores and cluster 12 butterfly geometry.

EXPERIMENTAL

The tri- and tetrametallic clusters were obtained, purified and identified according to established methods (see Table I). The chemical inertness of the products in acetonitrile, chloroform, methanol and *n*-hexane was tested by maintaining them in these solvents for several hours at room temperature and by monitoring the IR spectra (CO stretching region) of the solutions before and after the chromatographic experiments.

The chromatographic separations were performed using a Perkin-Elmer Series 3B chromatograph with a Rheodyne 7105 injection valve and an LC-75 variable-

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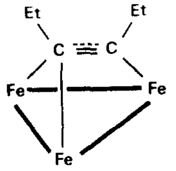
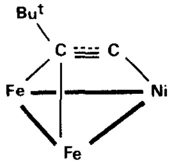
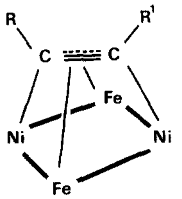
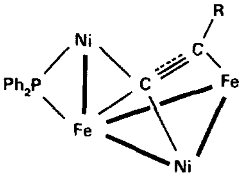
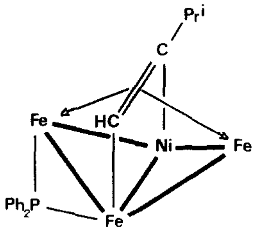
TABLE I

FORMULAS, ELECTRONIC ABSORPTION MAXIMA AND STRUCTURES OF THE CLUSTERS

*Compound**	*No.*	*$\lambda_{max.}$ (nm)***	*Structure****	*Ref.*
$Fe_3(CO)_9[C_2(C_2H_5)_2]$	1	270sh, 365sh		7, 8
$Fe_3(CO)_8[P(C_6H_5)_3]\ [C_2(C_2H_5)_2]$	2	260sh, 340sh		9
$Fe_3(CO)_7(dppm)\ [C_2(C_2H_5)_2]$	3	270sh, 385sh		10
$(cp)NiFe_2(CO)_6(tba)$	4	285, 331		11
$(cp)NiFe_2(CO)_5[P(C_6H_5)_3](tba)$	5	270, 340		9
$(cp)_2Ni_2Fe_2(CO)_6[C_2(C_2H_5)_2]$	6	330, 560, 625		12
$(cp)_2Ni_2Fe_2(CO)_6[C_2(C_6H_5)_2]$	7	330, 580, 620		12
$(cp)_2Ni_2Fe_2(CO)_6[HC_2\ (t\text{-}C_4H_9)]$	8	325, 550, 655		12
$(cp)_2Ni_2Fe_2(CO)_6[HC_2\ (i\text{-}C_3H_7)]$	9	325, 560, 625		12
$(cp)_2Ni_2Fe_2(CO)_5[P(C_6H_5)_2]\ [C_2(i\text{-}C_3H_7)]$	10	300sh		13
$(cp)_2Ni_2Fe_2(CO)_5[P(C_6H_5)_2](C_2C_6H_5)$	11	320sh		14
$(cp)NiFe_3(CO)_7[P(C_6H_5)_2]\ [HC_2(i\text{-}C_3H_7)]$	12	325sh		13

* dppm = bis(diphenylphosphino)methane; cp = η^5-cyclopentadienyl; tba = *tert.*-buthylacetylide.

** Solvent, hexane; sh = shoulder; all compounds exhibit an additional absorption maximum at $\lambda < 250$ nm.

*** Ni-bonded cyclopentadienyl and Fe-bonded σ-donor ligands (COs and phosphines) are omitted for clarity.

wavelength UV–visible detector. Stainless-steel columns (25 × 0.4 cm I.D.) filled with 10-μm LiChrosorb Si 60 or RP-8 (Merck) were used; the stability of the complexes towards stainless steel was tested as previously reported for other heterometallic clusters[4]. The flow-rate was generally 1 ml/min and the eluates were moni-

