CHROM. 16,159

Note

Gas chromatography of iron(III) chelates of hexadentate Schiff bases

S. DILLI* and E. PATSALIDES*
School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)
(Received July 22nd, 1983)

Attempts to determine iron by gas chromatography (GC) of volatile β-diketonate derivatives[1-6] have so far been largely unsuccessful due to the instability and reactivity of the chelates. Although iron β-diketonates appear stable during volatilisation, very poor chromatographic peaks are usually produced, even at microgram levels, because of adsorptive loading, peak broadening, elevated baselines and displacement, and memory effects[4,6,7]. At nanogram levels, such chelates are irreversibly retained on the column for reasons attributed[6] to dissociation in the stationary phase and adsorption at active sites on the support. These limitations have, to some extent, been overcome by addition of free ligand to the carrier gas[8-10], presumably to maintain equilibrium in favour of the undissociated chelate. Another investigation has abandoned chelate derivatives and examined an indirect method for determining iron by GC[11].

An alternative approach for improving the GC of iron chelates[6] involves forming chelates with higher dissociative stability than that of the β-diketonates. This can be accomplished by using multidentate ligands to maximize stability through the "chelate effect". In this paper we examine the hexadentate Schiff bases 4,4',4"-(neopentane-1,3,4-triyltriimino)tris(pent-3-en-2-one) (I), and 4,4',4"-(cyclohexane-*cis,cis*-1,3,5-triyltriimino)tris(pent-3-en-2-one) (II), for this purpose and report on the formation, stability and GC of the iron(III) chelates (III and IV).

EXPERIMENTAL

Preparation of ligands

Schiff bases I and II were prepared by refluxing each triamine (1 g) with pentane-2,4-dione (20 g) in benzene (200 ml) for 1 h. Water formed in the reaction was removed azeotropically and excess benzene and pentane-2,4-dione were removed on a rotary evaporator. In each case the tarry residue was placed under vacuum (0.1 Torr, 4 h) to remove residual pentane-2,4-dione, giving the crude solid ligand (approx. 98% yield). This was recrystallized from light petroleum (b.p. 100 120°C) with the aid of activated charcoal to obtain pure ligand. Of the two ligands characterised below, II has not been previously reported.

---

* Present address: Department of Inorganic Chemistry, University of Sydney, Sydney, N.S.W. 2006, Australia.

I

II

III

IV
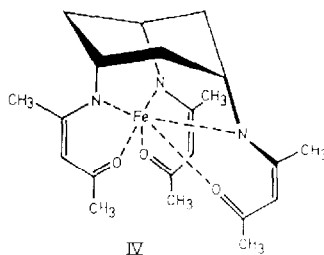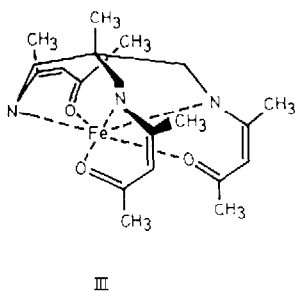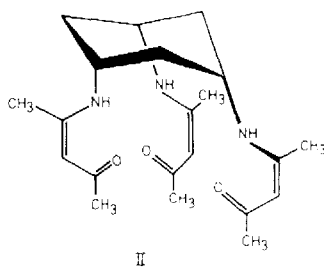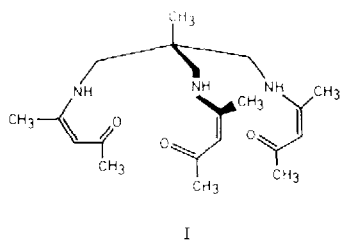
The triamines 1,1,1-triaminomethylethane and *cis,cis*-1,3,5-triaminocyclohexane were prepared[12] from the corresponding trihydric alcohols by forming the triazides followed by reduction with lithium aluminium hydride. Since *cis,cis*-1,3,5-trihydroxycyclohexane was unavailable commercially it was prepared[13] by catalytic hydrogenation of 1,3,5-trihydroxybenzene over Raney nickel.

