New Nickel(II) and Palladium(II) Complexes with Unsymmetrical Quadridentate Schiff Bases derived from 8-Amino-4-methyl-5-azaoct-3-en-2-one. Crystal and Molecular Structure of [4,10-Dimethyl-3-(nitroso-κ*N*)-5,9-(diaza-κ^2*N*)-trideca-3,10-diene-2,12-(dionato-κ*O*)(2−)]nickel(II)†

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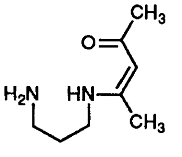
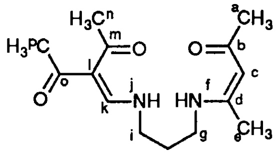
A monocondensation product of pentane-2,4-dione and 1,3-diaminopropane, 8-amino-4-methyl-5-azaoct-3-en-2-one, has been used as a precursor in preparation of three new unsymmetrical quadridentate Schiff-base ligands comprising a trimethylenedi-imine moiety. Nickel(II) and palladium(II) complexes of these ligands have been obtained and characterized by spectroscopic techniques. They are of essentially square-planar geometry and diamagnetic. The single-crystal structure of (4,10-dimethyl-3-nitroso-5,9-diazatrideca-3,10-diene-2,12-dionato)nickel(II) has been determined and shows the co-ordination of nickel by a nitroso group through the nitrogen atom. Crystallographic data: space group $P2_1/c$ (no. 14), a = 8.788(2), b = 7.562(2), c = 21.502(8) Å, β = 98.49(2)°, final R and R' 0.0422 and 0.0490, respectively.

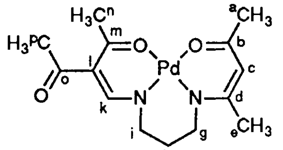
Recently, we have reported[1] that the reaction of pentane-2,4-dione with an excess of 1,3-diaminopropane yields the monocondensation product 8-amino-4-methyl-5-azaoct-3-en-2-one, HL^0. This compound had been used as a tridentate ligand in the preparation of di- and tri-nuclear copper complexes $[(CuL^0Cl)_2]$[2] and $[(CuL^0)_3OH][ClO_4]_2$,[1] respectively. Apart from being a ligand itself, HL^0 offers also the possibility of a synthetic route to unsymmetrical quadridentate Schiff bases by the condensation of its free primary amino group with a variety of reagents comprising carbonyl or alkoxymethylene substituents. A homologue of HL^0 derived from pentane-2,4-dione and 1,2-diaminoethane, 7-amino-4-methyl-5-azahept-3-en-2-one, had been extensively used for this purpose with success and a number of unsymmetrical quadridentate ligands along with their metal complexes obtained.[3–6] On the other hand, there have been few reports on metal complexes with unsymmetrical quadridentate Schiff bases comprising a trimethylenedi-imine moiety derived from 1,3-diaminopropane.[7] Therefore we decided to study whether HL^0 can be used as an efficient precursor in the synthesis of such ligands. In this paper we report the preparation of three new unsymmetrical quadridentate ligands with the use of HL^0, and their nickel(II) and palladium(II) complexes. The crystal and molecular structure of one of the new complexes, [4,10-dimethyl-3-(nitroso-κ*N*)-5,9-(diaza-κ^2*N*)trideca-3,10-dien-2,12-(dionato-κ*O*)(2−)]nickel(II), has been solved in order to determine the co-ordination mode of the nitroso substituent.

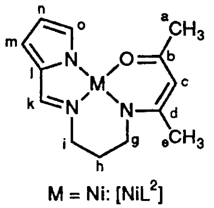

HL^0

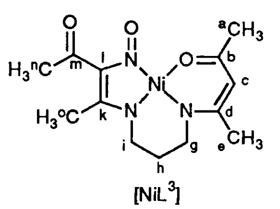
Results and Discussion

Ligands.—The precursor HL^0 reacts readily with 3-ethoxymethylenepentane-2,4-dione, 2-formylpyrrole, and 3-nitrosopentane-2,4-dione to form corresponding quadridentate unsymmetrical Schiff-base ligands H_2L^1, H_2L^2, and H_2L^3, respectively. Due to the formidable difficulties with recrystallization of H_2L^2 and H_2L^3, these ligands were isolated in crude form only as yellow solids, and their identity confirmed by the observation of molecular ions in their field desorption (f.d.) mass spectra. The ligand H_2L^1 was obtained in pure form by several recrystallizations from methanol–di-isopropyl ether, and characterized by mass, i.r., and n.m.r. spectrometry. In the f.d. mass spectrum the molecular peak appears at m/z = 266. The electron impact (e.i.) mass spectrum shows the fragmentation pattern typical of quadridentate Schiff bases,[3,4,8]


H_2L^1


$[PdL^1]$


M = Ni: $[NiL^2]$
M = Pd: $[PdL^2]$


$[NiL^3]$

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Spectroscopic data for the H_2L^1 ligand and metal complexes

