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The Structure and Redox Properties of Some Planar [$M^{II}N_4$] Compounds. Part V[†]. The Nickel(II) and Palladium(II) Compounds of Dianionic Ligands Derived from Diketones and 2-Pyridylhydrazine

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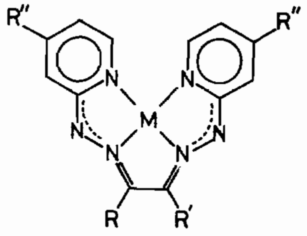
Abstract

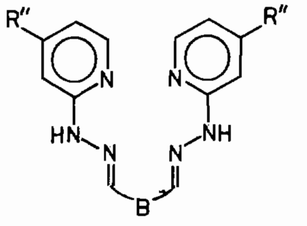
The quadridentate hydrazonato ligands, prepared by condensing two equivalents of a 2-pyridylhydrazine with an α-diketone, form two series of neutral compounds with nickel(II) and palladium(II). Monomeric species, of previously described type, are characteristic four-co-planar [$M(N_4)$] compounds, although the hydrazone ligands give them unusual electronic spectra. In addition, dimeric (and probably also polymeric) compounds are formed by the ligands derived from α-diketones. In the dimers, two metal atoms share two of the quadridentate ligands in an unusual arrangement, which is defined by the ligand steric effects. These also are four-co-planar [$M(N_4)$], diamagnetic species, but with a significant metal–metal bond. Details of a preparative study of the systems and related hydrazonato compounds of α-diketones are presented, together with the physiochemical data defining their structures, and the electronic spectra which are characteristic of the different types of compound obtained. A polarographic and cyclic voltammetric study extends the earlier work on one of the monomers, showing at least four electrode reactions: two oxidation processes, and two reduction processes. The dimeric compounds also undergo a series of one-electron oxidations and reductions.

Introduction

As part of a more general study of the redox behaviour of [$M^{II}N_4$] compounds [1–6], we have looked at the compounds **I** and related species derived from the ligands **II**.



I



II

Such compounds [I for R = R′ = Me, R″ = H and M = Ni, Cu, Pd] had been reported by Chiswell and Lions [7], and Holm *et al.* [8, 9] had shown that the Ni and Pd species undergo an interesting series of redox reactions.

Here we report a more extensive study of the Ni and Pd compounds, with a wider range of ligands, including also those prepared from γ-diketones.

In addition to the expected series of monomeric compounds **I**, a new series of dimeric species was found, and characterised by an X-ray structural analysis [6, 10].

In this paper, we describe preparations, the electronic and ^1H NMR spectra of the compounds, and details of an electrochemical survey.

Experimental

Preparation of Compounds

The Hydrazone Ligands

Most were made by the same procedure, of which the following is an example. The appropriate dione

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[†] For Part IV, see ref. [1].

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(20 mmol) in ethanol (10 ml) was added to a solution of the 2-pyridylhydrazine (40 mmol) in warm ethanol (30 ml). The mixture was heated on a steam-bath (20 min), cooled, and set aside at room temperature overnight. The white, or pale yellow crystalline product was filtered off, washed with iso-propanol and n-pentane and dried *in vacuo*. Yields were usually 75–90%.

For ligand (**III**–H, Me) a 30% aqueous solution of pyruvic aldehyde was used; for ligand {**IV**–$(CH_2)_4$} methanol was used as solvent; for ligand {**III**–$(CH_2)_5$} no crystals were obtained from methanol solution, so this solution was used directly for the metal compounds; for ligand **V**, again no crystals separated, so the solution was evaporated to dryness, and the resultant oil was crystallised from petroleum (40–60°). The ligands **VII** and **VIII** were not prepared in this study, but their metal compounds resulted from oxidative dehydrogenation of those of the saturated ligands **V** and **VI**.

Nickel Compounds

The same general procedure was used for all compounds, as given below for the compound of cyclo-heptane-1,2-dione-bis-(2′-pyridyl)-hydrazonate.

A hot MeOH solution (25 ml) of the ligand (1.5 g, 4.9 mmol) was added to a stirred solution of $NiCl_2 \cdot 6H_2O$ (1.2 g, 5.1 mmol) in a 1:3 water/methanol mixture (40 ml). The resultant clear solution was filtered into a hot aqueous solution (10 ml) of NaOH (0.40 g, 10 mmol) to give an intensely red-black coloured solution. After 30 min at room temperature, red-black crystals had formed. The product (compound **21**) was filtered off, washed with several small volumes of iso-propanol, then n-pentane, and dried *in vacuo*.

When the golden-black coloured filtrate was set aside overnight, a small quantity of black crystals of the monomer **5** crystallised out. These were collected as above.

