Chemistry of Polydentate Ligands. Part 1. Condensation Reactions of Aldehydes and Ketones with 6,6′-Dihydrazino-2,2′-bipyridylnickel(II) Perchlorate

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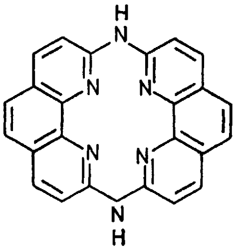
The complex 6,6′-dihydrazino-2,2′-bipyridylnickel(II) perchlorate has been prepared and its reactivity as a macrocyclic precursor investigated. This complex does not undergo cyclisation on reaction with acetone and other α-methyl ketones, or aldehydes, but preferentially forms a series of stable bis(hydrazone) complexes. The metal-free ligands have been isolated and manifest imino–azo tautomerism. This tautomerism has been studied by n.m.r. spectroscopy and evidence is presented for the formation of azo-hydroperoxide compounds.

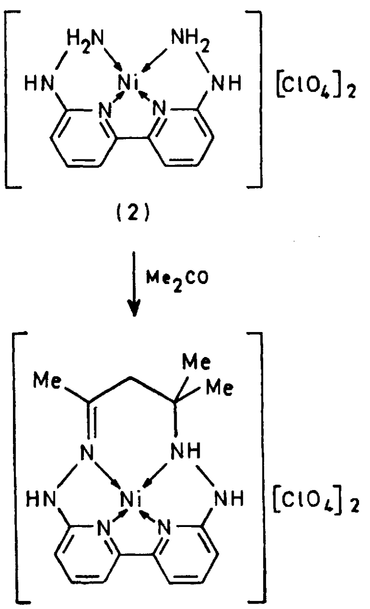
WHILST α-di-imines such as 2,2′-bipyridyl (bipy) and 1,10-phenanthroline (phen) have been extensively studied in their capacity as simple bidentate ligands which form complexes of high redox stability with many of the transition metals,[1] relatively little has been done to develop these compounds as multidentate and macrocyclic complexing agents. Only a single case appears to have been recorded in which bipy or phen has been incorporated into a macrocycle.[2] In this case two phen residues were coupled by way of secondary amine bridges, either in the absence of a metal, to form the macrocycle (1), or in the presence of copper(II) chloride to yield the copper(II) complex. Progress in this field has doubtless been retarded by the inaccessibility of suitably substituted 2,2′-bipyridyls and 1,10-phenanthrolines; however, recent work by Holm and his co-workers[3] has ameliorated this situation greatly in the case of bipy and has enormously widened the scope for the investigation of this compound.

We earlier communicated[4] the formation of 6,6′-dihydrazino-2,2′-bipyridyl and reported on the reactions of the nickel complex, (2), of this compound with pentane-2,4-dione and with acetone. Reaction with acetone was considered to yield the macrocycle (3) (Scheme 1). Additional evidence presented here now supports the bis(*N*′-isopropylidene) structure (Scheme 2).



(1)

RESULTS AND DISCUSSION



(2)

(3)

SCHEME 1

The reaction of 6,6′-dihydrazino-2,2′-bipyridylnickel(II) perchlorate, (2), with acetone[4] is not specific to acetone, analogous products being obtained with a variety of aldehydes and ketones simply by refluxing (2) in the respective aqueous aldehyde or ketone. The reaction appears to be a general one for these classes of compound. Besides formation of a cyclic product such as (3) (Scheme 1), another non-cyclic isomeric product is possible (Scheme 2).† Previous work,[5] such as with 3,6-diazaoctane-1,8-diaminenickel(II), provides a close analogy as this compound precedes the formation of a 13-membered macrocycle by a single bridge-forming condensation.[6,7] Providing the reaction proceeds by the incorporation of 2 mol of the acyl compound and loss of 2 mol of water, the cyclic product shown in Scheme 1 is produced. House and Curtis[8] synthesised a bis(*N*-isopropylidene) complex from tris(1,3-diaminopropane)nickel(II) perchlorate and acetone, but here the iso-

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† The actual mode of co-ordination of the ligand to the metal is discussed in the following paper.

