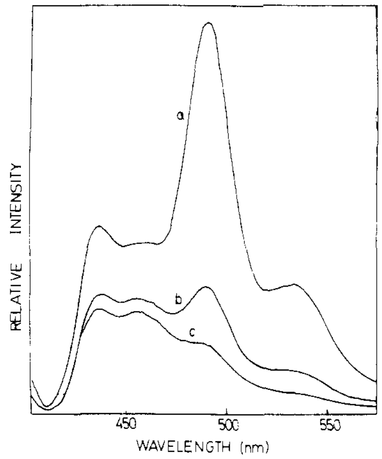

Figure 3. Emission spectra of biacetyl in deoxygenated methanol containing various concentrations of $Co(acac)_2N_3NH_3$. The exciting radiation was 430 nm, and the biacetyl concentration was 0.342M; the concentrations of $Co(acac)_2N_3NH_3$ were 0.0 M (a), 1.90×10^{-4} M (b), and 5.69×10^{-4} M (c).

^{3}benzophenone energy transfer and that sensitization occurs via an energy-transfer mechanism.

Concomitant with sensitizing the decomposition of $Co(acac)_2N_3NH_3$, benzophenone's phosphorescence is quenched by $Co(acac)_2N_3NH_3$. Emission-quenching determinations were carried out in deoxygenated solutions with a benzophenone concentration of 2.62×10^{-2} M. A plot of I_0/I (I is intensity), which is corrected for the fraction of exciting radiation absorbed by benzophenone, vs. $Co(acac)_2N_3NH_3$ concentration is given in Figure 2. As might be expected the quenching exhibits Stern–Volmer kinetics with a quenching constant of 2.16×10^3 M^{-1}.

Biacetyl emits both flourescence and phosphorescence in fluid solution. Excitation of a 3.34 M deoxygenated methanolic solution made 5.70×10^{-4} M in $Co(acac)_2N_3NH_3$ resulted in quenching 80% of the phosphorescence and 45% of the flourescence compared to a solution containing no $Co(acac)_2N_3NH_3$ (Figure 3). The extent to which the flourescence was quenched might be easily accounted for as a result of internal filtering by $Co(acac)_2N_3NH_3$. Zinc tetraphenylporphyrin fluoresces strongly at 603 and 654 nm. No significant fluoresces of the emission resulting from 400-nm excitation is observed when a 2.69×10^{-5} M zinc tetraphenylporphyrin solution is made 6.31×10^{-5} M in $Co(acac)_2N_3NH_3$. In addition, excitation into the 420-nm soret band of zinc tetraphenylporphyrin did not sensitize any photodecomposition of 5.79×10^{-5} M $Co(acac)_2N_3NH_3$.

Sensitized-photolysis results are consistent with the mechanistic proposals put forth in our previous communication.[1,2] Whereas the singlet-state emissions of excited molecules are not quenched by $Co(acac)_2N_3NH_3$, emitting triplet states are quenched by $Co(acac)_2N_3NH_3$. The emission quenching obeys Stern–Volmer kinetics and in the presence of oxygen exhibits kinetics consistent with competitive quenching between $Co(acac)_2N_3NH_3$ and O_2. Several molecules with low-energy triplet states sensitize the decomposition $Co(acac)_2N_3NH_3$ in the same manner as by direct photolysis. The lowest energy sensitizer, benzil, has a triplet energy of 18.5×10^3 cm^{-1}, thus bracketing the photoactive state energy within $(18.5–17.2) \times 10^3$ cm^{-1}.

Registry No. $Co(acac)_2N_3NH_3$, 38977-23-0.

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Oxidative Transformations in Nickel(II) Chelates of Tetradentate Schiff Bases

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Nickel(II) chelates of tetradentate β-keto enamines undergo aerial oxidation at the ethylene bridge to form a variety of monomeric nickel(II) chelate species. Chromatographic separation and identification of the products obtained from the oxidation of several chelates are reported, and, in some cases, structural isomers of the original and oxidized forms are identified. The sensitivity of the chelates to oxidation, studied by cyclic voltammetry and thermal analysis, are strongly influenced by substituents in the ligand. Oxidation of a Schiff base chelate with hydrogen peroxide removes the ethylene bridge, giving a ternary nickel(II) complex.

Tetradentate Schiff bases are known[2,3] to give highly stable chelates with bivalent metal ions. Indeed, certain chelates of Cu(II), Ni(II), Pd(II), and V(IV) are sufficiently stable to be volatilized and eluted intact from chromatographic columns at temperatures above 250 °C.[4-8] The stability of these derivatives, however, is markedly influenced by the substituents in the ligand. In the general structure I, a two-carbon bridge between the β-keto enamine rings, with fluoroalkyl substituents at R_1 or R_2, produces greatest chelate stability for a given bivalent metal ion, M. Longer bridging groups, or substituents in place of hydrogen at R_4 (such as halogens or alkyl groups), dramatically reduce stability,[7] probably by steric strain in the chelate rings.

Thermal stability of the chelates is limited by the dehydrogenation reaction which can occur at the two-carbon bridge. This reaction is affected by the type of substituent on the

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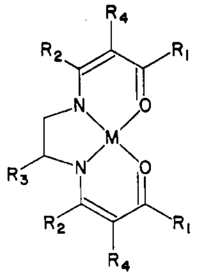

I

M = Cu(II), Ni(II), Co(II), Pd(II), V(IV)O

ligand.[7] Thus, it is promoted by alkyl or branched-alkyl groups whereas it is inhibited by fluoroalkyl substituents at R_1 or R_2.

A further source of instability in the Schiff base chelates derives from their susceptibility to aerial oxidation, a feature most evident in the Co(II) chelates.[2,9-12] Earlier, we reported[13] that the Ni(II) chelates are also air sensitive and react, presumably with oxygen, to give a variety of nickel-containing species. In this communication, further details of the separation, identification, and characterization of certain additional species are reported. Several of these new compounds, formed by irreversible oxidation at the carbon bridge of the original Schiff base chelates, have also been prepared by independent synthesis. The study includes an examination of the reactivity of the representative chelate [4,4′-(ethane-1,2-diyldiimino)-bis(pent-3-en-2-onato)(2−)]nickel(II) with selected oxidizing agents and the relationship between the oxidation potential in solution and the stability to oxidation in air of the various nickel Schiff base chelates.