This differential crystallisation of dimers and monomers also occurred for the Ni compounds of the cyclo-hexane ligands, but for all other ligands only monomers or dimers were obtained (Table I). Various attempts to define reaction conditions, that might lead wholly to one or the other, were unsuccessful.

For the preparation of the compounds **1**, **2**, **4**, **19** and **20** the ligands were dissolved in N,N′-dimethylformamide and added to $NiCl_2 \cdot 6H_2O$ in the water/methanol mixture. The further procedure was then as before.

Compound **13** was prepared by an oxidative dehydrogenation of compound **11** *in situ*. The reaction was carried out as in the above general method, using hexane-2,5-dione, and air was drawn through the reaction mixture for 5 min immediately after addition to the NaOH solution. The resultant dark-red solution was concentrated *in vacuo* to give black crystals of the product. Deliberate exclusion of oxygen, and the presence of an excess of pyridylhydrazine, are necessary for an efficient preparation of the saturated compound **11**.

The dehydrogenation that gives compound **14** is much more facile, and the corresponding saturated compound was not observed. It should, however, be obtainable under anaerobic conditions.

For one attempted preparation of compound **1** from MeOH, the ligand was largely undissolved when the metal solution was added. In this case, the product was an insoluble dark red-brown solid, which appears to be a polymer.

Palladium Compounds

The same method as used for the nickel compounds was adopted, with $PdCl_2$ as metal reagent. The initial reaction products for the preparations of compounds 7, 8, **9** and **10** were mainly the monomers, contaminated with small amounts of the dimers.

Each product in $CHCl_3$ was deposited on an Al_2O_3 column made up in $CHCl_3$. Elution with $CHCl_3$ developed a lower red-brown band (dimer) whilst the bulk of the material remained in a dark-green upper band. Elution with acetone was used to remove the red-brown dimer; elution with MeOH removed the green monomer.

For compounds **24**, **25** and **26**, the dimers were the major products, but here also, it was possible to demonstrate (by ^1H NMR spectroscopy) the presence of small amounts of the corresponding monomers in the filtrates.

From an attempted preparation of compound **12**, the product was largely the dehydrogenated species **15**. Complete conversion was achieved by dissolving the mixture in $CHCl_3$ and drawing air through the solution (2b). The crystalline product was obtained by adding MeOH and evaporating *in vacuo*. No further attempts were made to prepare a pure sample of compound **12**.

Physical Measurements

Details are given in refs. 3 and 4. The electrochemical data were obtained as follows:

oxidations: CH_2Cl_2 solutions (10^{-3} M) using a rotating Pt electrode;

reductions: DMF solutions (10^{-3}–10^{-4} M) using a dropping Hg electrode.

Results and Discussion

The compounds prepared are listed in Table I, together with the analytical data. Abbreviations for the ligand are in Table II.

TABLE I. The Compounds Prepared and Characterised. Each Compound is given a Unique Number. For Identification of the Ligand, refer Table II.

Compound number	Empirical formula	Ligand	m.pt. (°C)	Yield %	Analysis					
					Found			Calc.		
Monomers:					C	H	N	C	H	N
1	$NiC_{12}H_{10}N_6$	III–H, H	>300	13	48.7	3.4	28.5	48.5	3.4	28.3
2	$NiC_{13}H_{12}N_6$	III–H, Me	>300	56	50.4	3.9	27.3	50.2	3.9	27.0
3	$NiC_{14}H_{14}N_6$	III–Me, Me	>300	80	51.9	4.6	26.0	51.8	4.3	25.9
4	$NiC_{16}H_{16}N_6$	III–$(CH_2)_4$	>300	40	54.8	4.6	24.1	54.7	4.6	24.0
5	$NiC_{17}H_{18}N_6$	III–$(CH_2)_5$	>300	10	56.0	5.0	22.9	55.9	4.9	23.0
6	$NiC_{18}H_{20}N_6$	IV–$(CH_2)_4$	>300	20	57.1	5.4	22.2	57.1	5.3	22.2
7	$PdC_{12}H_{10}N_6$	III–H, H	>300	25	41.5	3.2	24.6	41.8	2.9	24.4
8	$PdC_{13}H_{12}N_6$	III–H, Me	>300	25	43.2	3.5	23.0	43.5	3.4	23.4
9	$PdC_{14}H_{14}N_6$	III–Me, Me	>300	22	44.7	3.8	22.1	45.1	3.8	22.6
10	$PdC_{15}H_{16}N_6$	III–Me, Et	>300	27	46.3	4.8	21.2	46.6	4.2	21.7
11	$NiC_{16}H_{18}N_6$	V	210	40	54.5	5.3	24.1	54.4	5.1	23.8
12	$PdC_{16}H_{18}N_6$	V								
13	$NiC_{16}H_{16}N_6$	VII	>300	10	54.9	4.7	24.0	54.7	4.6	24.0
14	$NiC_{18}H_{20}N_6$	VIII	218	32	57.1	5.7	22.3	57.0	5.3	22.2
15	$PdC_{16}H_{16}N_6$	VII	210	18	48.2	4.4	21.1	48.0	4.5	21.0
16	$NiC_{18}H_{14}N_6$	IX	212	50	58.2	4.0	22.8	57.9	3.8	22.5
17	$NiC_{20}H_{18}N_6$, MeOH	X	124	94	56.9	5.4	19.6	58.2	5.1	19.4
18	$PdC_{18}H_{14}N_6$	IX	185	20	50.5	3.5	17.8	50.4	3.4	20.0
Dimers:										
19	$NiC_{16}H_{16}N_6$, 2MeOH	III–$(CH_2)_4$	>300	33	53.3	5.3	22.1	53.3	5.2	22.0
20	$NiC_{17}H_{18}N_6$	III–$(CH_2)_2$–CHMe–CH_2	178	54	55.8	4.7	22.8	55.9	4.9	23.0
21	$NiC_{17}H_{18}N_6$	III–$(CH_2)_5$	>300	86	55.9	4.9	23.0	55.9	4.9	23.0
22	$NiC_{18}H_{20}N_6$, C_6H_6	IV–$(CH_2)_4$	205	60	60.6	5.7	20.4	60.4	5.5	20.1
23	$PdC_{12}H_{10}N_6$	III–H, H		~1	43.0	3.5	23.2	43.5	3.4	23.4
24	$PdC_{16}H_{16}N_6$, MeOH	III–$(CH_2)_4$	>300	55	47.5	4.7	19.5	47.4	5.0	19.6
25	$PdC_{17}H_{18}N_6$	III–$(CH_2)_2$–CHMe–CH_2	280	46	50.0	4.7	19.9	49.5	4.4	20.4
26	$PdC_{18}H_{20}N_6$, MeOH	IV–$(CH_2)_4$	>300	70	50.7	4.4	20.0	50.7	4.7	19.7

