Chemistry of Polydentate Ligands. Part 3.† Ring Closures effected by the Reaction of β-Diketones with 6,6′-Dihydrazino- and 6,6′-Di(*N*-methylhydrazino)-2,2′-bipyridylnickel(II) Diperchlorate

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Pentane-2,4-dione (Hpd) and benzoylacetone both react with 6,6′-dihydrazino-2,2′-bipyridylnickel(II) diperchlorate in a manner which leads to ring closure about each hydrazine moiety forming substituted derivatives of pyrazole. In contrast, the reaction of Hpd with 6,6′-di(*N*-methylhydrazino)-2,2′-bipyridyl in the presence of Ni^{II} leads to the formation of a complex containing a thirteen-membered macrocycle.

THE interaction of a single molecule of a β-diketone, such as pentane-2,4-dione, with a suitably disposed pair of co-ordinated amines has been used previously as a means of deriving macrocyclic systems from a linear tetra-amine precursor.[1-5] Hitherto only the cyclisation of aliphatic tetra-amines by this method has been reported. As a part of our continuing study of the chemistry of multidentate derivatives of 2,2′-bipyridyl we now report the cyclisation of 6,6′-di(*N*-methylhydrazino)-2,2′-bipyridyl (dmbipy) by reaction with pentane-2,4-dione, and elaborate on our earlier communication [6] of the reaction between 6,6′-dihydrazino-2,2′-bipyridyl (dhbipy) and 2 mol of a β-diketone, which leads to the formation of substituted pyrazole derivatives.

RESULTS AND DISCUSSION

Suspension of the square-planar complex 6,6′-dihydrazino-2,2′-bipyridylnickel(II) perchlorate in an ethanolic solution containing pentane-2,4-dione (Hpd) in excess of 2 mol equivalents resulted over a period of 1 h in the complete dissolution of the reactant. Addition of diethyl ether precipitated a product whose elemental analysis (Table 1) indicated that 2 mol of Hpd had condensed with the reactant. The i.r. spectrum, however, showed no ν(N–H), ν(O–H), or ν(C=O) absorptions, precluding simple monohydrazone formation on the part of each pentane-2,4-dione.

A method commonly employed in heterocyclic chemistry for the preparation of pyrazole ring systems involves the reaction of a hydrazine with a β-diketone,[7] and it became clear that it was a reaction of this type which had occurred to form (1). The spectral and magnetic properties of complex (1) (Table 2) are indicative of octahedral stereochemistry.[8] The ν(Cl–O) absorption in the i.r. spectrum does not show the typical splitting that would be expected were both perchlorate groups co-ordinated.[9] Thus, it appears likely that one perchlorate group and the one water molecule retained in the complex are used to complete the inner co-ordination sphere.

The nature of the ligand itself was verified by decomposition of the paramagnetic complex (1) with sodium cyanide so as to liberate the free ligand (2), which was amenable to ^1H n.m.r. spectroscopy. It was confirmed that the ligand (2) had been liberated from the metal

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† Part 2 is ref. 13.

[1] S. C. Cummings and R. E. Sievers, *J. Amer. Chem. Soc.*, 1970, **92**, 215.

[2] S. C. Cummings and R. E. Sievers, *Inorg. Chem.*, 1970, **9**, 1131.

[3] J. G. Martin, R. M. C. Wei, and S. C. Cummings, *Inorg. Chem.*, 1972, **11**, 475.

[4] N. F. Curtis, *Austral. J. Chem.*, 1974, **27**, 1167.

[5] J. G. Martin and S. C. Cummings, *Inorg. Chem.*, 1973, **12**, 1477.

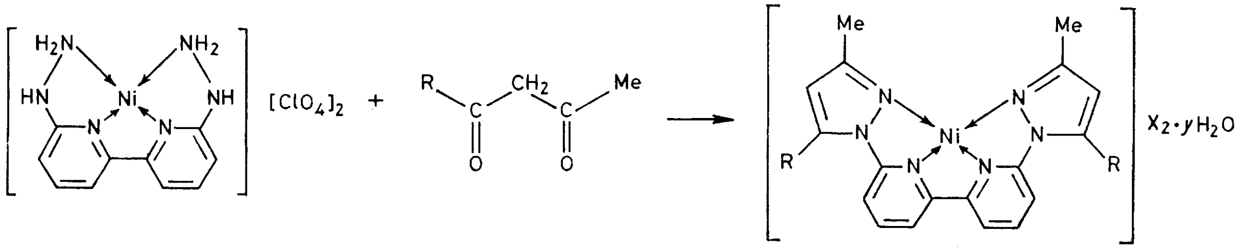
[6] J. Lewis and K. P. Wainwright, *J.C.S. Chem. Comm.*, 1974, 169.

[7] T. L. Jacobs in 'Heterocyclic Compounds,' vol. 5, ed. K. C. Elderfield, Wiley, New York, 1957, p. 48.

[8] L. Sacconi, 'Transition Metal Chemistry,' vol. 4, ed. R. L. Carlin, Edward Arnold, London, 1968, p. 199.