Compound	I.r.[a] (cm^{-1})	U.v.–visible,[b] $\lambda_{max.}$/nm(log ε)	^1H N.m.r.,[c] δ_H	^{13}C N.m.r., δ_C/p.p.m.
H_2L^1	1 520m 1 570s 1 605s 1 640s 3 190w	257(4.15) 299(sh) 309(4.40)	1.938(m, H^h), 1.927(s), 2.014(s), 2.261(s) 2.482(s), ($H^{a,e,n,p}$), 3.344(q, H^g), 3.519(q, H^i), 5.029(s, H^c), 7.773(d, H^k), 10.994(br, H^f), 11.062(br, H^j); $J(H^jH^k)$13, $J(H^fH^g) = J(H^gH^h) = J(H^hH^i) = J(H^iH^j) = 6.4$	18.77, 27.26, 28.88, 31.84($C^{a,e,n,p}$), 30.29(C^h), 39.15, 47.06($C^{g,i}$), 96.03(C^c), 111.89(C^l), 160.16, 162.94($C^{d,k}$), 194.45, 195.49, 200.60($C^{b,m,o}$)
[PdL^1]	1 515s 1 595s 1 645m	278(4.32) 324(3.97) 392(sh)	1.997(m, H^h), 2.022(s), 2.040(s), 2.306(s), 2.504(s), ($H^{a,e,n,p}$), 3.240(t, H^g), 3.356(t, H^i),[d] 4.951(s, H^c), 7.682(s, H^k); $J(H^gH^h)$ 5.5, $J(H^hH^i)$ 4.9	23.97, 24.12, 28.34, 29.45($C^{a,e,n,p}$), 30.95(C^h), 51.89, 58.57($C^{g,i}$), 99.73(C^c), 112.66(C^1), 159.20(C^k), 164.94(C^d), 176.08, 187.62($C^{b,m}$), 195.42(C^o)
[NiL^2]	1 515s 1 575s	235(4.26) 312(4.07) 344(3.97) 373(3.97) 500(sh)(2.2)	1.818(m, H^h), 1.851(s), 1.933(s), ($H^{a,e}$), 2.928(t, H^g), 3.043(t, H^i), 4.992(s, H^c), 6.055(m, H^n), 6.502(d, H^m), 6.604(d, H^o), 7.003(s, H^k); $J(H^gH^h)$ 5.0, $J(H^hH^i)$ 5.4, $J(H^mH^n)$ 3, $J(H^nH^o)$ 2	23.12, 23.64($C^{a,e}$), 29.46(C^h), 49.64, 52.23($C^{g,i}$), 100.45(C^c), 110.33(C^n), 144.61(C^m), 133.31(C^o), 137.40(C^l), 159.20(C^k), 166.90(C^d), 174.92(C^b)
[PdL^2]	1 510s 1 580s	280(sh) 326(4.10) 365(sh)(3.8)	1.906(m, H^h), 1.973(s), 1.993(s), ($H^{a,e}$), 3.294(t, H^g),[e] 3.310(t, H^i),[e] 4.899(s, H^c), 6.161(m, H^n), 6.610(m, H^m), 7.031(m, H^o), 7.327(s, H^k); $J(H^gH^h)$ 4.7, $J(H^hH^i)$ 5.6, $J(H^mH^n)$ 3.7, $J(H^nH^o)$ 1.8, $J(H^mH^o)$ 1.0	23.33, 24.68($C^{a,e}$), 31.77(C^h), 50.96, 53.67($C^{g,i}$), 98.91(C^c), 109.84(C^n), 115.47(C^m), 133.00(C^o), 137.57(C^l), 159.00(C^k), 163.02(C^d), 174.93(C^b)
[NiL^3]	1 200m 1 545s 1 575s 1 635s	233(4.31) 270(4.35) 350(3.94) 500(3.23)	1.999(m, H^h), 1.975(s), 2.024(s), 2.244(s), 2.955(s), ($H^{a,e,n,o}$), 3.147(t, $H^{g,i}$), 5.029(s, H^c); $J(H^gH^h) = J(H^hH^i) = 5.3$	17.93, 22.98, 24.34, 32.20($C^{a,e,n,o}$), 29.58(C^h), 48.09, 49.12($C^{g,i}$), 100.44(C^c), 152.72, 167.87($C^{d,k}$), 174.73, 176.41($C^{b,l}$), 191.94(C^m)

[a] s = Strong, m = medium, and w = weak. [b] H_2L^1, [PdL^1], [NiL^2], and [NiL^3] in methanol, [PdL^2] in acetonitrile, sh = shoulder. [c] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad; *J* in Hz. [d] Additional coupling $J(H^kH^i)$ 1.0 Hz. [e] Partially overlapped.

wherein the main pathway involves bond cleavage within the trimethylene bridge moiety.

