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VOLATILITY STUDIES OF METAL CHELATES

VIII. GAS CHROMATOGRAPHIC AND SPECTROSCOPIC STUDIES OF BIDENTATE β -KETOENAMINES AND THEIR COPPER(II) AND NICKEL(II) CHELATES

SERGIO DILLI*

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

ASHIT M. MAITRA

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

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SUMMARY

A series of bidentate β -ketoenamines has been synthesized by replacement of one oxygen atom in β -diketones by nitrogen. The ligands are of general structure $R_1COCH(R_3)C(NH_2)R_2$, where R_1 and R_2 are any two of the groups CH_3 , CH_2CH_3 , $CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$ and $CH_2CH_2CH_2CH_2CH_3$, and R_3 is H, CH_3 or CH_2CH_3 . The effects of alkyl chain-length on the thermoanalytical properties and gas chromatographic behaviour of the eleven ligands and their copper(II) and nickel(II) chelates are described. Isomerism and other structural features of the compounds are discussed with reference to mass and NMR (1H and ^{13}C) spectroscopic data.

INTRODUCTION

Although versatile ligands, the β -diketones have been successfully applied to the gas chromatographic (GC), trace level determination of only a small number of elements such as beryllium¹⁻⁵, chromium⁶⁻¹², cobalt^{13,14} and aluminium^{15,16}. The addition of other common elements to this group, however, has been frustrated by various unfavourable properties of the elements or the ligands. Investigations involving important common elements, such as copper and nickel, have met with limited success owing mainly to coordinative unsaturation in the chelates, whereas others, e.g. vanadium(III) undergo slow oxidation¹⁷ or imperfectly understood¹⁸ on-column reactions [as with iron(III) and manganese(III)].

The substitution of one oxygen atom in 1,1,1-trifluoropentane-2,4-dione by sulphur has proven beneficial for the sensitive trace analysis¹⁹ of nickel. However this ligand, like other monothio- β -diketones, is unsatisfactory for determining copper because of the simultaneous formation of copper(I) species²⁰ and oxidation of the

ligand, or of vanadium because of displacement²¹ of sulphur from the ligand.

Replacement of oxygen by nitrogen in an alternative ligand system has attracted relatively little attention to the resulting bidentate compounds although the related tetradentate Schiff bases have received extensive recent examination^{22,23}, and even have been applied with some success to the trace analysis of copper, nickel and vanadium^{24,25}. Understandably, the early papers concerned with the bidentate ketoenamines were interested in fundamental chemical aspects, but the range of compounds was rather narrow and derived from a few aromatic compounds such as salicylaldehyde and dimedones, or β -diketones, in reactions with ammonia and N-substituted amines. Notable in these studies was the interest in tautomerism, steric effects and structural isomerism. It was the studies of tautomerism²⁶⁻³⁸ that showed that the ketoenamine species prevails in non-donor solvents. Similarly, it has been shown^{30,39-44} that steric factors virtually determine the geometrical configuration and fix the *cis-s-cis* isomeric structures for the β -diketone-derived ligands in which there are no destabilising N-substituents. In addition, divalent metal chelates [such as the copper(II) and nickel(II) derivatives of 4-aminopent-3-en-2-one assume^{45,46} a square-planar *trans* configuration because of their higher symmetry. These chelates also have been resolved partially⁴⁷ into *d*- and *l*-optical forms, indicative of some distortion from simple square-planarity. Finally, structural isomerism in these ligands and chelates can result provided the parent β -diketones possess different terminal substituents, although a special case, involving selective condensation of diketones possessing both electronically and sterically differing substituents (namely, the methyl, trifluoromethyl and phenyl groups) to yield a single isomeric species, has been reported⁴⁸⁻⁵¹.

This paper reports the results of an extension to the modification of the β -diketone structure wherein a nitrogen atom replaces one oxygen atom to yield the bidentate β -ketoenamines of general structure $R_1COCH(R_3)C(NH_2)R_2$. The nature of the substituents (where R_1 and R_2 are any two of the groups CH_3 , CH_2CH_3 , $CH_2CH_2CH_3$, $CH_2CH_2CH_2CH_3$ and $CH_2CH_2CH_2CH_2CH_3$, and R_3 is H, CH_3 or CH_2CH_3) has been varied so that the increased influence of alkyl chain-length may be observed, in particular, upon thermoanalytical effects and the GC behaviour of the ligands and their copper(II) and nickel(II) chelates. Isomerism and other structural features of the compounds are also discussed, mainly with reference to mass and NMR spectroscopic data. This includes ¹³C NMR data presented in support of the existence of isomerism among the asymmetric compounds. The ligands referred to are 4-aminopent-3-en-2-one (Haai); 4-amino-3-methylpent-3-en-2-one (Hmaai); 4-amino-3-ethylpent-3-en-2-one (Heaai); 5-aminohept-4-en-3-one (Hhi); 2-aminohept-2-en-4-one [Hsi(2,4)]; 5-aminohept-4-en-3-one [Hsi(3,5)]; 2-aminooct-2-en-5-one [Hoi(2,4)]; 6-aminooct-5-en-4-one [Hoi(3,5)]; 2-aminonon-2-en-4-one [Hni(2,4)]; 3-aminonon-3-en-5-one [Hni(3,5)]; 6-aminonon-5-en-4-one [Hni(4,6)]. With the exception of Haai⁵²⁻⁵⁵, Hmaai⁵², Hhi⁵⁶ and Htfai⁵⁷, these ligands and their chelates have not been reported before.

EXPERIMENTAL

Instrumental

Thermoanalytical data were obtained on a combined tga-dta instrument (Ri-

gaku, Thermoflex M8076) using powdered solids or liquids (7.5 mg) heated at 5°C/min in a stream of pure nitrogen (100 ml/min). The $T_{0.5}$ and T_{\max} values refer to the temperature corresponding to 50% weight-loss and the maximum heating temperature, respectively. Sample residues are indicated as percent by weight for chelates only since no residues were obtained for the ligands. Other events recorded are fusion (F), volatilization (V) and decomposition (D).

GC data were obtained using freshly prepared solutions of ligands and chelates and an instrument (Packard Model 427) equipped with a flame ionization detector. High purity nitrogen, serving as the carrier gas (35 ml/min), was passed through borosilicate glass coils packed with a coated diatomite support (acid-washed, DMCS-treated, 80–100 mesh). Ligands were examined at 100°C on one column (1.6 m × 4 mm I.D., 5% SE-30 on Chromosorb W) whereas chelates were examined at 200°C on a shorter column (0.9 m × 4 mm I.D., 3% SE-30 on Chromosorb 750) after on-column silanization with HMDS and BSTFA (2 × 100 μl each). Relative retention (R_T) data are expressed relative to Haai, or its corresponding chelates.

Proton NMR spectra were recorded on a JEOL-FX-100 FT NMR spectrometer, equipped with digital quadrature detection using a 5-mm proton probe (temperature 25°C). The compounds were dissolved in deuteriochloroform or deuterobenzene (ca. 20% w/v). ^{13}C NMR spectra were obtained on a JEOL JNM FX-100 FT, using a 10-mm probe at the ambient temperature (20°C). Concentrated solutions of the compounds (ca. 1 M) were prepared in deuteriochloroform for this purpose. All chemical shifts are reported relative to tetramethylsilane (TMS).

A GEC-AEI MS12 single-focusing mass spectrometer and a GEC-AEI MS9 double-focusing magnetic mass spectrometer, provided with an AEI DS30 data acquisition system, were used. Compounds were introduced into the ion source (180–220°C) in borosilicate glass capillaries with a heated, direct-insertion probe. Operating conditions employed an accelerating voltage of 8 kV and an electron energy of 70 eV.

Syntheses

Synthesis of β -diketones. Apart from the commercially available pentane-2,4-dione (Hacac) and 1,1,1-trifluoropentane-2,4-dione (Htfa), it was necessary to synthesise all β -diketones [$\text{R}_1\text{COCH}(\text{R}_3)\text{COR}_2$]. The α -alkylation of Hacac was achieved⁵⁸ with methyl iodide or ethyl iodide yielding 3-methyl- ($\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{CH}_3$) and 3-ethylacac ($\text{R}_1 = \text{R}_2 = \text{CH}_3$; $\text{R}_3 = \text{C}_2\text{H}_5$), respectively. The remaining β -diketones were synthesised by a Claisen condensation of the appropriate ester (1.0 mole) and ketone (1.0 mole) in the presence of excess sodium hydride, essentially in accordance with the method⁵⁹ of Swamer and Hauser. Compounds prepared in this manner were hexane-2,4-dione ($\text{R}_1 = \text{CH}_2\text{CH}_3$, $\text{R}_2 = \text{CH}_3$, $\text{R}_3 = \text{H}$); heptane-2,4-dione ($\text{R}_1 = \text{CH}_2\text{CH}_2\text{CH}_3$, $\text{R}_2 = \text{CH}_3$, $\text{R}_3 = \text{H}$); heptane-3,5-dione ($\text{R}_1 = \text{R}_2 = \text{CH}_2\text{CH}_3$, $\text{R}_3 = \text{H}$); octane-2,4-dione ($\text{R}_1 = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{R}_2 = \text{CH}_3$, $\text{R}_3 = \text{H}$); octane-3,5-dione ($\text{R}_1 = \text{CH}_2\text{CH}_2\text{CH}_3$, $\text{R}_2 = \text{CH}_2\text{CH}_3$, $\text{R}_3 = \text{H}$); nonane-2,4-dione ($\text{R}_1 = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{R}_2 = \text{CH}_3$, $\text{R}_3 = \text{H}$); nonane-3,5-dione ($\text{R}_1 = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{R}_2 = \text{CH}_2\text{CH}_3$, $\text{R}_3 = \text{H}$) and nonane-4,6-dione ($\text{R}_1 = \text{R}_2 = \text{CH}_2\text{CH}_2\text{CH}_3$, $\text{R}_3 = \text{H}$). The diketones were purified through the copper chelates, and the purity confirmed by gas chromatography–mass spectrometry (GC–MS).