[9] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' 2nd edn., Wiley–Interscience, New York, 1970, p. 174.

unchanged by the fact that combination of (2) with nickel(II) perchlorate regenerates (1). Analytical and mass-spectral data were consistent with the proposed formulation. The ^1H n.m.r. spectrum of (2) in $CDCl_3$ shows two singlet methyl resonances at τ 7.20 and 7.59, a singlet due to the methine protons at τ 3.55, and a multiplet at τ 1.9 arising from the bipy protons. In accordance with the fact that 3,5-dimethylpyrazole has its methyl resonance at τ 7.73,[10] the methyl resonance at τ 7.69 was assigned to the methyl group on the carbon γ to the nitrogen carrying the bipy residue.



	R	X	y
(1)	Me	$[ClO_4]^-$	1
(3)	Me	Cl^-	1
(4)	Ph	$[ClO_4]^-$	2

TABLE 1

Analytical, melting point, and conductance data

Compound	Molecular formula	Analysis (%) Found C	H	N	Calc. C	H	N	Melting point (θ_c/°C)	Λ / S cm^2 mol^{-1}
(1)	$Ni(C_{20}H_{20}N_6)(OH_2)(ClO_4)_2$	39.0 38.8	3.80 3.70	13.7 [a] 13.4 [b]	38.7	3.60	13.6		191 [c]
(2)	$C_{20}H_{20}N_6$	69.3	5.85	24.0	69.7	5.85	24.4	220	
(3)	$Ni(C_{20}H_{20}N_6)(OH_2)Cl_2$	48.7	4.30	17.5	48.8	4.50	17.1		162 [c]
(4)	$Ni(C_{30}H_{24}N_6)(OH_2)_2(ClO_4)_2$	47.1	3.75	11.0	47.3	3.70	11.0		190 [c]
(5)	$C_{30}H_{24}N_6$	76.8	5.15	18.0	76.9	5.15	17.9	231	
(6)	$C_{30}H_{28}N_6O_2$	71.7	5.90	16.9	71.4	5.60	16.7	204	
(7)	$Ni(C_{20}H_{20}N_6)(NCS)_2$	50.6	4.00	21.7	50.9	3.90	21.6		*d*
(8)	$Ni(C_{30}H_{24}N_6)(NCS)_2$	59.4	3.90	17.2	59.7	3.75	17.4		*d*
(9)	$C_{12}H_{16}N_6$	58.9	6.60	34.8	59.0	6.60	34.4	155—156	
(10)	$C_{22}H_{28}N_6O_2$	64.8	7.00	20.9	64.7	6.90	20.6	230—233	
(11)	$C_{32}H_{32}N_6O_2$	72.2	6.30	16.0	72.2	6.05	15.8	224—226	
(12)	$Ni(C_{17}H_{19}N_6)I$	41.2	3.90	16.4	41.4	3.90	17.0		144 [e]
(13)	$Ni(C_{17}H_{19}N_6)(ClO_4)$	43.7	4.05	17.8	43.9	4.10	18.0		138 [e]
(14)	$Ni(C_{17}H_{19}N_6)(PF_6)$	39.8	3.80	16.5	39.9	3.75	16.5		130 [e]
(15)	$Ni(C_{17}H_{20}N_6)(PF_6)_2$	29.9	3.10	11.2	31.1	3.05	12.8		
(16)	$Cu(C_{12}H_{16}N_6)(ClO_4)_2$	28.6	3.20	16.2	28.4	3.20	16.6		198 [c]

[a] Prepared by reaction of $[Ni(dhbipy)][ClO_4]_2$ with pentane-2,4-dione. [b] Prepared by reaction of $[Ni(OH_2)_6][ClO_4]_2$ with (2). [c] 10^{-3} mol dm^{-3} in water at 22 °C. [d] Too insoluble. [e] 10^{-3} mol dm^{-3} acetonitrile at 22 °C. Typical values for 1 : 1 and 2 : 1 electrolytes are in the ranges 135—155 and 250—310 S cm^2 mol^{-1} respectively.[14]

TABLE 2

Spectral and magnetic properties of octahedral nickel(II) complexes

Complex	Electronic spectra (cm^{-1} ±1%) [a] $^3A_{2g}\rightarrow{}^3T_{2g}$ (10*Dq*)	$^3A_{2g}\rightarrow{}^1E_g$	$^3A_{2g}\rightarrow{}^3T_{1g}(F)$	$^3A_{2g}\rightarrow{}^1T_{2g}$	ν_2/ν_1	$\mu_{eff.}$ [b] / B.M.
(1)	10 380 (26)	12 850 (8)	15 720 (5)	21 500 (6)	1.51	3.21
(4)	10 410 (24)	12 280 (8)	16 230 (4)	21 510 (7)	1.56	3.11
(3)	10 380 (27)	12 770 (8)	15 390 (5)	21 600 (6)	1.48	3.18
(7)	9 970 [c]	12 590	17 670		1.77	3.17
(8)	10 250 [c]	12 260	17 450		1.70	3.09

[a] Absorption coefficients (ε/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [b] At 22 °C; 1 B.M. ≈ 9.27 × 10^{-24} A m^2. [c] Solid-state data.

On conducting the reaction under more acidic conditions the nature of the resulting ligand does not change. The interaction of Hpd and $[Ni(dhbipy)][ClO_4]_2$ in ethanol, to which sufficient HCl had been added to lower the pH to 2, resulted only in the formation of the dichloro-analogue (3) of (1). It was possible, also, to synthesise (2) by the direct reaction of dhbipy with Hpd.