4,4',4''-(Neopentane-1,3,4-triyltriimino)tris(pent-3-en-2-one) (I) was prepared from 1,1,1-triaminomethylethane and pentane-2,4-dione as a white solid, m.p. 89°C (Found: C, 66.1; H, 9.3; N, 11.6%). Calculated for $C_{20}H_{33}N_3O_3$: C, 66.1; H, 9.2; N, 11.6%, ^{1}H-NMR resonances (ppm) in C^2HCl_3 1.20 (bridgehead CH_3); 1.98, 2.04 (ketoenamine CH_3); 3.28, 3.35, CH_2; 5.10, CH; 11.20, NH. Mass spectrum (electron impact, EI) M^+, m/z 363 is most intense ion.

4,4',4''-(Cyclohexane-*cis,cis*-1,3,5-triyltriimino)tris(pent-3-en-2-one) (II) was prepared from *cis,cis*-1,3-5-triaminocyclohexane and pentane-2,4-dione as a white solid, m.p. 207°C (Found: C, 67.1; H, 8.2; N, 11.0%. Calculated for $C_{21}H_{33}N_3O_3$: C, 67.7; H, 8.8; N, 11.2%). ^{1}H NMR resonances (ppm) in C^2HCl_3, 1.95, 1.97, CH_3; 1.40, 2.22, 3.50, ring CH's; 4.94, CH; 10.83, NH. Mass spectrum (EI) M^+, m/z 375 is most intense ion.

Preparation of chelates

The iron chelates were prepared by refluxing a solution of each ligand (0.005 mole) with anhydrous iron(III) chloride (0.006 mole) and potassium *tert.*-butoxide (0.015 mole) in tetrahydrofuran (100 ml) for 1 h. After removal of solvent, the crude, deep violet chelates (yield approx. 60%) were purified by eluting from a column of alumina with toluene–ethyl acetate (2:1) and recrystallizing from light petroleum (b.p. 100–120°C). IV has not been reported previously.

[4,4',4''-(Neopentane-1,3,4-triyltriimino)tris(pent-3-en-2-onato)](−3)iron(III) (III): deep violet crystals, m.p. 230°C (dec.). (Found: C, 57.9; H, 7.4; N, 9.9; Fe, 13.2%. Calculated for $C_{20}H_{30}N_3O_3Fe$: C, 57.7; H, 7.3; N, 10.1; Fe, 13.4%.)

[4,4'.4''-(Cyclohexane-*cis,cis*-1,3,5-triyltriimino)tris(pent-3-en-2-onato)](— 3) iron(III) (IV): deep violet crystals, m.p. 225°C. (Found: C, 58.6; H, 6.8; N, 9.5; Fe, 12.6%. Calculated for $C_{21}H_{30}N_3O_3Fe$: C, 59.0; H, 7.1; N, 9.8; Fe, 12.9%.)

The Co(III) analogue of I and iron(III) β-diketonates were prepared as previously described[6,14].

Instrumentation

Thermoanalytical data were obtained on a Rigaku Denki Thermoflex Model M8076 combined differential thermal analysis (DTA) thermogravimetry (TG) instrument using 7.5 mg of compound and a scan rate of 5°C/min. Flow of high-purity nitrogen through the silica protection tube was 100 ml/min.

A Packard Becker Model 417 gas chromatograph equipped with a flame ionization detector was employed for the GC studies. Dry, high-purity nitrogen was used as carrier gas (30 ml/min and the temperatures of the injection block, column and detector were 230, 200 and 230°C, respectively. The column employed was a borosilicate glass coil (46 × 0.65 O.D.) packed with Gas Chrom Q AW DMCS (100 120 mesh) coated with 3% OV-101. This was silanized with 200 μl Silyl-8 (Pierce) at 200°C, then conditioned for several days before use. Chelate solutions were injected directly onto the column as benzene or carbon disulphide solutions.

Proton NMR spectra were run on a Varian HR 100 spectrometer with tetramethylsilane as internal reference and mass spectra on an AEI MS12 mass spectrometer employing EI ionization (70 eV).