To distinguish the monomers and dimers, various spectroscopic measurements were used. Especially useful were the electronic and ^1H NMR spectra, but IR and mass spectra also were used for the characterisations.

The mass spectra gave well-defined parent peaks for both monomers and dimers.

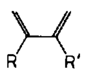
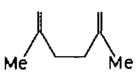
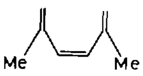
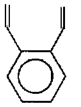
The IR spectra (both as paraffin oil mulls and in CH_2Cl_2 solution) in the region near 1600 cm^{-1} also appear to give a means of distinguishing the monomers from the dimers. The former had only one band in their spectra between 1610 and 1620 cm^{-1} whereas all dimers gave two bands in the region 1600–1630 cm^{-1}, separated by 10–15 cm^{-1}. The immediately appealing idea that the latter reflect the two different kinds of pyridyl in the dimers [10] is of doubtful significance, since other C=C, C=N (and perhaps also N=N) vibrations are expected to occur in the same region. However, the distinction seems to be a useful one.

Preparations

The general preparative method [7] involved deprotonation, with aqueous NaOH, of a methanol or a DMF solution of the appropriate metal chloro compound and the hydrazone ligand. Products were usually mixtures of monomer and dimer, and, despite a number of attempts, we have not defined conditions favouring the formation of one or the other. At various times, in the early preparations of the Ni compounds, different samples of pyridylhydrazine and different batches of solvent appeared to favour one or the other, but further investigation contradicted this. Variations in stoicheiometry of the reagents (up to 20%), use of different solvents, and changing the order of mixing the reagents were tried, but no systematic variations in products were observed.

However, there are some well-defined general trends for the products of the various preparative reactions:

TABLE II The Ligand Numbering and Abbreviation System The Basic Ligand Skeleton is that of Diagram II Numbers V to X are unique, but III and IV refer to a Series of Ligands with Differing R and R′ For These We use Systematic Abbreviations such as (III–Me, Me) for R = R′ = Me, (III–H, Me) for R = H and R′ = Me, (III–$(CH_2)_4$) for R + R′ = $(CH_2)_4$, *i e* the Ligand derived from Cyclohexane-1,2,-dione

Ligand number	B	R″
III		H
IV		Me
V		H
VI		Me
VII		H
VIII		Me
IX		H
X		Me

(a) In the Ni series, products usually crystallised as fairly pure samples of monomer or dimer That is, good fractional crystallisation generally was obtained from the reaction mixtures On the other hand, the Pd products were almost invariably mixtures which needed to be separated by chromatography

(b) The dimers were found more often and in greater proportion in the Pd than in the Ni series

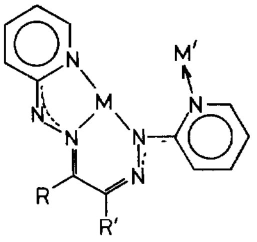
(c) Compounds of the ligands V → X were invariably monomeric