With benzoylacetone and $[Ni(dhbipy)][ClO_4]_2$ the

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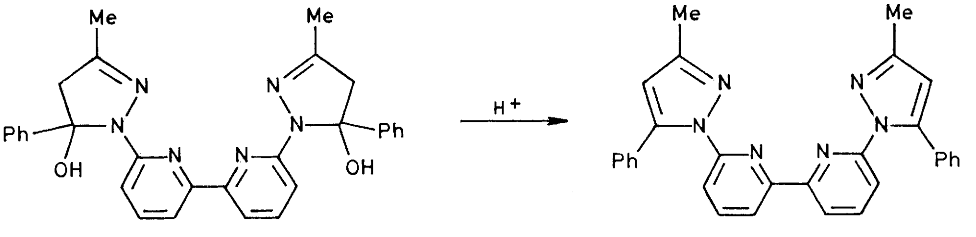
[10] 'Varian High Resolution N.M.R. Catalog,' vol. 2, spectrum no. 441.

reaction proceeded in the same general way as with Hpd, with the formation of the dihydrate (4). In this case, however, where a non-symmetrical β-diketone has been used, several different isomers are possible. It was of interest to ascertain which of these had formed since this would convey information concerning the relative reactivities of the amines in [Ni(dhbipy)][ClO_4]$_2$ which could be compared with the reactivities at the corresponding sites in free dhbipy. Thus the complex (4) was decomposed with Na[CN] and the ^{1}H n.m.r. spectrum of the free ligand, (5), recorded. In deuteriochloroform the ^{1}H n.m.r. spectrum shows only a single methyl resonance at τ 7.63 indicating that both methyl groups are bound at equivalent positions in the molecule and that only a single isomer is formed. In comparison with (2), the chemical shift of the observed signal strongly suggests that the methyl groups are attached to the carbon atom γ to the nitrogen carrying the bipy residue.



(6) (5)

For comparative purposes the direct reaction of benzoylacetone with free dhbipy was examined. After heating the two compounds under reflux for 2 h in methanol the product which precipitated, (6), was collected and purified. The ^{1}H n.m.r. spectrum of (6) together with its elemental analysis showed that it was not the expected product, but rather that it was a hydrated intermediate which probably owes its stability to internal hydrogen bonding. Compound (6) was readily dehydrated by warming it in acetic acid for a few minutes and gave (5).

Since benzoylacetone exists almost entirely in its enol form,[11] it is probable that initial attack by dhbipy (whether it is co-ordinated or not) takes place at the terminal position of the conjugated system, that is on the carbon bearing the methyl group. From the structure of the product it is obvious that it is the primary amine groups of dhbipy that attack at this position irrespective of the co-ordination of the dhbipy. Thus it appears, as has been anticipated from the geometry of dhbipy,[6] that the terminal amines of co-ordinated dhbipy are indeed quite labile and hence react as a nucleophilic centre. They then retain their basicity towards available electrophiles to an extent where they are still more basic than the adjacent secondary amines.

In order to establish whether the linear quadridentate ligands (2) and (5) are bonding to Ni^{II} in the *trans*, *cis*-α or *cis*-β configurations the perchlorate complexes (1) and (4) were converted into their thiocyanates, (7) and (8), respectively by metathesis with ammonium thiocyanate. Complexes (7) and (8) both exhibit spectral and magnetic properties which are characteristic of octahedral complexes[8] (Table 2) and their elemental analyses, as Ni(ligand)(NCS)$_2$, suggest that both anions are co-ordinated. The frequency of the ν(C–S) absorption falls in the range 780—860 cm^{-1} which is normally indicative of an *N*-co-ordinated isothiocyanate group.[12] The single sharp absorption at 2 099 cm^{-1} in the i.r. spectrum of (7) is consistent with a *trans* arrangement[13] of *N*-bonded isothiocyanate groups,[12] although a planar configuration of the ligand appears to be subject to extreme steric hindrance in molecular models. Complex (8) shows two groups of split C≡N bands which suggests that in the solid state it exists as either the *cis*-α or *cis*-β form.[13]

The preparation of 6,6′-di(*N*-methylhydrazino)-2,2′-bipyridyl (9) was effected in a manner analogous to that used for the preparation of dhbipy.[6] On reaction with 2 mol of Hpd both pentane-2,4-dione molecules bind simply as monohydrazones, forming (10). The structure shown for (10) was formulated on the basis of the ^{1}H n.m.r. spectrum which shows, in addition to the resonances arising from the bipy protons, just four signals: a singlet, integrating for two protons, at τ 4.85 attributable to the methine protons; a singlet at τ 6.58 arising from the nitrogen-bound methyl groups; and two singlets each integrating for six protons at τ 7.90 and 8.06 due to the methyl groups on the Hpd residue. These data lead to the following conclusions concerning the structure of (10). First, the precise ratio of 3 : 1 of either one of the signals at τ 7.90 or 8.06 to that at τ 4.85, together with the absence of any methylene resonance, establishes that virtually all of the Hpd residue exists in the enol form. Secondly, the presence of only two methyl resonances from the Hpd residue shows that only one configuration exists about the imino double bonds. Presumably this is the less sterically hindered in which the methyl group on the imino-carbon is *cis* to the tertiary nitrogen substituent.

