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## CHROMATOGRAPHIC AND OTHER PROPERTIES OF NOVEL TETRADENTATE TETRAKETO SCHIFF BASES AND CHELATES

### FURTHER EVIDENCE OF ISOMERISM IN BIDENTATE KETOENAMINES

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#### SUMMARY

The synthesis and characterisation of a new class of tetradentate Schiff bases obtained from the condensation of oxalyl chloride and the bidentate Schiff base 4-aminopent-3-en-2-one and its analogues are reported, together with their copper(II) and nickel(II) complexes. Data are presented from studies including gas chromatography, spectroscopy (infrared, mass and  $^1\text{H}$  NMR), thermal analysis, cyclic voltammetry and measurements of dipole moments.

In the chelates, the 1,2-dicarbonyl group at the bridge lowers their thermal stability, reverses the direction of the dipole moment with little change in magnitude, and gives rise to reversible electrochemical oxidation and reduction. Differences between chelates and the corresponding ligands are discussed in terms of electron delocalisation in the dicarbonyl bridge.

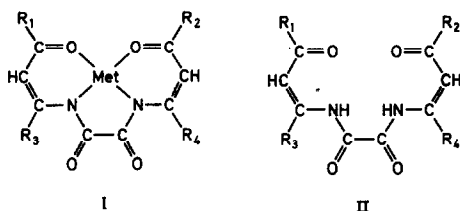
Chromatographic and spectroscopic evidence supports the existence of structural isomers in the unsymmetrical tetraketo compounds, and, hence, in the original bidentate Schiff bases used in their synthesis.

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#### INTRODUCTION

Tetraketo Schiff base chelates of the type examined in this paper (see Structure I) were first isolated<sup>1</sup> as stable products formed in the aerial oxidation of nickel(II) Schiff base chelates. Subsequently, several chelates were prepared from ligands (see Structure II) synthesised in simple condensation reactions involving the bidentate ketoenamines, and characterised mainly by  $^1\text{H}$  NMR spectroscopy. The application of these ligands as reagents for the determination of metal ions by gas chromatography (GC) has been discussed briefly<sup>2</sup> elsewhere.

This paper extends the synthesis and characterisation of this novel class of compounds and includes GC, spectroscopic (IR, mass and  $^1\text{H}$  NMR) and thermoanalytical data, together with the results of cyclic voltammetry and dipole moment measurements. Evidence is also presented for the existence of structural isomers in unsymmetrical tetraketo compounds to support the purely spectroscopic evidence previously given for isomerism in the bidentate Schiff bases<sup>3</sup> used in their preparation.



## EXPERIMENTAL

### Instrumentation

Experimental conditions for  $^1\text{H}$  NMR spectroscopy, mass spectrometry, and thermal analyses (differential thermal analysis and thermogravimetry, DTA-TG), including the symbols used to identify various events in the latter, are given in the earlier<sup>3</sup> communication.

IR spectra were obtained on a Hitachi EPI grating instrument with potassium bromide disks, halocarbon mulls and chloroform solutions (7 mg/ml). Cyclic voltammograms were obtained on a PAR Model 170 electrochemistry system, with a stationary platinum disc electrode and de-aerated solutions of the chelates ( $10^{-3}$  M in acetonitrile freed of readily oxidisable impurities and water<sup>4</sup>) containing 0.1 M tetraethylammonium perchlorate [dried, before use, for 1 week under vacuum and over phosphorus(V) oxide] as the supporting electrolyte. Dipole moments (in Debye units, D) were determined in benzene at 25°C by the refractivity method<sup>5</sup>. To calculate the molar distortion polarisation ( $P_D$ ) from the molar refraction ( $R_D$ ), the approximation  $P_D = 1.05R_D$  was used.

Column chromatography was carried out on silica gel (Merck, Kieselgel G for thin-layer chromatography).

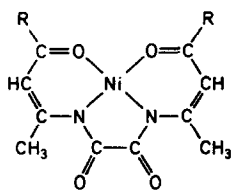
### Syntheses

**Ligands.** Ligands (see Structure II) were synthesised<sup>1</sup> as follows. Oxalyl chloride (12.6 g, 0.10 mole) in dichloromethane (50 ml) was added dropwise (over *ca.* 30 min, at room temperature) to a stirred solution of the appropriate bidentate Schiff base (0.20 mole) also in dichloromethane (50 ml) containing anhydrous potassium carbonate (20 g), followed by continuous stirring overnight (*ca.* 12–15 h at room temperature). Recovery involved water washes and removal of the solvent under vacuum, or by evaporation at room temperature.

4,4'-(Ethane-1,2-dioxo-1,2-diylidimino)bis(pent-3-en-2-one) [ $\text{H}_2\text{aaedO}_2$ ;  
 $R_1 = R_2 = R_3 = R_4 = \text{CH}_3$  in II]: recrystallised from methanol as white needles

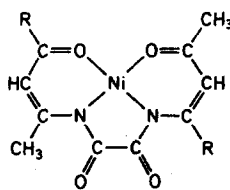
melting at 212–213°C. (Found: C, 56.7; H, 6.3; N, 10.8.  $C_{12}H_{16}N_2O_4$  requires C, 57.1; H, 6.3; N, 11.1%). DTA: F = 216°C; V = 275°C;  $T_{0.5}$  = 257°C;  $T_{max}$  = 310°C; residue 0.8%.

1,1,1,1',1',1' - Hexafluoro - 4,4' - (ethane - 1,2 - dioxo - 1,2 - diydiimino) - bis(pent - 3 - en - 2 - one) [ $H_2tfaedO_2$ ;  $R_1 = R_2 = CF_3$ ,  $R_3 = R_4 = CH_3$  in II]: purified as above and obtained as a white fluffy solid melting at 165–166°C. (Found: C, 40.3; H, 2.6; N, 7.6.  $C_{12}H_{10}F_6N_2O_4$  requires C, 40.0; H, 2.8; N, 7.8%). DTA: F = 176°C; V = 226°C;  $T_{0.5}$  = 209°C;  $T_{max}$  = 250°C; residue 0%.



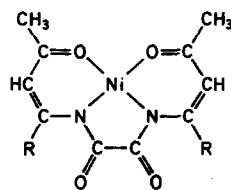
III

Isomer I



IV

Isomer II



V

Isomer III

5,5'-(Ethane-1,2-dioxo-1,2-diylidimino)bis(hex-4-en-3-one) [ $H_2hxedO_2$  and isomers;  $R = CH_2CH_3$  in III, IV and V]. The crude ligand was passed through a short silica gel column and the product eluted with ethyl acetate (10% v/v) in benzene. After vacuum-drying, the white solid melted at 98–100°C and was separated into two peaks by GC. (Found: C, 59.6; H, 7.3; N, 9.5.  $C_{14}H_{20}N_2O_2$  requires C, 60.0; H, 7.1; N, 10.0%).

6,6'-(Ethane-1,2-dioxo-1,2-diylidimino)bis(hept-5-en-4-one) [ $H_2hpodO_2(2,4)$  and isomers;  $R = CH_2CH_2CH_3$  in III, IV and V]: obtained, as for  $H_2hxedO_2$ , as colourless crystals melting at 111–113°C. This, also, was resolved into two peaks by GC. (Found: C, 62.2; H, 8.1; N, 8.7.  $C_{16}H_{24}N_2O_4$  requires C, 62.3; H, 7.8; N, 9.1%).