[1] L. F. Lindoy and S. E. Livingstone, *Co-ordination Chem. Rev.*, 1967, **2**, 173.

[2] S. Ogawa, T. Yamaguchi, and N. Gotoh, *J.C.S. Chem. Comm.*, 1972, 577.

[3] J. E. Parks, B. E. Wagner, and R. H. Holm, *J. Organometallic Chem.*, 1973, **56**, 53.

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

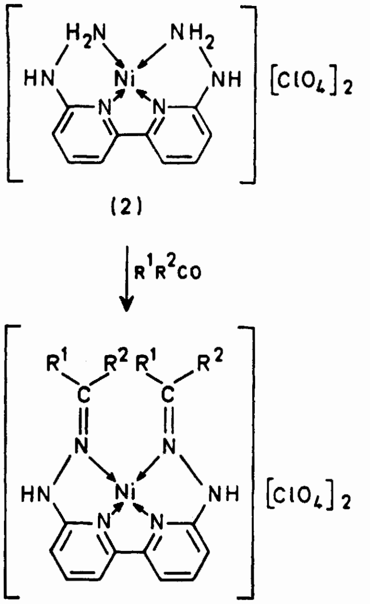
[5] N. F. Curtis, *Co-ordination Chem. Rev.*, 1968, **3**, 3.

[6] T. E. McDermott and D. H. Busch, *J. Amer. Chem. Soc.*, 1967, **89**, 5780.

[7] D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, 1964, **86**, 1331.

[8] D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, 1964, **86**, 223.

propylidene groups are almost certainly disposed *trans* to one another and hence cannot be considered to form a potentially cyclisable pair.



SCHEME 2

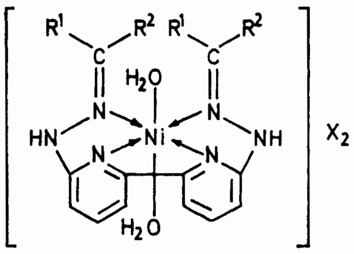
No definitive evidence in support of the two isomeric alternatives could be obtained by the application of the normal physical techniques. Chemically the complexes are resistant to hydrolysis of the imine moiety, and they were inert towards hydrogenation either with sodium tetrahydroborate or catalytically over palladium or platinum, making it impossible to determine the degree of unsaturation of the ligand.

In order to apply magnetic resonance spectroscopy to the problem, the paramagnetic nickel complexes were decomposed with sodium cyanide in a reaction which yields the free ligand and sodium tetracyanonickelate(II)[9] (the ligand recombining with nickel perchlorate and regenerating the original complex). Analytical data for the series of free ligands so formed are given in Table 2.

The 100-MHz ^1H n.m.r. spectrum of an undegassed solution of the ligand derived from the acetone condensation, (15), was recorded in deuteriomethanol. The chemical-shift data in the non-aromatic region were complex and appeared as follows: τ 7.68 (m); 7.97 (s); 8.01 (s); 8.04 (s). Accurate integration was not possible and assessments of relative intensity could only be made from the height of the signal. These data are not inconsistent with determinations made by Busch and his co-workers[10] on a macrocyclic metal complex involving the same bridging group, where three methyl resonances were also seen. The ^1H n.m.r. spectrum recorded in deuteriochloroform showed only two sharp singlets of equal intensity in the methyl–methylene region at τ 7.98 and at 8.11 as expected for the non-cyclic species derived from Scheme 2 (for the *cis* and *trans* environments of the methyl groups).