I.r., ^1H and ^{13}C n.m.r. data for the H_2L^1 ligand are collected in Table 1. In the i.r. spectrum a group of strong bands resulting from C=O, C=N, and C=C stretching vibrations is present in 1 450—1 640 cm^{-1} region. In this group the highest-frequency band at 1 640 cm^{-1} can be attributed to ν(C=O) in the acetyl group not involved in intramolecular hydrogen bonding to the enamine hydrogen atom. The broad absorption band resulting from the NH stretch is observed at 3 190 cm^{-1}.

The proton n.m.r. spectrum of the ligand shows clearly that it exists in solution entirely in the bis(ketoenamine) form (both acidic protons on enamine nitrogen atoms), like its closest homologue derived from 1,2-diaminoethane.[4] Enamine protons f and j give rise to two broad partially overlapping resonances separated by 0.07 p.p.m. The resonances of adjacent methylene groups, g and i, occur as two symmetrical quartets due to vicinal coupling with one enamine and two methylene h protons with virtually the same coupling constant, 6.4 Hz. The enamine–methine coupling (j–k) results in the splitting of the resonance of proton k into a doublet. The large value of the coupling constant $J(H^jH^k) = 13.0$ Hz is typical for *trans* coupling in H–C=N–H systems.[4] The methyl groups give rise to four singlets as the two acetyl groups n and p are not symmetry-related and give rise to two separate signals. In a 1:1 D_2O–CD_3CN mixture the labile enamine protons are readily exchanged with deuterons. In the ^1H n.m.r. spectrum of H_2L^1 dissolved in this solvent the enamine resonances are not present, and all vicinal couplings involving enamine protons f and j are removed, *i.e.* the methylene resonances g and i occur as two triplets, and the doublet of k is reduced to a singlet.

Since every carbon atom in H_2L^1 gives rise to a separate resonance, 14 lines are observed in its proton-decoupled ^{13}C n.m.r. spectrum (Table 1). Their assignment, based on the magnitudes of the chemical shifts and the multiplicity of signals in the proton-coupled spectrum, is straightforward.

Nickel and Palladium Complexes.—The ligands H_2L^1, H_2L^2, and H_2L^3 were used for the preparation of the complexes [PdL^1], [NiL^2], [PdL^2], and [NiL^3]. The complexes are neutral (two enamine groups are deprotonated in H_2L^1 and H_2L^3, one enamine and one pyrrole nitrogen atom in H_2L^2). In the fast atom bombardment (f.a.b.) mass spectrum of each complex a cluster of peaks corresponding to the molecular ion is observed. A complex pattern results from the superimposition of two peaks: M^+ and much more intense $[M + 1]^+$, each of them in turn split into components according to the natural abundance of nickel and palladium isotopes. The fragmentation is marginal, only peaks due to $[M - CH_3CO]$ being detected. The complexes are diamagnetic thus indicating a square-planar geometry around the central ion.

Absorption bands resulting from *d–d* transitions in the u.v.–visible spectra of red-brown [NiL^2] and red [NiL^3] (Table 1) appear around 500 nm. No bands are observed beyond 660 nm where octahedral and tetrahedral nickel complexes are expected to absorb,[9] and this is consistent with the square-planar geometry of the complexes. The *d–d* transitions in yellow [PdL^1] and yellow-brown [PdL^2] (Table 1) are obscured by much more intense u.v. transitions of a different nature.

In the i.r. spectra of the complexes (Table 1) no absorption is observed in the 3 000—3 500 cm^{-1} region in accord with the deprotonation of all NH groups upon complexation. Strong bands resulting from the stretching vibrations of C=C, C=N, and co-ordinated C=O groups appear at 1 510—1 600 cm^{-1}. A C=O stretch of the unco-ordinated carbonyl group in [PdL^1] and [NiL^3] gives rise to a strong absorption around 1 640 cm^{-1}. For [NiL^3] an additional absorption band observed at 1 200 cm^{-1} can be assigned to N=O stretching of the co-ordinated nitroso group. The position of this band indicates N-co-ordination, since it is known that in nitroso-β-ketoenamino metal complexes ν(NO) of the N-co-ordinated nitroso group appears in the range 1 188—1 285 cm^{-1}, whereas O-co-ordination results in a lower-frequency band at 1 098—1 155 cm^{-1}.[10]

Proton n.m.r. data for the diamagnetic nickel and palladium complexes are given in Table 1. They are fully consistent with the structures depicted. No NH resonances are present in the spectra due to the deprotonation upon complexation. The trimethylene fragment, common for all compounds, gives rise to

Table 2. Fractional atomic co-ordinates (× 10^4) for the complex [NiL^3]