Experimental Section

Ligands. A. Tetradentate Schiff Bases. The tetradentate Schiff bases used in this work are 4,4′-(ethane-1,2-diyldiimino)bis(pent-3-en-2-one) (H_2(aaed)), 5,5′-(ethane-1,2-diyldiimino)bis(hex-4-en-3-one) (H_2(hxed)), 5,5′-(ethane-1,2-diyldiimino)bis(hept-4-en-3-one) (H_2(hped)), 2,2′-dimethyl-5,5′-(ethane-1,2-diyldiimino)bis(hex-4-en-3-one) (H_2(ibaed)), 2,2,2′,2′-tetramethyl-5,5′-(ethane-1,2-diyldiimino)bis(hex-4-en-3-one) (H_2(paed)), 1,1′-diphenyl-3,3′-(ethane-1,2-diyldiimino)bis(but-2-en-1-one) (H_2(baed)), 1,1,1,1′,1′,1′-hexafluoro-4,4′-(ethane-1,2-diyldiimino)bis(pent-3-en-2-one) (H_2(tfaed)), 6,6,6,6′,6′,6′-hexafluoro-2,2,2′,2′-tetramethyl-5,5′-(ethane-1,2-diyldiimino)bis(hex-4-en-3-one) (H_2(tpmed)), 4,4′-(1-methylethane-1,2-diyldiimino)bis(pent-3-en-2-one) (H_2(aapd)), 5,5′-(1-methylethane-1,2-diyldiimino)bis(hex-4-en-3-one) (H_2(hxpd)), 5,5′-(1-methylethane-1,2-diyldiimino)bis(hept-4-en-3-one) (H_2(hppd)), 2,2,2′,2′-tetramethyl-(1-methylethane-1,2-diyldiimino)bis(hept-4-en-3-one) (H_2(papd)), and 6,6,6,6′,6′,6′-hexafluoro-2,2,2′,2′-tetramethyl-5,5′-(1-methylethane-1,2-diyldiimino)bis(hex-4-en-3-one) (H_2(tpmpd)). They were prepared by the 2:1 condensation of 1,2-diaminoethane or 1-methyl-1,2-diaminoethane with the appropriate β-diketone and purified by recrystallization from ethanol–water or by vacuum sublimation.

Only new compounds, not reported previously, are characterized below.

5,5′-(Ethane-1,2-diyldiimino)bis(hex-4-en-3-one) (H_2(hxed)): white crystals, mp 85 °C. Anal. Calcd for $C_{14}H_{24}N_2O_2$: C, 66.7; H, 9.5; N, 11.1. Found: C, 66.6; H, 9.8; N, 10.9.

5,5′-(Ethane-1,2-diyldiimino)bis(hept-4-en-3-one) (H_2(hped)): white crystals, mp 55 °C. Anal. Calcd for $C_{16}H_{28}N_2O_2$: C, 68.6; H, 10.0; N, 10.0. Found: C, 68.8; H, 10.3; N, 10.0.

5,5′-(1-Methylethane-1,2-diyldiimino)bis(hex-4-en-3-one) (H_2(hxpd)): white solid, mp 50 °C. Anal. Calcd for $C_{15}H_{26}N_2O_2$: C, 67.7; H, 9.8; N, 10.5. Found: C, 66.8; H, 10.0; N, 10.1.

5,5′-(1-Methylethane-1,2-diyldiimino)bis(hept-4-en-3-one) (H_2(hppd)): colorless liquid. Anal. Calcd for $C_{17}H_{30}N_2O_2$: C, 69.4; H, 10.2; N, 9.5. Found: C, 68.7; H, 10.5; N, 9.6.

B. Tetradentate Tetraketo Schiff Bases. The bidentate Schiff bases 4-aminopent-3-en-2-one, 5-aminohex-4-en-3-one, and 5-aminohept-4-en-3-one were prepared[14] by the addition of ammonia gas or water to an ethanolic solution of the corresponding β-diketones, pentane-2,4-dione, hexane-2,4-dione, and heptane-3,5-dione.

The novel tetraketo Schiff bases were prepared by the addition of oxalyl chloride (12.6 g, 0.10 mol) in dichloromethane (50 mL) to a stirred solution of the corresponding bidentate Schiff base (0.20 mol, in a similar volume of dichloromethane) and refluxing for 2 h. The solvent was removed under vacuum and the residue recrystallized from ethyl acetate–ethanol. The compounds were stable under ambient conditions.

4,4′-((1,2-Dioxoethane-1,2-diyl)diimino)bis(pent-3-en-2-one) (H_2(aaedO$_2$)): white needles, mp 215 °C (corrected). Anal. Calcd for $C_{12}H_{16}N_2O_4$: C, 57.1; H, 6.4; N, 11.1. Found: C, 57.2; H, 6.2, N, 11.0.

5,5′-((1,2-Dioxoethane-1,2-diyl)diimino)bis(hex-4-en-3-one) (H_2(hxedO$_2$)): white crystals, mp 98–100 °C. Anal. Calcd for $C_{14}H_{20}N_2O_4$: C, 60.0; H, 7.1; N, 10.0. Found: C, 59.6; H, 7.3; N, 9.4.

5,5′-((1,2-Dioxoethane-1,2-diyl)diimino)bis(hept-4-en-3-one) (H_2(hpedO$_2$)): white crystals, mp 101 °C. Anal. Calcd for $C_{16}H_{24}N_2O_4$: C, 62.3; H, 7.8; N, 9.1. Found: C, 62.2; H, 7.9; N, 9.1.

Chelates. A. Derivatives of Tetradentate Schiff Bases. The synthesis of the Ni(II), Co(II), Cu(II), Pd(II), and $V^{IV}O$ Schiff base chelates has been described elsewhere.[7] Nickel chelates not described previously[7] are characterized below.

[5,5′-(Ethane-1,2-diyldiimino)bis(hex-4-en-3-onato)(2−)]nickel(II) (Ni(hxed)): brown crystals, mp 135–137 °C. Anal. Calcd for $C_{14}H_{22}N_2O_2Ni$: C, 54.4; H, 7.2; N, 9.1, Ni, 19.0. Found: C, 54.7; H, 7.4; N, 9.0; Ni, 18.3.

[5,5′-(Ethane-1,2-diyldiimino)bis(hept-4-en-3-onato)(2−)]nickel(II) (Ni(hped)): brown crystals, mp 49–52 °C. Anal. Calcd for $C_{16}H_{26}N_2O_2Ni$: C, 57.0; H, 7.7; N, 8.3. Found: C, 57.4; H, 7.9; N, 8.6.

[5,5′-(1-Methylethane-1,2-diyldiimino)bis(hex-4-en-3-onato)-(2−)]nickel(II) (Ni(hxpd)) and [5,5′-(1-Methylethane-1,2-diyldiimino)bis(hept-4-en-3-onato)(2−)]nickel(II) (Ni(hppd)) were obtained as brown semisolids and could not be isolated as stable products having satisfactory elemental compositions.

B. Derivatives of Dehydrogenated Schiff Bases. [4,4′-(Ethene-1,2-diyldiimino)bis(pent-3-en-2-onato)(2−)]nickel(II) (Ni(aaed)dehyd). This stable chelate was prepared in 70% yield by refluxing 1.0 g of Ni(aaed) in 1,3,5-trimethylbenzene (ca. 30 mL) for 10–15 h in a stream of argon with 0.5 g of palladized carbon (10% palladium by weight on carbon). The product was separated from the more polar Ni(aaed) by eluting from silica gel with 5–10% v/v ethyl acetate in benzene and then purified by recrystallization from petroleum spirit (bp 100–120 °C): orange-brown crystals, mp 205 °C. Anal. Calcd for $C_{12}H_{16}N_2O_2Ni$: C, 51.7; H, 5.8; N, 10.0; Ni, 21.0. Found: C, 51.6; H, 5.6; N, 10.0; Ni, 21.1.

