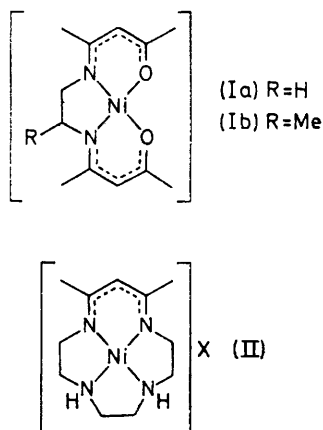


Hydrogen-1 and Carbon-13 Nuclear Magnetic Resonance Studies of Nickel(II) Complexes of Uninegative Quadridentate Ligands derived from Diamines and β -Diketones

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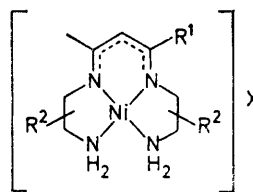
The preparation is described of a series of diamagnetic nickel(II) complexes, (III), of open-chain quadridentate ligands derived from the condensation *in situ*, in a 2 : 1 molar ratio, of ethylenediamine or propylenediamine with a β -diketone. A comparative ^1H and ^{13}C n.m.r. study of these and other related complexes is presented; the structures are discussed in terms of the n.m.r. data. Complex (IIIg), derived from (*RS*)-propylenediamine and pentane-2,4-dione, is assigned a symmetrical structure (IV) in which methyl substituents are attached to the carbon atoms adjacent to the co-ordinated amine groups. The data also indicate that the complex exists as *meso* and *rac* isomers which arise from different relative orientations of the methyl substituents. The ^{13}C n.m.r. data for the open-chain complexes derived from ethylenediamine, (IIIa)–(IIIe) and (IIIh), correlate well with similar data for a related macrocyclic ligand complex (II) in which the cyclic ligand is derived from 1 : 1 condensation of pentane-2,4-dione and 3,6-diazaoctane-1,8-diamine.

REACTION of pentane-2,4-dione with ethylenediamine in the presence of nickel(II) yields the well known nickel complex (Ia).¹ Prolonged heating of (Ia) in neat ethylenediamine does not induce further Schiff-base condensation at the terminal oxygen donors.^{2,3} Nevertheless other synthetic procedures have been successful in producing complexes of quadridentate ligands in which amine condensation has occurred at each end of a β -diketone moiety.³⁻⁷ One reaction of this type has been widely used to prepare a series of complexes of macrocyclic ligands of which (II) is a typical example;^{6,8}



these are obtained by condensation procedures *in situ* involving a linear quadridentate amine and the β -diketone. A range of investigations involving such complexes have now been reported.⁸⁻¹⁰ The existence of related open-chain analogues derived from *N*-methyl-

ethylenediamine (or ethylenediamine) and pentane-2,4-dione (in 2 : 1 molar ratio) have also been reported.⁵ Synthetic details for the preparation of the complex derived from ethylenediamine were not given originally



	R ¹	R ²	X
(III a)	Me	H	Cl
(III b)	Me	H	Br
(III c)	Me	H	I
(III d)	Me	H	SCN
(III e)	Me	H	ClO ₄
(III f)	Me	Me	I
(III g)	Me	Me	SCN
(III h)	Et	H	I

and this complex has since proved difficult to prepare.² Recently¹⁰ a reliable procedure for the synthesis of this complex has appeared (together with a discussion of its ^1H n.m.r. spectrum). We have also developed a related synthesis for this complex as well as for derivatives of the general type (III). We now report the results of a comparative ^1H and ^{13}C n.m.r. study of these various products.

Carbon-13 n.m.r. spectroscopy has been increasingly used to study organometallic compounds but has been employed less frequently to investigate bound organic ligands in co-ordination complexes. Thus the present

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² L. F. Lindoy, unpublished work.

³ T. J. Truex and R. H. Holm, *J. Amer. Chem. Soc.*, 1971, **93**, 285; 1972, **94**, 4529.