5,5'-(Ethane-1,2-dioxo-1,2-diylidimino)bis(hept-4-en-3-one) [ $H_2hpodO_2(3,5)$ ;  $R_1 = R_2 = R_3 = R_4 = CH_2CH_3$  in II]: obtained by the previous method as colourless crystals melting at 101°C. (Found: C, 62.3; H, 7.9; N, 9.1.  $C_{16}H_{24}N_2O_4$  requires C, 62.3; H, 7.8; N, 9.1%). DTA: unknown process at 92°C; F = 102°C; V = 286°C;  $T_{0.5}$  = 267°C;  $T_{max}$  = 310°C; residue 4.0%.

*Copper chelates.* The chelates (I where Met = Cu) were prepared by refluxing a dilute ethanolic solution (*ca.* 5% w/v) of the appropriate ligand (0.005 mole) together with an aqueous solution of copper acetate monohydrate (1.0 g, 0.005 mole) for 3 h. At the end of this period, when the solution developed a grey appearance, heating was discontinued and the cold solution filtered. Solvent was removed from the filtrate to obtain the crude products.

4,4'-(Ethane-1,2-dioxo-1,2-diylidimino)bis(pent-3-en-2-onato) (2-) -copper(II) [ $Cu \cdot aaedO_2$ ;  $R_1 = R_2 = R_3 = R_4 = CH_3$  in I]: purified from the crude product by elution from a column of silica gel with ethyl acetate (10% v/v) in benzene. The pure, olive green crystals melt at 218–219°C. (Found: C, 45.7; H, 4.5; N, 8.5.  $C_{12}H_{14}CuN_2O_4$  requires C, 45.9; H, 4.5; N, 8.9%). DTA: F = 232°C; D = 232°C;  $T_{max}$  = 320°C; residue 55%.

1,1,1,1',1',1' - Hexafluoro - 4,4' - (ethane - 1,2 - dioxo - 1,2 - diydiimino) -

bis(pent-3-en-2-onato) (2-)-copper(II), [Cu · tfaedO<sub>2</sub>, R<sub>1</sub> = R<sub>2</sub> = CF<sub>3</sub>, R<sub>3</sub> = R<sub>4</sub> = CH<sub>3</sub> in I]; this compound could not be purified by recrystallisation alone or by the previous method, owing to the presence of a more polar, green component which was difficult to remove, and is reflected in the microanalysis. The product consisted of dark violet crystals melting at 182°C. (Found: C, 33.3; H, 2.9; N, 7.6. C<sub>12</sub>H<sub>8</sub>F<sub>6</sub>CuN<sub>2</sub>O<sub>4</sub> requires C, 34.2; H, 1.9; N, 6.6%).

5,5'-(Ethane-1,2-dioxo-1,2-diyldiimino)bis(hept-4-en-3-onato) (2-)-copper(II) [Cu · hpedO<sub>2</sub>(3,5); R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = CH<sub>2</sub>CH<sub>3</sub> in I]; purified as for Cu · aaedO<sub>2</sub>. The greyish crystals melted at 149–150°C. (Found: C, 52.0; H, 6.0; N, 7.7. C<sub>16</sub>H<sub>22</sub>CuN<sub>2</sub>O<sub>4</sub> requires C, 52.0; H, 6.0; N, 7.6%). DTA: F = 156°C; D = 222°C; T<sub>max</sub> = 310°C; residue 46%.

*Nickel chelates.* As for the copper chelates, the general synthetic method for these compounds (I where Met = Ni) involved refluxing (1–2 h) a dilute ethanolic solution of the ligand (0.005 mole) and nickel acetate tetrahydrate (1.3 g, 0.005 mole), during which a reddish-brown colouration developed. The reaction mixture was cooled and filtered, and the solvent was removed in a rotary evaporator prior to the final purification step.

4,4'-(Ethane-1,2-dioxo-1,2-diyldiimino)bis(pent-3-en-2-onato) (2-)-nickel(II) [Ni · aaedO<sub>2</sub>; R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = CH<sub>3</sub> in I]; purified by elution from silica gel with ethyl acetate (10% v/v) in benzene, followed by recrystallisation from benzene to give reddish-brown crystals melting at 222–224°C. (Found: C, 46.8; H, 4.5; N, 9.4. C<sub>12</sub>H<sub>14</sub>NiN<sub>2</sub>O<sub>4</sub> requires C, 46.7; H, 4.5; N, 9.1%). DTA: F = 230°C; D = 290°C; T<sub>max</sub> = 350°C; residue 52%.

5,5'-(Ethane-1,2-dioxo-1,2-diyldiimino)bis(hex-4-en-3-onato) (2-)-nickel(II) [Ni · hxedO<sub>2</sub> and isomers; R = CH<sub>2</sub>CH<sub>3</sub> in III, IV or V]; prepared from the crude ligand and separated on a short silica gel column with ethyl acetate–benzene (1:9, v/v) and recovered as a reddish-brown solid. (Found: C, 50.5; H, 5.4; N, 8.2. C<sub>14</sub>H<sub>18</sub>NiN<sub>2</sub>O<sub>4</sub> requires C, 49.9; H, 5.4; N, 8.3%).

This product was resolved by GC into three distinct peaks and, on silica gel and alumina layers, was separated (with 10% ethyl acetate in benzene) into two distinct yet closely spaced pink spots. By slowly eluting the product (over 4 days) from a column of silica gel [with 0–4% (v/v) ethyl acetate in benzene], two pink bands were resolved and isolated. Fraction 1 had a molecular weight of 336 by electron impact mass spectrometry (EI-MS) (Found: C, 50.0; H, 5.6; N, 8.0%), and using GC (or repeated development on silica gel layers with 0–14% v/v ethyl acetate in benzene), was found to consist of two components. Similarly, Fraction 2 contained essentially a single species (Found: C, 49.5; H, 5.5; N, 8.3%. MW 336, by EI-MS).

6,6'-(Ethane-1,2-dioxo-1,2-diyldiimino)bis(hept-5-en-4-onato) (2-)-nickel(II) [Ni · hpedO<sub>2</sub>(2,4) and isomers; R = CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> in III, IV or V]; synthesised from the crude ligand and purified by slow elution (6–7 days) from a column of silica gel [with 0–4% (v/v) ethyl acetate in benzene], yielding two main fractions with MW 364. Fraction 1 (melting at 99–100°C) was resolved into two peaks by GC. (Found: C, 52.6; H, 6.3; N, 8.0. C<sub>16</sub>H<sub>22</sub>NiN<sub>2</sub>O<sub>4</sub> requires C, 52.6; H, 6.0; N, 7.7%. MW was found to be 364). Fraction 2, containing a single species (according to GC) and of MW 364, melted at 149–150°C (Found: C, 52.7; H, 6.2; N, 7.6%).

5,5'-(Ethane-1,2-dioxo-1,2-diyldiimino)bis(hept-4-en-3-onato) (2-)-nickel(II) [Ni · hpedO<sub>2</sub>(3,5); R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = R<sub>4</sub> = CH<sub>2</sub>CH<sub>3</sub> in I]; purified as for

Ni · aedO<sub>2</sub> giving pink crystals melting at 155–159°C. (Found: C, 53.2; H, 6.1; N, 7.7%). DTA: F = 161°C; VD = 315°C; T<sub>0.5</sub> = 298°C; T<sub>max</sub> = 340°C; residue 8.0%.