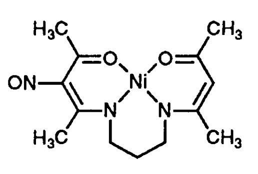
Atom	*x*	*y*	*z*
Ni	365(1)	338(1)	2 430(1)
O(1)	1 827(4)	254(5)	1 904(1)
O(2)	2 425(5)	1 227(8)	4 744(2)
O(3)	3 351(4)	−276(5)	3 040(2)
N(1)	−1 297(4)	587(5)	1 755(2)
N(2)	−777(5)	645(5)	3 090(2)
N(3)	2 007(4)	218(5)	3 106(2)
C(1)	3 197(7)	1 035(13)	1 084(3)
C(2)	1 705(6)	880(7)	1 340(2)
C(3)	340(6)	1 360(8)	991(2)
C(4)	−1 103(6)	1 101(7)	1 183(2)
C(5)	−2 484(8)	1 395(12)	674(3)
C(6)	−2 914(6)	287(9)	1 843(3)
C(7)	−3 102(7)	−500(9)	2 470(3)
C(8)	−2 491(6)	640(9)	3 008(3)
C(9)	−708(9)	1 488(11)	4 198(3)
C(10)	5(6)	955(6)	3 636(2)
C(11)	1 677(6)	747(7)	3 668(2)
C(12)	2 806(6)	1 045(8)	4 227(3)
C(13)	4 510(8)	1 170(13)	4 177(3)

Table 3. Bond distances (Å) and angles (°) for non-hydrogen atoms in [NiL^3]

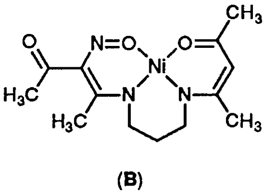
Ni–O(1)	1.832(3)	N(3)–C(11)	1.346(6)
Ni–N(1)	1.910(4)	C(1)–C(2)	1.500(7)
Ni–N(2)	1.870(4)	C(2)–C(3)	1.367(7)
Ni–N(3)	1.892(4)	C(3)–C(4)	1.404(7)
O(1)–C(2)	1.293(5)	C(4)–C(5)	1.526(8)
O(2)–C(12)	1.216(6)	C(6)–C(7)	1.505(9)
O(3)–N(3)	1.267(5)	C(7)–C(8)	1.479(9)
N(1)–C(4)	1.324(6)	C(9)–C(10)	1.495(8)
N(1)–C(6)	1.478(6)	C(10)–C(11)	1.469(7)
N(2)–C(8)	1.490(7)	C(11)–C(12)	1.458(7)
N(2)–C(10)	1.293(6)	C(12)–C(13)	1.520(8)
N(1)–Ni–O(1)	93.5(2)	C(3)–C(2)–C(1)	121.5(5)
N(2)–Ni–O(1)	167.4(2)	C(4)–C(3)–C(2)	124.0(5)
N(2)–Ni–N(1)	97.4(2)	C(3)–C(4)–N(1)	124.0(4)
N(3)–Ni–O(1)	87.0(2)	C(5)–C(4)–N(1)	120.8(5)
N(3)–Ni–N(1)	177.1(2)	C(5)–C(4)–C(3)	115.2(5)
N(3)–Ni–N(2)	81.8(2)	C(7)–C(6)–N(1)	114.2(5)
C(2)–O(1)–Ni	126.7(3)	C(8)–C(7)–C(6)	113.3(6)
C(4)–N(1)–Ni	123.0(3)	C(7)–C(8)–N(2)	109.7(5)
C(6)–N(1)–Ni	121.9(3)	C(9)–C(10)–N(2)	123.5(5)
C(6)–N(1)–C(4)	115.0(4)	C(11)–C(10)–N(2)	114.7(4)
C(8)–N(2)–Ni	123.9(4)	C(11)–C(10)–C(9)	121.8(5)
C(10)–N(2)–Ni	116.1(3)	C(10)–C(11)–N(3)	109.7(4)
C(10)–N(2)–C(8)	120.0(4)	C(12)–C(11)–N(3)	125.2(5)
O(3)–N(3)–Ni	123.1(3)	C(12)–C(11)–C(10)	125.2(5)
C(11)–N(3)–Ni	115.8(3)	C(11)–C(12)–O(2)	121.7(5)
C(11)–N(3)–O(3)	121.1(4)	C(13)–C(12)–O(2)	117.7(5)
C(1)–C(2)–O(1)	114.7(5)	C(13)–C(12)–C(11)	120.6(5)
C(3)–C(2)–O(1)	123.8(5)		

two symmetrical triplets (g,i) and a multiplet (h) usually overlapped by the methyl a,e resonances. In the spectrum of [PdL^2] the triplets are partially superimposed, and in the case of [NiL^3] they are entirely overlapped, appearing as one triplet of double intensity. The higher electronegativity of palladium[11] seems to be a primary cause for a downfield shift of some resonances in palladium complexes relative to the corresponding resonances in the nickel chelates.[3–5] The largest shift, *ca.* 0.3 p.p.m., is observed for protons separated from palladium by three bonds. For more distant protons (four bonds) the shift is smaller than 0.1 p.p.m.