Stable dehydrogenated analogues of ibaed, paed, papd, baed, and tfaed were prepared similarly by heating the chelates (0.5–1 g) in 1,3,5-trimethylbenzene or naphthalene for 10–15 h, as above. Yields were 30–90%.

[2,2′-Dimethyl-5,5′-(ethene-1,2-diyldiimino)bis(hex-4-en-3-onato)(2−)]nickel(II) (Ni(ibaed)dehyd): orange-brown crystals, mp 141 °C (cor). Anal. Calcd for $C_{16}H_{24}N_2O_2Ni$: C, 57.1; H, 7.0; N, 8.4; Ni, 17.5. Found: C, 59.1; H, 7.2; N, 8.5; Ni, 17.5.

[2,2,2′,2′-Tetramethyl-5,5′-(ethene-1,2-diyldiimino)bis(hex-4-en-3-onato)(2−)]nickel(II) (Ni(paed)dehyd): orange-brown crystals, mp 170 °C (cor). Anal. Calcd for $C_{18}H_{28}N_2O_2Ni$: C, 59.5; H, 7.8; N, 7.7; Ni, 16.2. Found: C, 59.7; H, 7.8; N, 7.6; Ni, 16.3.

[2,2,2′,2′-Tetramethyl-5,5′-(1-methylethene-1,2-diyldiimino)bis(hex-4-en-3-onato)(2−)]nickel(II) (Ni(papd)dehyd): orange-brown needles, mp 232 °C (DTA). Anal. Calcd for $C_{19}H_{30}N_2O_2Ni$: C,

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60.5; H, 8.0; N, 7.4; Ni, 15.6. Found: C, 60.2; H, 8.2; N, 7.1; Ni, 15.8.

[1,1′-Diphenyl-3,3′-(ethene-1,2-diyldiimino)bis(but-2-en-1-onato)(2−)]nickel(II) (Ni(baed)dehyd): brown crystals, mp 263 °C (DTA). Anal. Calcd for $C_{22}H_{20}N_2O_2Ni$: C, 65.6; H, 5.0; N, 6.9; Ni, 14.6. Found: C, 65.9; H, 5.5; N, 6.7, Ni, 14.1.

[1,1,1,1′,1′,1′-Hexafluoro-4,4′-(ethene-1,2-diyldiimino)bis(pent-3-en-2-onato)(2−)]nickel(II) (Ni(tfaed)dehyd): red crystals, mp 232 °C. Anal. Calcd for $C_{12}H_{10}N_2F_6O_2Ni$: C, 37.3; H, 2.6; N, 7.2; F, 29.5; Ni, 15.2. Found: C, 37.5; H, 2.7; N, 7.1; F, 29.7; Ni, 14.7.

In contrast, the following dehydrogenated compounds were isolated by column chromatography (see above) from the impure synthetic products. Again, all were stable compounds.

[5,5′-(Ethene-1,2-diyldiimino)bis(hex-4-en-3-onato)(2−)]nickel(II) (Ni(hxed)dehyd): orange crystals, mp 97–99 °C. Anal. Calcd for $C_{14}H_{20}N_2O_2Ni$: C, 54.8; H, 6.5; N, 9.1. Found: C, 55.0; H, 6.7; N, 9.1.

[5,5′-(Ethene-1,2-diyldiimino)bis(hept-4-en-3-onato)(2−)]nickel(II) (Ni(hped)dehyd): orange-red crystals, mp 78–79 °C. Anal. Calcd for $C_{16}H_{24}N_2O_2Ni$: C, 57.4; H, 7.2; N, 8.4. Found: C, 57.9; H, 7.1; N, 8.7.

[4,4′-(1-Methylethene-1,2-diyldiimino)bis(pent-3-en-2-onato)(2−)]nickel(II) (Ni(aapd)dehyd): orange-brown crystals, mp 186–187 °C. Anal. Calcd for $C_{13}H_{18}N_2O_2Ni$: C, 53.3; H, 6.2; N, 9.6. Found: C, 53.5; H, 6.0; N, 9.8.

[5,5′-(1-Methylethene-1,2-diyldiimino)bis(hex-4-en-3-onato)(2−)]nickel(II)(Ni(hxpd)dehyd): orange-brown crystals, mp 92–94 °C. Anal. Calcd for $C_{15}H_{22}N_2O_2Ni$: C, 56.1; H, 6.9; N, 8.7. Found: C, 55.4; H, 6.8; N, 8.6.

C. Derivatives of Oxidized Schiff Bases. Tetradentate Triketo Ni(II) Chelates. These were isolated by column chromatography on silica gel (see above). The compounds are stable at room temperature but decompose slowly (over 5–6 months).

[4,4′-((1-Methyl-2-oxoethane-1,2-diyl)diimino)bis(pent-3-en-2-onato)(2−)]nickel(II) (Ni(aapdO)): red-brown crystals, mp 129–130 °C (in air: 146 °C during thermal analysis in nitrogen). Anal. Calcd for $C_{13}H_{18}N_2O_3Ni$: C, 50.5; H, 5.8; N, 9.1. Found: C, 51.1; H, 5.8; N, 9.2.

[5,5′-((1-Methyl-2-oxoethane-1,2-diyl)diimino)bis(hex-4-en-3-onato)(2−)]nickel(II) (Ni(hxpdO)): initially a liquid, changes to a red-brown solid. Anal. Calcd for $C_{15}H_{22}N_2O_3Ni$: C, 53.5; H, 6.5; N, 8.3. Found: C, 53.2; H, 6.3; N, 8.2.

Tetradentate Tetraketo Ni(II) Chelates. These were isolated from oxidized chelates by chromatography, as above. They were synthesized by refluxing (1–2 h) an ethanolic solution of the ligand (0.005 mol) and $Ni(CH_3COO)_2·4H_2O$ (1.3 g, 0.005 mol). The solution was filtered when cold and then evaporated to dryness (rotary evaporator). The solid was recrystallized from benzene. Products are stable at room temperature.

[4,4′-((1,2-Dioxoethane-1,2-diyl)diimino)bis(pent-3-en-2-onato)(2−)]nickel(II) (Ni(aaedO₂)): reddish brown crystals, mp 222 °C. Anal. Calcd for $C_{12}H_{14}N_2O_4Ni$: C, 46.7; H, 4.5; N, 9.1; Ni, 19.0. Found: C, 46.8; H, 4.8; N, 9.1; Ni, 18.7.

[5,5′-((1,2-dioxoethane-1,2-diyl)diimino)bis(hex-4-en-3-onato)(2−)]nickel(II) (Ni(hxedO₂)): reddish brown crystals, mp 159–162 °C. Anal. Calcd for $C_{14}H_{18}N_2O_4Ni$: C, 49.9; H, 5.4; N, 8.3; Ni, 17.4. Found: C, 50.1; H, 5.6; N, 8.3; Ni, 16.9.