(d) For ligands of types III and IV, dimers were obtained most readily for the cyclohexyl and cycloheptyl ligands Indeed, only trace amounts of the Pd monomers of these ligands were detected in the reaction products

Compounds of the ligands VII and VIII resulted accidentally from oxidative dehydrogenation of the metal compounds of the ligands V and VI Such oxidative dehydrogenations are not uncommon in the metal compounds of macrocyclic and polycyclic $[N_4]$ ligands [11, 12] In the present case, rates of the reactions varied significantly The Ni compound of the ligand V was obtainable with only minor precautions against O_2, such as the use of an excess of the hydrazine in the preparative mixture Yet the dehydrogenation was so fast for the 4-Me analogue (ligand VI) that we did not attempt to characterise the aliphatic species The presence of an excess of OH^- in the preparative mixtures favoured the dehydrogenation

Some rationalisations can be made of the synthetic observations in terms of obvious steric effects from the X-ray structural analyses of the monomeric and dimeric species In a monomer I there is considerable cumulative ring strain [13] (C-strain) [14] The sum of the internal chelate ring angles is only 249° instead of an ideal 270°[†]

Much of the C-strain is relieved in the dimers [10] by an expansion of the middle chelate ring to a six-membered one, as shown in **XI** Then the remaining terminal pyridyl moiety prefers to bond to another metal (M′) in the dimer rather than form a strained four-membered chelate ring to M



XI

Thus we see the formation of the dimers as resulting, at least partially, from C-strain in the monomers Anything that increases this strain should favour the formation of the dimers, and this is indeed observed Pd, with its larger covalent radius than Ni, should favour the dimers [(b) above], and the widening of the chelate bond angles for R + R′ = $-(CH_2)_4-$ and $-(CH_2)_5-$ also is expected to have the same effect—again as observed [(d) above]

Such C-strain is largely relieved in the compounds of the ligands V to X, which have seven-membered middle chelate rings Here the formation of dimers would involve an enlarged eight-membered chelate ring

Electronic Spectra

The monomeric compounds have unusual electronic absorption spectra in the visible and near IR regions, with intense low energy bands These are clearly not of 'd–d' type, and appear to result from transitions between low-lying states of a delocalised system involving the ligands and the metal

The lowest energy bands occur in the spectra of the monomeric compounds of type I—that is, those of ligands of III and IV with a middle five-membered

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[†] Such distortion precludes another possible steric problem from overlap of the α-H atoms of the two pyridyl moieties The latter must, however, assume some significance in the compounds of ligands V to X, and here lead to non-coplanarity of these pyridyl residues with the co-ordination plane

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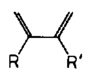
III		H
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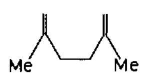
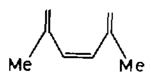
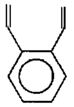
V		H
VI		Me
VII		H
VIII		Me
IX		H
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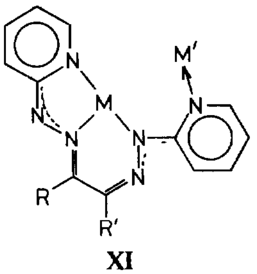

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TABLE III The Electronic Spectra Band Positions are given in 10^3 cm^{-1} and Extinction Coefficients (LM^{-1} cm^{-1}) are in Square Brackets Unresolved Bands, appearing as 'Shoulders' are given in Parentheses