Synthesis of β -ketoenamines. The compounds [of general structure* $R_1COCH(R_3)C(NH_2)R_2$] were prepared by the gradual addition of an excess of ammonia-water (15 M, 30 ml) to a stirred, ethanolic solution of the diketone (0.10 mole) contained in an ice-bath. After *ca.* 10 min, the mixture was transferred briefly to a boiling water-bath (*ca.* 20 min) and more ammonia-water (10 ml) added. Throughout the reaction, a single phase was maintained by the addition of ethanol, as required. The cold reaction mixture was extracted with an equal volume of chloroform, the extract was dried (over anhydrous sodium sulphate) and the solvent was removed in a rotary evaporator. Because of their considerable solubility in most solvents and low melting points, final purification of the products (5 g amounts) was conveniently achieved (at *ca.* 50°C and 0.2 Torr) by vacuum sublimation of solids, or by a form of vacuum distillation in a modified sublimator in the case of liquid products. In the latter, three fractions were normally collected but only the larger middle portion was used. Under these conditions, GC indicated virtually complete conversion of all diketones (except Htfa) into the corresponding β -ketoenamines.

4-Aminopent-3-en-2-one (Haai; $R_1 = R_2 = CH_3$, $R_3 = H$): white crystals, melting at 40–41°C (lit.^{52,55} 42–43°C. (Found: C, 60.0; H, 9.0; N, 13.8. Calc. for C_5H_9NO : C, 60.6; H, 9.1; N, 14.1%). DTA: F = 40°C; V = 140°C; $T_{0.5} = 127^\circ C$; $T_{max} = 170^\circ C$. $R_T = 1.0$ (2.5 min).

4-Amino-1,1,1-trifluoropent-3-en-2-one (Htfai; $R_1 = CH_3$, $R_2 = CF_3$, $R_3 = H$): white crystals, melting at 86–87°C (lit.⁵⁷ 87°C). (Found: C, 39.2; H, 3.9; N, 8.9. Calc. for $C_5H_6F_3NO$: C, 39.2; H, 3.9; N, 9.1%). DTA: F = 83°C; V = 142°C; $T_{0.5} = 130^\circ C$; $T_{max} = 180^\circ C$. $R_T = 1.1$ (2.8 min).

4-Amino-3-methylpent-3-en-2-one (Hmaai; $R_1 = R_2 = R_3 = CH_3$): off-white crystals from cyclohexane, melting at 102–103°C (lit.⁵² 105°C). (Found: C, 63.8; H, 9.7; N, 12.3. Calc. for $C_6H_{11}NO$: C, 63.7; H, 9.8; N, 12.4%). DTA: F = 109°C; V = 155°C; $T_{0.5} = 141^\circ C$; $T_{max} = 240^\circ C$. $R_T = 2.0$ (4.9 min).

4-Amino-3-ethylpent-3-en-2-one (Heaai; $R_1 = R_2 = CH_3$, $R_3 = CH_2CH_3$): white crystals melting at 55–56°C. (Found: C, 65.6; H, 10.6; N, 11.1. $C_7H_{13}NO$ requires C, 66.1; H, 10.2; N, 11.0%). DTA: F = 57°C; V = 156°C; $T_{0.5} = 145^\circ C$; $T_{max} = 200^\circ C$. $R_T = 2.9$ (7.3 min).

5-Aminohex-4-en-3-one (Hhi; $R_1 = CH_2CH_3$, $R_2 = CH_3$, $R_3 = H$): white crystals melting at 47–50°C (lit.⁵⁶ 45°C). (Found: C, 63.1; H, 10.0; N, 12.0. Calc. for $C_6H_{11}NO$: C, 63.7; H, 9.8; N, 12.4%). DTA: F = 30°C; V = 145°C; $T_{0.5} = 132^\circ C$; $T_{max} = 170^\circ C$. $R_T = 1.6$ (4.0 min).

2-Aminohept-2-en-4-one [Hsi(2,4); $R_1 = CH_2CH_2CH_3$, $R_2 = CH_3$, $R_3 = H$]: white crystals melting at 36–37°C. (Found: C, 66.1; H, 10.7; N, 11.0. $C_7H_{13}NO$ requires C, 66.1; H, 10.2; N, 11.0%). DTA: F = 34°C; V = 157°C; $T_{0.5} = 142^\circ C$; $T_{max} = 180^\circ C$. $R_T = 2.7$ (6.9 min).

5-Aminohept-4-en-3-one [Hsi(3,5); $R_1 = R_2 = CH_2CH_3$, $R_3 = H$]: white crystals melting at 43–44°C. (Found: C, 66.1; H, 10.4; N, 11.0. $C_7H_{13}NO$ requires C, 66.1; H, 10.2; N, 11.0%). DTA: F = 41°C; V = 155°C; $T_{0.5} = 142^\circ C$; $T_{max} = 200^\circ C$. $R_T = 2.6$ (6.7 min).

2-Amino-oct-2-en-4-one [Hoi(2,4); $R_1 = CH_2CH_2CH_2CH_3$, $R_2 = CH_3$,

* Structures given represent the major isomer possible in asymmetric ligands (or chelates).

$R_3 = H$]; colourless liquid. (Found: C, 68.6; H, 11.1, N, 9.2. $C_8H_{15}NO$ requires C, 68.1; H, 10.6; N, 9.9%). DTA: $V = 164^\circ C$; $T_{0.5} = 153^\circ C$; $T_{max} = 190^\circ C$. $R_T = 4.8$ (12.1 min).

6-Aminooct-5-en-4-one [Hoi(3,5); $R_1 = CH_2CH_2CH_3$, $R_2 = CH_2CH_3$, $R_3 = H$]; colourless liquid. (Found: C, 68.4; H, 10.9; N, 9.5. $C_8H_{15}NO$ requires C, 68.1; H, 10.6; N, 9.9%). DTA: $V = 162^\circ C$; $T_{0.5} = 150^\circ C$; $T_{max} = 200^\circ C$. $R_T = 4.3$ (11.0 min).

2-Aminonon-2-en-4-one [Hni(2,4); $R_1 = CH_2CH_2CH_2CH_2CH_3$, $R_2 = CH_3$, $R_3 = H$]; colourless liquid. (Found: C, 69.4; H, 11.0; N, 9.0. $C_9H_{17}NO$ requires C, 69.7; H, 11.0; N, 9.0%). DTA: $V = 178^\circ C$; $T_{0.5} = 164^\circ C$; $T_{max} = 230^\circ C$. $R_T = 8.7$ (21.9 min).

3-Aminonon-3-en-5-one [Hni(3,5); $R_1 = CH_2CH_2CH_2CH_3$, $R_2 = CH_3$, $R_3 = H$]; colourless liquid. (Found: C, 69.6; H, 11.1; N, 9.1. $C_9H_{17}NO$ requires C, 69.7; H, 11.0; N, 9.0%). DTA: $V = 172^\circ C$; $T_{0.5} = 160^\circ C$; $T_{max} = 200^\circ C$; $R_T = 8.0$ (20.3 min).

6-Aminonon-5-en-4-one [Hni(4,6); $R_1 = R_2 = CH_2CH_2CH_3$, $R_3 = H$]; colourless liquid. (Found: C, 70.2; H, 11.1; N, 8.9. $C_9H_{17}NO$ requires C, 69.7; H, 11.0; N, 9.0%). DTA: $V = 174^\circ C$; $T_{0.5} = 159^\circ C$; $T_{max} = 200^\circ C$. $R_T = 7.3$ (19.1 min).