[5,5′-((1,2-Dioxoethane-1,2-diyl)diimino)bis(hept-4-en-3-onato)(2−)]nickel(II) (Ni(hpedO₂)): reddish brown crystals, mp 159 °C. Anal. Calcd for $C_{16}H_{22}N_2O_4Ni$: C, 52.6; H, 6.0; N, 7.7; Ni, 16.1. Found: C, 53.2; H, 6.2; N, 7.7; Ni, 16.3.

Chelate of Ni(II) with Mixed Ligand. [4-Iminopent-2-en-2-olato-(2−)][4-iminopentane-2,3-dione]nickel(II) was prepared by dissolving 2.0 g of Ni(aaed) in 50 mL of ethanol–water and adding 5 mL of 30% v/v hydrogen peroxide dropwise over 20 min. The precipitate was filtered and recrystallized from ethanol (yield 32%): yellow solid, mp 280 °C dec. Anal. Calcd for $C_{10}H_{14}N_2O_3Ni$: C, 44.7; H, 5.2; N, 10.4; Ni, 21.9. Found: C, 44.7; H, 5.2; N, 10.2; Ni, 22.0. Molecular weight: calcd, 268.0358; found, 268.0357 (by mass spectrometry) and 267 in nitromethane at 50 °C (by vapor pressure osmometry). ^1H NMR (CD_3NO_2): δ 5.10 (ring CH=), 3.46 (NH, exchangeable with D_2O), 2.06 (CH_3) (proton counts were 1:1:12, respectively).

Chromatography. Separation of the oxidized forms of each Ni(II) Schiff base chelate (1.0 g) was obtained on a column of silica gel (Merck, Kieselgel H; 40 cm × 5 cm diameter) by eluting, in turn, with 5%, 10%, and 50% v/v ethyl acetate in benzene. Pressurized nitrogen (20 psi) was used to maintain an acceptable flow rate of solvent through the column. Fractions of the various colored bands were evaporated to dryness and the individual products recrystallized from petroleum spirit (bp 100–120 °C) or ethanol–water. Chromatograms were obtained on silica gel layers (20 cm × 10 cm, 0.5 mm thick) with developing solvents similar to those used for column chromatography. The separated spots were observed directly or by exposure to iodine vapor.

High-performance liquid chromatograms were obtained on a Du Pont 830 liquid chromatograph equipped with a Du Pont 837 variable-wavelength spectrophotometric detector operated at a wavelength of 300 nm. The column used was of stainless steel (28 cm × 2 mm i.d.) packed with Kieselgel H (300–400 mesh), operated isocratically at 0.3 mL/min (~300 psi) with deaerated 2:1 v/v toluene–hexane or 3% or 10% v/v ethyl acetate in toluene, depending on the chelates examined.

Physical Measurements. Analyses for carbon, hydrogen, and nitrogen were carried out by the Microanalytical Laboratory, School of Chemistry, University of New South Wales, and those for fluorine and nickel by the Australian National University Microanalysis Service. ^1H NMR spectra were obtained on a JEOL JNM-4H-100 spectrometer at 21 °C with solutions of chelates in deuteriochloroform (approximately 20% v/v), infrared spectra on a Hitachi EPI grating instrument with potassium bromide disks and halocarbon mulls, electron impact mass spectra (at 70 eV) on an AEI MS12 spectrometer, and chemical ionization mass spectra on a GEC-AEI M902 with isobutane as reagent gas. Cyclic voltammograms were obtained on a PAR Model 170 electrochemistry system using deaerated solutions of the chelates (10^{-3} M in acetonitrile) containing 0.1 M tetraethylammonium perchlorate as supporting electrolyte. Acetonitrile was purified[15] to remove readily oxidizable impurities and water, and the perchlorate dried over phosphorus pentoxide (for 1 week, under vacuum) before use.

Results and Discussion

Stability of Chelates in Air. The tendency of nickel chelates of tetradentate Schiff bases to undergo oxidation to form a number of derivatives in air was originally confirmed from observation of their chromatographic behavior[13] on silica gel. Although this adsorbent is also able to promote the oxidation of certain complexes, other chelates were found to oxidize readily in solution under ambient conditions. This diverse behavior is illustrated by Ni(aaed) ($R_1 = R_2 = CH_3$ in II), which can be stable[14] for long periods (~1 year) when stored as a solid in air or for several weeks as a solution in benzene. When it is adsorbed on silica gel, however, oxidation[16] in air can occur within hours (see Figure 1a) and the oxidation products are relatively stable compared with Ni(aaed). A similar reactivity was found for Ni(hxed) ($R_1 = C_2H_5$, $R_2 = CH_3$ in II) and Ni(aapd) ($R_1 = R_2 = CH_3$ in VI) whereas the homologous Ni(hped) ($R_1 = R_2 = C_2H_5$ in II), Ni(hxpd) ($R_1 = C_2H_5$, $R_2 = CH_3$ in VI), and Ni(hppd) ($R_1 = C_3H_7$, $R_2 = CH_3$ in VI) were somewhat more reactive and difficult to prepare in air without contamination from the various oxidized forms.

Chelates containing electron-donating substituents [such as Ni(ibaed), Ni(paed), and Ni(papd)] were even more reactive in solution than chelates in the previous group, a factor to be considered in any synthetic or purification work or, indeed, in analytical applications.[17,18] Nevertheless, solid samples of these compounds have been stored[14] in air for several years without significant oxidation occurring. In dilute solution, on the other hand, although freshly prepared solutions give a

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[15] O'Donnell, J. F.; Ayres, J. T.; Mann, C. K. *Anal. Chem.* **1965**, *37*, 1161.

[16] When it is examined by TLC, a greater number of nickel-containing species can be detected (with use of a simple decomposition procedure and dimethylglyoxime as reagent) than is shown in Figure 1a. The fact that no additional compounds were detected implies that all oxidation products contain nickel.

[17] Belcher, R.; Khalique, A.; Stephen, W. I. *Anal. Chim. Acta* **1978**, *100*, 503.

[18] Dilli, S.; Patsalides, E. *Anal. Chim. Acta* **1981**, *128*, 109.

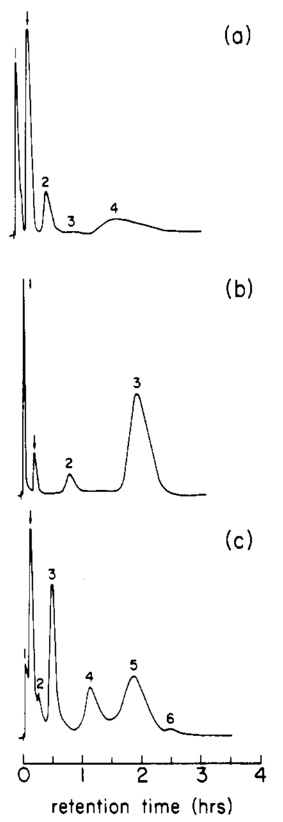


Figure 1. Liquid chromatograms of (a) Ni(aaed) after standing 15 h on silica gel and extracting with methanol (elution with 1:9 v/v ethyl acetate–toluene) and (b) Ni(paed) and (c) Ni(papd) left standing in hexane for 12 h (elution with 2:1 v/v toluene–hexane). Solutions were prepared from chelates or residues (1 mg/mL) in dichloromethane or hexane. Oxidized species are identified as unrelated numbered peaks and undecomposed chelates by an arrow. Other conditions are described in the Experimental Section.