Compound	Metal	Ligand type	Band positions and [extinction coefficients]							
1	Ni	III–H, H	39 5[20000]	33 5[10500]		24 9[10100]	19 6[1850]		10 7[2090]	(10 2)[2020]
2	Ni	III–H, Me	40 2[26500]	33 0[15400]	26 3[1260(	25 0[14000]	19 9[3020]	(19 0)[1500]	11 0[2500]	(10 4)[2440]
3	Ni	III–Me, Me	40 6	32 6	(26 6)	25 2	20 4		11 8	(10 9)
4	Ni	III–$(CH_2)_4$	40 0[28500]	32 8[17700]		25 2[15000]	20 0[3200]	(19 1)[2300]	11 2[2090]	(10 2)[2000]
5	Ni	III–$(CH_2)_5$	41 0[26500]	33 0[17700]	(26 5)[13800]	25 3[15500]	20 4[3670]	(19 4)[2870]	11 6[2200]	(10 6)[2060]
6	Ni	IV–$(CH_2)_4$	39 2[33700]	(33 0)[16800]	26 8[15000]	(25 3)[14000]	(20 4)[3800]		11 5[2300]	10 5[2200]
9	Pd	III–Me, Me	(38 5)[16400]	34 0[16500]		22 8[6600]			12 9[2560]	(11 9)[2400]
10	Pd	III–Me, Et		32 5[20000]		22 7[8100]			12 8[2260]	(11 8)[2060]
13	Ni	VII		34 8[25500]	(32 1)[23300]	24 2[12300]	20 2[9000]		17 2[6300]	15 8[11700]
14	Ni	VIII	37 0[19700]		(32 0)[15200]	25 8[8530]	20 1[5700]		17 1[4300]	15 7[7000]
15	Pd	VII	40 6[41500]		31 4[30500]	25 1[15500]	20 7[16600]		17 6[8000]	16 4[13900]
16	Ni	IX	39 6[29200]	35 0[23900]	29 0[12500]	25 5[13400]	23 6[24200]	(20 4)[11000]	19 4[15300]	17 2[8380]
17	Ni	X	39 5[38400]	34 9[33200]	29 0[15400]	(25 3)[16800]	23 2[37800]	(20 5)[14000]	18 4[19500]	17 3[12200]
18	Pd	IX	43 6[21300]	38 8[21600]	(29 5)[7000]	(24 8)[8000]	23 9[9410]	(20 2)[5500]	19 8[6100]	(18 0)[5200]
19	Ni	III–$(CH_2)_4$	43 7[42200]	39 3[44000]	23 4[17000]	20 5[15700]	(18 9)[14700]			
20	Ni	III–$(CH_2)_2$–CHMe–CH_2	43 5[46000]	38 6[43800]	23 5[15200]	20 3[13700]	(19 3)[12700]			
21	Ni	III–$(CH_2)_5$	42 4[49000]	38 4[51300]	23 4[18400]	20 6[11400]	(19 4)[14400]			
22	Ni	IV–$(CH_2)_4$	42 1[28100]	38 6[27400]	23 5[8160]	20 3[8000]	(19 2)[8160]			
23	Pd	III–H, H	42 5[23800]		27 4[9360]	20 6[10700]	(19 0)[9000]			
24	Pd	III–$(CH_2)_4$	42 6[27000]	(39 5)[22500]	26 2[12100]	20 9[12400]	(19 0)[8400]			
25	Pd	III–$(CH_2)_2$–CHMe–CH_2	42 5[25800]	(39 0)[20600]	26 2[11400]	20 9[11400]	(19 5)[9000]			
26	Pd	IV–$(CH_2)_4$	42 5[24500]	38 7[22300]	25 7[7600]	21 0[9300]	(19 5)[8000]			