TABLE 1

Analytical data for complexes of the type



Complex	Derived from	R^1	R^2	X	Analysis (%) Found C	Found H	Found N	Calc. C	Calc. H	Calc. N	Λ[a] S cm^2 mol^{-1}
(4)	Acetaldehyde	Me	H	ClO_4	29.7	3.5	15.2	30.0	3.4	15.0	196
(5)	Propionaldehyde	Et	H	ClO_4	32.4	4.1	14.4	32.6	4.1	14.2	177
(6)	Butyraldehyde	Pr	H	ClO_4	35.3	4.6	13.9	35.0	4.6	13.6	184[b]
(7)	Acetone	Me	Me	ClO_4	32.6	4.0	14.2	32.6	4.1	14.2	182
(8)	Ethyl methyl ketone	Et	Me	ClO_4	34.7	4.4	13.8	35.0	4.6	13.6	194
(9)	Diethyl ketone	Et	Et	ClO_4	36.6	5.0	13.2	37.2	5.0	13.0	189
(10)	Methyl n-propyl ketone	Pr	Me	ClO_4	36.6	4.8	12.8	37.2	5.0	13.0	190[b]
(11)[c]	Acetone	Me	Me	Cl	44.7	4.5	19.6	45.1	4.7	19.6	*d*

[a] For 10^{-3} mol dm^{-3} solutions in water. [b] Methanol (20%) was added to effect dissolution. [c] Crystallises as the anhydrous complex. [d] Insufficiently soluble.

Definitive evidence supporting the non-cyclic formulation comes from the ^{13}C n.m.r. spectrum of (15) in deuteriochloroform. Under proton decoupling two singlets occurred in the methyl region of the spectrum at 15.4 and 24.9 p.p.m. downfield from the carbon of

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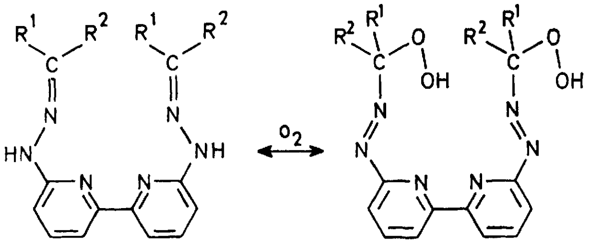
[9] N. F. Curtis, *J. Chem. Soc.*, 1964, 2644.

[10] L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, 1967, **89**, 703.

tetramethylsilane; upon proton coupling these signals split into two quartets, *J* 128 Hz. This spectrum is only consistent with the non-cyclic formulation.

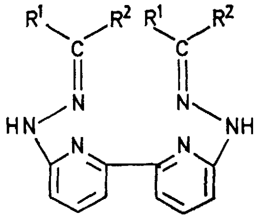
It was observed that solutions of these metal-free compounds gradually turned yellow on exposure to air. The onset of the yellow colouration is expected for hydrazone-type compounds as it has been shown [11–15] that a tautomeric equilibrium exists which results in the formation of azo-hydroperoxides (Scheme 3). The presence of the azo-hydroperoxide accounts not only for the yellow colour of solutions of the hydrazone, having a well established azo $n \rightarrow \pi^*$ transition at 410—425 nm,[14] but also for the presence of the anomalous third methyl peak in the methanolic ^1H n.m.r. spectrum of (15). (The loss of the imine bond will bring about equivalence of the two methyl groups and hence an additional resonance.) Work by Karabatsos and Taller [16] on the ^1H n.m.r. spectrum of acetone phenylhydrazone in deuteriobenzene supports this, as it has shown that the two methyl resonances at τ 8.16 and 8.72 have added to them a third resonance at τ 8.53 on introduction of oxygen to the system. The fact that no third signal appears in the deuteriochloroform solutions of (15) is possibly due to the deposition of the hydroperoxide from solution in impure form; solutions became cloudy and deposited a fine brown material from which no pure compound could be isolated.