⁴ W. Bradley and I. Wright, *J. Chem. Soc.*, 1956, 640; S. G. McGeachin, *Canad. J. Chem.*, 1968, **46**, 1903; J. E. Parks and R. H. Holm, *Inorg. Chem.*, 1968, **7**, 1408.

⁵ D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, 1969, **8**, 1611.

⁶ S. C. Cummings and R. E. Sievers, *J. Amer. Chem. Soc.*, 1970, **92**, 215; *Inorg. Chem.*, 1970, **9**, 1131; M. F. Richardson and R. E. Sievers, *J. Amer. Chem. Soc.*, 1972, **94**, 4134.

⁷ E. G. Jager, *Z. anorg. Chem.*, 1969, **364**, 177; *Z. Chem.*, 1964, **4**, 437; 1968, **8**, 30, 392.

⁸ L. F. Lindoy, *Chem. Soc. Rev.*, 1975, **4**, 421.

⁹ J. G. Martin, R. M. C. Wei, and S. C. Cummings, *Inorg. Chem.*, 1972, **11**, 475; C. J. Hipp, L. F. Lindoy, and D. H. Busch, *ibid.*, p. 1988; J. G. Martin and S. C. Cummings, *ibid.*, 1973, **12**, 1477; J. A. Cunningham and R. E. Sievers, *J. Amer. Chem. Soc.*, 1973, **95**, 7183; F. V. Lovecchio, E. S. Gore, and D. H. Busch, *ibid.*, 1974, **96**, 3109.

¹⁰ W. H. Elfring and N. J. Rose, *Inorg. Chem.*, 1975, **14**, 2759.

studies are of additional interest since they document the ^{13}C chemical shifts for a range of complexes derived from two very common ligand fragments, diamines and β -diketones.

N.M.R. Spectra.—The ^1H n.m.r. spectral assignments for the complexes (IIIa)—(IIIe) in CD_3OD or CDCl_3 are listed in Table 2. The assignments correlate well with those for (III; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$, $\text{X} = \text{PF}_6$) in $(\text{CD}_3)_2\text{CO}$

TABLE 1
Elemental analyses, conductance, visible, and i.r. spectral data

Complex	Analysis ^a (%)					Conductance ^b S cm ² mol ⁻¹	Visible spectra ^c		I.r. data ^d (cm ⁻¹)			
	C	H	N	Ni	X		$\lambda_{\text{max.}}$ / nm	ϵ/dm^3 mol ⁻¹ cm ⁻¹	$\nu(\text{N-H})$	$\delta(\text{N-H})$	$\nu(\text{C}\cdots\text{N}/\text{C}\cdots\text{C})$	Anion
(IIIa)	39.1 (38.95)	6.75 (6.90)	20.3 (20.2)	21.35 (21.15)	12.95 (12.8)	85	513	130	3 260 3 170 3 070	1 615	1 555 1 525	
(IIIb)	38.85 (33.6)	6.00 (5.95)	17.15 (17.4)	18.0 (18.25)	24.7 (24.8)	93	514	111	3 240 3 170 3 070	1 605	1 555 1 530	
(IIIc)	29.65 (29.3)	5.30 (5.20)	14.75 (15.2)	15.35 (15.9)		97	518	97	3 260 3 180 3 115	1 595	1 555 1 530	
(IIIId)	40.3 (40.0)	6.35 (6.40)	23.05 (23.35)	19.3 (19.55)		94	514	103	3 280 3 200 3 120	1 600	1 560 1 535	2 065
(IIIe)	31.8 (31.65)	5.45 (5.60)	16.7 (16.4)			107	512	137	3 320 3 270	1 600	1 560 1 530	1 090
(IIIIf)	33.5 (33.3)	5.90 (5.85)	13.85 (14.1)		32.15 (31.95)	105	522	108	3 240 3 180 3 090	1 590	1 555 1 535	
(IIIg)	44.05 (43.95)	6.95 (7.05)	21.5 (21.35)			95	520	115	3 240 3 190 3 090	1 590	1 555 1 535	2 040
(IIIh)	31.75 (31.35)	5.60 (5.55)	14.5 (14.65)			98	525	96	3 180 3 110	1 595	1 550 1 535	

^a Calculated values are given in parentheses. ^b *ca.* 10^{-3} mol dm⁻³ Solutions in methanol at 23 °C. ^c *ca.* 10^{-3} mol dm⁻³ Solutions in chloroform. ^d Nujol mulls.