TABLE IV The ^{1}H-NMR Spectra

Compound		Ligand	6-H	5-H	4-H	3-H	Other protons
[Ni]	1	III–H, H	6 38(D2)	5 88(T2)	6 93(T2)	6 10(D2)	5 47(S2)
	2	III–H, Me	6 43(D1)	5 88(T1)	6 91(T1)	6 08(D2)	5 45(S1)[H]
			6 33(D1)	5 56(T1)	6 83(T1)	–	1 56(S3)[Me]
	3	III–Me, Me	6 37(D2)	5 77(T2)	6 86(T2)	6 10(D2)	1 62(S6)
	4	III–$(CH_2)_4$	6 41(D2)	5 75(T2)	6 82(T2)	6 09(D2)	2 17(M4), 1 4(M4)[CH_2]
	5	III–$(CH_2)_5$	6 37(D2)	5 78(T2)	6 88(T2)	6 10(D2)	2 22(M4), 1 58(M6)[CH_2]
	6	IV–$(CH_2)_4$	6 34(D2)	5 65(D2)	–	5 98(S2)	2 16(M4), 1 42(M4)[CH_2], 1 42(S6)[Me]
[Pd]	7	III–H, H	6 90(M4)	5 90(T2)	b	6 22(D2)	5 34(S2)
	8	III–H, Me	6 86(M4)	5 85(M2)	b	6 26(D2)	5 40(S1)[H], 1 61(S3)[Me]
	9	III–Me, Me	6 78(M4)	5 74(T2)	b	6 21(D2)	1 59(S6)[Me]
	10	III–Me, Et	6 80(M4)	5 74(T2)	b	6 25(D2)	1 66(S3)[Me], 2 00(Q2), 1 00(T3)[Et]
[Ni]	11	V	6 74(D2)	5 88(T2)	6 98(T2)	6 32(D2)	2 41(M10)[CH_2, Me]
	13	VII	7 80(D2)	6 34(T2)	7 28(T2)	7 06(D2)	6 47(S2), 2 80(S6)[CH, Me]
	14	VIII	7 60(D2)	6 16(D2)	–	6 86(S2)	6 37(S2)[CH], 2 73(S6), 2.20(S6)[Me]
[Pd]	15	VII	7 95(D2)	6 38(T2)	7 31(T2)	7 15(D2)	6 45(S2), 2 80(S6)[CH, Me]
	16	IX	7 45(M)	6 20(T2)	7 20(T2)	6 69(D2)	9 01(S2)[CH], 7 45(M)[C_6H_4]
	17	X	7 21(D2)	6 03(T2)	–	6 48(D2)	8 90(S2)[CH], 7 43(M4)[C_6H_4], 2 14(S6)[Me]
[Pd]	18	IX	7 77(D2)	6 23(T2)	d	d	8 85(S2)[CH],[d] [C_6H_4]
[Ni]	19	III–$(CH_2)_4$	8 66(D1)	6 37(T1)	7 16(T1)	7 58(D1)	2 73(M4)[CH_2]
			5 45(D1)	5 68(T1)	6 96(T1)	6 67(D1)	1 72(M4)[CH_2]
	20	III–C_4H_7Me	8 66(D1)	6 42(T1)	7 20(T1)	7 59(D1)	3 19, 2 84, 2 39, 1 83
			5 46(D1)	5 70(T1)	6 98(T1)	6 71(D1)	1 34(M7)[CH, CH_2], 1 02(M3)[Me][c]
	21	III–$(CH_2)_5$	8 65(D1)	6 39(T1)	7 20(T1)	7 60(D1)	2 84(M4)[CH_2]
			5 42(D1)	5 66(T1)	6 94(T1)	6 65(D1)	1 66(M6)[CH_2]
	22	IV–$(CH_2)_4$	8 33(D1)	6 13(D1)	–	7 29(S1)	2 85(M4), 1 67(M4)[CH_2]
			5 27(D1)	5 52(D1)	–	6 47(S1)	2 06(S3), 1 99(S3)[Me]
[Pd]	24	III–$(CH_2)_4$	8 15(D1)	6 46(T1)	7 44(T1)	7 74(D1)	3 07(D2), 2 72(D2)[CH_2]
			6 34(D1)	5 92(T1)	7 11(T1)	6 88(D1)	1 76(S4)[CH_2]
	25	III–C_4H_7Me	8 14(D1)	6 47(T1)	7 44(T1)	7 74(D1)	4 44, 3 90, 2 38
			6 33(D1)	5 91(T1)	7 11(T1)	6 87(D1)	1 86(M7)[CH, CH_2], 1 04(M3)[Me][c]
	26	IV–$(CH_2)_4$	8 00(D1)	6 30(D1)	–	7 54(S1)	3 07(M4), 2 84(M4)[CH_2]
			6 23(D1)	5 80(D1)	–	6 74(S1)	2 26(S3), 2 07(S3)[Me]

[a] Resonances are given in p p m from TMS D, T, S *etc* have the usual meanings for multiplicities, and the accompanying figure in the parentheses is the relative intensity Typically, separations between components of the multiplets were 6-H, 10 Hz, 5-H, 12 Hz, 4-H, 8 Hz, 3-H, 8 Hz *Meta* coupling of the order of 1–1 5 Hz also was observed in most cases, but is neglected in this tabulation [b] These signals overlap with the 6-H multiplets [c] The methyl resonances appeared as an asymmetric 'triplet', suggesting overlapping doublets, resulting from both isomers of the methyl-cyclohexyl moiety [d] There is overlap here of the resonances of 4-H, 3-H and C_6H_4 centred at 7 26 (M8)

including *meta* and *para* coupling, spin decoupling experiments, and comparison with the 4-methyl-pyridyl species (IV)

Separation between resonances was significantly less in the Pd compounds, so that those for 6-H and 4-H generally overlapped

With the asymmetric ligands {**III** and **IV** for R ≠ R′}, different resonances were observed for each pyridyl ring In the nickel compounds, these were well-resolved, with the separations between the multiplets decreasing in the order 5-H > 6-H > 4-H > 3-H Such separations were again significantly smaller in the Pd compounds

The general ordering of resonances, from low-field to high-field was 4-H < 6-H < 3-H < 5-H However, with the conjugated ligands derived from γ-diketones {**VII** → **X**}, the 4-H and 6-H resonances inverted, and all resonances were at lower field Such changes appear to result from electron distributions in the ligands rather than from through space effects, such as ring current de-shielding

For the dimers, the spectra were quite characteristic, with the pyridyl resonances spread from 5 2 to 8 7 p p m Those for the two different pyridyl rings [10] were well separated and the ordering was different for each from low-field the observed order was usually 6-H (doublet) < 3-H (doublet) < 4-H (triplet) < 4′-H (triplet) < 3′-H (doublet) < 5-H (triplet) < 5′-H (triplet) < 6′-H (doublet) Again, separations between resonances were smaller for the palladıum compounds (2 2 p p m *vs* 3 2 p p m for Nı) and the relatıve posıtıons of the 5′ and 6′ protons were ınverted