SCHEME 3

TABLE 2

Analytical data for compounds of the type



				Analysis (%)						
				Found			Calc.			
Compound	Derived from	R^1	R	C	H	N	C	H	N	Melting point (θ_c/°C)
(12)	(4)	Me	H	62.6	6.2	31.2	62.7	6.0	31.3	206—207
(13)	(5)	Et	H	64.6	6.9	28.5	64.8	6.8	28.4	175—177
(14)	(6)	Pr	H	66.6	7.4	26.2	66.6	7.5	25.9	143—145
(15)	(7)	Me	Me	64.6	6.7	28.1	64.8	6.8	28.4	217—219
(16)	(8)	Et	Me	66.8	7.4	25.8	66.6	7.5	25.9	156—157
(17)	(9)	Et	Et	68.0	8.0	23.9	68.2	8.0	23.8	207—208
(18)	(10)	Pr	Me	68.5	8.3	24.0	68.2	8.0	23.8	153—155
(19)*	(17)	Et	Me	51.1	6.0	19.7	50.9	5.9	19.8	223—224

* (16) As its hydroperchlorate salt, formed during attempted acid hydrolysis.

Further evidence for the existence of the azo-hydroperoxide was gained from the mass spectrum of (15) where a metastable peak, usually more intense in aged samples of the compound, at *m*/*e* 267, corresponding to loss of O_2 from the azo-hydroperoxide of (15), *m*/*e* 328, to re-form (15) (*m*/*e* 296), occurred.

Complete ^1H n.m.r. data for the series of ligands is given in Table 3. Two sets of signals were seen for each alkyl group bonded to the imino-carbon, corresponding to residence in either the *cis* or *trans* position relative to the bipy residue. If one assumes that the more intense of the two signals is associated with the sterically less hindered configuration of the free ligand [17] (because of configurational instability [18] this may be different from the preferred co-ordinating configuration), then it is seen in the spectrum that protons on a carbon α to the double bond in the *cis* position resonate at higher field than when in the *trans* position and *vice versa* for protons on carbon atoms β and γ to the imino-carbon. This shift pattern has been observed in the spectra of 2,4-dinitrophenylhydrazones,[17] but differs from that found for phenylhydrazones where H_β behaves in the same manner as H_α.[16] The concentration of a substituent in a given position can thus be determined from the integrated values of the appropriate signals, and these values are tabulated. It is not possible to make a

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[11] R. O'Connor, *J. Org. Chem.*, 1961, **26**, 4375.

[12] R. O'Connor and G. Henderson, *Chem. and Ind.*, 1965, 850.

[13] A. J. Bellamy and R. D. Guthrie, *Chem. and Ind.*, 1964, 1575.

[14] A. J. Bellamy and R. D. Guthrie, *J. Chem. Soc.*, 1965, 2788.

[15] A. J. Bellamy and R. D. Guthrie, *J. Chem. Soc.*, 1965, 3528.

[16] G. J. Karabatsos and R. A. Taller, *J. Amer. Chem. Soc.*, 1963, **85**, 3625.

[17] G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Amer. Chem. Soc.*, 1962, **84**, 753.

[18] S. Patai, 'Chemistry of the Amino Group,' Interscience, London, 1968, p. 362.

determination of the amounts of the *syn* and *anti* isomers present because of an unknown concentration of the mixed *syn–anti* isomer. Evidence for the azo-hydroperoxide species is readily seen in the spectra of the aldehyde derivatives where the imino-methine proton provides a convenient probe with which to monitor the tautomerism. (This proton normally resonates at τ 1.9—2.2.[19]) Formation of the azo-hydroperoxide brings the methine proton into an environment where, in the absence of the hydroperoxide, it is known to resonate at *ca.* τ 4.3.[20] Accepting a downfield shift of *ca.* 1 p.p.m. for the presence of a hydroperoxide group, the signals at τ 3.5 arise from this methine proton and indicate the presence of the appropriate azo-hydroperoxide species. The intensity of this signal can be used to determine the percentage of the hydrazone which is present in the azo-form. These determinations are also tabulated and represent the state of the equilibrium 10 min after sample preparation. In the case of compounds derived from ketones such determinations must be made on the basis of signals which appear in the methyl–methylene region of the spectrum and it is only in the case of the compound derived from acetone that this region of the spectrum is sufficiently clear for meaningful measurements.