Synthesis of copper(II) chelates. The copper(II) chelates were readily* prepared in ca. 80% yields by adding an aqueous copper acetate solution (monohydrate, 2 g, 0.01 mole) to an ethanolic solution (10 ml) of sodium hydroxide (0.4 g, 0.01 mole) containing the β -ketoenamine (0.02 mole). The solution was heated briefly on a water-bath (15 min), and the product was filtered off and washed thoroughly with water and aqueous ethanol. The chelates were then recrystallised from aqueous methanol.

An alternative approach where an ammoniacal solution of a copper(II) salt is added to an alcoholic solution of the ligand was successful only if carried out under pressure to prevent loss of ammonia. Otherwise, as in the case of H-hi, the product consisted of $Cu(hi)_2$, a mixed chelate containing both β -diketone and β -ketoenamine residues, and the β -diketonate. From microanalyses and chemical ionisation MS, the ratio of these components was ca. 2:4:1 respectively.

Bis(4-aminopent-3-en-2-onato)copper(II), $Cu(aai)_2$: grey-purple crystals, melting at $185-186^\circ C$ (lit.^{60,61} $190-192^\circ C$). (Found: C, 45.8; H, 6.3; N, 10.2. Calc. for $C_{10}H_{16}CuN_2O_2$: C, 46.2; H, 6.2; N, 10.8%). DTA: $F = 186^\circ C$; unknown process at $193^\circ C$; $VD = 222^\circ C$; $T_{0.5} = 209^\circ C$; $T_{max} 290^\circ C$; residue 4.0%. $R_T = 1.0$ (3.1 min).

Bis(4-amino-1,1,1-trifluoropent-3-en-2-onato)copper(II), $Cu(tfai)_2$: purple crystals, melting at $188-190^\circ C$ (lit.⁵⁷ $188-189^\circ C$). (Found: C, 32.8; H, 2.7; N, 7.6. Calc. for $C_{10}H_{10}CuF_6N_2O_2$: C, 32.7; H, 2.7; N, 7.6%). DTA: $F = 187^\circ C$; $V = 215^\circ C$; $T_{0.5} = 193^\circ C$; $T_{max} = 270^\circ C$; residue 0.9%. $R_T = 0.5$ (1.7 min).

Bis(4-amino-3-methylpent-3-en-2-onato)copper(II), $Cu(maai)_2$: olive-green crystals, melting at $164-166^\circ C$ (lit.⁵² not given). (Found: C, 49.5; H, 7.1; N, 9.4. Calc. for $C_{12}H_{20}CuN_2O_2$: C, 50.1; H, 7.0; N, 9.7%). DTA: $F = 184^\circ C$; $DV = 210^\circ C$; $T_{0.5} = 209^\circ C$; $T_{max} = 260^\circ C$; residue 27.0%. Totally decomposed on GC column.

Bis(4-amino-3-ethylpent-3-en-2-onato)copper(II), $Cu(eaai)_2$: grey-green crystals melting at $136^\circ C$. (Found: C, 52.7; H, 7.7; N, 9.1. $C_{14}H_{24}CuN_2O_2$ requires C,

* Since $Cu(tfai)_2$ did not form readily, the reaction mixture was allowed to stand overnight before collecting the product and purifying it as in the general procedure.

53.2; H, 7.6; N, 8.9%). DTA: F = 243°C; DV = 208°C; $T_{0.5}$ = 207°C; T_{max} = 270°C; residue 27.0%. Totally decomposed on GC column.

Bis(5-aminohept-4-en-3-onato)copper(II), Cu(hi)₂: grey-purple crystals melting at 120–122°C (lit.⁵⁶ uncertain). (Found: C, 50.8; H, 7.1; N, 9.2. Calc. for C₁₂H₂₀CuN₂O₂: C, 50.1; H, 7.0; N, 9.7%). DTA: F = 128°C; VD = 229°C; $T_{0.5}$ = 217°C; T_{max} = 270°C; residue 10.0%. R_T = 1.7 (5.2 min).

Bis(2-aminohept-2-en-4-onato)copper(II), Cu(si-2,4)₂: purple crystals melting at 88–89°C. (Found: C, 52.8; H, 7.8; N, 8.6. C₁₄H₂₄CuN₂O₂ requires C, 53.2; H, 7.6; N, 8.9%). DTA: F = 98°C; VD = 237°C; $T_{0.5}$ = 225°C; T_{max} = 260°C; residue 9.0%. R_T = 2.6 (8.0 min).

Bis(5-aminohept-4-en-3-onato)copper(II), Cu(si-3,5)₂: purple crystals melting at 135–137°C. (Found: C, 53.9; H, 7.7; N, 8.6. C₁₄H₂₄CuN₂O₂ requires C, 53.2; H, 7.6; N, 8.9%). DTA: F = 139°C; unknown process at 125°C; VD = 236°C; $T_{0.5}$ = 223°C; T_{max} = 270°C; residue 8.0%. R_T = 2.6 (8.0 min).

Bis(2-aminooct-2-en-4-onato)copper(II), Cu(oi-2,4)₂: grey-purple crystals, melting at 85–86°C. (Found: C, 56.0; H, 8.2; N, 8.0. C₁₆H₂₈CuN₂O₂ requires C, 55.9; H, 8.2; N, 8.2%). DTA: F = ca. 84°C; VD = 242°C; $T_{0.5}$ = 236°C; T_{max} = 280°C; residue 14.0%. R_T = 4.7 (14.7 min).

Bis(6-aminooct-5-en-4-onato)copper(II), Cu(oi-3,5)₂: grey-purple crystals melting at 78–80°C. (Found: C, 55.6; H, 8.3; N, 8.0. C₁₆H₂₈CuN₂O₂ requires C, 55.9; H, 8.2; N, 8.2%). DTA: F = 80°C; VD = 239°C; $T_{0.5}$ = 229°C; T_{max} = 260°C; residue 15.0%. R_T = 4.1 (12.7 min).

Bis(2-aminonon-2-en-4-onato)copper(II), Cu(ni-2,4)₂: purple crystals melting at 46–47°C. (Found: C, 58.8; H, 8.9; N, 7.5. C₁₈H₃₂CuN₂O₂ requires C, 58.1; H, 8.6; N, 7.5%). DTA: F = 47°C; DV = 246°C; $T_{0.5}$ = 242°C; T_{max} = 290°C; residue 21.0%. R_T = 9.1 (28.2 min).

Bis(3-aminonon-3-en-5-onato)copper(II), Cu(ni-3,5)₂: purple crystals melting at 48–51°C. (Found: C, 58.9; H, 8.9; N, 7.5. C₁₈H₃₂CuN₂O₂ requires C, 58.1; H, 8.6; N, 7.5%). DTA: F = 46°C; DV = 248°C; $T_{0.5}$ = 243°C; T_{max} = 280°C; residue 17.0%. R_T = 7.6 (23.6 min).

Bis(6-aminonon-5-en-4-onato)copper(II), Cu(ni-4,6)₂: grey-purple crystals melting at 68°C. (Found: C, 58.4; H, 8.8; N, 7.4. C₁₈H₃₂CuN₂O₂ requires C, 58.1; H, 8.6; N, 7.5%). DTA: unknown process at 41°C; F = 67°C; DV = 247°C; $T_{0.5}$ = 230°C; T_{max} = 290°C; residue 14.0%. R_T = 6.3 (19.5 min).

Synthesis of nickel(II) chelates. The red-brownish red nickel(II) chelates were prepared (in yields of ca. 60%) by adding an excess of an ammoniacal solution of nickel chloride (ca. pH 10) to an ethanolic solution (20 ml) of ligand (0.01 mole). The mixture was heated on a water-bath (1–2 h) with occasional stirring, then the product was filtered off, washed with water and recrystallised from methanol or aqueous methanol. In the case of Ni(tfai)₂, the reaction mixture was kept at ambient temperature for 2–3 days and the red solid which formed then treated as above.

Bis(4-aminopent-en-2-onato)nickel(II), Ni(aai)₂: melts at 245–246°C (lit.⁶² 246°C). (Found: C, 47.0; H, 6.5; N, 11.0. Calc. for C₁₀H₁₆NiN₂O₂: C, 47.1; H, 6.3; N, 11.0%). DTA: FV = 246°C; $T_{0.5}$ = 233°C; T_{max} = 270°C; residue 0.3%. R_T = 1.0 (4.4 min).

Bis(4-amino-1,1,1-trifluoropent-3-en-2-onato)nickel(II), Ni(tfai)₂: melts at 199–200°C (lit.⁶³ 201°C). (Found: C, 32.9; H, 2.7; N, 7.7. Calc. for

$C_{10}H_{10}F_6NiN_2O_2$: C, 33.1; H, 2.8; N, 7.7%). DTA: F = 197°C; V = 200°C; $T_{0.5}$ = 191°C; T_{max} = 250°C; residue 0.2%. R_T = 0.4 (1.7 min).

