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Note

Volatility and gas chromatography of some derivatives of Schiff base chelates

S. DILLI*

School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)

A. M. MAITRA

School of Chemistry, Macquarie University, North Ryde, N.S.W. 2113 (Australia)

and

E. PATSALIDES

School of Chemistry, University of Sydney, Sydney, N.S.W. 2006 (Australia)

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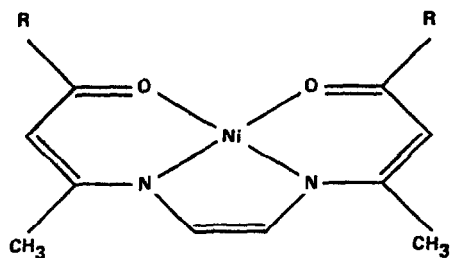
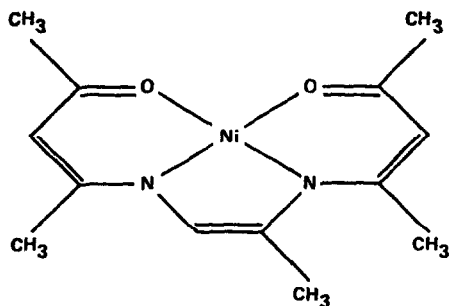
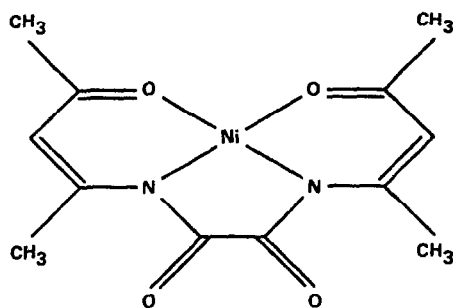
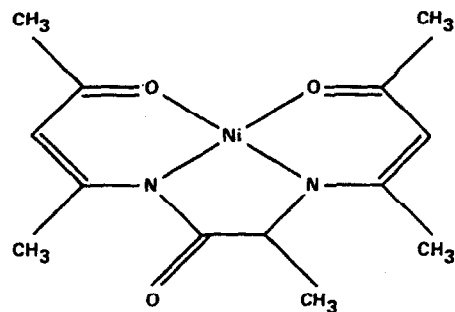
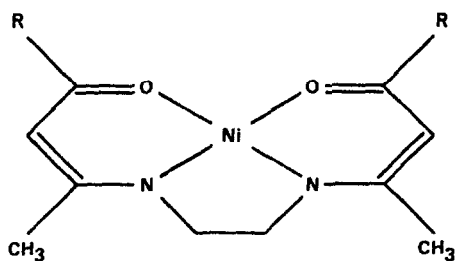
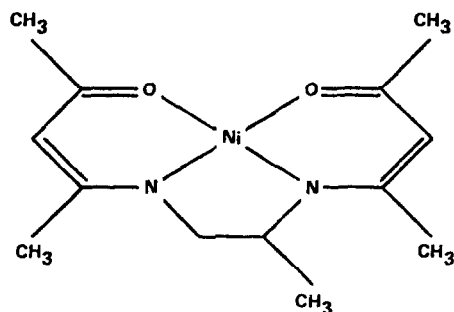
Schiff bases derived from β -diketones¹⁻⁵, or their sulphur analogues⁶, have proved to be versatile reagents for the gas chromatographic (GC) determination of an increasing number of transition metal ions, including copper(II), cobalt(II) and cobalt(III), nickel(II), palladium(II), platinum(II), zinc(II), cadmium(II), iron(III) and oxovanadium(IV)^{1,6}.

A related group of Schiff base chelates, potentially useful for analytical purposes, are I-V and their analogues. These new compounds have recently been isolated from the aerial oxidation⁷ of the corresponding Schiff base chelates VI-VIII, and appear to have good air and chemical stability. Chelate IV also possesses a 1,2-dicarbonyl group which can endow this non-fluorinated species with a high sensitivity⁸ for electron-capture detection. In this communication, we examine the thermal and GC properties of these new chelates and briefly examine their potential as derivatives in determining transition metal ions by GC.

EXPERIMENTAL

The synthesis and purification of the chelates have been reported^{2,5,7} elsewhere. Thermoanalytical data were obtained on a Rigaku instrument (Thermoflex Model M8076) combining differential thermal analysis and thermogravimetry (DTA-TG), modified for the collection of condensable material. Scans were made on 7.5 mg powdered samples in open aluminium cups at 5°C/min with a mobile atmosphere of high purity dry nitrogen (100 ml/min). DTA data are presented as temperatures of peak maxima for the various transitions.