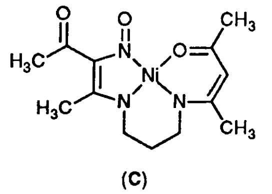
The assignment of the resonances in the ^{13}C n.m.r. spectra of the complexes (Table 1) is based on the magnitudes of the chemical shifts and the multiplicity of the signals in a proton-coupled spectrum. The resonances of the carbonyl carbon atoms of the free unco-ordinated acetyl group (in [PdL^1], [NiL^3], and H_2L^1) appear invariably in the range 191—201 p.p.m., whereas the co-ordination of these groups to nickel or palladium causes an upfield shift of these signals of *ca.* 20 p.p.m. This probably results from the partial overlapping of filled d_{xz} and d_{yz} metal orbitals with the C=O π orbital, thus increasing the electron density on the carbonyl carbon atom. It is interesting that the complexation of H_2L^1 with palladium (H_2L^1–[PdL^1] transition) causes no substantial change in the chemical shift of carbon atoms d,k linked to the enamine nitrogen atoms also involved in co-ordination, since the C–N bond is predominantly single in character and no additional orbital overlapping can be expected. Similarly to the ^1H n.m.r. spectra, substitution of nickel by palladium in the complex (as in the case of [NiL^2] and [PdL^2]) causes a *ca.* 1.4 p.p.m. downfield shift of the resonances associated with carbon atoms g,i, separated from palladium by two single bonds, due to the higher electronegativity of palladium. However, when one of these two bonds has double or even partially delocalized character this effect is not observed.



(A)



(B)



(C)

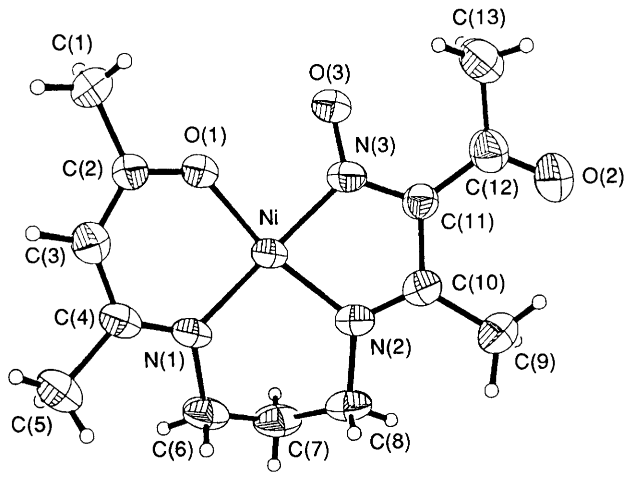


Figure 1. A perspective view of [NiL^3] including the atom numbering scheme

Structure of the Complex [NiL^3].—The ligand H_2L^3 can co-ordinate to nickel(II) ion to form a square-planar diamagnetic complex in three alternative ways; (**A**), (**B**), or (**C**). Several complexes of the types (**B**) and (**C**) have been reported. For example, the close analogue of [NiL^3], 4,9-dimethyl-3-nitroso-

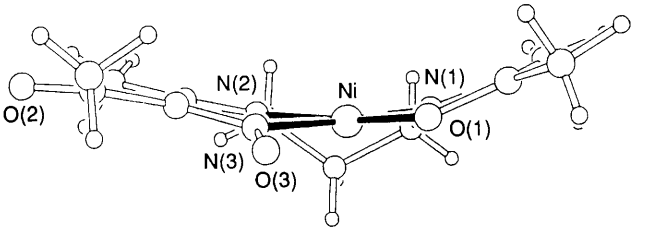


Figure 2. A view of $[NiL^3]$ showing the distortion from planarity

5,8-diazadodeca-3,9-diene-2,11-dionato)nickel(II), differing only in the shorter polymethylene bridge, is a mixture of isomers (**B**) and (**C**).[12] Also the crystal structure of 4,9-dimethyl-3,10-dinitroso-5,8-diazadodeca-3,9-diene-2,11-dionato)nickel(II) shows both types of co-ordination in one molecule: one nitroso group is co-ordinated through its oxygen atom, the second one through nitrogen.[10] In the case of $[NiL^3]$ the strain within the molecule should favour structure (**C**); to determine the actual co-ordination type its crystal and molecular structure have been determined.

A perspective view of the complex $[NiL^3]$ is shown in Figure 1. The final atomic co-ordinates, bond distances and angles are given in Tables 2 and 3, respectively. The crystal structure consists of discrete, roughly square-planar $[NiL^3]$ molecules. The doubly deprotonated ligand L^3 is quadridentate and binds to the Ni^{II} *via* the nitrogen atom of the nitroso group, the two nitrogens of the trimethylenedi-imine moiety, and the oxygen atom of the pentane-2,4-dione functionality [structure (**C**)]. This multidentate binding leads to the formation of two adjacent six-membered chelate rings and one five-membered chelate ring (6-6-5). The complex is visibly folded about the O(1)···N(1) and N(2)···N(3) vectors with the Ni atom displaced approximately 0.07 Å out of the O(1), N(1), N(2), N(3) plane (see Figure 2).