Reaction of benzoylacetone in a similar way produces (11). The structure indicated for this compound assumes that the primary amine of dmbipy attacks in the usual way at the terminus of the conjugation existing

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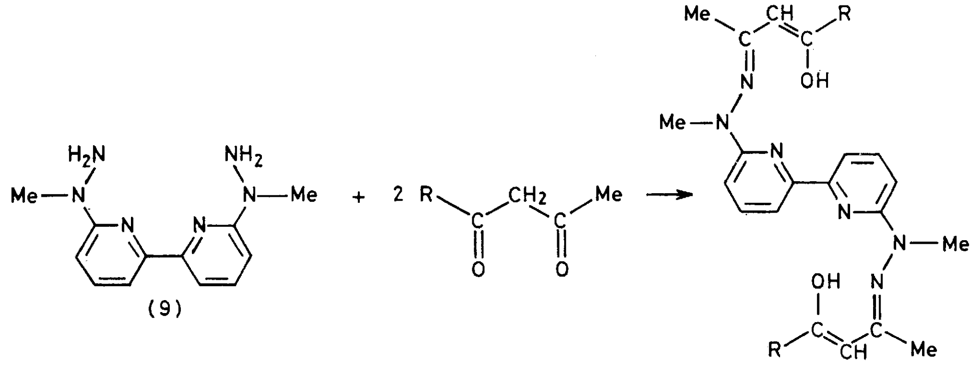
[11] R. T. Morrison and R. N. Boyd, ' Organic Chemistry,' 2nd edn., Allyn and Bacon, Boston, 1968, p. 947.

[12] J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 1961, 4590.

[13] J. Lewis and K. P. Wainwright, *J.C.S. Dalton*, 1977, 739.

in the enolic form of benzoylacetone. The ^1H n.m.r. spectrum of (11) in deuteriochloroform shows, besides the expected signals, a singlet due to the methyl group in the benzoylacetone residue at τ 7.90. This, together with the fact that the other signals are displaced slightly downfield from their position in (10) due to the phenyl group, suggests that in the spectrum of (10) the resonance at τ 8.06 is that due to the imino-methyl group whilst that at τ 7.90 is due to the olefinic methyl group.


(9)

(10) R = Me
(11) R = Ph

Following the general procedure of Cummings and Sievers,[2] compound (10) was heated under reflux in water, which had been acidified to pH 5 with acetic acid, with nickel(II) acetate. Addition of this solution to a saturated aqueous solution of sodium iodide resulted in the precipitation of a red crystalline material. Its observed diamagnetism and visible spectrum (Table 3) showed that it was a square-planar nickel(II) complex[8] and analytical data confirmed that it had the stoicheiometry shown in structure (12). The molar conductivity in acetonitrile was in the range normally observed in this solvent for 1 : 1 electrolytes.[14] The mass spectrum of (12) shows as its highest mass peak that corresponding to the *m*/*e* expected for the cationic part of the molecule alone. This observation is in accordance with Martin and Cummings[5] who observed the equivalent peak in the spectrum of the corresponding macrocyclic product derived from 3,7-diazanonane-1,9-diamine.

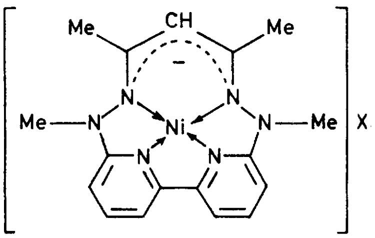

(12) $X = I^-$
(13) $X = [ClO_4]^-$
(14) $X = [PF_6]^-$

TABLE 3

Electronic-spectral data (cm^{-1} + 1%; ε/dm^3 mol^{-1} cm^{-1} in parentheses) for square-planar nickel(II) complexes

Complex	$^1A_{1g} \rightarrow {}^1A_{2g}$	Solvent
(12)	20 080 (227)	MeCN
(13)	20 100 (241)	MeCN
(14)	20 080 (252)	MeCN
(15)	23 200	Solid State

The addition of sodium perchlorate or ammonium hexafluorophosphate to the reaction solution containing the macrocyclic species results in the precipitation of the more soluble perchlorate (13) and hexafluorophosphate (14) salts respectively. The ^1H n.m.r. spectra of these two complexes were recorded in $S(CD_3)_2O$ and are fully in agreement with the proposed structure.

The rate of formation of this cyclic system decreases significantly if the pH is allowed to rise above 5. This suggests that acid hydrolysis of one of the imine moeities is responsible for the initiation of the reaction. It then appears that the resulting free amine attacks the acyl group of the bound pentane-2,4-dione, which, because of the metal-template effect, is favourably positioned for attack. Two observations support this suggestion. First, no cyclic product is obtained in the absence of a metal, as also noted by Martin and Cummings[5] and suggests the necessity for metal-template orientation. Secondly, attempts to cyclise the benzoylacetone derivative (11) in the same manner as (10) gave no result. The compound did not react at all. This is reasonable in view of what has been suggested since attack at the benzoyl carbon atom, which would be necessary for cyclisation, is known to be less favourable than attack at an acetyl carbon atom. Hence, with (11), the tendency after the initial elimination of one benzoylacetone molecule is to recombine with that same benzoylacetone molecule, by attack at the acetyl carbon, rather than attack at the benzoyl position of the bound benzoylacetone as required for cyclisation.