Examination of chelates eluted from the column

To determine whether chelates eluting from the column at 220°C were decomposing, samples were collected in cooled glass capillaries affixed to the flame ionization detector jet, as previously described[15], and examined on alumina layers with toluene ethyl acetate (2:1) and by mass spectrometry.

RESULTS AND DISCUSSION

Thermal analyses of chelates III and IV revealed that both decompose near 230°C without appreciable volatilisation (see Fig. 1)*. The ligands, were more stable and volatilised at higher temperature with some decomposition. For comparison, the thermogram of the iron(III) derivative of pentane-2,4-dione is included in Fig. 1. The limited stability of the Schiff base chelates, compared to derivatives of tetradentate Schiff bases[16], may stem from steric strain of the chelate rings. Models show that the bridge groups linking the nitrogen atoms in III and IV prevent these donor atoms from occupying true octahedral co-ordination sites. Furthermore, bridge types other than those in I and II produce chelates with more strained co-ordination, implying a lower thermal stability for such compounds compared to III and IV.

Despite limited stabilities, III and IV were found to chromatograph at temperatures up to 230°C without apparent decomposition. This was confirmed by collecting eluents from the column, and observing, in each case, that intact chelate was the only species present. Sharp, symmetrical peaks (see Fig. 2) were obtained for the

---

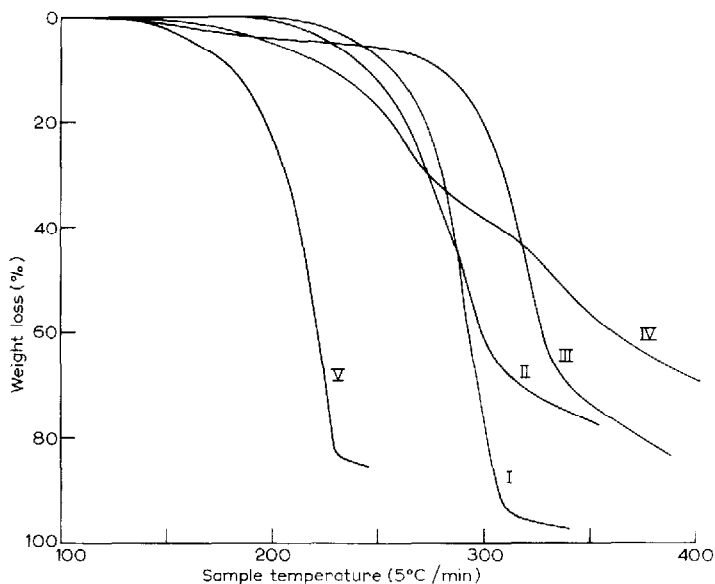* A similar instability was observed for the Co(III) analogue of I.

Fig. 1. TG curves for Schiff bases I and II, their corresponding iron(III) chelates, III and IV respectively and Tris(pentane-2,4-dionato)iron(III), (V). DTA data (not shown) indicated decomposition, with peaks at 228°C (endothermic), 230°C (exothermic) and 238°C (endothermic) for III and at 225°C (endothermic) for IV. The ligands did not give sharp decomposition peaks.
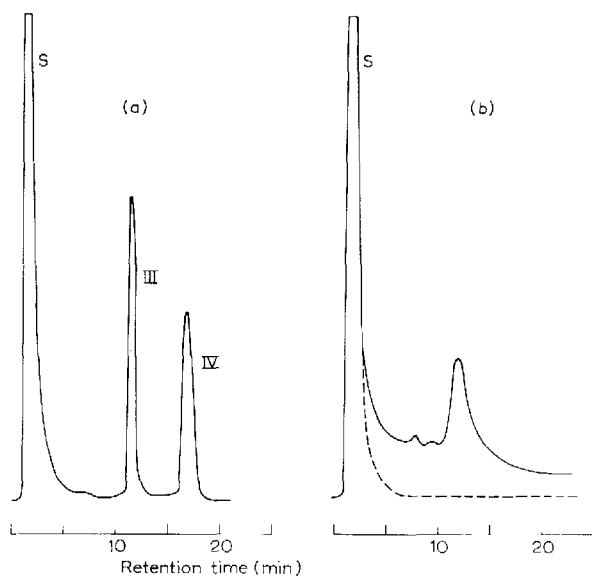