The Electrochemıcal Data

The monomerıc nıckel compounds of the α-dıketones (lıgand systems **III** and **IV**) generally show [8] two oxıdatıon and two reductıon waves (Table V) The two oxıdatıon waves and the first reductıon wave are usually well-defined reversıble one-electron processes, but the second reductıon wave (sometımes obscured by medıum breakdown) ıs ınvarıably ırreversıble, and appears to be a two-electron process

TABLE V The Electrochemıcal Data

Compound		Cell[a]	$E_{1/2}$[b]	$E_{3/4} - E_{1/4}$[c]	i_d/c[d]	PS[e]	Process
1	[Nı, III–H, H]	1	f				
			−1 13	−62	3 4	105	0 → −1
			−1 75	−63	6 2	CR[g]	k
2	[Nı, III–H, Me]	1	0 55	67	3 4	170	+1 → +2
			0 17	62	3 6	160	0 → +1
			−1 22	−60	3 5	105	0 → −1
			−1 82	−67	6 3	CR	k
3	[Nı, III–Me, Me]	1	0 53	68	3 2	170	+1 → +2
			0 14	63	3 5	160	0 → +1
			−1 32	−56	3 2	110	0 → −1
			−1 92	−67	6 0	CR	k
4	[Nı, III–$(CH_2)_4$]	1	0 52	67	3 3	170	+1 → +2
			0 12	65	3 5	155	0 → +1
			−1 31	−61	3 4	110	0 → −1
			−1 90	−62	6 2	CR	k
5	[Nı, III–$(CH_2)_5$]	1	0 60	67	3 4	165	+1 → +2
			0 16	63	3 7	155	0 → +1
			−1 34	−56	3 2	110	0 → −1
			−1 94	−63	6 3	CR	k
6	[Nı, IV–$(CH_2)_4$]	1	0 47	67	3 2	170	+1 → +2
			0 06	59	3 5	155	0 → +1
			−1 37	−63	3 6	110	0 → −1
8	[Pd, III–H, Me]	2	0 77	120	4 2	220	+1 → +2
			0 21	80	3 8	200	0 → +1
			−1 22	−80	1 2	I	0 → −1
9	[Pd, III–Me, Me]	2	0 75	95	3 6	200	+1 → +2
			0 19	90	4 2	210	0 → +1
			−1 31	−50	1 7	I	0 → −1
10	[Pd, III–Me, Et]	2	0 75	110	4 5	200	+1 → +2
			0 16	90	3 8	225	0 → +1
			−1 29	−130	1 9	I	0 → −1
			−2 0[h]	−130	3 3		−1 → −2
11	[Nı, V]	1	0 45	83	2 8	I	+1 → +2
			0 21	79	3 3	I	0 → +1
			−1 37	−77	3 3	I	0 → −1
13	[Nı, VII]	1	0 41	56	3 5	170	0 → +1
			−1 18	−63	3 3	105	0 → −1
			−2 14	−89	3 0	I, CR	−1 → −2
14	[Nı, VIII]	2	0 33	95	4 5	250	0 → +1
			−1 15	−70	4 1		0 → −1
			−1 97	−65	3 8		−1 → −2

(contınued on facıng page)

TABLE V *(continued)*

Compound		Cell[a]	$E_{1/2}$[b]	$E_{3/4} - E_{1/4}$[c]	i$_d$/c[d]	PS[e]	Process
15	[Pd, VII]	2	0 86	90	4 3	240	+1 → +2
			0 45	110	6 5	200	0 → +1
			−1 30	−75	3 7		0 → −1
			−1 81	−65	2 8	I	−1 → −2
16	[Ni, IX]	1	0 43	111	3 3	I, CR	0 → +1
			−1 15	−65	3 6	100	0 → −1
			−2 1[h]	−80	3 2	I, CR	−1 → −2
17	[Ni, X]	2	0 57	150	5 6	CR	0 → +1
			−1 15	−80	4 1		0 → −1
			−2 1	−85	3 8		−1 → −2
18	[Pd, IX]	2	0 51	80	3 3	CR	0 → +1
			−1 33	80	3 5		0 → −1
			−1 82	−70	3 1		−1 → −2
			−2 0[h]	−60	3 0	I	
19	[Ni, III–(CH$_2$)$_4$]$_2$	1	1 1			CR	
			0 52	67	3 5	140	+1 → +2
			0 21	62	3 7	160	0 → +1
			−1 49	−57	3 7	110	0 → −1
			−1 69	−69	3 2	CR	−1 → −2
20	[Ni, III–C$_4$H$_7$Me]$_2$	1	1 0			CR	
			0 48	67	3 3	170	+1 → +2
			0 18	61	3 6	155	0 → +1
			−1 55	−62	3 8	150	0 → −1
			−1 75	−71	3 3	CR	−1 → −2
21	[Ni, III–(CH$_2$)$_5$]$_2$	1	0 60	65	3 4	170	+1 → +2
			0 24	62	3 6	160	0 → +1
			[j]				
22	[Ni, IV–(CH$_2$)$_4$]$_2$	2	0 48	125	4 2	280	+1 → +2
			0 08	85	3 9	200	0 → +1
			−1 59	−60	3 2		0 → −1
			−1 79	−80	2 8	CR	−1 → −2
24	[Pd, III–(CH$_2$)$_4$]$_2$	2	1 13	100	4 3	250	+2 → +3
			0 57	85	3 3	220	+1 → +2
			0 26	80	3 2	180	0 → +1
			−1 66	−40	3 0		0 → −1
			−1 99[h]	−50	2 1	I	1 → −2
25	[Pd, III–C$_4$H$_7$Me]$_2$	2	1 12	110	7 5	270	
			0 51	85	4 4	220	+1 → +2
			0 25	75	3 8	220	0 → +1
			−1 67	−40	3 0		0 → −1
			−2 01[h]	−55	1 8	I	−1 → −2
26	[Pd, IV–(CH$_2$)$_4$]	2	1 12	125	5 4	270	
			0 52	120	4 3	240	+1 → +2
			0 21	100	3 6	230	0 → +1
			−1 71	−50	4 0		0 → −1
			−2 07[h]	−70	3 1	I	?