The final step in the reaction involves deprotonation of the γ-carbon atom in the pentane-2,4-dione residue to form the delocalised π-electron system. With the compounds under discussion, the system is fully deprotonated under the prevailing reaction conditions, *i.e.* at pH 5, and it is only necessary to add an appropriate counter ion to precipitate the complex containing the deprotonated

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[14] E. S. Gore and D. H. Busch, *Inorg. Chem.*, 1973, **12**, 1.

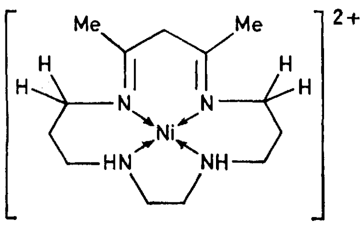
ligand. This is in contrast to the macrocyclic systems derived from aliphatic tetra-amines where it has generally been found necessary to adjust the reaction solution to pH 10 before any precipitation of the product can be effected.[1-5] It is possible that the ease with which the negative charge is stabilised in this ligand system is due to the delocalisation of the charge into the bipyridyl system by way of conjugation through the metal. This is consistent with the ^{1}H n.m.r. data from both (13) and (14) where the bipy protons are seen to resonate *ca.* 0.6 p.p.m. to higher field than they do in cases where they form part of a neutral co-ordinated ligand system.[13]

Protonation of the uninegative ligand was effected by treating (14) with 2 mol dm^{-3} hexafluorophosphoric acid. In this way the red suspended solid was converted into a yellow compound (15). Owing to its high acidity and low solubility in sufficiently protic solvents, satisfactory analytical data could not be obtained. The solid-state i.r. spectrum, however, showed a well resolved ν(C=N) stretch at 1 601 cm^{-1}, in contrast to the co-ordinated uninegative ligand which showed a broad unresolved band between 1 605 and 1 520 cm^{-1}. No band is seen in the spectrum of (15) in the 2 250—2 700 cm^{-1} region which would suggest that protonation of a tertiary amine, rather than of the pentane-2,4-dione residue, has occurred.

Attempts were made to free the macrocycle from the metal by treating the complex with Na[CN]. However, in accordance with observations made by Cummings on this type of system, no demetallation could be effected.[15]

The reaction of copper(II) acetate with (10) was investigated and was found not to produce the macrocyclic product. Instead, hydrolysis of both Schiff-base groups occurred forming the $[Cu(dmbipy)]^{2+}$ complex, which was precipitated as its perchlorate salt (16). In the past, the ability of a macrocycle of this type to form around Ni^{II} but not Cu^{II} has been taken as being illustrative of the fact that one is approaching the strain limit that is acceptable for the ligand.[5] This observation has been prompted by pK_a determinations which show that, of the two geometrical possibilities, the uninegative and the neutral macrocycle, Cu^{II} always has a greater tendency to stabilise the more strain-free, protonated, form of the ligand. Thus, the fifteen-membered macrocycle (17), in which there are unfavourable steric interactions due to the adjacent six-membered rings, will not form around Cu^{II}, and with Ni^{II} can only be formed in the more strain-free protonated form.[5]

It appears that in the reaction under study the macrocyclic system formed exhibits as much internal strain as such systems will tolerate. We are currently investigating the possibility of forming a macrocycle containing, instead of the 2,2′-bipyridyl residue present in (12)—(15), a 1,10-phenanthroline group.[16] The formation or otherwise of such a system will establish whether it is possible to impose any further constraints on thirteen-membered systems having this geometry.



(17)

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on a Varian HA-100 spectrometer using internal $SiMe_4$ as lock. Infrared spectra were determined as Nujol mulls using a Perkin-Elmer 237 spectrometer. Conductance data were determined using a Wayne–Kerr Universal Bridge. Magnetic moments were measured using a Newport Gouy balance and are corrected for ligand and inner-core diamagnetism using Pascall's constants.[17] Electronic spectra were recorded on a Unicam SP 700A u.v. and visible spectrometer. Molecular weights were determined by mass spectrometry, where possible, using an A.E.I. MS12 spectrometer. Microanalyses were by the University Chemical Laboratory Microanalytical Department.

Di-isothiocyanatotetra(pyridine)nickel(II) was prepared by the standard procedure.[18] 6,6′-Dibromo- and 6,6′-dihydrazino-2,2′-bipyridyl were prepared as reported previously.[6,19]

Aqua[6,6′-*bis*(3,5-*dimethylpyrazolyl*)-2,2′-*bipyridyl*]-*nickel*(II) *Diperchlorate* (1).—Pentane-2,4-dione (0.16 g) was added to a stirred refluxing suspension of 6,6′-dihydrazino-2,2′-bipyridylnickel(II) diperchlorate (0.25 g) in ethanol (40 cm^3). After 1 h, complete dissolution of the reactant marked the completion of the reaction. The green solution was filtered and was reduced in volume to *ca.* 5 cm^3 by evaporation under reduced pressure. Addition of diethyl ether precipitated the pure complex as pale green plates (0.28 g, 85%).