TABLE 2
100-MHz N.m.r. spectral assignments (δ values) for the complexes ^a

Complex	Solvent ^b	-CH=	-NH ₂ ^c	=N-CH ₂ -	-CH ₂ - ^d	-CH ₃
(IIIa) ^e	CD_3OD	4.71	3.30	3.16 (t) (<i>J</i> 6 Hz)	2.53 (6 peaks) ^f	1.91
(IIIc)	CDCl_3	4.69	3.60 (t) (<i>J</i> 5 Hz)	3.19 (t) (<i>J</i> 6 Hz)	2.68 (5 peaks)	1.90
(IIIh)	CDCl_3	4.70	3.58	3.21 (br, t) (<i>J</i> 6 Hz)	2.66 (br, m)	1.92 ^g

^a In p.p.m., relative to SiMe_4 . The assignments for (IIIg) are given in the text. All the signals showed relative intensities in accord with the assignments. ^b Concentration *ca.* 0.3 mol dm⁻³. ^c Appeared as a broad signal which disappeared on addition of one drop of $\text{Na}[\text{OD}]-\text{D}_2\text{O}$. ^d Adjacent to amine group; simplified to a triplet on addition of $\text{Na}[\text{OD}]-\text{D}_2\text{O}$. ^e The spectra of (IIIb), (IIIId), and (IIIe) in CD_3OD were also determined; the spectra are very similar to that of (IIIa) with all the resonances within ± 0.02 p.p.m. ^f From which $J(\text{HC}-\text{CH})$ *ca.* 6 and $J(\text{HC}-\text{NH})$ *ca.* 3 Hz. ^g Et resonances: $-\text{CH}_2-$, 2.24 p.p.m., q, *J* 7.3 Hz; $-\text{CH}_3$, 1.06 p.p.m., t, *J* 7.3 Hz.

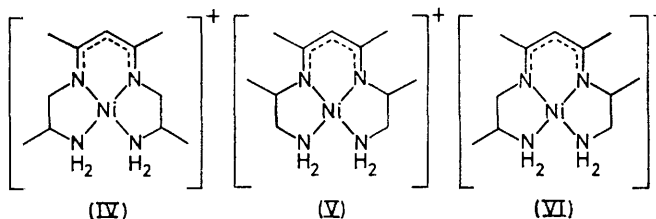
RESULTS AND DISCUSSION

Analytical, conductance, and spectral data for the complexes (III) are listed in Table 1. In accord with the uninegative nature of the co-ordinated ligands, the conductance values indicate that the complexes are 1 : 1 electrolytes.¹¹ The visible spectra are typical of diamagnetic square-planar nickel(II) complexes¹² and the i.r. spectra of the complexes containing thiocyanate or perchlorate anions exhibit the expected bands for these anions when they are not co-ordinated.^{13,14} The mass spectra of the complexes did not show a $[\text{P}]^+$ ion, but all contained a $[\text{P} - \text{X}]^+$ and/or a $[\text{P} - \text{HX}]^+$ ion; further analyses of the spectra were not attempted because of decomposition and hydrogen migrations during fragmentation.

¹¹ W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

¹² G. Maki, *J. Chem. Phys.*, 1958, **29**, 162, 1129; R. D. Archer, *Inorg. Chem.*, 1963, **2**, 292.

reported previously.¹⁰ For (IIIh), the incorporation of a non-symmetric β -diketone backbone is not sufficient to cause observable n.m.r. non-equivalence of correspond-



ing protons in the two diamine sections of the ligand (however, the resonances were broader than the analo-

¹³ B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.