Bis(4-amino-3-methylpent-3-en-2-onato)nickel(II), Ni(maai)₂: melts at 250°C. (Found: C, 51.2; H, 7.4; N, 10.0. $C_{12}H_{20}NiN_2O_2$ requires C, 50.9; H, 7.1; N, 9.9%). DTA: F = 252°C; V = 268°C; $T_{0.5}$ = 259°C; T_{max} = 300°C; residue 0.2%. R_T = 3.2 (14.0 min).

Bis(4-amino-3-ethylpent-3-en-2-onato)nickel(II), Ni(eaai)₂: melts at 174°C. (Found: C, 53.8; H, 7.5; N, 9.2. $C_{14}H_{24}NiN_2O_2$ requires C, 54.1; H, 7.7; N, 9.0%). DTA: F = 177°C; V = 265°C; $T_{0.5}$ = 255°C; T_{max} = 300°C; residue nil. R_T = 4.7 (20.7 min).

Bis(5-aminohept-4-en-3-onato)nickel(II), Ni(hi)₂: melts at 183–184°C (lit.⁵⁶ 187–188°C). (Found: C, 51.4; H, 7.1; N, 10.0. Calc. for $C_{12}H_{20}NiN_2O_2$: C, 50.9, H, 7.1; N, 9.9%). DTA: F = 186°C; V = 243°C; $T_{0.5}$ = 226°C; T_{max} = 300°C; residue nil. R_T = 1.6 (7.1 min).

Bis(2-aminohept-2-en-4-onato)nickel(II), Ni(si-2,4)₂: melts at 166°C. (Found: C, 53.8; H, 7.8; N, 9.0. $C_{14}H_{24}NiN_2O_2$ requires C, 54.1; H, 7.7; N, 9.0%). DTA: F = 166 and 170°C; V = 250°C; $T_{0.5}$ = 236°C; T_{max} = 265°C; residue nil. R_T = 2.5 (10.8 min).

Bis(5-aminohept-4-en-3-onato)nickel(II), Ni(si-3,5)₂: melts at 199–200°C. (Found: C, 54.5; H, 8.1; N, 9.0. $C_{14}H_{24}NiN_2O_2$ requires C, 54.1; H, 7.7; N, 9.0%). DTA: F = 203°C; V = 245°C; $T_{0.5}$ = 233°C; T_{max} = 300°C; residue nil. R_T = 2.5 (10.8 min).

Bis(2-aminooct-2-en-4-onato)nickel(II), Ni(oi-2,4)₂: melts at 162–163°C. (Found: C, 56.8; H, 8.5; N, 8.0. $C_{16}H_{28}NiN_2O_2$ requires C, 56.7; H, 8.3; N, 8.3%). DTA: F = 168°C; V = 265°C; $T_{0.5}$ = 251°C; T_{max} = 280°C; residue 1.0%. R_T = 4.0 (7.3 min).

Bis(6-aminooct-5-en-4-onato)nickel(II), Ni(oi-3,5)₂: melts at 145–146°C. (Found: C, 56.5; H, 8.3; N, 8.3. $C_{16}H_{28}NiN_2O_2$ requires C, 56.7; H, 8.3; N, 8.3%). DTA: F = 149°C; V = 260°C; $T_{0.5}$ = 244°C; T_{max} = 310°C; residue nil. R_T = 3.4 (14.7 min).

Bis(2-aminonon-2-en-4-onato)nickel(II), Ni(ni-2,4)₂: melts at 121–122°C. (Found: C, 58.9; H, 8.6; N, 7.4. $C_{18}H_{32}NiN_2O_2$ requires C, 58.9; H, 8.7; N, 7.6%). DTA: F = 121 and 125°C; V = 285°C; $T_{0.5}$ = 259°C; T_{max} = 300°C; residue nil. R_T = 6.2 (26.9 min).

Bis(3-aminonon-3-en-5-onato)nickel(II), Ni(ni-3,5)₂: melts at 110–111°C. (Found: C, 58.6; H, 9.0; N, 7.5. $C_{18}H_{32}NiN_2O_2$ requires C, 58.9; H, 8.7; N, 7.6%). DTA: F = 99 and 111°C; V = 260°C; $T_{0.5}$ = 259°C; T_{max} = 300°C; residue nil. R_T = 6.2 (26.9 min).

Bis(6-aminonon-5-en-4-onato)nickel(II), Ni(ni-4,6)₂: melts at 103–104°C. (Found: C, 58.9; H, 8.7; N, 7.6. $C_{18}H_{32}NiN_2O_2$ requires C, 58.9; H, 8.7; N, 7.6%). DTA: F = 118°C; V = 260°C; $T_{0.5}$ = 251°C; T_{max} = 300°C; residue 2.0%. R_T = 5.3 (23.1 min).

RESULTS AND DISCUSSION

Thermal properties

Ligands. Thermograms for the ligands (see Fig. 1) show that these compounds

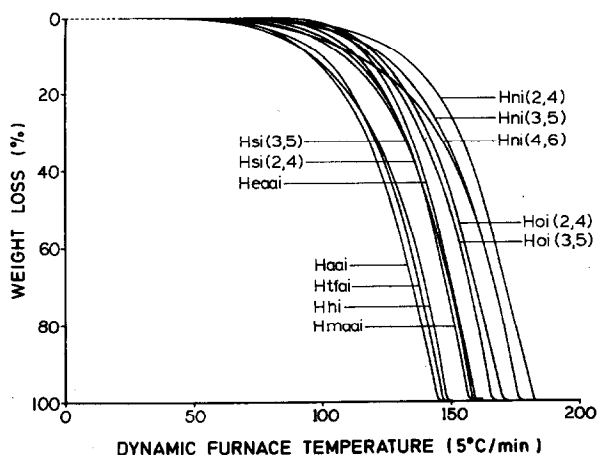


Fig. 1. Thermogravimetric curves for bidentate β -ketoenamines.

are thermally stable, sublime without decomposition in the range 140–180°C. The stability of the compounds was confirmed by GC examination of the colourless sublimes. The following order* of decreasing volatility was observed: Hhai > Htfai > Hhi > Hmaai > Hsi(3,5), Hsi(2,4) > Heaai > Hoi(3,5) > Hoi(2,4) > Hni(4,6) > Hni(3,5) > Hni(2,4).

Based on these results, several comments may be made regarding the influence of substituents in the ligands. Because of the similarity of these substituents, variations in volatility probably reflect differences in the packing geometry.

(i) Progressive increase of the carbon chain-length is accompanied by a gradual reduction in volatility.

(ii) Greater asymmetry in the molecule introduced by variation in the terminal substituents (R_1 and R_2) leads to a reduction in volatility. This is evident among the larger molecules, particularly in Hni(2,4) which is appreciably less volatile than its symmetrical isomer Hni(4,6). Volatility differences of this type tend to diminish as the difference in the chain-length of the two alkyl substituents, and hence the overall molecular asymmetry, is reduced. This relationship holds in other isomers also [e.g. Hoi(3,5) and Hoi(2,4), and Hsi(3,5) and Hsi(2,4)].

(iii) The α -substituted ligands, Hmaai and Heaai, are less volatile than their straight-chain isomers, Hhi and Hsi. Here the order of volatility, based on molecular symmetry, does not appear to hold.

(iv) The fluorinated ligand Htfai is only slightly less volatile than its non-fluorinated analogue, Hhai.

Chelates. Thermal data for nickel and copper chelates establish that the nickel compounds vaporise below 285°C without decomposition (see Fig. 2). In marked contrast (see Fig. 3) and with the exception of the sole fluorinated chelate examined, $\text{Cu}(\text{tfai})_2$, all copper chelates decomposed to some extent, leaving various amounts

* This sequence is based (as are the series for copper and nickel chelates) on a comparison of temperatures corresponding to 50% weight-loss of samples during volatilisation.

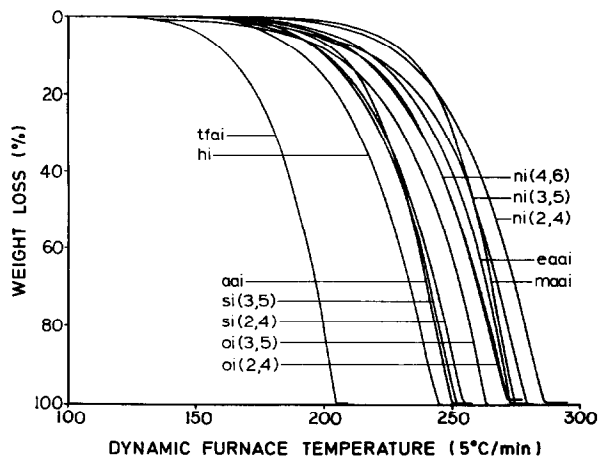


Fig. 2. Thermogravimetric curves for nickel chelates of the bidentate β -ketoenamines.

of residues in the sample cups. Of these, $\text{Cu}(\text{aai})_2$ appeared to be the most stable (with 4% residue) whereas the α -substituted compounds, $\text{Cu}(\text{maai})_2$ and $\text{Cu}(\text{eaii})_2$, were the least stable (with residues of 27%). As the chain-length of the substituents increased, the copper chelates tended to be more unstable thermally. In this regard, the trend is similar to that reported for the β -diketonates⁶⁴. However, smaller residues were observed for the chelates of the symmetrical, isomeric ketoenamines [e.g. the copper(II) chelates of Hni]. From the thermal data, the descending order of volatility is as follows: [for nickel(II) chelates] $\text{Htfai} \gg \text{Hhi} > \text{Haai} > \text{Hsi}(3,5) > \text{Hsi}(2,4) > \text{Hoi}(3,5) > \text{Hoi}(2,4)$, $\text{Hni}(4,6) > \text{Heaii} > \text{Hmaai} > \text{Hni}(3,5) > \text{Hni}(2,4)$; [for copper(II) chelates, excluding those of Hmaai and Heaii] $\text{Htfai} > \text{Haai} > \text{Hhi} > \text{Hsi}(3,5) > \text{Hsi}(2,4) > \text{Hoi}(3,5) > \text{Hoi}(2,4) > \text{Hni}(4,6) > \text{Hni}(2,4) > \text{Hni}(3,5)$.