Alternatively, 6,6′-bis(3,5-dimethylpyrazolyl)-2,2′-bipyridyl (2) (0.2 g) was suspended in ethanol (25 cm^3) and the solution heated under reflux. Hexa-aquanickel(II) diperchlorate (0.25 g) was added, and the solution was heated under reflux until all of the reactant had dissolved. The pure product was then isolated from the resulting solution in the manner described above (0.31 g, 89%). Infrared spectrum in Nujol: 3 400s, 1 604s, 1 585m, 1 566s, 1 490s, 1 426s, 1 333s, 1 310s, 1 275m, 1 194w, 1 182w, 1 150—1 030s, 990m, 925w, 848w, 792s, and 715m cm^{-1}.

6,6′-*Bis*(3,5-*dimethylpyrazolyl*)-2,2′-*bipyridyl* (2).—Complex (1) (0.2 g) was dissolved in methanol (25 cm^3) and the solution heated under reflux. Sodium cyanide (0.075 g) was then added and the solution heated under reflux for another 15 min before evaporating to dryness under reduced pressure. The residue was extracted with hot chloroform

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[15] L. F. Lindoy and D. H. Busch in ' Preparative Inorganic Reactions,' ed. W. L. Jolly, Wiley, New York, 1971, vol. 6, p. 1.

[16] J. Lewis, T. O'Donoghue, and K. P. Wainwright, unpublished work.

[17] B. N. Figgis and J. Lewis, ' Modern Co-ordination Chemistry,' eds. J. Lewis and R. E. Wilkins, Interscience, New York, 1960, p. 400.

[18] G. B. Kauffman, R. A. Albers, and F. L. Marlan, *Inorg. Synth.*, 1970, **12**, 251.

[19] F. H. Burstall, *J. Chem. Soc.*, 1938, 1662.

(2 × 20 cm^3) and the extract filtered, before evaporating it to dryness under reduced pressure to yield the crude product. Recrystallisation, once, from chloroform–light petroleum gave the pure compound as white needles (0.1 g, 87%).

Alternatively, 6,6′-dihydrazino-2,2′-bipyridyl (0.4 g) was suspended in refluxing methanol; to the suspension was added Hpd (0.4 cm^3) and glacial acetic acid (two drops). The suspension was heated under reflux for 1 h before filtering off the white precipitate which formed. The precipitate was washed with methanol (2 × 10 cm^3) and dried *in vacuo* to give the pure product (0.6 g, 94%). Hydrogen-1 n.m.r. spectrum in CDCl$_3$: τ 1.7—2.2 (m, 6 H), 3.95 (s, 2 H), 7.20 (s, 6 H), and 7.69 (s, 6 H). Infrared spectrum in Nujol: 1 586m, 1 578m, 1 562s, 1 282w, 1 143w, 1 095m, 1 072m, 1 041m, 982w, 968s, 793s, 770s, and 697s cm^{-1}. Mass spectrum: *m/e* of parent ion 344 (calc. 344).

[6,6′-*Bis*(3,5-*dimethylpyrazolyl*)-2,2′-*bipyridyl*]*dichloronickel*(II) *Hydrate* (3).—6,6′-Dihydrazino-2,2′-bipyridylnickel(II) (0.2 g) was suspended in ethanol (20 cm^3), and concentrated aqueous hydrochloric acid (11.5 mol dm^{-3}) was added until the solution attained pH 2. Pentane-2,4-dione (0.13 g) was then added and the solution heated under reflux for 1 h. The solution was then filtered and reduced in volume under reduced pressure to *ca.* 5 cm^3, whereupon bright green crystals of the pure product precipitated. The product was filtered off, washed sparingly with water, and dried *in vacuo*, yield 0.15 g (72%). Infrared spectrum in Nujol: 3 400s, 1 600m, 1 560s, 1 339m, 1 307m, 1 272m, 1 196m, 1 125s, 1 028m, 990m, 919w, 850w, 803s, and 796s cm^{-1}.

Diaqua[6,6′-*bis*(3-*methyl*-5-*phenylpyrazolyl*)-2,2′-*bipyridyl*]*nickel*(II) *Diperchlorate* (4).—Benzoylacetone (0.26 g) and [Ni(dhbipy)][ClO$_4$]$_2$ (0.25 g) were heated under reflux in 95% ethanol (40 cm^3) until, after 5 h, complete dissolution of the reactant marked the end of the reaction. The pure product was isolated from the resulting green solution in the same manner as derivative (1). Yield 0.36 g (89%). As for (1), complex (4) was also prepared by the direct interaction of [Ni(OH$_2$)$_6$][ClO$_4$]$_2$ with 6,6′-bis(3-methyl-5-phenylpyrazolyl)-2,2′-bipyridyl in ethanol. Infrared spectrum in Nujol: 3 400s, 1 600m, 1 581m, 1 575m, 1 481s, 1 435s, 1 335m, 1 310m, 1 279m, 1 205m, 1 150—1 030s, 986m, 975m, 930m, 849m, 815m, 793m, and 696s cm^{-1}.

6,6′-*Bis*(3-*methyl*-5-*phenylpyrazolyl*)-2,2′-*bipyridyl* (5).—Compound (5) was prepared from its nickel complex (4) in the same manner as (2) was derived from (1). Recrystallisation (once) from methanol gave the pure compound.