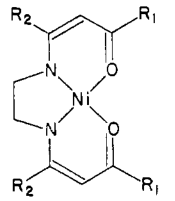
single peak of the undecomposed chelate, complete oxidation can take place in 1–2 days. Figure 1b,c shows chromatograms of dilute, 1-day old solutions of Ni(paed) and Ni(papd) in hexane. Oxidized species are shown (see peaks 1–3 and 1–6, respectively), and, in each case, undecomposed chelate also remains. In striking contrast, fluorinated chelates appeared stable to oxidation in solution or on silica gel and no oxidation products were observed.

The aerial stability of the nickel chelates was also examined by thermal analysis. Data from differential-thermal analysis show that the nonfluorinated chelates Ni(aaed), Ni(hxed), Ni(ibaed), and Ni(paed) decompose in air by a series of endothermic and exothermic reactions starting at about 260 °C. In an inert atmosphere of nitrogen these chelates volatilize without extensive decomposition, although dehydrogenated forms can be detected in the sublimates.[7] Again, the fluorinated chelates volatilize in air at 210–320 °C without decomposing since dehydrogenation of these chelates can be achieved only by employing[19] forceful conditions.

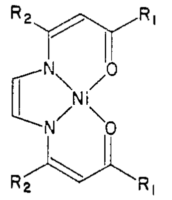
Other metal chelates of this group of Schiff base ligands are also air sensitive although their reactivity appears to be different to that of Ni(II). The reversible interaction of Co(aaed) with air by metal ion centered reactions to give dioxygen complexes is, of course, well-known and has been extensively studied.[9-12] Such Co(II) chelates produce peroxide-bridged species or are oxidized to monomeric Co(III) complexes. There is no evidence to date, however, that irreversible oxidation of the Co(II) chelates gives bridge-oxidized species of the type (see Structures III–V and VII–VIII) described here for Ni(II). Nonfluorinated chelates of Cu(II), Pd(II), and $V^{IV}O$ were found to slowly dehydrogenate on silica gel but did not give oxidation products similar to those observed in the Ni(II) chelates.

No evidence of air sensitivity was found for any of the free Schiff base ligands. In contrast to the chelates, the ligands were resistant to dehydrogenation and neither C–N nor C–C dehydrogenation could be effected with the vigorous conditions referred to above.

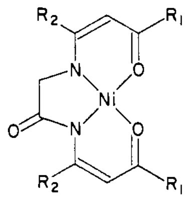
Products in the Oxidation of Ni(II) Chelates. Oxidized compounds present in Ni(aaed), Ni(hxed), Ni(hped), Ni(aapd), Ni(hxpd), and Ni(hppd) were identified, following purification on open columns of silica gel of high capacity and efficiency, by elemental and spectroscopic analyses. These compounds were monomeric and diamagnetic chelates of type III–V (derived from II) and VII–VIII (from VI). Chelates of type IV were not isolated in pure form and appeared to convert readily to the corresponding chelates V. The order of elution of the compounds from columns was III, II, IV, V and VII, VI, VIII, respectively. No dimeric or peroxide-bridged complexes were isolated.



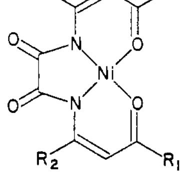
II



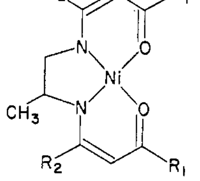
III



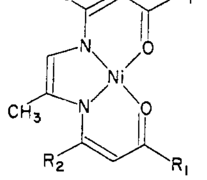
IV



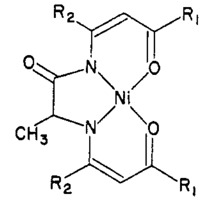
V



VI



VII



VIII

The most convincing evidence supporting structures II–VIII is provided by the NMR data given in Table I. Identification of R_1 and R_2, where these are not identical, was based on the large upfield shift of the proximal (R_2) substituent in an aromatic solvent compared with that in a nonaromatic solvent[20,21] such as chloroform. However, oxidized and parent compounds generally gave prominent $(M + 1)^+$ peaks in CI mass spectra, with less intense peaks also at $(M + 39)^+$ and $(M + 57)^+$. EI mass spectra were characterized by prominent molecular ions (M^+). In both types of spectra, nickel-containing fragment ions displayed a typical pattern due to the isotopes ^{58}Ni and ^{60}Ni of natural abundance[22] about 2.6:1.

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(19) As an example, yellow Ni(tfaed) is converted to red Ni(tfaed)dehyd on prolonged heating in boiling naphthalene in the presence of palladized carbon.

(20) Dudek, G. O.; Holm, R. H. *J. Am. Chem. Soc.* **1961**, *83*, 2099.

(21) Dilli, S.; Patsalides, E. *Aust. J. Chem.* **1978**, *31*, 765.

(22) Weast, R. C., Ed. "Handbook of Chemistry and Physics"; Chemical Rubber Publishing Co.: Cleveland, OH, 1970–1971.

Table I. 100-MHz ^{1}H NMR Spectral Assignments for Ni(II) Chelates in Deuteriochloroform

		proton resonances, δ^a								
		R_1		R_2						
chelate	struct type	CH_3	CH_2	CH_3	CH_2	diketone =CH–	bridge =CH–	bridge –CH_2–	bridge CH_3	bridge CH–
Ni(aaed)	II	1.85 s		1.85 s		4.86 s		3.08 s		
Ni(hxed)	II	1.02 t	2.12 q (J^e = 7.8)	1.90 s		4.89 s		3.14 s		
Ni(hped)	II	1.04 t	2.22 q (J = 7.6)	1.03 t	2.14 q (J = 7.6)	4.89 s		3.02 s		
Ni(aapd)^b	VI	1.79 s		1.79 s		4.84 s, 4.88 s		3.19 m	1.27 d (J = 6.4)	2.62 m
Ni(aaed)dehyd	III	2.13 s		2.13 s		5.26 s	6.11 s			
Ni(hxed)dehyd^c	III	1.13 t	2.38 q (J = 7.8)	2.15 s		5.29 s	6.15 s			
Ni(hped)dehyd	III	1.15 t	2.39 q (J = 7.5)	1.13 t	2.51 q (J = 7.5)	5.31 s	6.18 s			
Ni(aapd)dehyd	VII	2.08 s		2.16 s, 2.28 s		5.17 s, 5.21 s	5.96 s		2.08 s	
Ni(hxpd)dehyd	VII	1.11 t	2.34 q (J = 7.5)	2.08 s, 2.30 s		5.18 s, 5.23 s	5.97 s		2.15 s	
Ni(aaedO_2)	V	2.35 s		2.02 s		5.32 s				
Ni(hxedO_2)^d	V	2.35 s		1.06 t	2.25 q (J = 7.5)	5.35 s				
Ni(hpedO_2)	V	1.06 t	2.27 q (J = 7.4)	1.08 t	2.77 q (J = 7.5)	5.40 s				
Ni(aapdO)	VIII	1.87 s 2.00 s		1.87 s 2.29 s		4.94 s, 5.25 s			1.46 d	3.54 q (J = 6.6)