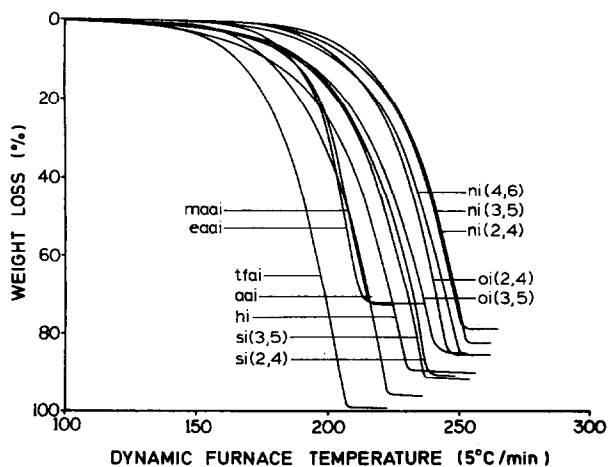


Fig. 3. Thermogravimetric curves for copper chelates of the bidentate β -ketoenamines.

Irrespective of the metal ion, several trends in volatility are notable and dictated by the substituents.

(i) As for the ligands, increasing the chain-length of the substituent reduces the volatility, as expected. Ni(hi)₂, which is appreciably more volatile than Ni(aai)₂, is an exception.

(ii) As for the ligands, the presence of alkyl groups in the α -position of the β -diketone reduces the volatility of the nickel chelates. This may be due to an inductive (+I) effect operating to increase the electron density of the conjugated π -system and its greater interaction with metal ions in other molecules^{65,66}, or in metal-nitrogen interaction⁶⁷ owing to an increase in the Lewis basicity of nitrogen in the molecule.

(iii) Although substitution of a trifluoromethyl group for a methyl group reduces the volatility of the ligand, there is a dramatic improvement in the observed volatility of both chelates. This implies a more uniform electron distribution following chelation, accompanied by a reduction of the molecular dipole due to the inductive effect (-I) of the CF₃ group and the basicity of the nitrogen atom in the molecule. As a consequence, the dipole moment of the chelate should depend largely on the Lewis acidity of the metal ion to control the order of volatility of the chelates of the same ligand. Thus, the greater volatility of the copper chelates applies generally (with the exception of the fluorinated chelate), although the effect is obscured by their lower thermal stability.

(iv) As with the ligands, a reduction in volatility accompanies a change in molecular symmetry of the chelates. Some minor exceptions exist, however, such as the higher volatility of Ni(hi)₂ compared with Ni(aai)₂, and of Cu(ni-2,4)₂ relative to Cu(ni-3,5)₂.

Gas chromatography

Ligands. Under the experimental conditions employed, the elution of the ligands on the non-polar stationary phase SE-30 followed the same order as their volatility. Thus, the resolution between any two compounds within the series of ligands is controlled by the difference in their volatilities as determined by thermal analysis. Fig. 4 illustrates the resolution of isomeric ketoenamines synthesised from isomeric β -diketones. On this non-polar column, the separation of relatively small molecules, such as Hsi(2,4) and Hsi(3,5), is poor, and the partial separation shown in Fig. 4c was achieved on only a very polar stationary phase. It may be noted that although separation of the isomeric forms of the bidentate ketoenamines [*i.e.* R₁COCH=C(NH₂)R₂ and R₂COCH=C(NH₂)R₁] has not been successful even with comparatively long-chain molecules [such as Hni(2,4) and Hni(3,5)], their existence is established by the successful resolution of a group of related tetradentate ligands. Details of this work are given in ref. 71.

Chelates. The retention times for the elution of both nickel and copper chelates follow the same order as their volatilities based on thermal analysis and, because of the differences in volatility which exist, a good separation of copper and nickel chelates is attainable. The main difficulty lies, however, in the lability of the copper chelates, observable even for amounts above the microgram level. Elevated baselines, indicating the slow elution of volatile decomposition products, are characteristic of these chelates. In parallel with the thermoanalytical data, extremes of lability were

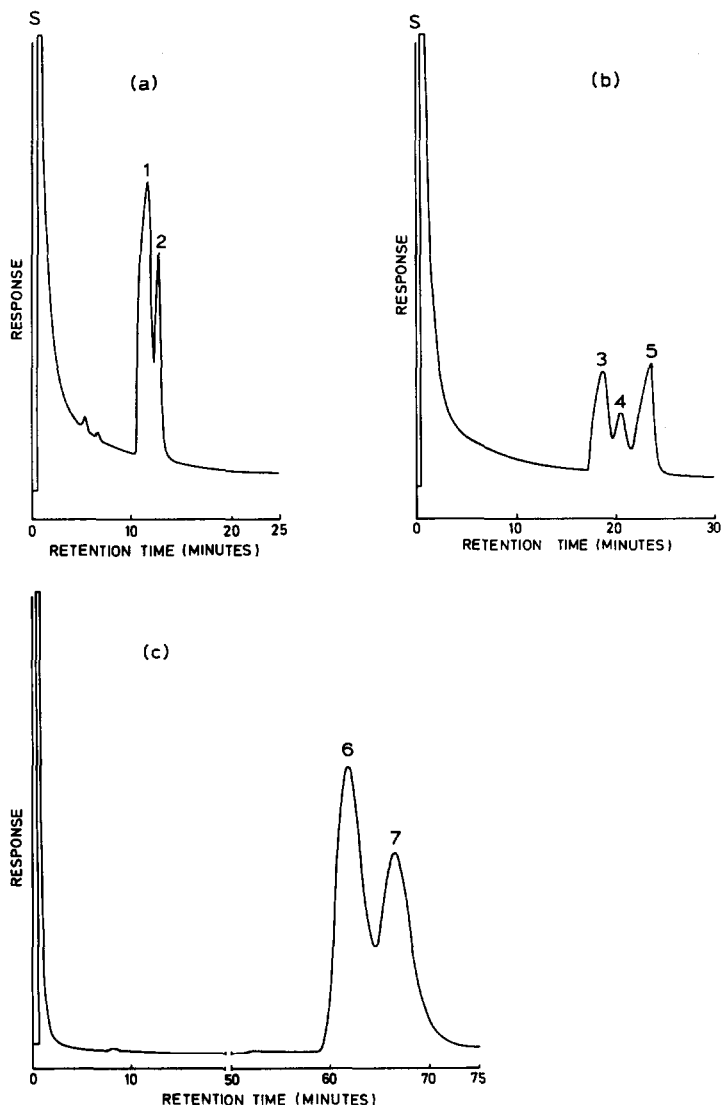


Fig. 4. Chromatograms showing the separation of ligand isomers of (a) Hoi, (b) Hni and (c) Hsi. Peaks: 1 = Hoi(3,5); 2 = Hoi(2,4); 3 = Hni(4,6); 4 = Hni(3,5); 5 = Hni(2,4); 6 = Hsi(3,5); 7 = Hsi(2,4); S = solvent.

demonstrated by the copper chelates of Hmaai and Heaai where the only obvious peaks to be seen eluted close to the solvent peak. Again, regardless of its adequate thermal stability and excellent volatility, the copper chelate of Htfai behaved poorly on the column and was not separated from the nickel compound.