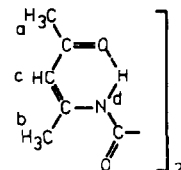
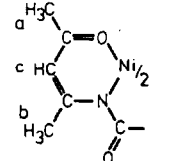
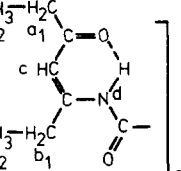
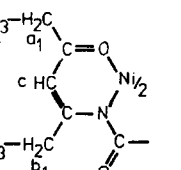
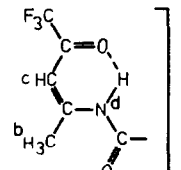
RESULTS AND DISCUSSION

Occurrence of isomers

These ligands and chelates represent an interesting system in that proof of the

TABLE I

PROTON CHEMICAL SHIFTS FOR SELECTED TETRAKETO SCHIFF BASES AND NICKEL CHELATES

Compound	Solvent	Proton chemical shifts (ppm)*			
		a	b	c	d**
	C <sup>2</sup> HCl <sub>3</sub>	2.19	2.43	5.52	13.49
	C <sub>6</sub> <sup>2</sup> H <sub>6</sub>	2.08	1.69	4.77	13.65
	C <sup>2</sup> HCl <sub>3</sub>	2.02	2.35	5.36	—
	C <sub>6</sub> <sup>2</sup> H <sub>6</sub>	2.11	1.41	4.61	—
	C <sup>2</sup> HCl <sub>3</sub>	2.50 <sup>a</sup> , 1.12 <sup>t</sup>	2.85 <sup>a</sup> , 1.18 <sup>t</sup>	5.55	13.61
	C <sub>6</sub> <sup>2</sup> H <sub>6</sub>	2.61 <sup>a</sup> , 0.98 <sup>t</sup>	2.00 <sup>a</sup> , 0.91 <sup>t</sup>	4.98	13.82
	C <sup>2</sup> HCl <sub>3</sub>	2.27 <sup>a</sup> , 1.07 <sup>t</sup>	2.77 <sup>a</sup> , 1.09 <sup>t</sup>	5.42	—
	C <sub>6</sub> <sup>2</sup> H <sub>6</sub>	2.65 <sup>a</sup> , 1.00 <sup>t</sup>	1.81 <sup>a</sup> , 0.82 <sup>t</sup>	4.92	—
	C <sup>2</sup> HCl <sub>3</sub>	—	2.61	5.87	13.12
	C <sub>6</sub> <sup>2</sup> H <sub>6</sub>	—	1.84	5.20	12.78

\* Signals are singlets unless stated otherwise. Abbreviations: d = doublet; t = triplet; q = quartet. Coupling constants for a and b multiplets are 7.4 ± 0.2 Hz.

\*\* A broad singlet which disappears on <sup>2</sup>H<sub>2</sub>O exchange.

existence of isomers (see Structures III–V) among these compounds provides strong evidence that the original building blocks, the bidentate  $\beta$ -ketoenamines, also exist as structural isomers<sup>3</sup>. For the purpose of studying these isomers,  $\text{Ni} \cdot \text{hxedO}_2$  and  $\text{Ni} \cdot \text{hpedO}_2$  were chosen not merely for their ready characterisation by NMR spectroscopy but also because their intense colour and stability on columns are of value in facilitating chromatographic separations. Generally, as indicated in the Experimental section, the separation of the isomers of these chelates by column chromatography was difficult, and it remains to be seen if preparative high-performance liquid chromatography is more effective in this regard. Nevertheless, the fractions collected from these two chelates gave consistent molecular weights (by EI-MS) and structures (by NMR).

As with other Schiff bases derived from  $\beta$ -diketones, the ligands considered here may exist in a number of tautomeric forms. From the NMR data discussed below (see Table I), the absence of chemical shifts indicative of methylene groups in the ligands excludes the ketoimine form in favour of the ketoenamine or enolimine forms. In addition, the presence of a strong absorption band near  $1700 \text{ cm}^{-1}$  in the IR spectra (see later) eliminates the enolimine tautomer involving the dicarbonyl bridge. Beyond these points, further clarification of the structure is not possible from the NMR data, although the appearance of the acidic proton near 13 ppm suggests that the equilibrium lies closer to the enolimine tautomer.

Support for the presence of isomers is provided by the chromatograms of Fig. 1, in which both the ligands examined show two components. Evidence for isomers in the corresponding nickel chelates is illustrated in Figs. 2 and 3, where each chromatogram for microanalytically pure, but isomerically impure material (see Figs. 2a and 3a), shows three components to be present. Fractions referred to in the Experimental section are seen to consist of two compounds in the case of Fractions 1 (Figs.

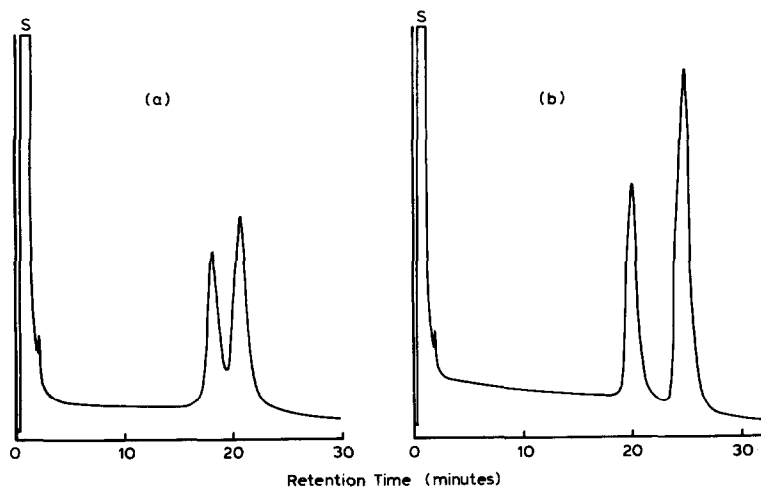


Fig. 1. Chromatograms showing isomers in (a)  $\text{H}_2\text{hxedO}_2$  and (b)  $\text{H}_2\text{hpedO}_2(2,4)$ . Conditions: glass column ( $1.2 \text{ m} \times 4 \text{ mm I.D.}$ ) packed with 5% SE-30 on Chromosorb 750 silanised with HMDS and BSTFA ( $2 \times 100 \mu\text{l}$  each); column temperature, (a)  $200^\circ\text{C}$  and (b)  $210^\circ\text{C}$ ; flame ionisation detector and port temperatures held at  $230^\circ\text{C}$ ; carrier gas (nitrogen) flow-rate,  $35 \text{ ml/min}$ . Solvent (peak S) in all chromatograms was dichloromethane.