[a] Relative to tetramethylsilane in $CDCl_3$. Relative intensities of the peaks are in accord with the structures assigned. Key: singlet, s; doublet, d; triplet, t; quartet, q; complex multiplet, m. [b] The ^{1}H NMR spectrum of this chelate has been examined in detail by Larsen and Schaumberg.[42] [c] The isomeric form isolated is derived from IX. [d] The isomeric form isolated is derived from XI. [e] J values given in Hz.

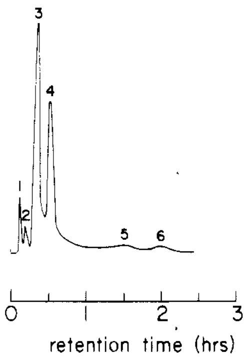
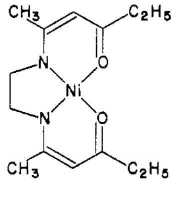


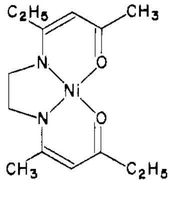
Figure 2. Liquid chromatograms of Ni(hxed) showing the separation of isomeric species with 3% v/v ethyl acetate–toluene eluent. Other conditions were as in Figure 1. See text for identification of peaks 1–4. Peaks 5 and 6 are unknown.

Infrared spectra were also able to distinguish the chelates since all products showed strong absorption near 1580 and 1520 cm^{-1}, characteristic of β-keto enamine chelates, and structures IV, V, and VIII displayed strong absorption near 1700 cm^{-1} associated with the bridge carbonyl groups. Thus, chelates of type VIII absorbed strongly at 1690 cm^{-1} while those of type V containing a 1,2-dicarbonyl system absorbed strongly at 1700 cm^{-1}.

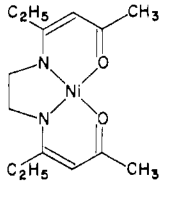
Although the subject of a later communication, it may be noted that the occurrence of isomeric forms of these chelates is common[14] when $R_1 \neq R_2$ in II and gives rise to a greater number of oxidized species, as was observed for Ni(hxed) and Ni(hxpd). Thus, the Schiff base H_2(hxed), hitherto thought to exist in only one isomeric form,[23] is shown in Figure 2 to exist in two of the isomeric forms IX–XI of Ni(hxed) prepared from the *crude*[24] ligand. Isomers IX and X (peaks 3 and 4, respectively) and the corresponding dehydrogenated chelates (peaks 1 and 2, respectively) were identified from NMR and mass spectroscopic examination of bands collected from the column.[25] Evidently XI is less stable than IX or X and is converted into its oxidized forms.



IX

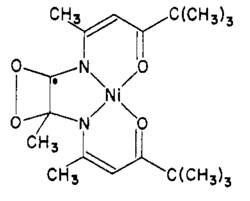


X



XI

Previous studies[26,27] have reported the development of paramagnetism in aged solutions of certain Schiff base chelates, indicating the formation of high-spin Ni(II) chelates or stable free radicals of low-spin Ni(II) chelates. When examined directly by mass spectrometry, the identity of compounds produced[28] in Ni(aaed) and Ni(papd), as representative compounds, was simplified by the prominent molecular ions and the characteristic nickel isotope ratio. Thus, residues isolated from Ni(aaed) gave the following peaks in the electron-impact mass spectrum: m/z 278, 280; 280, 282; 294, 296; 308, 310; corresponding to the species III, II, IV, and V, respectively (where $R_1 = R_2 = CH_3$ in each case). In addition, peaks at m/z 324, 326 and 340, 342 can be attributed to *N*-oxides of V or peroxides isomeric with these, although no attempt was made to isolate or further characterize these species. Similarly, for the residues from Ni(papd), the following ions were observed: m/z 376, 378; 378, 380; 392, 394; corresponding to species of the type VII, VI, and VIII, respectively (where R_1 = *t*-Bu and $R_2 = CH_3$). Prominent peaks at m/z 407 and 409 with masses 407.1480 and 409.1456, respectively, correspond to a composition $C_{19}H_{29}N_2O_4Ni$, suggesting the free radical species XII. However, examination of a benzene solution of the residue by ESR did not support this. Again, the alternative



XII

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[23] Lindoy, L. F.; Moody, W. E.; Taylor, D. *Inorg. Chem.* **1977**, *16*, 1962.

[24] This means a microanalytically pure but not isomerically pure ligand.

[25] Evidence for the third isomer XI was obtained after isolation (on a preparative column) as a small quantity of the corresponding nickel chelate containing the 1,2-dione bridge (structure V).

[26] Bluck, R. S.; Odell, A. L.; Olliff, R. W. *J. Chem. Soc.* **1964**, 4660.

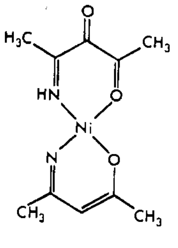
[27] Powers, C. R.; Everett, G. W. *J. Am. Chem. Soc.* **1969**, *91*, 3468.

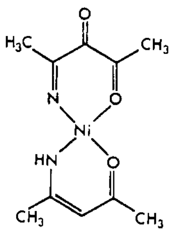
[28] After reaction on silica gel, any products were exhaustively extracted with methanol.

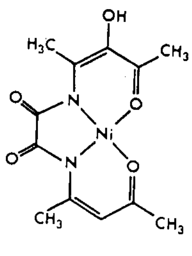
and plausible explanation that the ions originated from the fragmentation of hydroxy- or peroxide-bridged complexes related to XII was not supported by the observation of such molecular ions in EI or CI mass spectra.

Chemical Oxidation of Ni(aaed). The susceptibility of the Ni(II) Schiff base chelates to aerial oxidation suggested the use of other reagents for the selective oxidation of the C–C bridge in Ni(aaed) and, indeed, several reactions with this chelate are of interest. Of these, dehydrogenation was achieved[29] selectively with a number of reagents. One method[13] involved refluxing the compound in 1,3,5-trimethylbenzene (bp 165 °C) with palladized carbon under a cover of argon for 36 h. Selective introduction of oxygen functional groups at the C–C bridge without destruction of the chelate itself proved difficult and was not accomplished with the reagents and conditions examined[32].