Alternatively, dhbipy (0.3 g) and benzoylacetone (0.45 g) were heated under reflux for 3 h. The white precipitate which formed was collected by filtration and recrystallised twice from methanol. This product was found to be 6,6′-bis(4,5-dihydro-5-hydroxy-3-methyl-5-phenylpyrazolyl)-2,2′-bipyridyl (6); it was dissolved in glacial acetic acid (10 cm^3) and stirred at room temperature for 20 min before adding ethanol (90 cm^3) and allowing the solution to cool overnight in a refrigerator. The white crystals which formed were filtered off and recrystallised once from methanol to yield the pure compound (0.6 g, 92%). Hydrogen-1 n.m.r. spectrum in CDCl$_3$: τ 2.3 (d of d, J 8.0, J' 1.0, 2 H), 2.52 (t, J 8.0, 2 H), 2.72 (s, 10 H), 3.22 (d of d, J 8.0, J' 1.0 Hz, 2 H), 3.7 (s, 2 H), and 7.63 (s, 6 H). Infrared spectrum in Nujol: 1 584m, 1 565s, 1 556s, 1 544s, 1 194w, 1 146w, 1 105w, 1 071w, 1 017w, 992m, 971s, 909w, and 810s cm^{-1}. Mass spectrum: *m/e* of parent ion 468 (calc. 468).

6,6′-*Bis*(4,5-*dihydro*-5-*hydroxy*-3-*methyl*-5-*phenylpyrazolyl*)-2,2′-*bipyridyl* (6).—This compound was isolated in the manner described above. Hydrogen-1 n.m.r. spectrum in CDCl$_3$: τ 2.4—2.8 (m, 14 H), 3.25 (d of d, J 7.0, J' 1.0, 2 H), 4.05 (s, 2 H), 6.73 (d, J 18, 2 H), 7.05 (d, J 18 Hz, 2 H), and 7.94 (s, 6 H). Infrared spectrum in Nujol: 3 400m, br, 1 572s, br, 1 309m, 1 249w, 1 211w, 1 156w, 1 091w, 1 071m, 1 034w, 1 019w, 977w, 911w, 872m, 796s, and 772s cm^{-1}. Mass spectrum: *m/e* for parent ion 504 (calc. 504).

[6,6′-*Bis*(3,5-*dimethylpyrazolyl*)-2,2′-*bipyridyl*]*di-isothiocyanatonickel*(II) (7).—The corresponding perchlorate salt (1) (0.2 g) was dissolved in methanol (20 cm^3). Ammonium thiocyanate (0.08 g) was added to the solution which was then stirred for 30 min. The pale blue precipitate was filtered off and purified by washing with methanol (2 × 10 cm^3), yield quantitative. Infrared spectrum in Nujol: 2 099s, 1 602s, 1 585m, 1 569s, 1 551m, 1 326w, 1 305w, 1 269w, 1 192m, 1 174w, 1 127m, 1 037w, 1 017w, 990m, 819m, 811m, and 787s cm^{-1}.

[6,6′-*Bis*(3-*methyl*-5-*phenylpyrazolyl*)-2,2′-*bipyridyl*]-*di-isothiocyanatonickel*(II) (8).—The corresponding perchlorate salt (4) was treated as described above for the preparation of (7). The pale green product was obtained in quantitative yield. Infrared spectrum in Nujol: 2 077s, 2 061s, 2 048s, 2 036s, 1 600m, 1 578m, 1 565m, 1 309m, 1 278m, 1 204m, 1 175w, 1 157w, 1 036s, 1 002w, 989m, 976m, 846w, 828m, and 797s cm^{-1}.

6,6′-*Bis*(N-*methylhydrazino*)-2,2′-*bipyridyl* (9).—6,6′-Dibromo-2,2′-bipyridyl (3.0 g) was added to methylhydrazine (50 cm^3) which had been refluxing in a stream of nitrogen for 10 min. The resulting solution was heated under reflux for 1 h before removing 40 cm^3 of the methylhydrazine by distillation. The residue was allowed to cool and was diluted with water (20 cm^3). The yellow crystalline material was filtered off and washed with water (2 × 10 cm^3). Recrystallisation (once) from methanol gave the pure product as yellow prisms (1.8 g, 77%). Hydrogen-1 n.m.r. spectrum in D$_2$O + one drop of CH$_3$CO$_2$H): τ 1.92 (d of d, J 7.0, J' 8.0, 2 H), 2.33 (d of d, J 7.0, J'' 1.0, 2 H), 2.79 (d of d, J' 8.0, J'' 1.0 Hz, 2 H), and 6.49 (s, 6 H). Infrared spectrum in Nujol: 3 310m, 3 206w, 1 633m, 1 572s, 1 390m, 1 325w, 1 127w, 974s, 911m, and 790s cm^{-1}. Mass spectrum: *m/e* of parent ion 244 (calc. 244).