The general features of the nickel co-ordination sphere are not unusual. The observed angular distortions from a regular square-planar geometry are consistent with similar distortions seen in related compounds.[13,14] For example, A–Ni–B angles associated with five-membered chelate rings are invariably smaller than those associated with six-membered rings. For $[NiL^3]$, the N(2)–Ni–N(3) angle associated with the five-membered ring is 81.8(2)° while the O(1)–Ni–N(1) and N(1)–Ni–N(2) angles associated with the six-membered rings are 93.5(2) and 97.4(2)°, respectively. Corresponding values observed in related structures[13,14] range from 82.6 to 83.5° for five-membered rings and from 92.4 to 97.6° for six-membered rings. The acuteness of the N(2)–Ni–N(3) angle is attributed in part to the steric strain imparted to the system by the presence of the two adjacent six-membered rings. The rather long Ni–N(3) distance observed, *i.e.* 1.892(4) Å, is also consistent with this. For comparison, Ni–N(oxime) bonds in other closely related complexes range from 1.86 to 1.88 Å (based on *X*-ray analyses). Finally, the observed lengthening in the Ni–N(1) metal–imine bond *versus* the Ni–N(2) bond [1.910(4) *vs.* 1.870(4) Å] again appears to be a reflection of the steric constraints imposed by the ligand molecule. Related Ni–N(imine) distances in the literature range from 1.856 to 1.890 Å. The Ni–O(1) distance of 1.832(3) Å is normal and in excellent agreement with the average Ni–O(pentanedione) distance of 1.836(5) Å reported for bis(dipivaloylmethanido)nickel.[15]

The structural features of the ligand itself are in a good agreement with the results from comparable studies. The pentanedione end of the ligand exhibits C(2)–O(1), C(2)–C(3), C(3)–C(4), and N(1)–C(4) bond distances of 1.293(5), 1.367(7), 1.404(7), and 1.324(6) Å, respectively. These are very close to the values 1.294(8), 1.379(15), 1.408(11), and 1.299(8) Å reported for a related copper(II) complex,[16] and are indicative of partial delocalization of the ketoenamino end of the nickel-bound L^3 ligand. The nitroso end is characterized by N(3)–O(3), N(3)–C(11), C(10)–C(11), and N(2)–C(10) distances of 1.267(5), 1.346(6), 1.469(7), and 1.293(6) Å, comparable to corresponding distances of 1.269(2), 1.336(2), 1.458(2), and 1.292(2) Å reported in a related study by McConnell *et al.*[14] The trimethylenedi-imine moiety is normal. The six-membered chelate ring arising *via* co-ordination of this moiety to the Ni^{II} exhibits a half-boat conformation, in contrast to the essentially planar six-membered ring derived from the delocalized ketoenamine group.

Lastly, it is noted that the $[NiL^3]$ molecules pack together one on the top of the other giving rise to infinite stacks of these dish-like molecules in the solid state, the result being that loosely associated zigzag chains of Ni atoms are found to extend throughout the crystal lattice. The magnitude of the Ni···Ni distances [3.854(1) Å] rather excludes any significant interactions between the metal ions.

Experimental

Materials.—8-Amino-4-methyl-5-azaoct-3-en-2-one (HL^0), 3-nitrosopentane-2,4-dione, and 3-ethoxymethylenepentane-2,4-dione were prepared according to the literature procedures.[1,17,18] All other chemicals were reagent grade and used without further purification.

Ligands.—3-*Acetyl*-10-*methyl*-5,9-*diazatrideca*-3,10-*diene*-2,12-*dione*, H_2L^1. Freshly prepared 3-ethoxymethylenepentane-2,4-dione (3.12 g, 0.02 mol) in dichloromethane (10 cm^3) was added dropwise to a solution containing HL^0 (3.12 g, 0.02 mol) in dichloromethane (20 cm^3), and the mixture was stirred at 0 °C for 30 min. Partial evaporation of the solvent yielded a red precipitate, which was removed by filtration, redissolved in methanol–di-isopropyl ether (1:1, 50 cm^3), and decolourized with charcoal. The resulting pale yellow solution was then partially evaporated to yield a white precipitate of the crude ligand. The precipitate was recrystallized twice from methanol–di-isopropyl ether and finally 1.60 g of H_2L^1 were obtained in the form of white plates, m.p. 94 °C [Found: C, 63.1; H, 8.3; N, 10.6%; M^+ 266 (100% in f.d. mass spectrum). $C_{14}H_{22}N_2O_3$ requires C, 63.1; H, 8.3; N, 10.5%; *M* 266]. E.i. mass spectrum: *m*/*z* 266 (52, M^+), 223 (8, *M* − CH_3CO), 168 [10, $(CH_3CO)_2CCHNH(CH_2)_3$], 154 [13, $(CH_3CO)_2CCHNH(CH_2)_2$], 126 [100, $(CH_3CO)_2CCHNH$ and $CH_3COCHC(CH_3)NH(CH_2)_2$], 112 [59, $CH_3COCHC(CH_3)NHCH_2$], and 98 [56%, $CH_3COCHC(CH_3)NH$].