In the particular case of hydrogen peroxide, provided an excess was avoided, an orange-yellow solid was isolated. Based on the ^{58}Ni isotope, the mass number of 268.0358 for this compound, together with the elemental analysis and molecular weight in solution, indicates a monomeric species of molecular formula $C_{10}H_{14}N_2O_3Ni$, consistent with structures of the tautomeric ternary complexes XIII or XIV. The infrared spectrum of this compound was similar to that of Ni(aaed) in having intense absorption at 1590 and 1510 cm^{-1} indicative of at least one intact β-keto enamine ring. An intense band at 1670 cm^{-1}, absent in the spectrum of Ni(aaed), is also attributed to a free carbonyl group in the product. Furthermore, the absence of resonances at δ 3.0–3.2 in the ^{1}H NMR spectrum of this compound confirms the absence of bridge hydrogens, while resonances at δ 5.10, 3.46 (broad) and 2.06 correspond to methine, imino, and methyl hydrogens, respectively. Fragments in electron-impact mass spectra (see Table II) support these assignments and favor XIII rather than XIV. Thus, the formation of ions *m/z* 196, 198 and 155, 157 from the parent ions (*m/z* 268, 270) can be rationalized by the fragmentation of XIII shown in Scheme I.


XIII


XIV

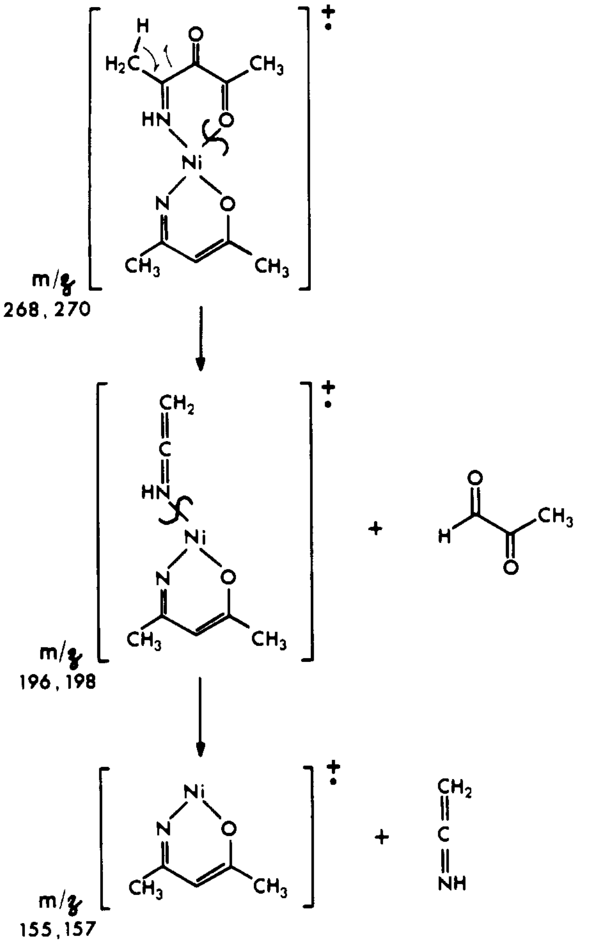

XV

Summarizing these results, the formation of XIII from Ni(aaed) implies that the mechanism for oxidation by hydrogen peroxide involves two levels of activity. Whereas initial oxidation of the C–C bridge probably gives V as an intermediate, further reaction leads to attack of a methine carbon with nucleophilic displacement of the methine hydrogen to give XV, which, in turn, eliminates carbon monoxide thermally and rearranges to XIV.

Table II. Fragment and Metastable Ions Identified in the Electron Impact Mass Spectrum of Compound XIII

m/z	identity	% rel abund	transn (metastable ion)
268, 270	$M^{+\cdot}$	58	
224, 226	$M^{+\cdot} - CH_3CHO$	16	268 → 224 (187.2) 270 → 226 (189.2)
196, 198	$M^{+\cdot} - CH_3COCHO$	47	
183, 185	$M^{+\cdot} - CH_3COCOCH_2\cdot$	27	
155, 157	$M^{+\cdot} - CH_3COCOC(CH_3){=}NH$ or (196, 198) $- CH_2{=}C{=}NH$	95	196 → 155 (122.6) 198 → 157 (124.5)
140, 142	155, 157 $- CH_3\cdot$	19	
99, 101	NiN=C(CH$_3$)	100	
58, 60	Ni$^+$	32	

Scheme I



Electrochemical Behavior. The electrochemical behavior of the Schiff base chelates, mainly their cathodic reactions, has been investigated by a number of workers.[34–37] Here, the

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[29] Dehydrogenation was also effected by refluxing the chelate in toluene–xylene in a stream of air for 4–5 h or following the addition of di-*tert*-butyl peroxide or by photolysis in acetone with ultraviolet light (254 nm from a low-pressure Hg arc lamp). Reaction with 3-phenyl-2-*tert*-butyloxazirane in boiling toluene yielded Ni(aaed)dehyd but produced no less than six other unidentified, nickel-containing compounds. Attempts to achieve dehydrogenation with trityl tetrafluoroborate and sodium borohydride,[30] dichlorodicyanobenzoquinone, or selenium dioxide[31] were unsuccessful.

(30) Truex, T. J.; Holm, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 4529.

(31) Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967.

(32) For example, heating Ni(aaed) with sodium peroxide, lead dioxide, or bismuth pentoxide in refluxing xylene did not result in significant oxidation. Reaction with ozone was unselective and resulted in decomposition of the chelate. Bromine caused decomposition mainly (probably due to the formation of HBr) but produced a small quantity of the brown chelate Ni(aaedBr$_2$) in which the bromine is incorporated by nucleophilic displacement of the two methine hydrogens.[33]

(33) Lindoy, L. F.; Hip, H. C.; Moody, W. E. *J. Chem. Soc., Dalton Trans.* **1974**, 44.

(34) Kodama, M.; Fujii, Y.; Sakurai, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1729.

(35) Carter, M. J.; Engelhardt, L. M.; Rillema, D. P.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1973**, 810.

(36) Brockway, D. J.; West, B. O.; Bond, A. M. *J. Chem. Soc., Dalton Trans.* **1979**, 1891.

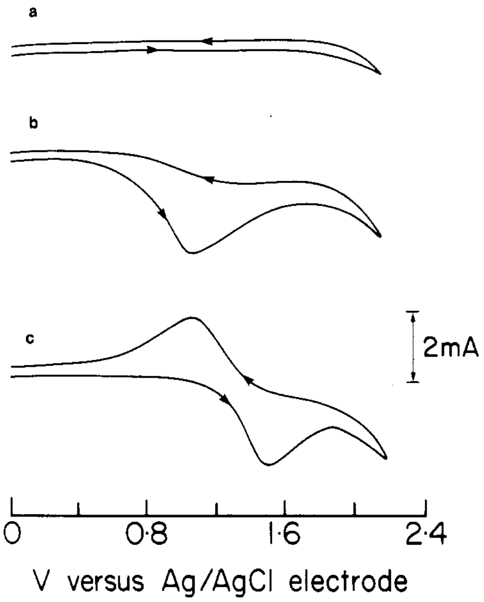


Figure 3. Cyclic voltammograms for (a) H_2(aaed), (b) Ni(aaed), and (c) Ni(tpmpd). Conditions were as given in the Experimental Section.