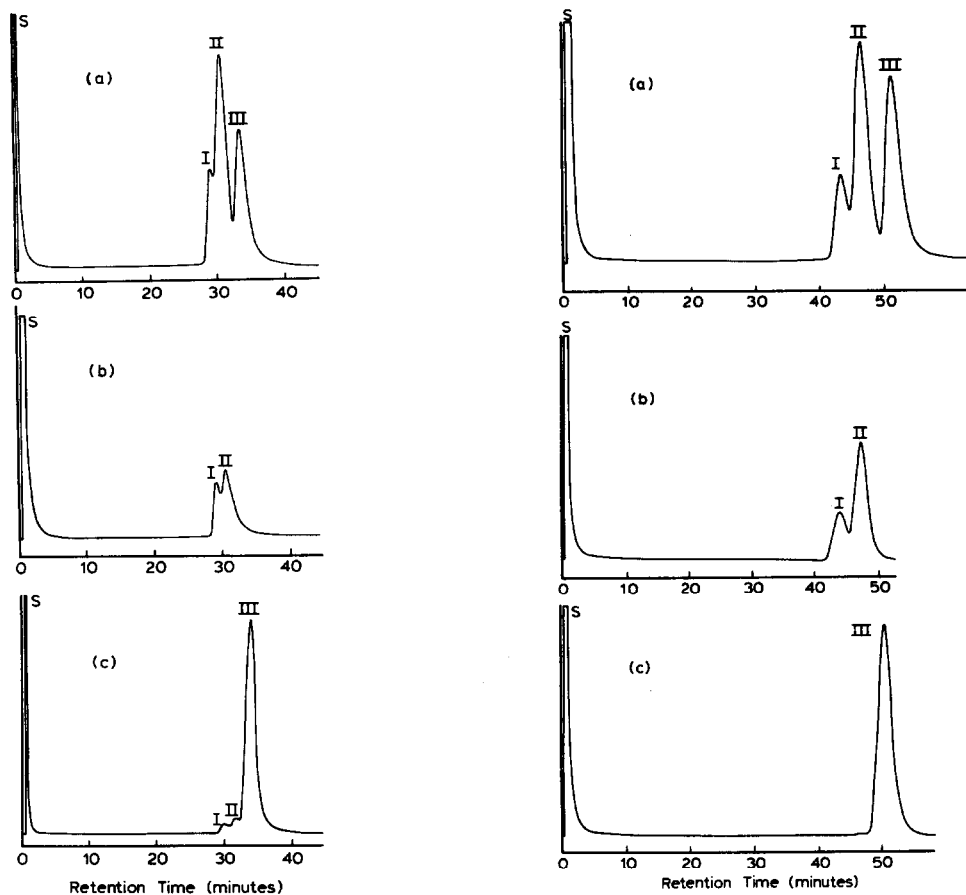


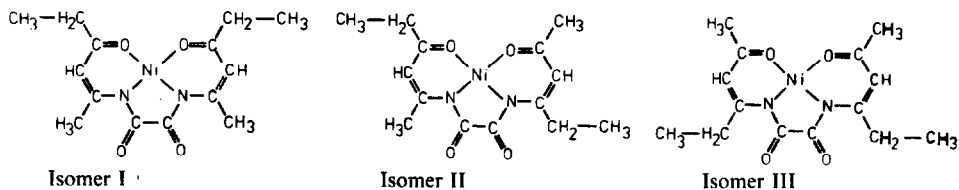
Fig. 2. Chromatograms of the isomers of Ni · hxedO<sub>2</sub> showing (a) all three isomers, (b) Isomers I and II in Fraction 1, and (c) the nearly pure Isomer III of Fraction 2 (see Experimental section). Column temperature, 220°C; other conditions as in Fig. 1.

Fig. 3. Chromatograms showing (a) the three isomers of Ni · hpedO<sub>2</sub>(2,4), (b) the two isomers present in Fraction 1 referred to in the text, and (c) the pure Isomer III from Fraction 2. Conditions as in Fig. 2.

2b and 3b) and the essentially pure compounds of Structure V in each Fraction 2.

Proton NMR data for several ligands and chelates, uncomplicated by the existence of isomers, are shown in Table I. The structures shown in the table were assigned<sup>6-8</sup> on the basis that resonances for protons near the bridge (the proximal position) were differentiated from those at the terminal positions by considerably larger upfield shifts for the former in aromatic solvents<sup>7</sup> such as benzene. The basis of this phenomenon in the Schiff bases and chelates is due to charge delocalisation from the nitrogen and carbons in the ketoenamine ring to the terminal and bridge carbonyl oxygens (see later discussion also). This gives rise to preferred solvation by benzene in which the proximal and terminal protons are shielded or deshielded to different degrees. In the terminal group, the proximity of the negative carbonyl oxy-

TABLE II

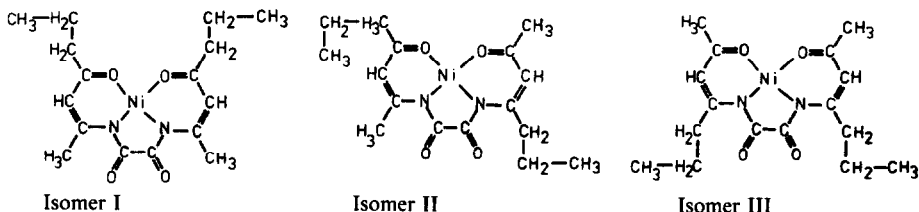
PROTON CHEMICAL SHIFTS FOR ISOMERS OF Ni · hxedO<sub>2</sub>

Compound	Solvent	Proton chemical shifts (ppm)*			
		-CH <sub>3</sub> (ethyl)	-CH <sub>2</sub> -	-CH <sub>3</sub>	=CH-
Fraction 1 (mixture of Isomers I and II)	C <sup>2</sup> HCl <sub>3</sub>	1.08 <sup>t</sup>	2.76 <sup>q</sup> , 2.26 <sup>q</sup>	2.36, 2.03	5.40, 5.36
	C <sub>6</sub> <sup>2</sup> H <sub>6</sub>	0.78 <sup>t</sup> , 0.98 <sup>t</sup>	2.60 <sup>q</sup> , 1.75 <sup>q</sup>	2.13, 1.43	4.72, 4.77
Fraction 2 (Isomer III)	C <sup>2</sup> HCl <sub>3</sub>	1.06 <sup>t</sup>	2.26 <sup>q</sup>	2.36	5.35
	C <sub>6</sub> <sup>2</sup> H <sub>6</sub>	0.81 <sup>t</sup>	1.78 <sup>q</sup>	2.17	4.76
Isomer I**	C <sup>2</sup> HCl <sub>3</sub>	1.08 <sup>t</sup>	2.76 <sup>q</sup>	2.03	5.40
	C <sub>6</sub> <sup>2</sup> H <sub>6</sub>	0.98 <sup>t</sup>	2.60 <sup>q</sup>	1.43	4.72

\* Abbreviations: *t* = triplet; *q* = quartet. Splittings in both were 7.4 ± 0.1 Hz.

\*\* Structure deduced from the chemical shifts of Fractions 1 and 2.

TABLE III

PROTON CHEMICAL SHIFTS FOR ISOMERS OF Ni · hpedO<sub>2</sub>(2.4)

Compound	Solvent	Proton chemical shifts (ppm)*				
		-CH <sub>3</sub> (propyl)	-CH <sub>2</sub> -	-CH <sub>2</sub> -	-CH <sub>3</sub>	=CH-
Fraction 1 (mixture of Isomers I and II)	C <sup>2</sup> HCl <sub>3</sub>	0.92 <sup>t</sup> , 0.93 <sup>t</sup>	1.57 <sup>m</sup>	2.69 <sup>t</sup> , 2.21 <sup>t</sup>	2.35, 2.02	5.39, 5.38, 5.35
	C <sub>6</sub> <sup>2</sup> H <sub>6</sub>	0.71 <sup>t</sup> , 0.87 <sup>t</sup> , 0.89 <sup>t</sup>	~1.45 <sup>s</sup>	2.61 <sup>t</sup> , 1.79 <sup>t</sup>	2.16, 1.47	4.81, 4.79
Fraction 2 (Isomer III)	C <sup>2</sup> HCl <sub>3</sub>	0.92 <sup>t</sup>	1.54 <sup>s</sup>	2.20 <sup>t</sup>	2.36	5.34
	C <sub>6</sub> <sup>2</sup> H <sub>6</sub>	0.72 <sup>t</sup>	1.35 <sup>s</sup>	1.80 <sup>t</sup>	2.17	4.80
Isomer I**	C <sup>2</sup> HCl <sub>3</sub>	0.93 <sup>t</sup>	1.52 <sup>s</sup>	2.69 <sup>t</sup>	2.02	5.39/5.38
	C <sub>6</sub> <sup>2</sup> H <sub>6</sub>	0.87 <sup>t</sup> , 0.89 <sup>t</sup>	1.45 <sup>s</sup>	2.61 <sup>t</sup>	1.47	4.81/5.79

\* Abbreviations: *t* = triplet; *m* = multiplet (possibly two slightly non-equivalent sextets) value quoted is mid-point of multiplet; *s* = sextet; *s'* = an apparent sextet(s) overlapped by another singlet. Splittings range between 7.1 and 7.4 Hz.