7-*Methyl*-1-(*pyrrol*-2′-*yl*)-2,6-*diazadeca*-1,7-*dien*-9-*one*, H_2L^2, *and* 4,10-*dimethyl*-3-*nitroso*-5,9-*diazatrideca*-3,10-*diene*-2,12-*dione*, H_2L^3. Ligand HL^0 (3.12 g, 0.02 mol) in dichloromethane (40 cm^3) was added dropwise to a stirred mixture containing 2-formylpyrrole (1.90 g, 0.02 mol) or 3-nitrosopentane-2,4-dione (2.58 g, 0.02 mol), respectively, in dichloromethane (40 cm^3). Then solid anhydrous magnesium sulphate (3 g) was added and the mixture refluxed with stirring for 1 h. The partially hydrated magnesium salt was removed by filtration and the filtrate evaporated to dryness to give both ligands in the form of oily residues. Attempts to prepare the ligands in crystalline form were not successful, therefore the products were characterized by the observation of molecular ions in the f.d. mass spectra of the crude ligands [M^+, *m*/*z* 233 (100) and 267 (100%) for H_2L^2 and H_2L^3, respectively].

Complexes.—[3-*Acetyl*-10-*methyl*-5,9-*diazatrideca*-3,10-*diene*-2,12-*dionato*(2 −)]*palladium*(II), $[PdL^1]$. To a suspension of palladium chloride (0.355 g, 2 mmol) in methanol–water (2:1, 30 cm^3) were added H_2L^1 ligand (1.065 g, 4 mmol) and 1 mol dm^{-3} sodium hydroxide (3.5 cm^3), and the mixture was refluxed

Table 4. Structure determination summary for the complex [NiL^3]

Crystal data	
Empirical formula	$C_{13}H_{19}N_3NiO_3$
Colour and habit	Dark red needles
Size	0.12 × 0.20 × 0.45 mm
Space group	$P2_1/c$ (no. 14)
Unit-cell dimensions	$a = 8.788(2), b = 7.562(2), c = 21.502(8)$ Å, $\beta = 98.49(2)°$
U/Å^3	1 413.2(7)
Z	4 molecules per cell
D_c/g cm^{-3}	1.52
$F(000)$	680
M	324.0
Data collection	
Radiation	Mo (0.710 73 Å)
Monochromator	Highly oriented graphite crystal
Temperature	Ambient (294 K)
hkl Limits	0—11, 0—10, −25 to 25
Scan range	0.9 on either side of $K_{\alpha 12}$
Background measurement	Stationary crystal and counter at beginning and end of scan, total background-to-scan time ratio of 0.5
Reflections collected	2 187 total, 1 859 independent
Absorption coefficient	13.58 cm^{-1}
No of φ-scan reflections	5
Refinement	
System used	MicroVAX II, Nicolet SHELXS/SHELXTL PLUS
Solution	Sharpened Patterson (PATT)
Final residuals	$R = 0.0422, R' = 0.0490$[a]
Goodness of fit, S	1.61[b]
Largest |shift/e.s.d.|	0.001
Number of variables	257
Data-to-parameter ratio	5.5:1
Maximum/minimum excursions	0.73, −0.30 e Å^{-3}

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = [\Sigma(w||F_o| - |F_c||^2)/\Sigma w|F_o|^2]^{\frac{1}{2}}$ $w = [\sigma^2(F) + |g|F^2]^{-1}, g = 0.000\,500$. [b] $S = [\Sigma(w||F_o| - |F_c||^2)/(M - N)]^{\frac{1}{2}}$ where M is the number of observed reflections and N the number of parameters refined.

for 1.5 h. Then the unreacted palladium salt was removed by filtration, and slow evaporation of the solvent from the filtrate yielded 0.252 g of microcrystalline [PdL^1] complex, m.p. 111 °C (Found: C, 45.7; H, 5.5; N, 7.6. $C_{14}H_{20}N_2O_3Pd$ requires C, 45.4; H, 5.4; N, 7.6%). F.a.b. mass spectrum: *m/z* 371, $[M + 1]^+$.

[*7-Methyl-*1*-*(*pyrrol-*2′*-yl*)*-*2,6*-diazadeca-*1,7*-diene-*9*-onato-*(2−)]*nickel*(II), [NiL^2]. A solution of nickel acetate tetrahydrate (1.24 g, 5 mmol) in methanol (10 cm^3) was combined with crude H_2L^2 (1.17 g, *ca.* 5 mmol) in methanol (50 cm^3). The red-brown mixture was stirred for 2 h at room temperature upon which a dark coloured precipitate formed. The precipitate was removed by filtration, washed with methanol, and recrystallized from methanol–dichloromethane to give [NiL^2] (0.60 g) as red-brown crystals, m.p. 150 °C (Found: C, 53.7; H, 5.9; N, 14.4. $C_{13}H_{17}N_3NiO$ requires C, 53.8; H, 5.9; N, 14.5%. F.a.b. mass spectrum: *m/z* 290, $[M + 1]^+$.