¹⁴ K. Nakamoto and P. J. McCarthy, 'Spectroscopy and Structure of Metal Complex Compounds,' Wiley, New York, 1968.

gous resonances for the complexes derived from pentane-2,4-dione).

For the complexes (III f) and (III g) three structures (IV)—(VI) are possible. The ^1H n.m.r. spectra of these complexes derived from (*RS*)-propylenediamine are somewhat complicated and there is some difficulty in distinguishing unambiguously between structures (IV) and (V) solely from proton spectra, although the spectra indicate that structure (VI) is most unlikely (see below). Assignments are aided by the fact that it was possible to obtain the spectra of these complexes in CDCl_3 as well as in D_2O . The spectrum of the thiocyanate salt (III g) in each solvent is shown in Figure 1. In CDCl_3 , there were five distinct areas of resonance of relative intensity 1 : 2 : 8 : 6 : 6 at 4.65, 3.77, 3.01 (position of major peak), 1.89, and 1.29 p.p.m., respectively. The peaks at 4.65 and 1.89 p.p.m. were both sharp singlets and, in accord with the similar assignments in Table 1, are assigned respectively to the =CH- and CH_3 protons of the backbone derived from pentane-2,4-dione. The broadened

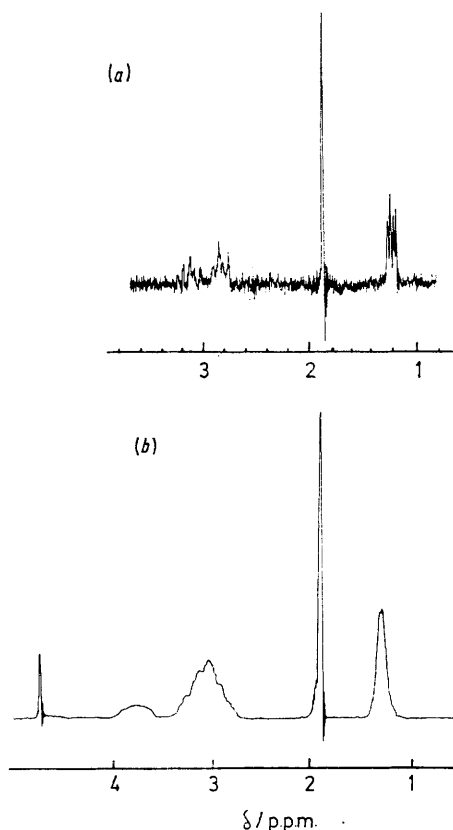


FIGURE 1 100-MHz ^1H n.m.r. spectra of complex (III g) prepared from (*RS*)-propylenediamine: (a) in D_2O ; (b) in CDCl_3

(six-proton) peak at 1.29 p.p.m. is assigned to the methyl groups on the portions of the molecule derived from (*RS*)-propylenediamine. Spin decoupling at the frequency of the eight-proton multiplet results in this peak at 1.29 p.p.m. becoming a sharp doublet [Figure 2(a) and 2(b)].

In D_2O the spectrum of (III g) [Figure 1(a)] showed three areas of resonance: a complex multiplet at 2.89

p.p.m. (position of major peak), a sharp singlet at 1.88 p.p.m., and a four-peak signal centred at 1.19 p.p.m. (The position of the CH resonance was masked by the HDO peak of the solvent in this case.) Owing to