\*\* Structure deduced from the chemical shifts of Fractions 1 and 2.



gen leads to smaller upfield shifts than in the proximal substituent, which resides in a positively charged part of the molecule. Thus, in the particular case of  $H_2tfaedO_2$ , it may be concluded that the methyl groups occupy the proximal positions in the molecule because of the upfield movement (*i.e.*, shielding) of the methyl resonances (*ca.* 0.8 ppm) in deuterobenzene.

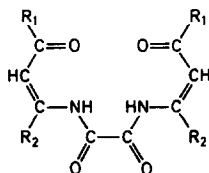
Utilising proton counts and extending this interpretation to the NMR data of Tables II and III, identified the structures of the compounds isolated as Fractions 2 are identified as isomers III (*i.e.* Structure V) of  $Ni \cdot hxedO_2$  and  $Ni \cdot hpedO_2$ , respectively. Although the spectra of the products referred to as Fractions 1 (see Tables II and III) can be representative only of the structures of isomers II, the relative peak intensities are not consistent with this unless isomer I is also present in the ratios indicated by the chromatograms (a and b) of Figs. 2 and 3. The structure assigned to isomer I is deduced from resonances not common to the spectra of Fractions 1 and 2 (in each case) and are those with high area integrals.

#### Mass spectra and further evidence for isomers

The MS fragmentation of the ligands  $H_2aaedO_2$ ,  $H_2hpedO_2(3,5)$  and  $H_2tfaedO_2$  is summarised in Table IV. In general, these compounds yield simple mass spectra (see Scheme 1) in which the main feature is homolysis at the bridge, producing the base-peak  $\frac{1}{2}M^+$ . The stability of this even-electron species probably results from

TABLE IV

ELECTRON-IMPACT (70 eV) MASS SPECTRAL DATA FOR TETRAKETO SCHIFF BASES



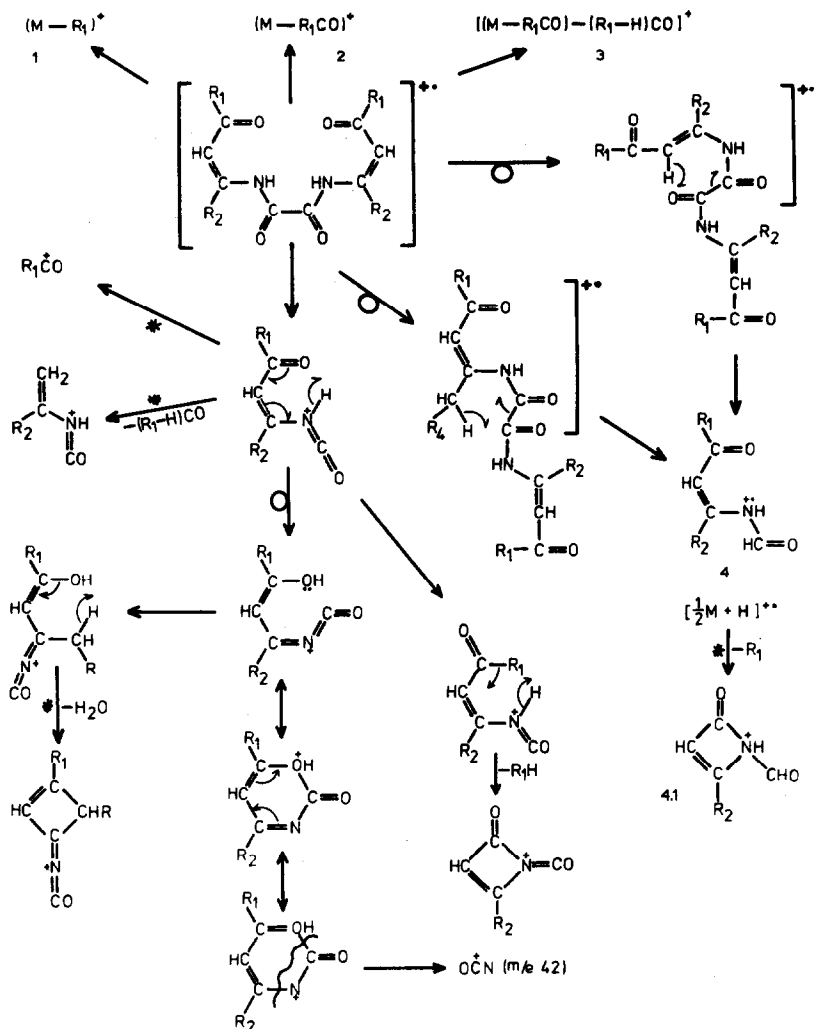
$M^{++}$  = molecular ion.

Fragment ion	<i>m/z</i> (% abundance relative to most intense peak)		
	$H_2aaedO_2$	$H_2hpedO_2(3,5)$	$H_2tfaedO_2$
$M^{++}$	252 (1)	308 (4)	360 (40)
$[M - R_1]^+$	—	279 (1)	291 (6)
$[M - R_1CO]^+$	209 (<1)	251 (1)	263 (5)
$[(M - R_1CO) - (R_1 - H)CO]^+$	167 (1)	195 (2)	—
$[\frac{1}{2}M + H]^+$	127 (6)	155 (8)	181 (7)
$\frac{1}{2}M^+$	126 (100)	154 (100)	180 (100)
$[(\frac{1}{2}M + H) - R_1]^+$	112 (2)	126* (3)	112 (2)
$[\frac{1}{2}M - R_1H]^+$	110 (3)	124 (5)	110 (70)
$[\frac{1}{2}M - H_2O]^+$	108 (4)	136* (1)	—
$[\frac{1}{2}M - (R_1 - H)CO]^+$	84 (23)	98* (27)	—
$R_1CO^+$	43 (47)	57* (16)	97 (3)
$(R_1 - H)CO^{++}$	42 (21)	56 (5)	—
$OCN^+$	42 (21)	42 (2)	42 (20)
$R_1^+$	—	29 (16)	69 (22)

\* Indicates metastable peak for the proposed transition.

extended conjugation following cyclisation of the fragment. One important fragmentation mode, particularly in the spectrum of  $\text{H}_2\text{tfaedO}_2$ , is the loss of a saturated hydrocarbon molecule from  $\frac{1}{2}\text{M}^+$  which, as the molecule  $\text{CHF}_3$ , is a common event among fluorinated compounds<sup>9,10</sup>. The spectra also contain fragment ions characteristic of the tetradentate Schiff bases containing saturated hydrocarbon bridges<sup>8</sup> (see fragments 1, 2, 3, 4 and 4.1 in Scheme 1), and for which the molecular ion is in very low (*ca.* 1%) abundance.

