Factors Influencing the Chelate Linkage Isomerism of Some Oxime Complexes of Nickel(II)

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^{1}H N.m.r. and i.r. spectroscopy show that the (4-iminopentane-2,3-dione 3-oximato) ligand forms a five-membered chelate ring in (4-iminopentane-2,3-dione 3-oximato)(4-aminopent-3-en-2-onato)nickel(II) but a six-membered chelate ring in (3-methyliminobutan-2-one oximato)(4-iminopentane-2,3-dione 3-oximato)nickel(II). The stability of these and related mixed-ligand complexes of nickel(II) is attributed to the presence of intramolecular hydrogen bonding between the imino hydrogen atom of one ligand and the oximino oxygen atom of the other.

THERE has been interest recently in the chelate linkage isomerism of oxime complexes with transition metals.[1-7] We have observed that tetra-amminenickel(II) nitrite reacts with pentane-2,4-dione in refluxing ethanol to yield deep red needles of (4-iminopentane-2,4-dione 3-oximato)(4-aminopent-3-en-2-onato)nickel(II) (I). The preferred structural configuration of this complex and related stable mixed-ligand complexes is that in which one ligand forms a five-membered chelate ring and the other a six-membered chelate ring with the nickel atom.

EXPERIMENTAL

^{1}H N.m.r. spectra were determined on a Varian HA 100 spectrometer in $CDCl_3$ solutions at 28·5 °C. Chemical shifts are reported in p.p.m. relative to internal tetramethylsilane (τ = 10·00 p.p.m.). I.r. spectra (paraffin mulls) were measured on a Perkin-Elmer grating spectrometer and the wavenumbers ($\pm 0{\cdot}5$ cm^{-1}) reported in the present studies were obtained using ten-fold expanded scales calibrated against ammonia and water vapour. Group wavenumbers were assigned by comparison with those obtained by isotopic substitution of related complexes.[1,5] Mass spectra were determined on a G.E.C.–A.E.I. MS 12 spectrometer (direct insertion probe, *ca.* 200°) at 70 eV.

(4-*Iminopentane*-2,3-*dione* 3-*oximato*)(4-*aminopent*-3-*en*-2-*onato*)*nickel*(II) (I).—*Method* (*i*). A suspension of tetra-amminenickel(II) nitrite [8] (1·1 g) in absolute ethanol (30 ml) containing pentane-2,4-dione (1·0 g) was heated to gentle reflux. The supernatant liquor slowly turned red over 10 min. After 30 min at reflux, the mixture was filtered hot and the combined filtrate and washings allowed to stand to yield red needles (0·25 g). The compound was recrystallised from ethanol.

Method (*ii*). The compound was synthesised by mononitrosation of bis(4-aminopent-3-en-2-onato)nickel(II) (IV), which was prepared by a published procedure.[9] Its ^{1}H n.m.r. spectrum reported previously [10] contains an erroneous assignment of the NH resonance {τ 5·01 (b, NH), 5·17 [d, *J*(NH,CH) 2·6 Hz, $-CH=$], 8·13 [d, *J*(NH,CH) 0·8 Hz, $CH_3C(=NH)-$], 8·28 [s, $CH_3C(=O)-$]}. The reaction mixture of (IV) (1·27 g), isopentyl nitrite (1·34 ml), and glacial acetic acid (1 ml) in absolute ethanol (20 ml) was refluxed for 1 h. The mixture turned deep red as the nickel complex reacted and crystals of the product began to appear rapidly. The product was filtered off (1·1 g) and recrystallised from ethanol. Its ^{1}H n.m.r., i.r., and mass spectra were identical to those of the compound formed by method (i) [Found: C, 42·05; H, 5·2; N, 14·5. $C_{10}H_{15}N_3NiO_3$ requires C, 42·30; H, 5·32; N, 14·80%. Molecular ion, *m/e* 283 (Ni = 58)]. ^{1}H N.m.r. spectra (4-iminopentane-2,3-dione 3-oximato) ligand: τ 2·75 (b, NH), 7·66 [d, *J*(NH,CH) 1·5 Hz, $CH_3C(=NH)-$], 7·67 [s, $CH_3C(=O)-$]. (4-Aminopent-3-en-2-onato) ligand: τ 3·42 (b, NH), 5·01 [d, *J*(NH,CH) 2·6 Hz, $-CH=$], 7·94 [d, *J*(NH,CH) 1·0 Hz, $CH_3C(=NH)-$], 8·12 [s, $CH_3C(=O)-$].