Fig. 2. Chromatograms showing (a) sharp, symmetrical peaks for 0.05 μg of III and IV (at 220°C) and (b) a typical, non-ideal peak obtained for 0.05 μg of an iron(III) β-diketonate, in this case tris(1,1,1,2,2-penta-fluoro-6,6-dimethylheptane-3,5-dionato)iron(III) on the same column (column temperature 140°C). S = Solvent (also broken line in b).

iron chelates even at nanogram levels, in marked contrast to derivatives of the β-diketones. Adsorptive loading, elevated baselines and other abnormal characteristics typical of iron(III) β-diketonates were absent in the chromatograms. Detection limits (flame ionization detection) were 0.9 and 1.2 ng for III and IV, corresponding to 0.1 and 0.15 ng of iron, respectively.

Although utilization of the Schiff bases for determining low concentrations of iron by GC appeared promising, repeated attempts to prepare and extract the chelates from aqueous solution were unsuccessful. For example, attempts to form III at various pH values between 4 and 14 gave either the pentane-2,4-dione complex or iron(III) hydroxide. A plausible explanation is the hydrolytic instability of the Schiff base chelates, for which there is much evidence in the literature[17,18]. However, III was found to be stable in boiling aqueous solutions over this pH range. It is possible also that chelate formation is not favoured in an aqueous medium, or that the actual ligand undergoes hydrolysis[19]. This property, of course, restricts the derivatization reaction to non-aqueous systems which, from the practical viewpoint, is severely limiting.

Currently, related hexadentate reagents are being examined in an effort to overcome these limitations.

REFERENCES

1 R. W. Moshier and J. E. Schwarberg, *Talanta*, 13 (1966) 445.
2 G. P. Morie and T. R. Sweet, *Anal. Chim. Acta*, 34 (1966) 314.
3 R. E. Sievers, J. W. Connolly and W. D. Ross, *J. Gas Chromatogr.*, 5 (1967) 241.
4 P. C. Uden and C. R. Jenkins, *Talanta*, 16 (1969) 893.
5 T. P. O'Brien and J. W. O'Laughlin, *Talanta*, 23 (1976) 805.
6 S. Dilli and E. Patsalides, *J. Chromatogr.*, 176 (1979) 305.
7 S. Dilli and K. Robards, unpublished results.
8 T. Fujinaga, T. Kuwamoto and S. Murai, *Anal. Chim. Acta*, 71 (1971) 141.
9 T. Fujinaga, T. Kuwamoto and S. Murai, *Talanta*, 18 (1971) 429.
10 K. W. M. Siu, M. E. Fraser and S. S. Berman, *J. Chromatogr.*, 256 (1983) 455.
11 M. A. Ditzlor and W. F. Gutknecht, *Anal. Chem.*, 52 (1980) 614.
12 E. B. Fleischer, A. E. Gebala, A. Levey and P. A. Tasker, *J. Org. Chem.*, 36 (1971) 3042.
13 R. A. D. Wentworth and J. J. Felton, *J. Amer. Chem. Soc.*, 90 (1968) 621.
14 K. Hiraki, M. Onishi and K. Hamada, *Chem. Lett.*, (1978) 117.
15 E. Patsalides, B. J. Stevenson and S. Dilli, *J. Chromatogr.*, 173 (1979) 321.
16 S. Dilli and E. Patsalides, *Aust. J. Chem.*, 34 (1981) 1579.
17 D. F. Martin and F. F. Cantwell, *J. Inorg. N. Chem.*, 26 (1964) 2219.
18 R. H. Holm, F. Rohrscheid and G. W. Everett Jr., *Inorg. Synth.*, 11 (1968) 72.
19 K. Dixon and J. V. Greenhill, *J. Chem. Soc., Perkin Trans II*, (1974) 164.