Despite the advantage of a rapid reaction in chelate formation which is typical of the non-fluorinated ligands, these Schiff bases appear to be unsuitable reagents for the trace determination of copper. On the other hand, all nickel chelates elute with

TABLE I
 PROTON CHEMICAL SHIFTS FOR BIDENTATE SCHIFF BASES AND THEIR NICKEL(II) DERIVATIVE

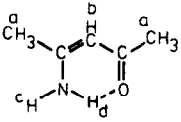
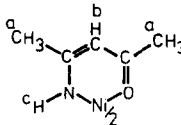
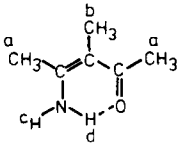
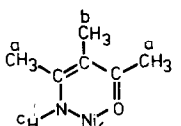
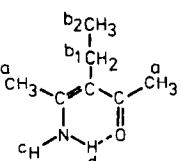
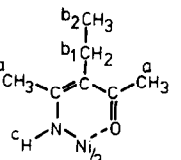
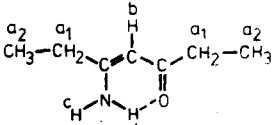
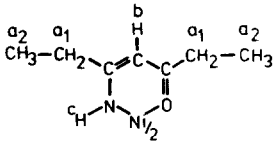
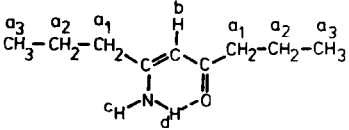
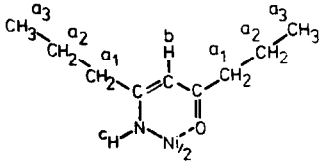
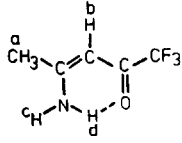
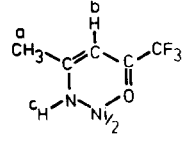
Compound	Solvent	Proton chemical shifts (ppm)*			
		a	b**	c***	d [†]
	C ² HCl ₃	1.91, 2.00 ^{§§}	4.98	5.85	9.7
	C ₆ ² H ₆	1.49, 1.92	4.82	5.81	9.9
	C ² HCl ₃	1.72, 1.88	4.83 ^d (J=2.5)	4.95	—
	C ₆ ² H ₆	1.25, 1.73	4.71 ^d	5.20	—
	C ² HCl ₃	1.95, 2.12	1.81	5.80	10.0
	C ₆ ² H ₆	1.46, 2.03	1.57	§§§	§§§
	C ² HCl ₃	1.79, 1.94	1.68	5.23	—
	C ₆ ² H ₆	1.34, 1.82	1.49	5.45	—
	C ² HCl ₃	1.98, 2.16	2.24 ^a , 1.02 ^t	§§§	10.0
	C ₆ ² H ₆	1.48, 2.09	2.04 ^a , 0.87 ^t	§§§	10.10
	C ² HCl ₃	1.83, 1.99	2.10 ^a , 0.91 ^t	5.21	—
	C ₆ ² H ₆	1.41, 1.86	1.93 ^a , 0.81 ^t	5.48	—
	C ² HCl ₃	2.17 ^a , 2.30 ^a ; 1.09 ^t , 1.16 ^t	5.01	5.40	9.7
	C ₆ ² H ₆	1.78 ^a , 2.24 ^a ; 0.87 ^t , 1.13 ^t	4.91	5.38	9.9

TABLE I (continued)

Compound	Solvent	Proton chemical shifts (ppm)*			
		a	b**	c***	d [§]
	C ² HCl ₃	1.98 ^a , 2.15 ^a ; 0.96 ^t , 1.09 ^t	4.85 ^d (<i>J ca.</i> 2.8)	5.09	
	C ₆ ² H ₆	1.66 ^a , 2.06 ^a ; 0.71 ^t , 1.04 ^t	4.86 ^d	5.36	—
	Neat	2.10 ^m ; 1.58 ^m ; 0.88 ^t , 0.90 ^t	4.94	7.43	9.8
	C ² HCl ₃	2.15 ^m ; 1.59 ^a ; 0.88 ^t , 0.91 ^t , 0.91 ^t	4.97	6.03	9.8
	C ₆ ² H ₆	1.94 ^t , 2.20 ^t ; 1.55 sm ; 0.83 ^t , 0.89 ^t	4.94	6.50	10.00
	C ² HCl ₃	1.99 ^t , 2.07 ^t ; 1.46 ^m ; 0.83 ^t , 0.91 ^t	4.79	5.01	—
	C ₆ ² H ₆	2.04 ^t (<i>J</i> = 7.2) [†] ; —; 0.64 ^t , 0.86 ^t	4.84	5.30	—
	C ² HCl ₃	2.09	5.34	6.77	10.0
	C ₆ ² H ₆	1.25	5.12	5.78	9.8
	C ² HCl ₃	2.06	5.39 ^d (<i>J</i> = 3.0)	5.81	—
	C ₆ ² H ₆	0.86	5.14 ^d	5.50	—

* Signals are singlets unless stated otherwise. Abbreviations used are: *d* = doublet; *t* = triplet; *q* = quartet; *s* = sextet which under an expanded scale appears to be two slightly non-equivalent sextets distinguishing the carbonyl and the amino ends of the molecule; *m* = complex multiplet, the value quoted describes the middle of the range; *sm* = multiplet, possibly two overlapping sextets, middle position of the multiplet quoted. Coupling constants vary between 7.0 and 7.5 Hz unless stated otherwise.

** Weak acidity of the methine proton is often indicated by the reduction of signal after ²H₂O exchange in the ligands.

*** Broad singlet (almost absent in Heaai) which disappears after ²H₂O exchange of the ligands. This proton does not seem to be exchangeable in the few nickel(II) chelates studied.

§ Broad singlet which disappears upon deuteration; δ values quoted are those obtained by triangulation and are given to ± 0.1 ppm.

§§ Terminal and proximal protons are not distinguished here.

§§§ This is a very broad signal.

† Value indicates the chemical shift of the methylene protons (*a*₁) at the carbonyl end. Owing to the solvent shift effect two complex multiplets appear in the spectrum for the proton resonances (*a*₁ at the amino end and *a*₂ methylene protons at both ends of the molecule), exact positions of which have not been ascertained. The *a*₃ protons give rise to the expected triplets.

symmetrical peaks, a feature which is maintained well below microgram amounts. It is not surprising, therefore, that a detection limit of 50 pg has been reported⁶⁹ for Ni(tfai)₂.

NMR data

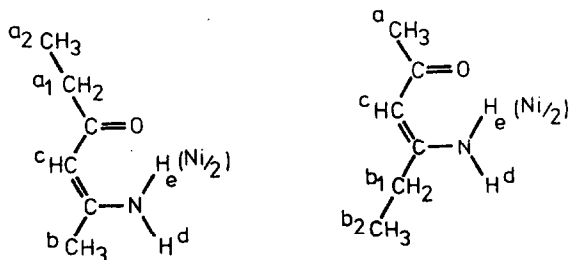
Table I summarises the ¹H NMR data for the β-ketoenamines and nickel chelates examined. For all the ligands, the NH resonances in the low-field region suggest that hydrogen bonding exists between the amino group and the oxygen atom of the carbonyl group²⁸. This forces the *cis-s-cis* geometry for the ligands^{39,44}, as shown in Table I.

Briefly, the data show that weakly acidic methine protons appear at *ca.* 4.9 ppm. There is a shift downfield by *ca.* 0.4 ppm in the case of Htfai, consistent with an increased acidity due to the electron-withdrawing CF₃ group. In Hmaai, the α-methyl protons appear further upfield than do any of the terminal methyl signals (in deuteriochloroform), and Heai shows the expected first-order coupling required to produce a quartet and triplet due to the α-ethyl protons. In addition, the first-order spin-spin coupling is also maintained to some extent among the protons in terminal substituents, but with increased alkyl chain-length there is a departure from the simple first-order splitting. One additional complication in the spectra of compounds containing longer alkyl substituents [*e.g.*, Hni(4,6) and its nickel(II) derivative], is the slight non-equivalence of the corresponding protons of the terminal substituents in the molecule, and this gives rise to overlapping resonance signals. For this reason, identification of resonances was difficult in a number of Schiff bases [such as Hni(2,4) or its nickel(II) derivative].

An interesting, although apparently obscure, feature of the spectra of Hmaai

TABLE II

PROTON CHEMICAL SHIFTS FOR AN ISOMERIC MIXTURE OF 5-AMINOHEX-4-EN-3-ONE AND ITS NICKEL(II) CHELATES



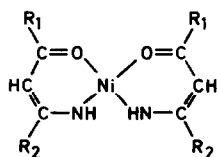
Solvent deuterobenzene.