[*7-Methyl-*1*-*(*pyrrol-*2′*-yl*)*-*2,6*-diazadeca-*1,7*-diene-*9*-onato-*(2−)]*palladium*(II), [PdL^2]. To a suspension of palladium chloride (0.355 g, 2 mmol) in acetone (100 cm^3) were added crude H_2L^2 ligand (0.466 g, *ca.* 2 mmol) and triethylamine (0.405 g, 4 mmol). The mixture was refluxed for 3 h until most of the palladium salt dissolved, then filtered and solvent removed from the filtrate to yield a brown precipitate, which was recrystallized from methanol–di-isopropyl ether to give [PdL^2] (0.135 g) as a yellow-brown microcrystalline solid, m.p. 190 °C (Found: C, 45.9; H, 5.0; N, 12.4. $C_{13}H_{17}N_3OPd$ requires C, 46.2; H, 5.1; N, 12.4%). F.a.b. mass spectrum: *m/z* 338, $[M + 1]^+$.

[4,10*-Dimethyl-*3*-*(*nitroso-*κN)*-*5,9*-*(*diaza-*κ^{2}N)*trideca-*3,10*-diene-*2,12*-*(*dionato-*κO)(2−)]*nickel*(II), [NiL^3]. This compound was obtained in a similar way to [NiL^2] with the crude ligand H_2L^3 (1.26 g, *ca.* 5 mmol). Recrystallization from methanol–dichloromethane yielded [NiL^3] (0.68 g) as dark red needles, m.p. 189 °C (Found: C, 48.3; H, 5.9; N, 13.0. $C_{13}H_{19}N_3NiO_3$ requires C, 48.2; H, 5.9; N, 13.0%). F.a.b. mass spectrum: *m/z* 324, $[M + 1]^+$.

Physical Measurements.—Elemental analyses were performed on a Carlo Erba MOD 1106 elemental analyzer. Field desorption mass spectra of the ligands (accelerating voltage 8 kV, extraction voltage −3 kV, emitter current 10 mA) and the 70-eV (*ca.* 1.12 × 10^{-17}J) electron impact mass spectrum of H_2L^1 was recorded on a Varian Mat 711 spectrometer. Fast atom bombardment mass spectra of the complexes were recorded using a *m*-nitrobenzyl alcohol matrix on a VG 30-250 spectrometer (VG Instruments Inc.) at the probe temperature; xenon was used as the primary beam gas and the ion gun operated at 8 kV and 100 μA. Proton and ^{13}C n.m.r. spectra were run on a 300-MHz Nicolet spectrometer in $CDCl_3$ solution with $SiMe_4$ as internal reference. U.v.–visible spectra were recorded on a Perkin-Elmer 402 and i.r. spectra (1 000—4 000 cm^{-1} region) on a Perkin-Elmer 621 spectrometer in Nujol and hexachlorobutadiene mulls.

X-Ray Crystallography of the Complex [NiL^3].—A suitably large crystal of [NiL^3] was isolated, cut to the desired dimensions, mounted on a glass fibre with epoxy cement, and transferred to a Syntex P$\bar{1}$ four-circle diffractometer for characterization and data collection. Unit-cell parameters were determined from the angular settings of 15 well centred reflections ($22 < 2\theta < 31$). Axial photographs and a limited search through an octant of reciprocal space revealed systematic absences and symmetry consistent with the monoclinic space group $P2_1/c$ (no. 14). Crystal data are summarized in Table 4.

Data collection parameters are given in Table 4. One quadrant of data ($+h$, $+k$, $\pm l$) was collected in the 2θ—θ scan mode with 2θ ranging from 3.0 to 45.0°. Scan speeds varied from 1.5 to 4.0° min^{-1}. A total of 2 187 reflections were measured, and corrected for Lorentz-polarization and absorption effects (empirical correction based on five azimuthal reflections; minimum and maximum transmission factors 0.579 and 0.836, respectively). Three standard reflections were remeasured for every 37 reflections as a means of monitoring instrument and crystal stability during the course of the experiment. The intensities of those standards showed a random drift or variation ranging from 0.9269 to 1.0000 with no observable decomposition in the sample. A correction curve from those standards was used to scale the general data to account for the observed drift. Data processing yielded 1 859 unique reflections of which 1 422 had $F > 6\sigma(F)$ with $R_{\text{int}} = 0.0246$ for the averaging of equivalent reflections.

The structure was successfully solved by heavy-atom methods (SHELXS/PATT)[19] in the monoclinic space group $P2_1/c$ (no. 14), and refined by full-matrix least squares. Refinement of the data converged to $R = 0.0912$ with all atoms isotropic, and $R = 0.0623$ with the atoms anisotropic. Subsequent least-square cycles included positional and isotropic thermal parameters for the hydrogen atoms, absorption-corrected data, and a weighting scheme based on $\sigma(F)$. All of the H-atom parameters were free to vary. The final values for the refinement indices are given in Table 4 while fractional atomic co-ordinates for non-hydrogen atoms are in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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