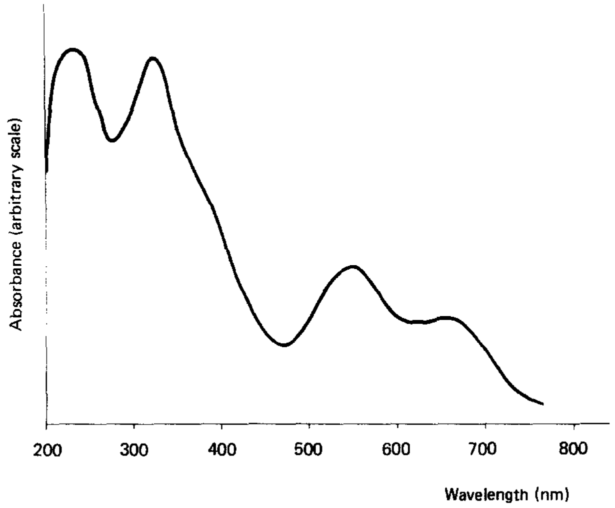


Fig. 1. Electronic spectrum of 8 in *n*-hexane.

tored at 265 or 330 nm, depending on the positions of the absorption maxima. The UV–VIS spectra of all the compounds were recorded on a Jasco 505 spectrophotometer (Table I); one of them (compound 8) is shown in Fig. 1.

Acetonitrile or *n*-hexane solutions (5 μl) of the compounds were injected; *n*-hexane–chloroform was the mobile phase for the Si 60 column and acetonitrile–methanol for the RP-8 column. Solvents were of HPLC grade (Carlo Erba).

DISCUSSION

The mixtures of clusters chromatographed on the RP-8 and Si 60 columns are listed in Table II. Fig. 2–4 show three of the separations reported in Table II.

TABLE II

RETENTION TIMES, ELUENT AND COLUMN MATERIALS

Mixtures of compounds and retention times (min) in parentheses*	*Column*	*Eluent***	*Flow-rate (ml/min)*	*Note*
3 (4.1), 1 (4.5), 2 (5.2)	RP-8	M–A (50:50)	1.0	Fig. 2
4 (4.6), 5 (5.2)	RP-8	M–A (50:50)	1.0	–
7 (6.4), 9 (6.5), 6 (6.6), 8 (6.7)	RP-8	M–A (45:55)	1.8	–
10 (5.0), 12 (5.3), 9 (5.4)	RP-8	M–A (90:10)	1.0	–
11 (5.4), 10 (5.5)	RP-8	M–A (50:50)	1.0	–
1 (9.2), 3 (9.3), 2 (14.7)	Si 60	H–C (80:20)	1.0	–
4 (3.4), 5 (4.3)	Si 60	H–C (90:10)	1.0	Fig. 3
8 (3.2), 9 (3.3), 6 (3.4), 7 (3.8)	Si 60	H–C (95:5)	1.0	–
9 (2.9), 12 (3.0), 10 (3.2), 11 (3.3)	Si 60	H–C (70:30)	1.0	Fig. 4

* Compound numbers as in Table I.

** M = methanol; A = acetonitrile; H = *n*-hexane; C = chloroform.

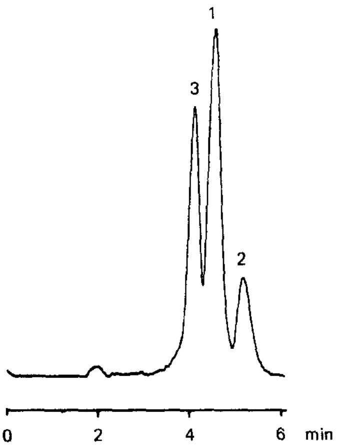


Fig. 2. Separation of 1, 2 and 3 on RP-8. Mobile phase, methanol–acetonitrile (50:50); flow-rate, 1 ml/min; detection, UV (265 nm). Resolution (R_s), 0.7 and 1.0; plate numbers (N), 1063, 895 and 896.

The separations of these clusters were slightly difficult, with close retention times. However, further information on the chromatographic behaviour of metal carbonyl clusters was achieved and in some instances valuable results in terms of effective separations were obtained.