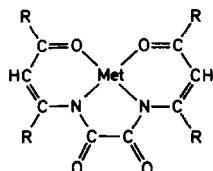
Two features of the spectra (see Table V and Scheme 2) of the chelates of the tetraketo compounds are (i) the occurrence of an intense molecular ion, and (ii) homolysis at the bridge to yield the base-peak,  $[\text{M} - \frac{1}{2}\text{L}]^+$ . Furthermore, the fact that the molecular ions for the nickel chelates are more intense than the analogous



Scheme 1. Proposed MS (70 eV) fragmentation pathways for the tetraketo Schiff bases. \* indicates the existence of metastable ions for the particular transition. The arrow with circle indicates a rearrangement (see also Scheme 1 on p. 354).

TABLE V

ELECTRON-IMPACT (70 EV) MASS SPECTRAL DATA FOR THE COPPER AND NICKEL CHELATES OF SELECTED TETRAKETO SCHIFF BASES



where Met = Cu(II) or Ni(II)

 $M^{++}$  = molecular ion; L = ligand moiety.

Fragment ion	$m/z$ (% abundance relative to most intense peak)			
	Copper chelate		Nickel chelate	
	<i>CuaaedO<sub>2</sub></i>	<i>CuhpedO<sub>2</sub>(3,5)</i>	<i>NiaaedO<sub>2</sub></i>	<i>NihpedO<sub>2</sub>(3,5)</i>
$M^{++}$	313 (25)	369 (21)	308 (65)	364 (74)
$[M - CO]^+$	—	—	280 (5)	336 (8)
$[M - \frac{1}{2}L]^+$	188 (100)	216* (100)	183 (100)	211* (100)
$[(M - \frac{1}{2}L) - CO]^+$	160 (29)	188 (16)	155 (44)	183 (32)
$[(M - \frac{1}{2}L) - NHCO]^+$	145 (10)	173* (2)	140 (14)	168 (21)
$[(M - \frac{1}{2}L - CO) - CO]^+$	—	—	127 (3)	155* (22)
$[(M - \frac{1}{2}L - CO) - C_2H_4]^+$	—	—	—	155* (22)
$[(M - \frac{1}{2}L) - MetR]^+$	110 (20)	124 (8)	110 (4)	124 (2)
Met <sup>+</sup>	63 (22)	63 (8)	58 (21)	58 (10)
RCO <sup>+</sup>	43 (55)	57 (29)	43 (78)	57 (71)
R <sup>+</sup>	—	29 (28)	—	29 (53)

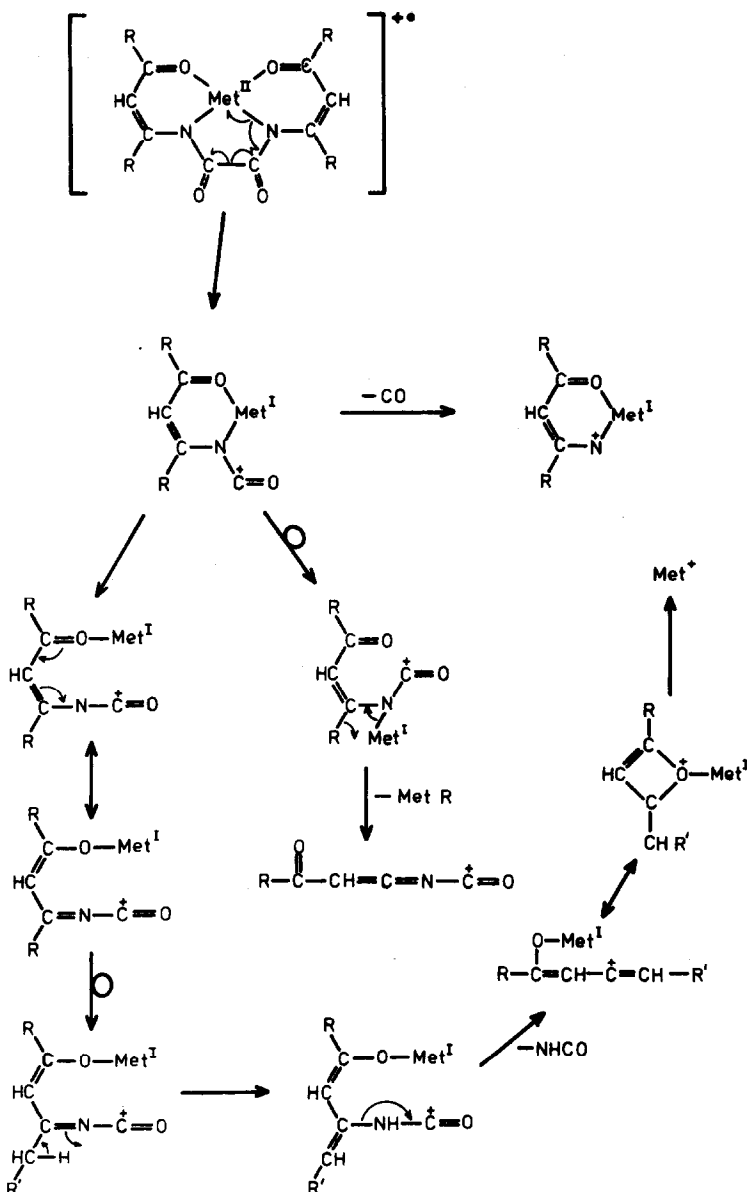
\* Presence of metastable ion for the proposed transition.

copper chelates is consistent with their relative stability indicated in the thermogravimetric data and with the superior performance of nickel chelates during GC.

Provided the isomers are separated, EI-MS can be used to clarify their structures. This follows from a comparison of Schemes 1 and 2, where it is apparent that the same mass spectra of the ligands are richer in structural information than those of the chelates. Hence, the variety of characteristic fragmentation paths of the ligand ions gives many opportunities to identify the groups  $R_1$  and  $R_2$ . In contrast, there seems to be only one pathway for the nickel chelates able to supply this information. This involves the loss of  $RNi$  from the ion  $[M - \frac{1}{2}L]^+$ , where R is the proximal substituent. Unfortunately, the ions concerned are in low abundance, although the copper chelates seem to be more suitable in this respect. Nonetheless, distinct ions (ca. 4% abundance) were observed for the loss of  $C_2H_5Ni$  and  $C_3H_2Ni$  from the  $[M - \frac{1}{2}L]^+$  ions of Isomers III of *NihxedO<sub>2</sub>* and *NihpedO<sub>2</sub>*, respectively (and both at  $m/z$  110 and 112), but of negligible abundance (less than 1%) for the loss of  $CH_3$  in both cases (i.e., at  $m/z$  124 and 126, and at 138 and 140, respectively). This, therefore, corroborates Structures III assigned from the NMR data.

#### IR and dipole moment data

Detailed IR and dipole moment studies of a number of tetradentate Schiff bases and their chelates have been reported<sup>11-14</sup>. From these and other studies<sup>15-22</sup>,



Scheme 2. Major MS fragmentation (70 eV) pathways proposed for the chelates of the tetraketo Schiff bases.

it has been established that resonance effects contribute significantly to the bonding and polarity of these compounds. For example, in Ni · aed\* the resonance form VI is thought to be largely responsible for the high dipole moment (4.5 D) of this com-

\* The abbreviation Ni · aed is used for the nickel chelate of the parent compound 4,4'-(ethane-1,2-diyldiimino)bis(pent-3-en-2-one).