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[a] Two different cells were used Their characteristics are noted in c → e

[b] In volts *vs* S C E CH$_2$Cl$_2$ solutions were used for the oxidations, and DMF solutions for the reductions

[c] A reversibility criterion (in mV) For cell 1, $E_{3/4} - E_{1/4} = 60 \pm 10$ mV for a reversible one-electron process For cell 2, $E_{3/4} - E_{1/4} = 90 \pm 10$ mV The compound [N(n-Bu)$_4$]$_2$[Ni{S$_4$C$_4$(CN)$_4$}] was used to establish these criteria

[d] In μamp/mmol The reference compound (see c) gave values of 3 6 for cell 1 and 4 0 for cell 2 for reversible one-electron processes

[e] PS = peak separation (mV) For reversible one-electron processes in cell 1, PS = 165(±10) mV in CH$_2$Cl$_2$ and 105(±10) mV in DMF, and in cell 2, PS = 230(±10) mV in CH$_2$Cl$_2$

[f] Oxidation waves not measured because of insufficient solubility in CH$_2$Cl$_2$.

[g] CR indicates a chemical reaction occurring on the reverse wave of the cyclic voltammogram

[h] The wave tails into that for base electrolyte decomposition

[i] Return wave irreversible

[j] Reduction waves not measured

[k] These appear to be two-electron reductions

The related palladium compounds are generally similar in electrode behaviour, but here all reduction waves are irreversible, and the oxidation waves occur at higher potentials, especially those of the second process

Data are available for only one compound of a saturated γ-diketone (compound **11**), and the observed electrode processes are not fully reversible However, the overall pattern does seem to be much the same as for the α-diketones, and this is in keeping with the long C–C bond found linking the two halves of the ligand in the X-ray structural determination [9] of the compound **3**

The introduction of unsaturation into the γ-diketone (compounds **13** → **18**) leads to significantly different electrochemical behaviour—generally a single (irreversible) process at higher potential

The comparisons from compound to compound must be tentative, since we have not sought information on the nature of the products Oxidations of such nickel compounds have been shown to involve either oxidation to nickel(III) [17, 18] or oxidation of the ligand to a radical cation [19–21] In at least one case [22] both of these have been identified as arising from the same nickel(II) species Similar remarks apply to the reduction processes *e g*, either Ni(I) or a radical anion However, at least for compounds **3** and **9**, Holm and co-workers [8] have obtained EPR data on the -1 and $+1$ species suggesting but not proving ligand-based radicals

We think that the closeness of the potentials for the Ni and Pd compounds of the same ligand suggests that these are essentially ligand-based oxidations and reductions

Methyl group substituents generally make the half-wave potentials more negative, as observed in other related sets of data [12, 17]

The pattern of two readily accessible oxidation waves has a number of parallels in related $[NiN_4]^\circ$ species, including ligands derived from *o*-aminobenzaldehyde [4] and a number of macrocyclic systems [20, 23, 24], but the pattern is not repeated in the compounds of a series of pyrrole-2-aldehyde-base ligands [3] (single oxidation near 1 volt), nor in hydrazone-based macrocyclic ligands [12]

The dimers (compounds **19** → **26**) also show a rich series of one-electron (per dimer) electrode processes Oxidation of $[Ni_2L_2]^\circ$ species with $AgPF_6$ in CH_2Cl_2 gives a green solution of the oxidised species $[Ni_2L_2]^+$, and a green solid can be isolated However, despite earlier optimism [6], this product has not been fully characterised

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