6,6′-*Bis*[(3-*hydroxy*-1-*methylbut*-2-*enylidene*)-N-*methylhydrazino*]-2,2′-*bipyridyl* (10).—Compound (9) (0.45 g) was dissolved in ethanol (60 cm^3) and the solution heated under reflux. Pentane-2,4-dione (0.3 g) was added and the solution heated under reflux for 1 h. As the reaction proceeded the crude product precipitated from the solution; it was filtered off and purified by washing with methanol (2 × 10 cm^3), yield 0.7 g (93%). Hydrogen-1 n.m.r. spectrum in CDCl$_3$: τ 2.16 (d, J 8.0, 2 H), 2.41 (t, J 8.0, 2 H), 3.29 (d, J 8.0 Hz, 2 H), 4.85 (s, 2 H), 6.58 (s, 6 H), 7.90 (s, 6 H), and 8.06 (s, 6 H). Infrared spectrum in Nujol; 3 170s, br, 1 610s, 1 568s, 1 301m, 1 277m, 1 216w, 1 191w, 1 120w, 1 078w, 1 015m, 978m, 874m, and 788s cm^{-1}. Mass spectrum: *m/e* of parent ion 408 (calc. 408).

6,6′-*Bis*[(3-*hydroxy*-1-*methyl*-3-*phenylprop*-2-*enylidene*)-N-*methylhydrazino*]-2,2′-*bipyridyl* (11). Compound (11) was prepared as for (10) but with pentane-2,4-dione being replaced by benzoylacetone. It was filtered off, washed with methanol (2×5 cm^3), and dried *in vacuo* (0.61 g, 93%). Hydrogen-1 n.m.r. spectrum in $CDCl_3$: τ 2.0—2.7 (m, 14 H), 3.21 (d, *J* 8.0 Hz, 2 H), 4.12 (s, 2 H), 6.51 (s, 6 H), and 7.90 (s, 6 H). Infrared spectrum in Nujol: 1 602s, 1 571s, 1 549s, 1 537m, 1 341m, 1 284m, 1 203m, 1 127m, 1 042w, 1 069m, 1 029w, 979m, 894m, 850s, 790s, and 758s cm^{-1}. Mass spectrum: *m/e* of parent ion 532 (calc. 532).

[2,4,6,8-*Tetramethyl*-1,14:9,13-*dinitrilo*-2,3,7,8-*tetra-aza-cyclononadeca*-9,11,15,17-*tetraenato*(1—)]*nickel*(II) *Iodide*, [NiL]I (12).—Compound (10) (0.1 g) was suspended in boiling water (15 cm^3). Nickel(II) acetate (0.08 g) was added and the pH adjusted to 5 with acetic acid. After heating under reflux, with stirring, for 3 h, the ligand had completely dissolved to yield a deep red solution. This solution was filtered into an aqueous solution of NaI (5 g NaI in 15 cm^3 water). The resulting flocculent red precipitate was filtered off and washed with water (2×10 cm^3) to give the product (0.1 g, 83%). Further purification for analytical purposes was effected by recrystallisation from pyridine–diethyl ether. Infrared spectrum in Nujol: 1 605—1 520m, br, 1 160m, 1 080w, 1 031m, 975w, 812m, and 781s cm^{-1}. Mass spectrum: *m/e* of parent cation 365 (calc. 365).

$[NiL][ClO_4]$ (13).—The reaction solution, prepared as described for complex (12), was filtered into an aqueous solution of sodium perchlorate. The resulting red precipitate was collected and purified as for (12). Infrared spectrum in Nujol: 1 605—1 520m, br, 1 170m, 1 090s, 990m, and 787s cm^{-1}. Hydrogen-1 n.m.r. spectrum in $S(CD_3)_2O$: τ 2.50—3.13 (m, 6 H), 5.51 (s, 1 H), 6.97 (s, 6 H), and 8.09 (s, 6 H).

$[NiL][PF_6]$ (14).—This complex was prepared in the same manner as (13) using, instead, an aqueous solution of ammonium hexafluorophosphate. Hydrogen-1 n.m.r. spectrum in $S(CD_3)_2O$: τ 2.63—3.29 (m, 6 H), 5.66 (s, 1 H), 7.10 (s, 6 H), and 8.21 (s, 6 H). Infrared spectrum in Nujol: 1 605—1 520m,br, 850s, and 788s cm^{-1}.

$[Ni(HL)][PF_6]_2$ (15).—Hexafluorophosphoric acid was added to the reaction solution, prepared as described above for complex (12). A red precipitate first formed, but more acid was added until this was completely yellow. The yellow precipitate was stirred for 1 h, filtered off on an acid-washed sinter, and washed once with concentrated hydrochloric acid. Infrared spectrum in Nujol: 1 601s, 1 565s, 1 302s, 1 169s, 1 094w, 1 065w, 1 046m, 969m, 901m, and 900—860s, br cm^{-1}.

6,6′-*Bis*(N-*methylhydrazino*)-2,2′-*bipyridylcopper*(II) *Diperchlorate* (16).—Compound (10) (0.15 g) was suspended in boiling water. The pH was adjusted to 5 with acetic acid before adding copper(II) acetate monohydrate (0.072 g). The resulting green solution was heated under reflux for 3 h. At this stage the product was isolated and purified in the same manner as (13), yield 0.18 g (96%). Infrared spectrum in Nujol: 3 290s, 1 630s, 1 605m, 1 520m, 1 310m, 1 220s, 1 100s,br, 1 018m, 965w, and 786s cm^{-1}.

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