For the GC studies, a Packard Becker Model 427 gas chromatograph, equipped with a flame ionization and an electron-capture detector, was employed. Columns were borosilicate glass coils (1.2-1.5 m long and 4 mm I.D.) packed with 5% SE-30, 3% QF-1 or 3% Apiezon-L on Chromosorb 750 (80-100 mesh), silanized and conditioned as previously^{2,4} described. Carrier gas was high purity, dry nitrogen

I $R = \text{CH}_3$ in $\text{Ni}(\text{AAED})\text{DEHYD}$ II $R = \text{CF}_3$ in $\text{Ni}(\text{TFAED})\text{DEHYD}$ III $\text{Ni}(\text{AAPD})\text{DEHYD}$ IV $\text{Ni}(\text{AAED})\text{O}_2$ V $\text{Ni}(\text{AAPD})\text{O}$ VI $R = \text{CH}_3$ in $\text{Ni}(\text{AAED})$ VII $R = \text{CF}_3$ in $\text{Ni}(\text{TFAED})$ VIII $\text{Ni}(\text{AAPD})$

(35–40 ml/min). For the dehydrogenation studies, a bed of powdered palladium (5 mm long) was inserted into the injection port-end of the column. For this work, chelates were prepared as 0.1% (w/v) solutions in dichloromethane or benzene, and diluted as required.

RESULTS AND DISCUSSION

Thermal analyses (see Table I and Figs. 1 and 2) revealed that the majority of the chelates were sufficiently volatile and stable for GC. Chelate IV, however, showed marginal stability, decomposing at 290–350°C, while decomposition was also observed for Cu(AAED)DEHYD and VO(AAED)DEHYD. Excellent stability was exhibited by VII and the dehydrogenated chelates I–III, with no evidence of decomposition being observed*. The latter chelates** appear to be more stable⁹ than the corresponding Schiff base chelates and are not prone to further dehydrogenation.

TABLE I

DTA DATA FOR VARIOUS NICKEL CHELATES

F = fusion, D = decomposition and V = volatilization. Temperatures quoted are those representing 50% weight loss.

Chelate	Temperature (°C)	Residue (%w/w)
I	206 (F), 298 (V)	1.0
II	234 (F), 286 (V)	0.1
III	193 (F), 305 (V)	0
IV	230 (F), 290 (D)	52
V	146 (F), 271 (V)	1.5
VI	210 (F), 303 (V)	2
VII	278 (F), 311 (V)	4
VIII	156 (F), 287 (V)	1

From Figs. 1 and 2 the new chelates are seen to have volatilities comparable with the parent chelates. Distinct trends in the volatilities are also apparent and can be rationalized in terms of molecular parameters such as dipole moment, polarizability and substituent effects. For this purpose, it is assumed that volatility bears an inverse relationship to the total intermolecular forces per mole of volatilizing chelate. Thus, apart from non-directional dispersion forces, stronger dipole, quadrupole and dipole-induced dipole interactions will, as well as more specific interactions due to co-ordinative unsaturation and hydrogen bonding, lower volatility. On the other hand, steric effects can impede the stronger interactions, thereby enhancing volatility.

Reference to Figs. 1 and 2 reveals the following trends. Firstly, I is more vol-

* As further evidence of the stability of these chelates, electron impact mass spectra (at 70 eV) showed little fragmentation and were dominated by the parent molecular ion.

** Nickel chelates are unaffected by treatment with H₂S or aqueous solutions of acid, cyanide or EDTA whereas the parent Schiff base chelates readily react with these reagents to produce the free ligand.