TABLE VI

INFRARED ASSIGNMENTS FOR CARBONYL BANDS IN SCHIFF BASES AND CHELATES, AND REFERENCE COMPOUNDS

Compound	IR absorption bands ( $\text{cm}^{-1}$ )	
	Carbonyl ring	Carbonyl bridge
H <sub>2</sub> aaed	1610	
H <sub>2</sub> aaedO <sub>2</sub>	1652	1712
H <sub>2</sub> hpedO <sub>2</sub> (3,5)	1647	1717
H <sub>2</sub> tfaedO <sub>2</sub>	1680	1735
Ni · aaedO <sub>2</sub>		1702
Cu · aaedO <sub>2</sub>		1686
Ni · hpedO <sub>2</sub> (3,5)		1705
Cu · hpedO <sub>2</sub> (3,5)		1685
Benzil		1665
Oxamide (as KBr disk)		1670
Oxanilide		1665

pound. In an effort to determine the effects of the 1,2-dicarbonyl bridging group, we have compared the carbonyl group IR frequencies and the dipole moments of the ethylene- and dicarbonyl-bridged compounds shown in Tables VI and VII. In the ethylene-bridged ligands (such as H<sub>2</sub>aaed), intense bands near  $1600 \text{ cm}^{-1}$  have been assigned<sup>11</sup> to carbonyl vibrations. The abnormally low frequency for these bands is consistent with extensive delocalisation in the ligands. However, in the tetraketo

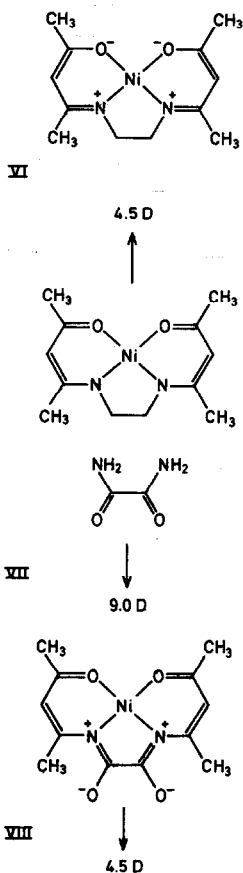
TABLE VII

DIPOLE MOMENTS AND RELATED DATA FOR ETHYLENE- AND DICARBONYL-BRIDGED LIGANDS AND CHELATES

$\alpha = \Sigma \Delta \epsilon / \epsilon_1 \cdot \Sigma w_2$  and  $\beta = \Sigma \Delta d / d_1 \cdot \Sigma w_2$  where  $\Delta \epsilon$  and  $\Delta d$  are the measured incremental changes from pure benzene of the relative permittivities and densities for solutions with solute weight fractions  $w_2$ ;  $\epsilon_1$  and  $d_1$  are the values for pure benzene;  $P_T$  is the total molar polarization and  $R_D$  is the molar refraction;  $\mu$  is the dipole moment in Debye units<sup>5</sup>.

Compound	Concentration range (%, w/w solute)	Experimental parameters				
		$\alpha$	$\beta$	$P_T$ ( $\text{cm}^3$ )	$R_D$ ( $\text{cm}^3$ )	$\mu$ (D)
H <sub>2</sub> aaed	0.0–1.8	2.34	0.190	288	73	$3.23 \pm 0.02$
H <sub>2</sub> aaedO <sub>2</sub>	0.0–0.6	0.532	0.255	106	64	$1.4 \pm 0.1$
H <sub>2</sub> hpedO <sub>2</sub> (3,5)	0.0–0.56	0.493	0.206	133	83	$1.5 \pm 0.2$
Ni · aaed	0.0–0.6	3.65	0.388	497	75	$4.53 \pm 0.02$
Cu · aaed	0.0–0.6	3.85	0.375	534	77	$4.70 \pm 0.03$
Ni · aaedO <sub>2</sub>	0.0–0.25	3.65	0.438	539	79	$4.7 \pm 0.1$
Cu · aaedO <sub>2</sub>	0.0–0.35	3.71	0.450	557	72	$4.85 \pm 0.05$
Ni · hpedO <sub>2</sub> (3,5)	0.0–0.40	3.43	0.357	615	94	$5.02 \pm 0.06$

ligands these carbonyl bands are at higher frequencies, near  $1660\text{ cm}^{-1}$ , while intense bands near  $1720\text{ cm}^{-1}$  are assigned to the bridging carbonyl groups. Since the latter bands are close to those observed<sup>23</sup> in open-chain, aliphatic 1,2-diketones (at  $1710\text{--}1740\text{ cm}^{-1}$ ), it can be concluded that electron delocalisation in this dicarbonyl bridge is not greatly favoured. In contrast, related 1,2-dicarbonyl compounds such as benzil, oxamide and oxanilide (which apparently exhibit such delocalisation) have bands near  $1620\text{ cm}^{-1}$  (see Table VI). Thus, in the tetraketo ligands it seems that competition between the carbonyls in the bridge and ketoenamine moieties for electron delocalisation prevails in the latter system owing to its greater stabilisation.



A comparison of carbonyl group frequencies for the corresponding chelates shows the absence of carbonyl bands near  $1600\text{ cm}^{-1}$ , owing to the involvement of the carbonyls in coordination. Bands due to the bridge carbonyls, on the other hand, occur at  $1705\text{--}1686\text{ cm}^{-1}$ , marginally lower than those of the free ligands. Chelation, therefore, does not appear greatly to affect bonding in these groups. However, incorporating 1,2-dicarbonyl groups in five-membered rings, as accomplished here by chelation, could be expected to enhance band frequencies<sup>24</sup> by  $30\text{--}50\text{ cm}^{-1}$  so that the bands should be observed at  $1750\text{--}1760\text{ cm}^{-1}$ . Since these bands occur at lower

frequency, it can be concluded that the chelates exhibit a compensating resonance effect where electron delocalisation in the 1,2-dicarbonyl group is favoured. This does not appear to be the case for the corresponding ligands.

Analysis of the dipole moments of the tetraketo chelates provides additional evidence for a significant contribution of resonance to the chelate structure. This can be established by assuming that the chelates are planar and the dipole vector lies along the  $C_2$  symmetry axis. Such assumptions are reasonable, although rotation about the C–C bond of the bridge allows the planar chelate rings to be inclined up to  $15^\circ$  (at least in the crystalline state<sup>19</sup>). As seen in Table VII, the dipole in Ni · aeed which is oriented as shown in VII has a magnitude of 4.5 D, whereas the experimental dipole moment for Ni · aeedO<sub>2</sub> is 4.7 D. Although bond moment corrections<sup>2,5</sup> were applied to Ni · aeed, the calculated value\* for Ni · aeedO<sub>2</sub> was found to be close to zero (0.5 D). Clearly, this approach is unable to predict reasonable values of dipole moments in the tetraketo chelates, although an improvement can be achieved by assuming that polar resonance forms such as VIII contribute significantly to the bonding structure. In this method, vector addition of the dipoles of Ni · aeed and the polar *cis*-oxamide (dipole moment 9.0 D)<sup>26</sup>, as shown in VII, can be used to approximate the contribution of VIII to the overall dipole moment. The resultant is a vector 4.5 D, acting in the *opposite* direction to that in Ni · aeed, in close agreement (as are the calculated values of 4.3 and 4.5 D for Ni · hpedO<sub>2</sub>(3,5) and Cu · aeedO<sub>2</sub>, respectively) with the experimental value given in Table VII.