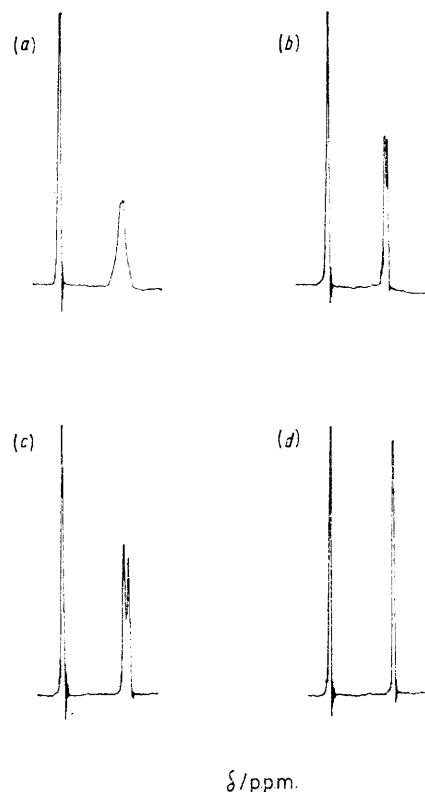


FIGURE 2 100-MHz ^1H n.m.r. spectra of complex (III g) in CDCl_3 : (a) complex prepared from (*RS*)-propylenediamine; (b) spectrum (a) spin decoupled at 3.01 p.p.m.; (c) complex prepared from (*R*)-propylenediamine; (d) spectrum (c) spin decoupled at 3.01 p.p.m.

deuterium exchange, the NH resonances were no longer present. The relative intensities of the observed resonances were 1 : 1 : 1 (*i.e.* 6 : 6 : 6). The nearly equal intensities of the four peaks which comprise the methyl signal at 1.19 p.p.m. suggests that this pattern is derived from two overlapping doublets, one at 1.20 and the other at 1.18 p.p.m., both with J ca. 6 Hz. Spin decoupling of the six-proton multiplet at 2.89 p.p.m. results in the four peaks collapsing to two at 1.20 and 1.18 p.p.m. To aid the assignment of this portion of the spectrum the analogous complex from (*R*)-propylenediamine was synthesised and its spectrum determined. In this case the above resonance appeared as a doublet reduced to a sharp singlet at 1.18 p.p.m. on spin decoupling of the six-proton multiplet [Figure 2(c) and 2(d)]. Clearly the two doublets observed for the methyl resonance in the D_2O spectrum of the complex derived from (*RS*)-propylenediamine arise from the presence of *meso* and *rac* isomers. The *rac* form gives rise to the signal at 1.18 p.p.m. and the *meso* form to that at 1.20 p.p.m.

The loss of two protons from the multiplet at 3.01

p.p.m. and the disappearance of the two-proton peak at 3.77 p.p.m. (δ values for the complex in CDCl_3) in D_2O indicate that there are two types of NH protons. The eight-proton multiplet observed for the complex in CDCl_3 thus results from the presence of two sets of three protons on each portion of the ligand derived from propylenediamine plus two of the four NH protons. Thus the observed signal is very complex since it arises from four overlapping signals, each of which is coupled in a different way. Because of this the signal is poorly resolved at 100 MHz but resolution was greatly improved at 270 MHz (Figure 3). In this case this multiplet was

doublet of doublets, while for (VIII) this will only occur if there is no further coupling to the NH protons. If the latter were the case the two NH resonances might be expected to have the same shape: for example, each a doublet with the same coupling constant. This is not observed in the spectrum; one resonance is clearly a doublet while the other is too broad to decide its multiplicity. Thus, based on the ^1H n.m.r. assignments (Figure 3), these data suggest that (IV) is the correct structure rather than (V). The above spectral data are not in accord with the alternate structure (VI).