Compound	Proton chemical shifts (ppm)*								
	a ₁	a ₂	a	b	b ₁	b ₂	c	d	e
Hhi	2.21 ^{qJ}	1.11 ^{tJ}	1.94 ^s	1.49 ^s	1.73 ^{qJ}	0.87 ^{tJ}	4.86 ^s	<i>ca.</i> 5.50 ^{bs}	<i>ca.</i> 9.90 ^{bs}
Ni(hi) ₂	2.03 ^{qJ}	1.02 ^{tJ}	1.77 ^s	1.35 ^s	1.67 ^{qJ}	0.72 ^{tJ}	4.75 ^m	<i>ca.</i> 5.20 ^{bs}	—

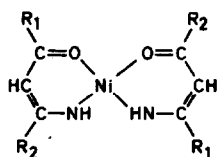
* Abbreviations: *s* = singlet; *bs* = broad singlet; *t* = triplet; *q* = quartet; *m* = a distorted triplet (*J* = 1.8 and 2.5 Hz) due to contributions from three isomers. *J* splitting of 7.5 Hz.

and Heai is the frequent occurrence of very broad resonances for the free NH and hydrogen-bonded NH. These are often unrecognisable and have area integrals showing either depleted proton counts or none at all. In the corresponding nickel(II) complexes (see also Table I), the free NH signals are relatively sharp and give correct proton counts. However, these free NH protons consistently move upfield (by as much as 1.2 ppm more than in the free ligands) indicating an increased covalency. Only with the spectra of Hsi(3,5) and Ni(si-3,5)₂, in deuterobenzene, is this difference absent. In the nickel(II) complexes, other protons remain virtually unchanged or undergo a slight upfield shift by *ca.* 0.2 ppm relative to the analogous protons in the free bases. Methine protons in the chelates split into doublets ($J = 2.5\text{--}3$ Hz), indicative of non-equivalence due to a slight departure⁷⁰ from a strictly square-planar structure.

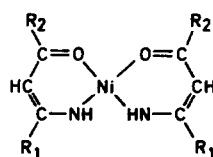
It may be noted that, with the exception of Htfai and Ni(tfai)₂, all species in Table I are symmetrically substituted. For the unsymmetrical compounds, assignment of a particular isomeric structure is dependent on the unambiguous recognition of the terminal substituents (R_1 and R_2), and is facilitated by the upfield displacement of the resonances⁷¹ of protons nearer the nitrogen atom when examined in an aromatic solvent, such as deuterobenzene. The upfield shift observed for the methyl singlet in Htfai and its chelate (0.84 and 1.20 ppm, respectively, in the spectra of these compounds in benzene relative to chloroform) confirms the structure shown in Table I.



Structure I



Structure II



Structure III

Proton chemical shifts for another unsymmetrical ligand, Hhi, and its nickel(II) chelate are given in Table II. In this case, the spectrum of the ligand can be rationalised by reference to the two isomeric structures shown (see also Structures I and II), to the proton counts, and to the displacement of chemical shifts referred to above. In addition, from the intensity ratio of the resonances of the *a* and *b* protons, an approximate proportion of 7:3 for the two isomers exists, with the isomer represented by Structure I being the major isomer of Hhi. In fact, although supporting data are not presented here*, the major isomer in related asymmetric bidentate Schiff bases is the one containing the larger alkyl substituent adjacent to the carbonyl group.

Spectra of the nickel(II) chelates are less straightforward than for the ligands as a result of the presence of three isomers (see Structure III). The NMR data for Ni(hi)₂ can be rationalised in terms of only the two isomeric structures shown in

* This statement is based on the proton spectra of Hsi(2,4), Hoi(2,4), Hoi(3,5), Hni(2,4) and Hni(3,5). The data are not included because of their complexity, arising from the presence of isomeric forms and the tendency of the spectra to deviate from first-order coupling as the chain-length of the alkyl substituent increases.

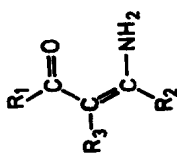
TABLE III
CARBON-13 CHEMICAL SHIFTS OF SELECTED β -KETOENAMINES

H- \bar{a} ai	H-eaai		H-hi		H-si(3,5)		H-si(2,4)		H-ni(4,6)		H-ni(3,5)	
	1	2	1	2	1	2	1	2	1	2	1	2
C _{1.1}	C _{1.1}	C _{1.1}	C _{1.1}	C _{1.1}	C _{1.2}	C _{1.1}	C _{1.3}	C _{1.1}	C _{1.3}	C _{1.2}	C _{1.2}	C _{1.4}
C ₁₌₀	C ₁₌₀	C ₁₌₀	C ₁₌₀	C ₁₌₀	C ₁₌₀	C _{1.2}	C _{1.2}	C ₁₌₀	C _{1.2}	C _{1.1}	C _{1.1}	C _{1.3}
C ₂	C _{2.1-C₂}	C _{2.1-C₂}	C ₂	C ₂	C ₂	C _{1.1}	C _{1.1}	C ₂	C _{1.1}	C _{1.1}	C ₁₌₀	C _{1.2}
C _{3-NH₂}	C _{3-NH₂}	C _{3-NH₂}	C _{3-NH₂}	C _{3-NH₂}	C ₂	C ₂	C ₁₌₀	C _{3-NH₂}	C ₁₌₀	C ₂	C ₂	C _{1.1}
C _{3.1}	C _{3.1}	C _{3.1}	C _{3.1}	C _{3.1}	C _{3.1}	C _{3.1}	C _{3-NH₂}	C _{3.1}	C _{3.1}	C _{3-NH₂}	C _{3-NH₂}	C ₁₌₀
					C _{3.2}	C _{3.2}	C _{3.1}	C _{3.2}	C _{3.1}	C _{3.1}	C _{3.1}	C ₂
					C _{3.1}	C _{3.1}	C _{3.1}	C _{3.3}	C _{3.1}	C _{3.2}	C _{3.2}	C _{3.1}
					C _{3.2}	C _{3.2}	C _{3.2}	C _{3.3}	C _{3.2}	C _{3.2}	C _{3.3}	C _{3.2}

Compound Carbon-13 chemical shifts (ppm)

Compound	C ₁	C ₂	C ₃	C _{1.1}	C _{1.2}	C _{1.3}	C _{1.4}	C _{2.1}	C _{2.2}	C _{3.1}	C _{3.2}	C _{3.3}	C _{3.4}
Haai	196.5	95.6	161.4	29.2	—	—	—	—	—	22.1	—	—	—
Hmaai	197.3	99.0	159.3	28.5	—	—	—	14.4	—	21.7	—	—	—
Heaai	197.0	106.1	160.1	27.3	—	—	—	20.6	15.3	21.9	—	—	—
Hhi: 1	200.4	94.5	161.7	35.2	12.2	—	—	—	—	22.2	—	—	—
Hhi: 2	197.0	94.1	167.0	29.3	12.2	—	—	—	—	29.3	9.4	—	—
Hsi(3,5)	200.7	93.1	166.9	35.3	12.2	—	—	—	—	29.3	9.9	—	—
Hsi(2,4): 1	199.5	94.9	162.6	42.2	23.0	14.0	—	—	—	22.5	—	—	—
Hsi(2,4): 2	196.3	94.5	166.9	29.2	—	—	—	—	—	36.1	22.0	13.3	—
Hni(4,6)	199.4	94.5	165.5	44.6	21.4	14.1	—	—	—	38.5	19.9	13.7	—
Hni(3,5): 1	200.1	93.6	166.1	36.2	14.0	—	—	—	—	35.3	28.3	22.4	10.0
Hni(3,5): 2	200.4	93.8	167.1	42.3	29.4	22.7	12.2	—	—	30.3	13.8	—	—