It is interesting that in the free tetraketo ligands, reasonable values were also obtained for dipole moments calculated by using bond moments correction, and assuming a *cis*-planar geometry. For example, the value calculated for H<sub>2</sub>aeedO<sub>2</sub> was 0.8 D, compared with the experimental value of 1.4 D.

Tentatively, we conclude that the chelates show an enhanced aromaticity relative to the ligands, owing to the presence of the transition ion and the planarity of the ketoenolate rings. This favours delocalisation of the electrons into the dicarbonyl system of the chelates, an interpretation supported by the enhanced dipole moment of Ni · hpedO<sub>2</sub>(3,5) relative to Ni · aeedO<sub>2</sub> and, presumably, a result of the electron-releasing action of the ethyl substituents in the former compound. The presence of extra polar groups in the tetraketo Schiff bases, and their copper and nickel chelates, is totally consistent with the need for column temperatures that are 20–30°C higher than required for GC of the parent Schiff bases and their chelates.

#### *Electrochemical behaviour*

We complete this discussion by noting that chelates of the tetraketo ligands exhibit interesting electrochemical properties since both the transition-metal ion and ligand moieties are electroactive. A consequence of the ready electrochemical reduction of Ni · aeedO<sub>2</sub> is that this compound, like its related fluorinated chelates, should generally exhibit a high electron-capture cross-section giving prominent molecular ions in negative-ion mass spectra. For the same reason, high sensitivity in GC with electron-capture detection is expected and, indeed, has been found<sup>2</sup>.

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\* This analysis uses the dipole moment of Ni · aeed (4.5 D), and the bond moments of the C–H (0.0 D) and C=O (2.3 D) groups. Assuming  $sp^2$  hybridization at the bridge carbons, a resultant of 0.5 D (i.e.  $4.5 - 2 \times 2.3 \sin 60^\circ$ ), acting in the direction of the original dipole, is obtained.

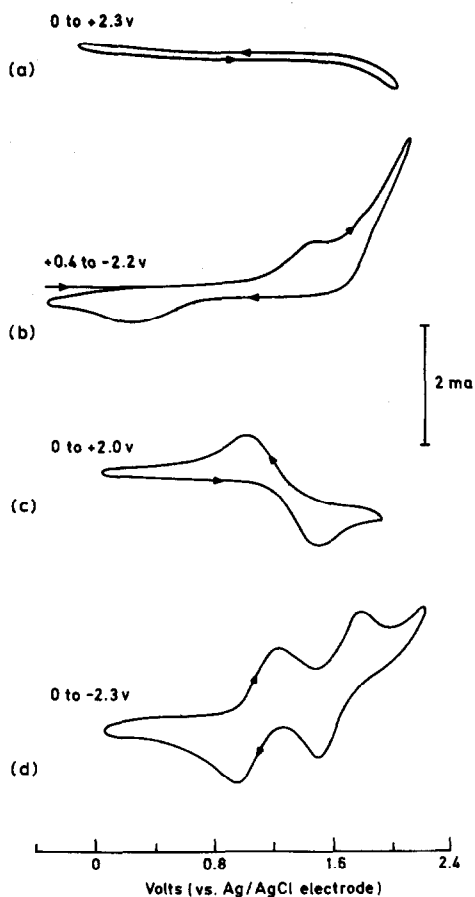


Fig. 4. Anodic and cathodic cyclic voltammograms for  $H_2aaedO_2$  (a and b) and  $Ni \cdot aaedO_2$  (c and d). See Experimental section for details.

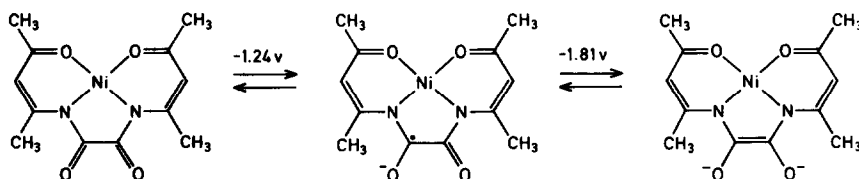
In a study confined to  $H_2aaedO_2$  and its nickel(II) chelate, the ligand was found to be inactive for anodic scans (0 to +2.0 V) but active for cathodic scans (0 to -2.0 V) and with a reduction peak near -1.4 V, attributed to initial formation of the radical anion  $H_2aaedO_2^{\cdot-}$  (Fig. 4a and b). On repeated scanning, this species gradually becomes depleted because of further unidentified reactions at the electrode surface. At potentials more negative than -1.6 V there is an unlimited current rise, ascribed to the liberation of hydrogen from the ligand or the reduced species. The anodic peak near -0.2 V, observed on the reverse cycle, may be due to irreversible re-oxidation of the radical anion.

The chelate  $Ni \cdot aaedO_2$  was electroactive in both anodic and cathodic scans. In the anodic reaction (Fig. 4c), the peak voltage is observed at +1.44 V, close to that observed<sup>1</sup> for the fluorinated Schiff base chelates. The reaction is ascribed to a single-electron oxidation at the electrode giving rise to the radical cation  $Ni \cdot aaedO_2^{\cdot+}$ . Evidence for this oxidation is derived from the fact that identical peak currents were obtained for the oxidation or reduction of the same molar concentra-



tions of cobalt(II) chloride and  $\text{Co} \cdot \text{aed}$ , both known to undergo one-electron reactions. Furthermore, the reaction is quasi-reversible since the heights of anodic and cathodic peaks are equal (although the difference between these peaks is greater<sup>27</sup> than 0.06 mV at a slow scan-rate, such as 0.1 V/s) and the peak-to-peak voltage increases with increasing scan-rates. The chemical reversibility of this oxidation, in contrast to that of the parent Schiff base chelate  $\text{Ni} \cdot \text{aed}$ , is attributed to the absence of hydrogen at the bridging carbons since, in  $\text{Ni} \cdot \text{aed}$ , hydrogen may be abstracted<sup>1</sup> to give electro-inactive species.

The cathodic reactions for  $\text{Ni} \cdot \text{aedO}_2$  comprise two clearly separated quasi-reversible one-electron reductions with peak voltages at  $-1.24$  V and  $-1.81$  V (Fig. 4d). These may be either both ligand-based (see Scheme 3) or one ligand-based, and one due to the reduction of nickel(II) to nickel(I). Of course, this distinction need not be made since reductions of the complex as a whole are being observed. Related ethylene-bridged nickel chelates, such as  $\text{Ni} \cdot \text{aed}$ , generally lack characteristic cathodic peaks although fluorinated analogues give single chemically reversible peaks<sup>28</sup> at  $-1.5$  V to  $-1.7$  V. In the latter compounds the strongly electron-withdrawing trifluoromethyl substituents are thought to enhance the stability of the nickel(I) complex by lowering the energy levels of unoccupied d-orbitals in the nickel(II) chelates.



Scheme 3. Proposed mechanism for the electrochemical reduction of  $\text{Ni} \cdot \text{aedO}_2$ .

Incidentally, but still of relevance to their possible further use in GC, both the copper and nickel chelates of the tetraketo ligands exhibit considerable thermal instability. This was apparent from their incomplete volatilisation and the large residues (see Experimental section) after thermal analysis. Despite this, the nickel chelates respond to GC below  $250^\circ\text{C}$  on a non-polar stationary phase, as shown in Figs. 2 and 3. More recent work<sup>29</sup> has shown the distinctly better behaviour of members of this class of chelates on capillary columns.

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