Carbon-13 n.m.r. assignments for representative

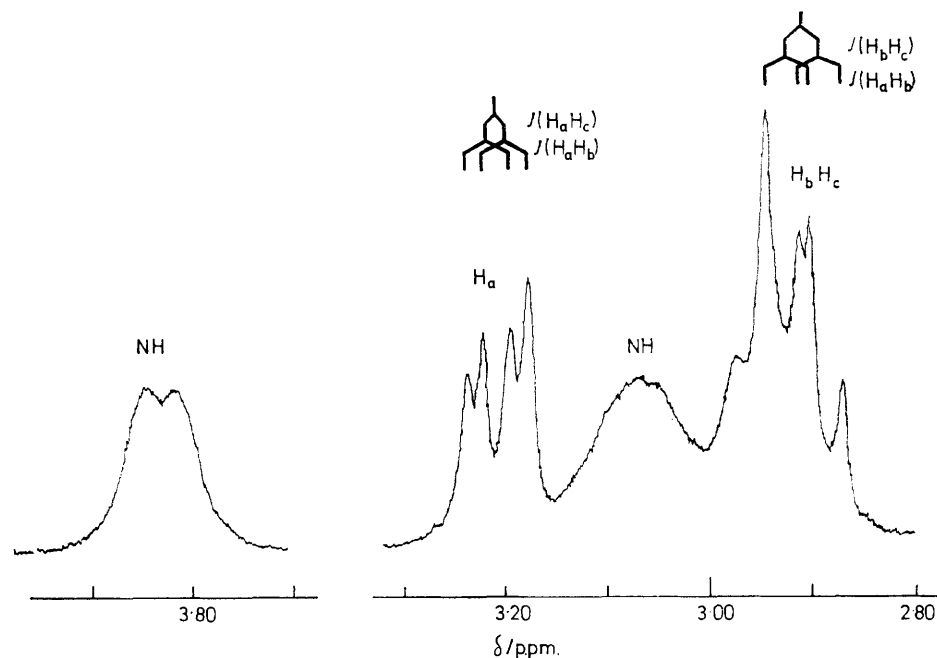
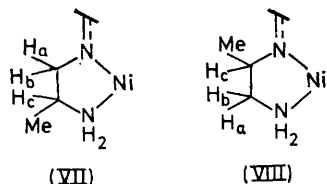


FIGURE 3 270-MHz ^1H n.m.r. spectrum of (IIIg) (prepared from (*R*)-propylenediamine) in the region of the complex multiplet

resolved into three separate signals, a doublet of doublets, a broad poorly structured peak, and a doublet of doublets superimposed on another signal. The relative intensities of these peaks were *ca.* 1 : 1 : 2. Because of its broadness, the central resonance is assigned to a pair of NH protons.

The remaining two signals therefore result from H_a , H_b , and H_c [see (VII) and (VIII)]. Two of these protons



each appeared as a doublet of doublets, a situation which can only be realised by H_a and H_b in either (VII) or (VIII). The broad signal under the lower-field doublet of doublets is assigned to H_c ; this proton is expected to be extensively coupled and thus should give rise to a broad resonance. In (VII), H_a and H_b will both be a

complexes are summarised in Table 3, in which the spectra of complexes (Ia) and (Ib) are included for reference. Similarly, for comparison, the previously reported⁹ related macrocyclic ligand derivative (II) was prepared and its ^{13}C n.m.r. spectrum recorded.

Relative to the spectrum of (Ia), introduction of the methyl group in the diamine chelate ring to yield (Ib) results in two significant changes: first, the imine carbon atoms in the rings derived from pentane-2,4-dione become non-equivalent; and secondly the carbons of the diamine backbone then appear as a triplet at 59.1 p.p.m. and a doublet at 57.5 p.p.m. [in contrast to the single triplet at 52.9 p.p.m. found for (Ia)]. In addition, the presence of the methyl group in (Ib) results in a downfield shift of both diamine backbone carbons of *ca.* 5–7 p.p.m. Analogous shifts in the backbone carbon resonances of co-ordinated propylenediamine relative to co-ordinated ethylenediamine have recently been reported.¹⁵ In (IIIc) the carbon atoms of both diamine


¹⁵ L. E. Erickson, J. E. Sarneski, and C. N. Reilley, *Inorg. Chem.*, 1975, **14**, 3007.

sections of the molecule occur as triplets (at 54.1 and 43.5 p.p.m.). By comparison with the spectrum of (Ia), the triplet at 54.1 p.p.m. can thus be assigned as the carbon atom adjacent to the imine nitrogen.