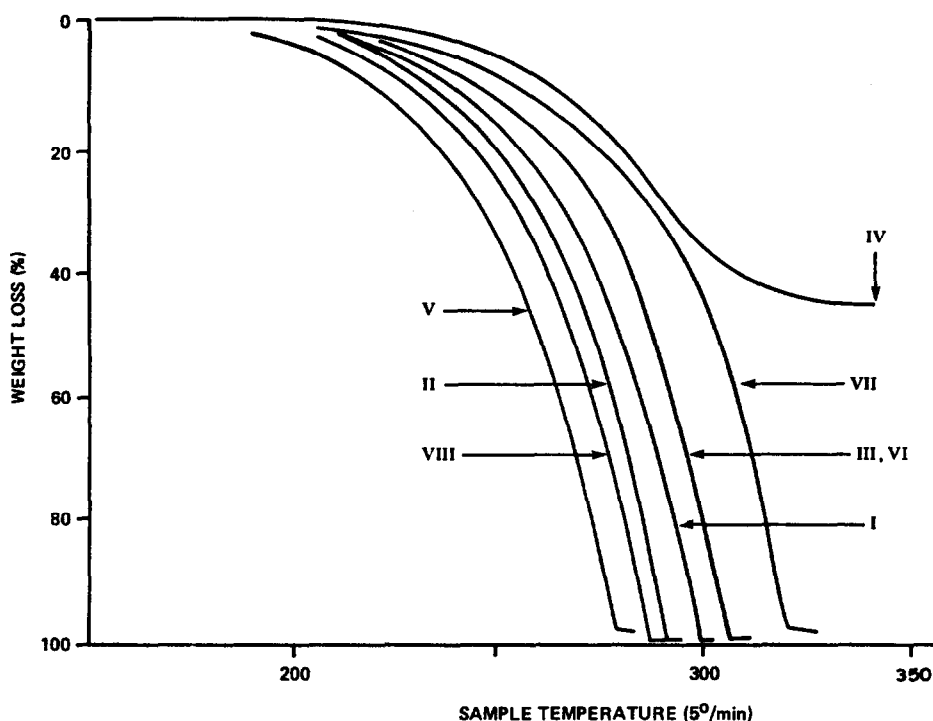


Fig. 1. Thermogravimetric data for eight nickel chelates.

atile than the parent chelate VI due largely to a lower polarity* in the dehydrogenated form I. This apparently general trend² in the analogues of I is most pronounced in the fluorinated chelate II where the fluoroalkyl substituent in the conjugated system lowers both the polarity and polarizability relative to VII. Interestingly, this trend is reversed for chelates containing a methyl substituent at the ethylene bridge, such as Ni(AAPD)DEHYD. Of the two contributing effects to this reversal, one is the removal of the steric effect of the methyl group [which gives a greater volatility in Ni(AAPD) relative to Ni(AAED)], since in Ni(AAPD)DEHYD this substituent occupies a fixed equatorial position. The second effect is attributed to an enhanced polarizability in Ni(AAPD)DEHYD relative to Ni(AAED)DEHYD due to the inductive effect of the bridge methyl group on the conjugated system of the chelate. Again, this is a general trend² for analogues of III.

The metal ion has an important effect on chelate volatility⁵ and also influences the direction and extent of volatility changes produced by structural variations in the ligand moiety. From Fig. 2 it can be seen that dehydrogenation of the AAED chelates produces no significant gain in volatility in the case of copper, a gain for nickel and vanadium, and a decrease for palladium. The reason for this is not clear although the result seems to be due to opposing polarity and polarizability effects, both of which are affected by the metal ion. Curiously, chelates IV and V, containing car-

* Dipole moments measured for I and VI in benzene were 2.85 and 4.52 Debye, respectively.