(4-*Methyliminopentane*-2,3-*dione* 3-*oximato*)(4-*aminopent*-3-*en*-2-*onato*)*nickel*(II) (II).—3-Hydroxyiminopentane-2,4-dione [11] (1·3 g) and methylamine (3 ml, 30% aqueous solution) were added to nickel acetate (2·5 g) in aqueous ethanol (50%, 20 ml). The mixture was heated on the steam-bath for 5 min (dark brown solution) and then cooled to room temperature. An ethanolic solution of 4-aminopent-3-en-2-one [9] (1·0 g) was then added slowly with stirring whereupon a reddish brown precipitate rapidly formed. The mixture was filtered and the precipitate washed and dried (0·8 g). The mother liquor was heated on a steam-bath for a further 30 min, then cooled to room temperature to yield a further quantity of red precipitate (0·6 g). The combined precipitates were crystallised twice from ethanol [Found: C, 44·55; H, 5·5; N, 14·1. $C_{11}H_{17}N_3NiO_3$ requires C, 44·34; H, 5·75; N, 14·10%. Molecular ion, *m/e* 297 (Ni = 58)]. ^{1}H N.m.r. spectra (4-methyliminopentane-2,3-dione 3-oximato) ligand: τ 7·00 (b, NCH_3), 7·66 [s, $CH_3C(=O)-$], 7·79 [bs, $CH_3C(=NCH_3)-$]. (4-Aminopent-3-en-2-onato) ligand: τ 3·38 (b, NH), 5·00 [d, *J*(NH,CH) 2·5 Hz, $-CH=$], 7·96 [bs, $CH_3C(=NH)-$], 8·09 [s, $CH_3C(=O)-$].

(3-*Methyliminobutan*-2-*one oximato*)(4-*iminopentane*-2,3-*dione* 3-*oximato*)*nickel*(II) (VII).—Diacetyl monoxime (0·8 g)

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and methylamine (3 ml, 30% aqueous solution) were added to nickel acetate (2·0 g) in aqueous ethanol (50%, 20 ml). The mixture was heated on a steam-bath for 5 min and an aqueous ammoniacal solution of 3-hydroxyiminopentane-2,4-dione (1·0 g) was then added slowly with stirring. After warming for a further 5 min, the reaction mixture was allowed to cool whereupon yellow-brown crystals slowly formed. The suspension was filtered and the precipitate washed with ethanol and dried (1·5 g). It was recrystallised from ethanol–benzene [Found: C, 40·25; H, 5·25; N, 18·65. $C_{10}H_{16}N_4NiO_3$ requires C, 40·18; H, 5·39; N, 18·74%. Molecular ion, *m/e* 298 (Ni = 58)]. (3-Methyliminobutan-2-one oximato) ligand: τ 6·96 (b, NCH_3), 7·87 [q, *J*(NCH_3,CH) 0·8 Hz, $CH_3C(=NCH_3)$–], 8·06 [bs, $CH_3C(NO)$=]. (4-Iminopentane-2,3-dione 3-oximato) ligand: τ 0·74 (b, NH), 7·49 [s, $CH_3C(=O)$–], 7·53 [d, *J*(NH,CH) 1·2 Hz, $CH_3C(=NH)$–].

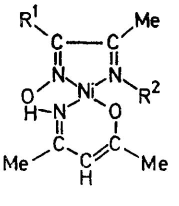
(3-*Methyliminobutan*-2-*one oximato*)(4-*aminopent*-3-*en*-2-*onato*)*nickel*(II) (III).—Diacetyl monoxime (1·0 g) and methylamine (3 ml, 30% aqueous solution) were added to nickel acetate (2·5 g) in aqueous ethanol (50%; 20 ml). The mixture was heated on a steam-bath for 5 min and an ethanolic solution of 4-aminopent-3-en-2-one (1·0 g) was then added dropwise with stirring to the hot dark brown solution. A precipitate rapidly formed. After heating for a further 2—3 min, the mixture was allowed to cool to room temperature and the yellow-brown crystals filtered (1·9 g). The product was recrystallised from ethanol–benzene [Found: C, 44·5; H, 6·2; N, 15·75. $C_{10}H_{17}N_3NiO_2$ requires C, 44·49; H, 6·35; N, 15·56%. Molecular ion, *m/e* 269 (Ni = 58)]. (3-Methyliminobutan-2-one oximato) ligand: τ 7·08 (bs, NCH_3), 7·98 [m, $CH_3C(=NCH_3)$–], 8·12 [bs, $CH_3C(NO)$=]. (4-Aminopent-3-en-2-onato) ligand: τ 3·00 (b, NH), 5·01 [d, *J*(NH,CH) 2·7 Hz, –CH=], 7·98 [m, $CH_3C(=NH)$–], 8·10 [s, $CH_3C(=O)$–].