TABLE IV
MASS SPECTRAL DATA FOR SELECTED BIDENTATE SCHIFF BASES

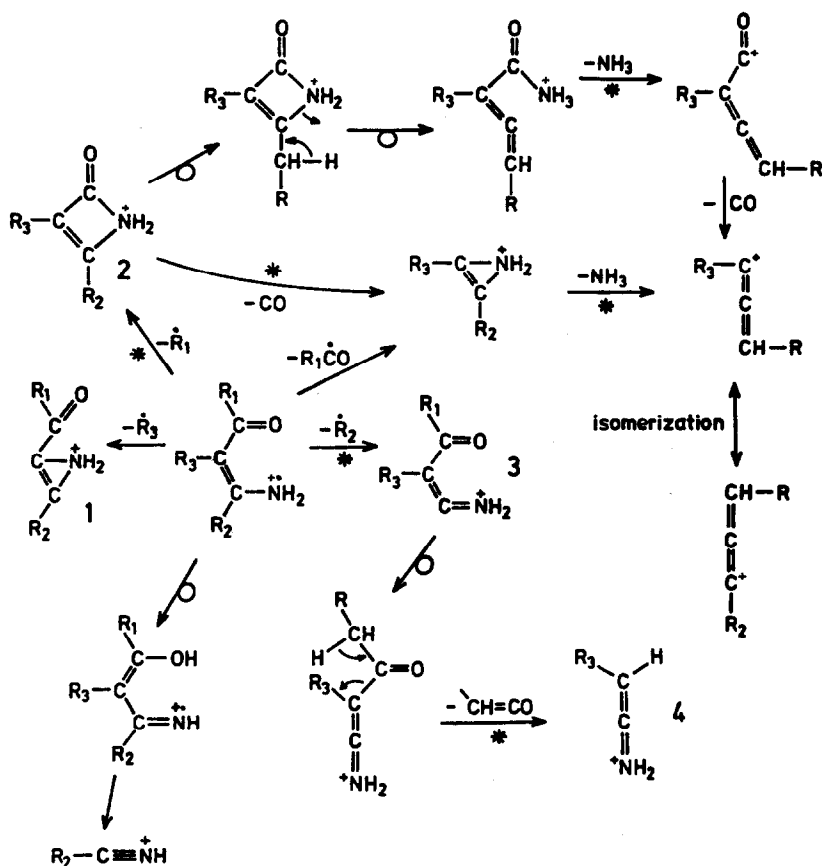


Fragment ion	<i>m/e</i> (% abundance relative to most intense peak)						
	<i>Haa</i> ($\text{R}_1 = \text{R}_2 = \text{CH}_3$, $\text{R}_3 = \text{H}$)	<i>Hsi</i> (3,5) ($\text{R}_1 = \text{R}_2 = \text{CH}_3\text{CH}_2$, $\text{R}_3 = \text{H}$)	<i>Hni</i> (4,6) ($\text{R}_1 = \text{R}_2 = \text{CH}_3\text{CH}_2\text{CH}_2$, $\text{R}_3 = \text{H}$)	<i>Hfy</i> ($\text{R}_1 = \text{CF}_3$, $\text{R}_2 = \text{CH}_3$, $\text{R}_3 = \text{H}$)	<i>Hma</i> ($\text{R}_1 = \text{R}_2 =$ $\text{R}_3 = \text{CH}_3$)	<i>Hea</i> ($\text{R}_1 = \text{R}_2 = \text{CH}_3$, $\text{R}_3 = \text{CH}_3\text{CH}_2$)	
MH^+	100(6)	128(10)	156(4)	154(4)	114(9)	128(9)	
M^+	99(78)	127(98)	155(23)	153(60)	113(98)	127(97)	
$[\text{M}-\text{R}_3]^+$	98(1)	126(2)	154(4)	—	84(11)	84(20)	
$[\text{MH}-\text{R}_1]^+$	85*(6)	99*(20)	113(9)	85(4)	99(9)	113*(13)	
$[\text{M}-\text{R}_1]^+$	84*(100)	98*(100)	112*(100)	84(100)	98*(100)	112*(100)	
$[(\text{M}-\text{R}_1)-\text{R}_2\text{R}_3]^+$	68(2)	68(10)	68(5)	68(9)	68(4)	68(9)	
$[(\text{M}-\text{R}_1)-\text{NH}_3]^+$	67*(2)	81*(4)	95(<1)	67(2)	81(<1)	95(<1)	
$[(\text{M}-\text{R}_1)-\text{CO}]^+$	56*(3)	70*(7)	84*(6)	56(2)	70*(40)	84*(20)	
$[\text{M}-\text{R}_1\text{CO}]^+$	56(3)	70(7)	84(6)	56(2)	70(40)	84(20)	
$[\text{M}-\text{C}_2\text{H}_4]^+$	—	—	127*(5)	—	—	99(5)	
$[(\text{M}-\text{C}_2\text{H}_4)-\text{C}_2\text{H}_4]^+$	—	—	99*(<1)	—	—	—	
$[\text{M}-\text{C}_2\text{H}_5\text{CO}]^+$	—	—	—	—	—	70*(78)	
R_1CO^+	43(39)	57(15)	71(11)	—	43(36)	43(60)	
$[(\text{M}-\text{R}_2)-\text{CH}_2\text{CO}]^+$	42(19)	56*(49)	70(15)	—	56(13)	70*(78)	
R_2CNH^+	42(19)	56(49)	70(15)	—	42(24)	42(37)	
$[(\text{M}-\text{R}_2)-(\text{R}_1-\text{H})\text{CO}]^+$	42(19)	42(15)	42(7)	42(59)	56(13)	70(78)	
$[(\text{M}-\text{R}_1-\text{CO})-\text{NH}_3]^+$	39(5)	53(12)	67*(<1)	39(8)	53*(8)	67*(12)	
$[(\text{M}-\text{R}_1-\text{NH}_3)-\text{CO}]^+$	39(5)	53(12)	67(<1)	39(8)	53(8)	67(12)	
R_1^+	—	29(25)	43(18)	69(10)	—	—	

* Presence of metastable peak for the transition.

Table II. Furthermore, a major difference in the interpretation of the spectra is that for the chelate, proton counts cannot be explained by assuming the presence of only two isomers. This is only an indirect proof of a third chelate isomer and, of course, unambiguous proof must await their isolation. However, synthesis of nickel(II) complexes of new tetradentate ligand containing a dione bridge is a step in this direction, and is the subject of a later paper in this series⁷¹.

Additional evidence of isomerism in Schiff bases is provided by ¹³C NMR spectroscopy, as shown in Table III for the ligands Haai, Hmaai, Heaai, Hhi, Hsi(3,5), (Hsi(2,4), Hni(4,6) and Hni(3,5). Values assigned are comparable with those previously reported^{43,72-75} for related compounds, and it is significant that two similar resonances of unequal intensities appear for each carbon in the spectra of the asymmetric Schiff bases [namely, Hhi, Hsi(2,4) and Hni(3,5)] and can only be rationalised by assuming that two isomeric structures exist for each compound. Sym-



R₂ and R₃ are changed to the equivalent RCH₂ to clarify mechanisms.

* indicates the existence of metastable ions for the particular transition.

$\xrightarrow{\text{O}}$ indicates a rearrangement.

Scheme 1.

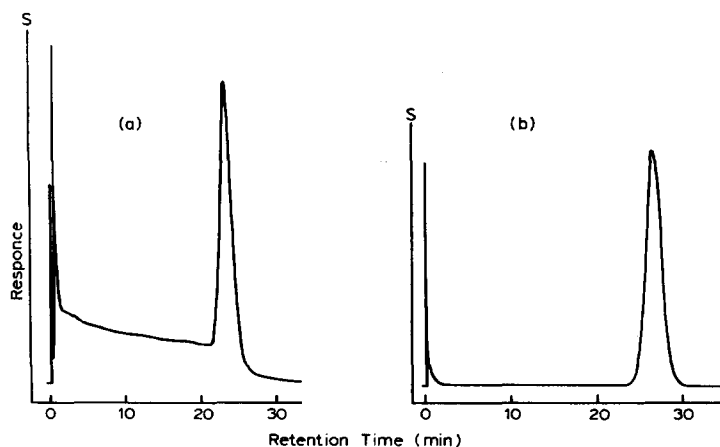


Fig. 5. Chromatograms of (a) $\text{Cu}(\text{ni-3,5})_2$ and (b) $\text{Ni}(\text{ni-3,5})_2$.

metrical compounds, on the other hand, give rise to a single resonance signal for each carbon. Thus, among others, the spectrum of Haai showed, five different resonances, whereas Hmaai and Hni(4,6) gave six and nine, respectively.

Mass spectral data

For the ligands, the relative abundances of the major fragments resulting from electron impact are presented in Table IV. The most prominent features of the spectra of these compounds are (i) the strong molecular ion ($\text{M}^{+\cdot}$), (ii) loss of the alkyl group R_1 from $\text{M}^{+\cdot}$ to yield the base-peak, (iii) low abundance (*ca.* 2%) of the protonated molecular ion and its subsequent elimination of R_1 . Scheme 1 summarises mechanisms proposed for the major fragmentation pathways.

An interesting fragmentation route for the α -alkyl-substituted ligands is the loss from $\text{M}^{+\cdot}$ of the radical R_3CO . This elimination, involving alkyl-migration, is prominently displayed in the case of Heai and results from a concerted mechanism supported by the corresponding metastable ion.

The mass spectrum of Htfai, the sole unsymmetrical ligand in Table IV, contains the ion $(\text{M} - \text{R}_1)^+$ but not the ion due to $(\text{M} - \text{R}_2)^+$. Apart from the ease⁷⁶ of losing the trifluoromethyl group, this is probably due to the higher stability of fragment ion 2 (over that of ion 3) because of cyclisation and the tendency of nitrogen to minimise the number of double bonds²⁹. In addition, the absence of the fragment ion 4 from the spectrum is in accord with the conclusion drawn from the NMR data, namely, that this compound contains the CF_3 group only at the terminal position near the carbonyl group. The case of other asymmetrical ligands is less straightforward and is made more complex by the presence of isomers. Thus, in the spectra of these compounds, the appearance of metastable peaks corresponding to both fragmentation routes involving $[(\text{M} - \text{CH}_3) - \text{C}_2\text{H}_4\text{CO}]^+$ and $[(\text{M} - \text{CH}_2\text{CH}_3) - (\text{CH}_2\text{CO})]^+$ reinforces the earlier inference, based on NMR data, that the theoretically predicted isomers do really exist.

Although the mass spectra of the chelates are not discussed here, generally the chelates gave good spectra with strong molecular ions.

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