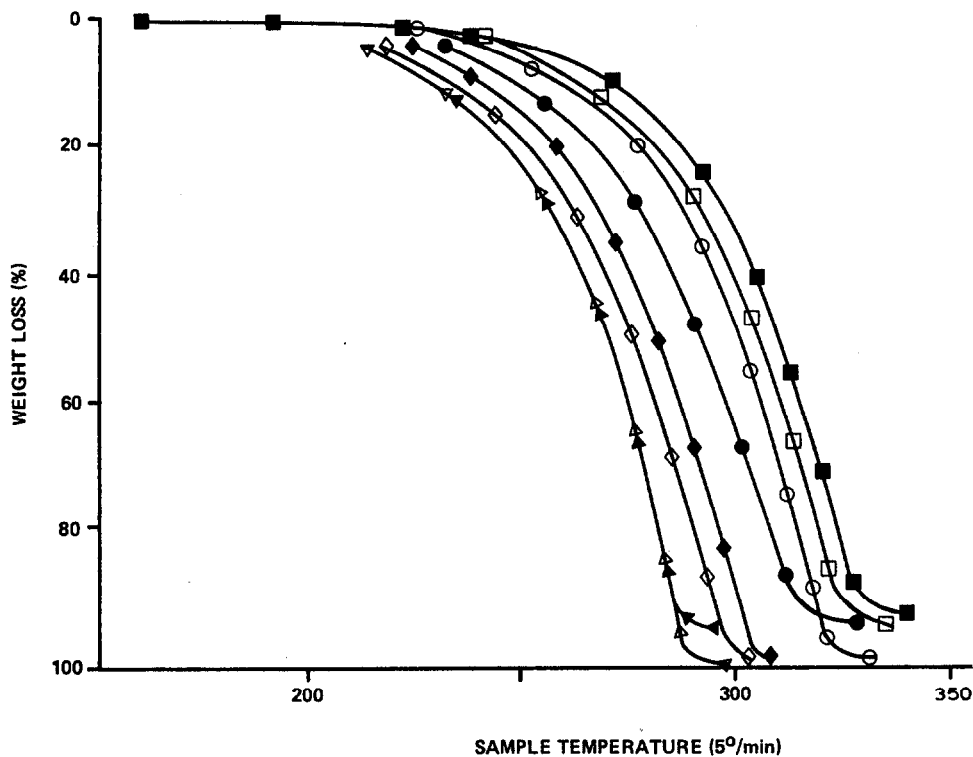


Fig. 2. Thermogravimetric data for the Schiff base chelates (structure VI, solid symbols) and their corresponding dehydrogenated forms (structure I, open symbols); copper chelates (▲), nickel chelates (◆), palladium chelates (●) and vanadium chelates (■).

bonyl groups in the bridge, are at the extremes of volatility. The exceptional volatility of Ni(AAPD)O may be due to a reduced dipole moment brought about by the bridge keto group. From this consideration it would seem that IV would be more volatile than V but the bridge dicarbonyl group in this chelate seems², by a resonance effect, to enhance the polarity considerably. Further studies of the dielectric properties of a range of these compounds are being made to better assess their role in chelate volatility.

All chelates reported herein produced satisfactory GC peaks. Fig. 3 illustrates typical chromatograms obtained for the nickel chelates. Of these, IV elutes with tailing but without apparent decomposition at 250°C although it decomposes near 300°C. With the exception of IV, all chelates gave sharp peaks at the nanogram level on the deactivated non-polar SE-30 column. As expected, chelate IV showed good sensitivity to the electron-capture detector, but with less than 10 ng quantities, irreversible adsorption prevented a lower detection limit from being attained.

Retention data (for a non-polar phase) are given in Table II for the nickel chelates. Similar data showing the separation of the Schiff base and dehydrogenated chelates of three transition ions are given in Table III. Thus, complete separation of these chelates can be achieved on the polar QF-1 phase, with the dehydrogenated forms eluting first in each case. This selectivity is attributable to polarity differences between the chelate pairs.

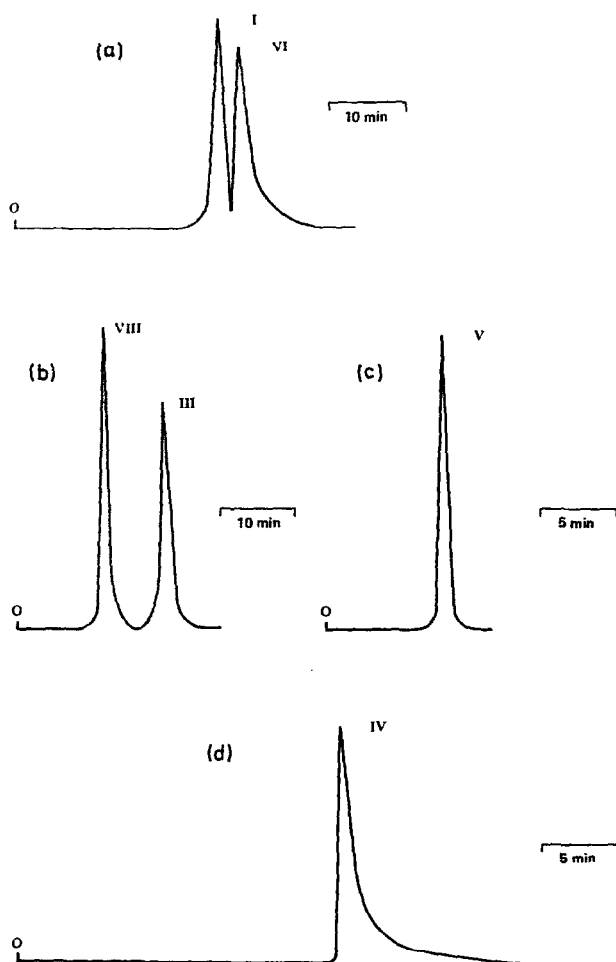


Fig. 3. Chromatograms for the nickel chelates ($0.1 \mu\text{g}$) on an SE-30 column at 200°C (a), 220°C (b), and 250°C (c and d). See text for compound identification.