DISCUSSION

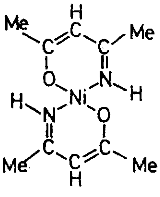
Vicinal oxime-imine ligands, such as the (4-iminopentane-2,3-dione 3-oximato) ligand, can chelate in two possible ways, involving bonding of the oximino nitrogen atom or the oximino oxygen atom to the metal atom.[1-7] The ^1H n.m.r. spectrum of (I) demonstrates that it is not a mixture of chelate linkage isomers, nor is it an equimolar mixture of bis(4-iminopentane-2,3-dione 3-oximato)nickel(II) [1,4] (V) and (IV). The NH proton of the (4-aminopent-3-en-2-onato) ligand of (I) resonates at a much lower field strength (τ 3·42) than that of (IV) (τ 5·01), which indicates a structure for (I) in which an intramolecular hydrogen bond can form between this NH group and the oximino oxygen atom of the other ligand. *X*-Ray crystallographic data have demonstrated the presence of such bonding in the molecule of (4-methyliminopentane-2,3-dione 3-oximato)(4-iminopentane-2,3-dione 3-oximato)nickel(II) (VI).[7]

Additional support for the conclusion that the (4-iminopentane-2,3-dione 3-oximato) ligand is bonded by way of its oximino nitrogen atom in (I) is found in its i.r. spectrum. The carbonyl stretching wavenumber for the unco-ordinated acetyl group (1630 cm^{-1}) is of the order expected [5] for a five-membered chelate ring of this type (1660—1630 cm^{-1}). Also there is no strong absorption *ca.* 1200 cm^{-1}, demonstrating the absence of an oxygen-bonded oxime group.[5]

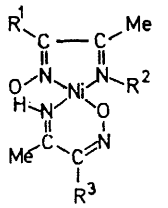
A similar structure is found when the imino hydrogen atom of the oxime ligand is replaced by a methyl group, as in (II). The NH proton resonance (τ 3·38) of the (4-aminopent-3-en-2-onato) ligand is again significantly downfield of that of (IV), while the i.r. spectrum of (II) shows features analogous to those discussed for (I) [ν(C=O) at 1652 cm^{-1}; no strong absorption *ca.* 1200 cm^{-1}].



(I) R^1 = Ac, R^2 = H
(II) R^1 = Ac, R^2 = Me
(III) R^1 = R^2 = Me



(IV)



(V) R^1 = R^3 = Ac, R^2 = H
(VI) R^1 = R^3 = Ac, R^2 = Me
(VII) R^1 = R^2 = Me, R^3 = Ac

Complex (VII) was synthesised in order to see which mode of chelation is adopted by the (4-iminopentane-2,3-dione 3-oximato) ligand in this case. Its ^1H n.m.r spectrum demonstrates quite clearly that the mode of chelation exhibited by this ligand is not the same as that found in (I). Thus, the NH proton resonance (τ 0·74) in the spectrum of (VII) is significantly downfield of that of the same ligand in the spectrum of (I) (τ 2·75) but is comparable to that in the spectrum of (VI) (τ 1·25).[7] The N–H stretching frequency (3115 cm^{-1}) is comparable to that reported (3164 cm^{-1}) for (VI), of known structure,[7] while ν(C=O) for the unco-ordinated acetyl group is observed as a doublet at 1688 and 1683 cm^{-1}, as expected[5] for a six-membered chelate ring of this type (1690—1670 cm^{-1}). Moreover, there is a strong absorption at 1191 cm^{-1} [coupled ν(N–O)], supporting the presence of an oxygen-bonded oxime group.

It is clear that the preferred structures adopted by these mixed-ligand complexes are those in which one ligand (vicinal oxime-imine) forms a five-membered chelate ring while the second ligand forms a six-membered chelate ring with the nickel atom. The second ligand must have an imino-hydrogen atom and can be derived from either a vicinal oxime-imine, as in (VII), or a β-aminoketone, as in (III). Thus, the NH proton resonance of (III) (τ 3·00) is comparable to that observed for the (4-aminopent-3-en-2-onato) ligands of (I) and (II), consistent with the presence of intramolecular hydrogen bonding. Also, there are no strong absorption bands at 1600—1700 cm^{-1} and *ca.* 1200 cm^{-1} in the i.r. spectrum of (III), confirming that the oxime ligand does not possess an unco-ordinated carbonyl group nor is it bonded to the nickel atom by its oxygen atom.

There are very few mass spectra reported of mixed-ligand chelate complexes which do not disproportionate to some extent in the gas phase prior to ionisation. The 70 eV mass spectra of compounds (I)—(III), and (VII) show abundant molecular ions and no ions attributable to products of disproportionation [*e.g.* ions *m/e* 254 and 312 from (I)].*

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* Details of the mass spectra of these compounds have been deposited in Supplementary Publication No. 20940 (2 pp.). For details of this deposition scheme see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are sent as full-size copies).