Comparison of the spectrum of (IIIg) with those of (Ia), (Ib), and (IIIc) provides further strong evidence

backbone carbon atoms which are adjacent to the imine nitrogens. Thus, in an analogous manner, if (VI) were the correct structure for the complex derived from propylenediamine then the different positions of the diamine methyl substituents might be expected to cause non-equivalence in the chemical shifts of both imine

TABLE 3
Carbon-13 n.m.r. spectral assignments (δ values) for the complexes ^a

Complex	CH ₃ -	-CH=		$\begin{matrix} -\text{CH}_2-\text{N}=\text{C} \\ -\text{CH}(\text{CH}_3)-\text{N}=\text{C} \\ \text{CH}_2-\text{NH}-\text{CH}_2- \end{matrix}$	$\begin{matrix} -\text{CH}_2-\text{NH}_2 \\ -\text{CH}(\text{CH}_3)-\text{NH}_2 \end{matrix}$	Others
(Ia)	24.2 (q) (O) (<i>J</i> 127.5)	99.4 (d) (<i>J</i> 160)	176.8 (s) (O)	52.9 (t) (<i>J</i> 138)		
(Ib)	20.9 (q) (N) (<i>J</i> 128)		164.5 (s) (N)			
	24.4 (q) (O) (<i>J</i> 125)	99.6 (d) (<i>J</i> 160)	176.8 (s) (O)	59.1 (t) (<i>J</i> 138)		19.88 (q) (-CH-CH ₃) (<i>J</i> 126)
	21.1 (q) (N), 21.5 (q) (N) (<i>J</i> 126)		165.1 (s) (N), 163.0 (s) (N)	57.6 (d) (<i>J</i> 137)		
(IIIc)	21.0 (q) (<i>J</i> 129)	98.8 (d) (<i>J</i> 168)	159.1 (s)	54.1 (t) (<i>J</i> 138)	43.5 (t) (<i>J</i> 143)	
(IIIg) ^c	21.1 (q) (<i>J</i> 127)	98.5 (d) (<i>J</i> 161)	159.0 (s)	60.5 (t) (<i>J</i> 139)	51.6 (d) (<i>J</i> 141)	18.6 (q) (-CH-CH ₃) (<i>J</i> 126)
(IIIh)	21.2 (q) (<i>J</i> 123)	97.4 (d) (<i>J</i> 164)	152 (s), 138.2 (s)	54.0 (t) (<i>J</i> 140)	43.5 (t) (<i>J</i> 140)	27.4 (t) (-CH ₂ -CH ₃) (<i>J</i> 125)
				53.2 (t) (<i>J</i> 140)		13.0 (q) (-CH ₂ -CH ₃) (<i>J</i> 123)
(II)	19.6 (q) (<i>J</i> 130)	98.8 (d) (<i>J</i> 170)	158.7 (s)	56.3 ^d (t) (<i>J</i> 135)		
				52.4 ^d (t) (<i>J</i> 140)		
				50.5 ^d (t) (<i>J</i> 143)		

^a In p.p.m., relative to SiMe₄. Proton-coupled and proton-decoupled spectra were determined for all the complexes. Spectra for (R) complexes in CDCl₃ near saturation. *J* in Hz. ^b Tabulated resonances correspond to carbon in italics. ^c Prepared from (R)-propylenediamine. ^d Cannot be unambiguously assigned to specific methylene groups on the evidence available.

that this complex has structure (IV) as suggested by the ¹H n.m.r. spectral data. First, the presence of the methyl groups causes the expected downfield shifts in the diamine backbone carbon resonances [observed shift *ca.* 6–8 p.p.m.; *cf.* spectrum of (IIIc)]. The position of the triplet at 60.5 p.p.m. immediately identifies this methylene carbon as adjacent to the imine linkage [*cf.* spectrum of (Ib)]. Further, the position of the doublet at 51.6 p.p.m. (which arises from the carbon to which the methyl group is attached) would not be expected at such a high-field position if it were adjacent to an imine linkage [*cf.* spectrum of (Ib)].