The results concerning the two series of clusters, 1–3 and 4 and 5, confirm the

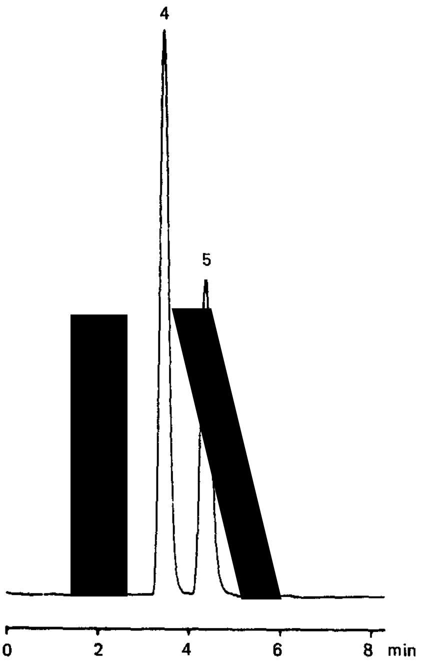


Fig. 3. Separation of 4 and 5 on Si 60. Mobile phase, n-hexane–chloroform (90:10); flow-rate, 1 ml/min; detection, UV (265 nm). Resolution (R_s), 1.6; plate numbers (N), 740 and 825.

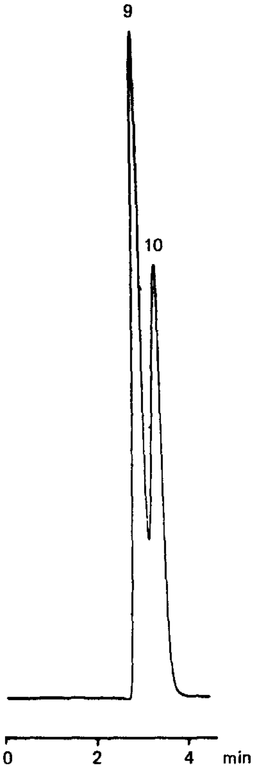


Fig. 4. Separation of 9 and 10 on Si 60. Mobile phase, *n*-hexane–chloroform (70:30); flow-rate, 1 ml/min; detection, UV (330 nm). Resolution (R_s), 0.8; plate numbers (N), 538 and 489.

general tendency observed[3,5] that triphenylphosphine monosubstituted clusters (2 and 5 in this work) give longer retention times than the parent clusters (1 and 4, respectively). In contrast, compound 3, which contains the bridging ligand 1,2-bis-(diphenylphosphino)methane, exhibits almost the same retention time as the parent compound 1 on silica and, surprisingly, is eluted before it in reversed-phase conditions. This behaviour could be related to the high solubility of 3 in all common organic solvents. It is worth noting that the tri-iron clusters 1, 2 and 3 are strongly retained on silica and hence they can be easily separated from the corresponding nickel-containing derivative (*e.g.*, cluster 6).

The chromatographic behaviour of the series of quasi-planar clusters 6–9 and of the spiked triangular clusters 10 and 11 are essentially determined by the nature of the organic radical on the alkyne ligand. On silica the phenyl derivatives are eluted after the alkyl derivatives and the order appears to be related to the Taft polar substituent constant[16,17], σ, as previously observed[2,4]: the retention time increases as σ increases ($\sigma_{C_6H_5} > \sigma_{C_2H_5} > \sigma_{i\text{-}C_3H_7} > \sigma_{t\text{-}C_4H_9}$). On the RP-8 column an opposite elution order is observed, as expected, with the exception of clusters 9 and 6, which maintain the order exhibited on silica.

The clusters 9, 12 and 10, all containing the isopropyl radical, are eluted in this order on silica. Both 10 and 12 carry a diphenylphosphido ligand but differ in shape (spiked triangular and butterfly, respectively) and in the Ni:Fe ratio, and therefore it is difficult to rationalize the chromatographic results in terms of separate effects. However, the different retention times of 9 and 10, which have the same Ni:Fe ratio, appear to be due to the presence in 10 of the diphenylphosphido ligand, if one disregards the effects of the shape (quasi-planar and spiked triangular, respectively). In reversed-phase conditions the opposite elution order is observed and cluster 10 is eluted first.

In conclusion, it is interesting to note the different effects exerted by the PPh_3 ligand and the PPh_2 moiety: the presence of the former in a cluster always produces higher retention times in both normal and reversed-phase conditions, whereas the latter appears to be sensitive to the chromatographic conditions used.

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