Table III. Anodic Peak Voltages (E_p) for Various Ni(II) Chelates (Conditions as in Figure 3)

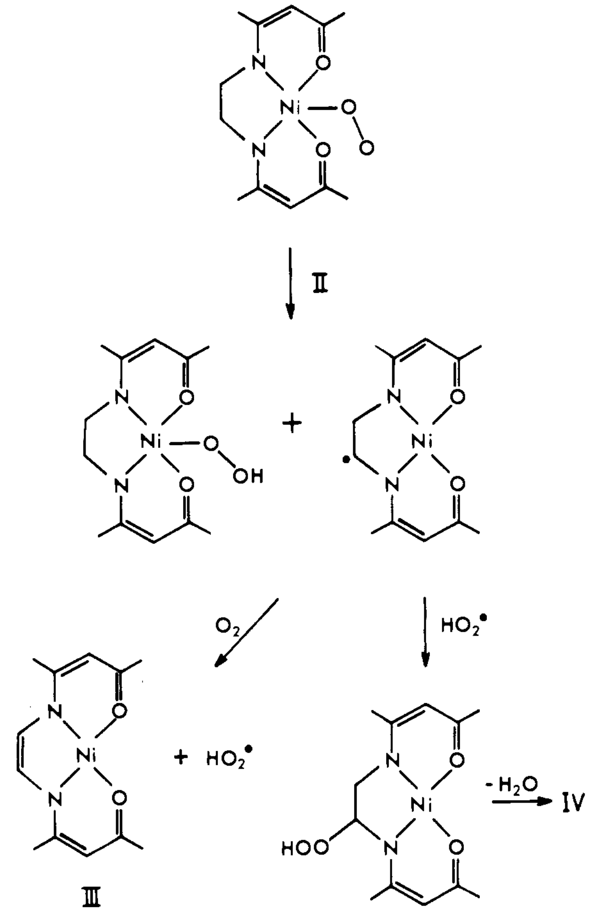
chelate	E_p, V	chelate	E_p, V
Ni(paed)	+0.95	Ni(aapd)	+1.05
Ni(baed)	+0.98	Ni(tpmed)	+1.35
Ni(ibaed)	+1.02	Ni(tfaed)	+1.42
Ni(hxed)	+1.04	Ni(tbmed)	+1.45
Ni(aaed)	+1.05	Ni(tpmpd)	+1.52

anodic reactions of the chelates were examined to observe the relationship between oxidation potentials and aerial stability.

Cyclic voltammograms for H_2(aaed) and Ni(aaed) are shown in Figure 3. Although the ligand is electrochemically inactive in the range 0.0 to +2.3 V, the chelate is oxidized irreversibly near +1.0 V in a reaction which probably involves loss of 1 electron/molecule to give Ni(aaed)$^+$, corresponding to the oxidation of Ni(II) to Ni(III). Evidently this ion undergoes a rapid irreversible reaction to produce an electrode-inactive species because Ni(aaed)$^+$ is not detected during the cathodic sweep in the voltammogram. The mode of decay of the electrode-generated Ni(aaed)$^+$ has not been established but may involve the loss of H^+ as occurs in Ni(III) cyclam chelates;[38] however, H^+ (or HB^+ when B is a basic solvent) was not detected in the cathodic sweep of a cyclic voltammogram run from −1.8 to +1.8 V.

As seen in Figure 3, with the exception of Ni(tpmpd), the oxidation of the nickel chelates at the platinum electrode was irreversible at a scan rate of 2 V/s so that reversible oxidation potentials for the chelates could not be measured. Nevertheless, the relative order of the oxidation potentials can be determined from the anodic peak voltages. Thus, the data of Table III show that substituents have a marked effect on the oxidation potential, a finding which agrees with previous studies[39-41] reporting substituent effects in the reversible reduction potentials of various chelate types. There is also a parallel between the oxidation potential and aerial stability of the nickel chelates. For example, the anodic peak voltages for Ni(paed), Ni(aaed), and Ni(tfaed) are +0.95, +1.05, and +1.42 V, respectively, which is the order of increasing stability in air. Values for the other chelates also reflect their relative stability in air.

Scheme II



At this stage, any mechanism accounting for the aerial oxidation of the nickel chelates can only be speculative. Two mechanisms possibly operate, depending upon the reaction temperature. At low temperatures the reaction in solution, or on silica gel, possibly involves a dioxygen adduct similar to that of Co(II) chelates, followed by intra- or intermolecular reactions to produce (as shown in Scheme II) an unstable hydroperoxide which decomposes to III or IV or V. At higher temperatures (~120 °C) where addition of oxygen is less favored, a mechanism not requiring a metal ion centered intermediate may operate. In this case, oxidation is probably initiated by cleavage of a weak C–H bond at the bridge, with further reaction[38,43,44] involving oxygen responsible for the stable products III, IV, and V.

Registry No. H_2(hxed), 81294-25-9; H_2(hped), 81294-26-0; H_2(hxpd), 81294-27-1; H_2(hppd), 81294-28-2; H_2(aaed), 7275-44-7; H_2(aaedO_2), 36684-35-2; H_2(hxedO_2), 81294-29-3; H_2(hpedO_2), 81294-30-6; Ni(hxed), 55519-92-1; Ni(hped), 81315-98-2; Ni(hxpd), 81315-99-3; Ni(hppd), 81340-06-9; Ni(paed), 55524-07-7; Ni(papd), 80011-43-4; Ni(tpmpd), 80011-46-7; Ni(aapd), 40792-91-4; Ni(baed), 53109-27-6; Ni(ibaed), 62816-08-4; Ni(tpmed), 66973-43-1; Ni(tfaed), 40792-92-5; Ni(tbmed), 81316-00-9; Ni(aaed), 36802-27-4; Ni(aaed)dehyd, 71294-54-7; Ni(ibaed)dehyd, 81316-01-0; Ni(paed)dehyd, 81316-02-1; Ni(papd)dehyd, 81316-03-2; Ni(baed)dehyd, 81316-04-3; Ni(tfaed)dehyd, 81316-05-4; Ni(hxed)dehyd, 81316-06-5; Ni(hped)dehyd, 81316-07-6; Ni(aapd)dehyd, 81316-08-7; Ni(hxpd)dehyd, 81316-09-8; Ni(aapdO), 81316-10-1; Ni(hxpdO), 81316-11-2; Ni(hxedO_2), 81316-12-3; Ni(hpedO_2), 81316-13-4; Ni(aaedO_2), 81316-14-5; [4-iminopent-2-en-2-olato(2−)][4-iminopentane-2,3-dione]nickel(II), 81316-15-6.

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