Despite the generally favourable stability and gas chromatographic properties of these chelates, several limitations confront their utilization for analytical purposes. A major limitation seems to be the difficulty of preparing ligands for the derivatizing reaction. Several attempts to synthesize ligands* related to chelates I and V or, indeed, to isolate these ligands from the corresponding chelates, were unsuccessful.

One alternative considered² in attempts to overcome the problem of synthesis was the somewhat less-practical conversion of the Schiff base chelates to derivatives of type I by on-column dehydrogenation with a catalyst in the form of either a powdered metal or a free-radical initiator, such as di-*tert.*-butyl peroxide. The former

* In our hands, the preparation of $\text{H}_2(\text{AAED})\text{DEHYD}$ by the catalytic or free radical dehydrogenation of $\text{H}_2(\text{AAED})$ were unsuccessful, as were attempts to prepare $\text{H}_2(\text{AAPD})\text{O}$ from the condensation of 2-bromopropionyl bromide and 4-aminopent-3-en-2-one.

TABLE II

RETENTION DATA FOR NICKEL CHELATES ON AN SE-30 COLUMN AT 220°C

<i>Chelate</i>	<i>Retention time (min)</i>
I	9.8
II	5.8
III	15.0
IV	17.1
V	8.4
VI	9.9
VII	8.8
VIII	8.4

TABLE III

RETENTION DATA FOR SCHIFF BASE CHELATES AND THEIR DEHYDROGENATED FORMS ON POLAR AND NON-POLAR COLUMNS

<i>Ion</i>	<i>Stationary phase</i>	<i>Column temperature (°C)</i>	<i>Retention time (min)</i>	
			<i>Schiff base chelate</i>	<i>Dehydrogenated chelate</i>
Cu(II)	Apiezon L	225	35.0	35.0
	QF-1	200	13.0	9.3
Ni(II)	Apiezon L	225	39.8	36.0
	QF-1	200	16.7	12.1
VO(IV)	Apiezon L	225	44.8	44.4
	QF-1	200	54.9	44.5

approach can be illustrated by the complete dehydrogenation of Ni(AAED) at 220°C on a pre-column packed with palladium powder. In fact, although dehydrogenation has also been observed for the corresponding copper, vanadium and palladium chelates, extensive decomposition occurs with these compounds. Indeed, undesired dehydrogenation reactions of this type have been noted in the GC of reactive Schiff base chelates^{2,10}. In these instances, dehydrogenation occurs either prior to their introduction onto the column, or on the column itself, aided by high injection port temperatures (about 200°C), or the possible presence of residual decomposition products from previous injections.

Studies are continuing on the GC of IV on capillary columns and synthesis of ligands represented by compound V.

REFERENCES

- 1 P. C. Uden and D. E. Henderson, *Analyst (London)*, 102 (1977) 889.
- 2 S. Dilli and A. M. Maitra, unpublished data.

- 3 S. C. Cummings and R. E. Sievers, *Inorg. Chem.*, 11 (1972) 1483.
- 4 S. Dilli and E. Patsalides, *J. Chromatogr.*, 270 (1983) 354.
- 5 S. Dilli and E. Patsalides, *J. Chromatogr.*, 130 (1977) 251.
- 6 E. Patsalides, B. J. Stevenson and S. Dilli, *J. Chromatogr.*, 173 (1979) 321.
- 7 S. Dilli, A. M. Maitra and E. Patsalides, *Inorg. Chem.*, 21 (1982) 2832.
- 8 J. Vessman, in A. Zlatkis and C. F. Poole (Editors), *Electron Capture, Theory and Practice in Chromatography (J. Chromatogr. Library Series, Vol. 20)*, Elsevier, Amsterdam, Oxford, New York, 1981, p. 142.
- 9 S. Dilli, A. M. Maitra and E. Patsalides, *Chem. Commun.*, (1979) 133.
- 10 R. Belcher, A. Khaliq and W. I. Stephen, *Anal. Chim. Acta*, 100 (1978) 503.