Without exception the values of the C-H coupling constants for the diamine methylene carbons [complexes (Ia), (Ib), (IIIc), and (IIIg)] correlate well. It is diagnostically useful in assigning the proposed structure for (IIIg) that in each case the *J*(C-H) value for the carbon adjacent to an imine linkage is slightly less than when it is adjacent to an NH₂ moiety.

In order to further confirm these assignments, the spectrum of (IIIh) was determined. In this complex the imine carbon atoms are no longer equivalent and this results in n.m.r. non-equivalence of the two diamine

carbons as well as of both methyl carbons of the β -diketone portion of the ligand. No such non-equivalence was observed in the spectrum thus indicating that structure (VI) is unlikely. Clearly the ¹H n.m.r. data together with the internal consistency of the ¹³C assignments listed in Table 3 strongly support structure (IV) for this complex.

The spectrum of complex (II) is in accord with the assignments already discussed (Table 3). The spectrum is generally similar to that of (IIIc) except that it contains an additional triplet resulting from the presence of the extra methylene carbon atoms.

EXPERIMENTAL

Microanalyses were by the Microanalytical Department of the University Chemical Laboratory, Cambridge, or by Mr. J. Kent, Microanalytical Laboratory, University of Queensland. Nickel was determined by atomic absorption spectroscopy. Hydrogen-1 n.m.r. spectra were recorded on Jeol JNM-MH-100 (100 MHz) and Bruker HX-270 spectrometers (270 MHz); the 270-MHz spectra were run at the National NMR Centre, Australian National University. Carbon-13 n.m.r. spectra were obtained on Varian Associates

XL-100 or Jeol JNM FX-60 spectrometers in the Fourier-transform mode. I.r. spectra were recorded on a Jasco IRA-1 spectrophotometer using Nujol mulls; all the spectra were calibrated with respect to a polystyrene standard. Visible spectra were obtained on a Beckman ACTA IV spectrophotometer. Mass spectra were determined on a Jeol JMS-D100 mass spectrometer. Conductance measurements were made using a Philips type PR9500 bridge.

Preparations.—The starting materials were obtained commercially and used without further purification. Optically pure (*R*)-propylenediamine was separated from (*RS*)-propylenediamine by the published method.¹⁶ All complexes were dried over P_4O_{10} .

Complexes (Ia) and (Ib) were prepared¹⁷ and characterised¹⁸ as previously described; (II) was prepared by the published method⁶ (Found: C, 33.7; H, 5.55; N, 14.1. Calc. for $C_{11}H_{21}IN_4Ni$: C, 33.45; H, 5.35; N, 14.2%).

General Procedure for the Synthesis of Complexes (IIIa)—

¹⁶ F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Amer. Chem. Soc.*, 1959, **81**, 290.

¹⁷ P. J. McCarthy, R. J. Hovey, K. Ueno, and A. E. Martell, *J. Amer. Chem. Soc.*, 1955, **77**, 5820.

(IIIh).—The complex $[Ni(diamine)_2Cl_2]$ (0.05 mol) was dissolved in water (100 cm³) and the solution adjusted to pH 5 with acetic acid. The β -diketone (0.05 mol) was then added and the mixture was heated under reflux for 3–5 h, during which time the colour changed from light to dark green. The solution was then cooled to 80 °C and a concentrated solution of Na[OH] was added slowly with stirring until a dense green-grey precipitate formed. The mixture was stirred at 80 °C until a deep red colour developed (usually 3–5 h). The solution was filtered (to remove any nickel hydroxide present) and excess of the desired anion in water (as its sodium or potassium salt) was added. The crude product, which crystallises on standing, may be recrystallised from ethanol, acetone, or a mixture of both to give red crystals.

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[6/421 Received, 2nd March, 1976]

¹⁸ L. F. Lindoy, H. C. Lip, and W. E. Moody, *J.C.S. Dalton*, 1974, 44.