TABLE 3

Proton magnetic resonance data (in τ, *J* values in Hz)

Compound	Solvent	Hydroxylic + amino	Aromatic + iminomethine	Amino–methine	Methyl + methylene	Remarks (all percentages ±5)
(12)	$CDCl_3$	1.3—2.0 (br, m) (2 H)	2.1—3.0 (m) (7 H)	3.37 (q) (*J* 5.5) (1 H)	8.09 (d) (*J* 6.0) *trans*-Me 8.12 (d) (*J* 6.0) *cis*-Me } (3 H) 8.15 (d) (*J* 5.5) (azo compound) (3 H)	50% azo-hydroperoxide 39% of Me groups are *trans* 11% of Me groups are *cis*
(13)	$CDCl_3$	1.3—2.2 (br, m)(2 H)	2.25—3.0 (m) (7.6 H)	3.48 (t) (*J* 5.0) (0.4 H)	7.67 (d of q) (J_1 7.5) (J_2 5.0) (4 H) 8.80 (t) (*J* 7.5) *cis*-Me 8.88 (t) (*J* 7.5) *trans*-Me } (6 H)	20% azo-hydroperoxide 30% of alkyl groups are *cis* 50% of alkyl groups are *trans*
(14)	$CDCl_3$	1.3—2.2 (br, m) (2 H)	2.25—3.2 (m) (7. 6 H)	3.48 (t) (*J* 5.0) (0.4 H)	7.78 (q) (*J* 6.5) (4 H) 8.48 (sxt) (*J* 7.0) (4 H) 9.00 (t) (*J* 7.5) *cis*-Me 9.06 (t) (*J* 7.5) *trans*-Me } (6 H)	20% azo-hydroperoxide 48% of alkyl groups are *trans* 32% of alkyl groups are *cis*
(15)	$CDCl_3$	2.2—2.3 (s) (2 H)	2.3—2.9 (m) (6 H)		7.98 (s) } (12 H) *trans*-Me 8.11 (s) *cis*-Me	No azo-hydroperoxide apparent
	CD_3OD		2.2—3.0 (m) (6 H)		7.86 (m) 7.97 (s) 8.01 (s) 8.04 (s) } (12 H)	15% azo-hydroperoxide 85% hydrazone
(16)	$CDCl_3$	2.1 (s) (2 H)	2.25—2.9 (m) (6 H)		7.67 (q) (*J* 7.5) (4 H) 7.98 (s) *trans*-Me 8.14 (s) *cis*-Me } (6 H) 8.79 (t) (*J* 7.5) *cis*-Me 8.88 (t) (*J* 7.5) *trans*-Me } (6 H)	no azo-hydroperoxide apparent 85% of Me are *cis*
(17)	$CDCl_3$	2.06 (s) (2 H)	2.25—2.9 (m) (6 H)		7.67 (q) (*J* 7.5) (4 H) } *trans*-CH_2 7.69 (q) (*J* 7.5) (4 H) } *cis*-CH_2 8.86 (t) (*J* 7.5) (12 H)	no azo-hydroperoxide apparent no splitting observed for the Me group
(18)	$CDCl_3$	2.19 (s) (2 H)	2.25—2.9 (m) (6 H)		7.70 (t) (*J* 7.5) *trans*-CH_2 7.71 (t) (*J* 7.5) *cis*-CH_2 } (4H) 7.98 (s) *trans*-Me 8.13 (s) *cis*-Me } (6H) 8.39 (sxt) (*J* 7.5) (4H) 8.99 (t) (*J* 7.5) *cis*-Me 9.04 (t) (*J* 7.5) *trans*-Me } (6H)	83% of Me *cis* no azo-hydroperoxide apparent

The solid-state i.r. spectra of these ligands showed no ν(C=N) frequency that is distinguishable from that in the bipy residue. This observation is in accordance with the findings of Fabian *et al.*[21] who, after a comprehensive survey, concluded that the imine stretching frequency in hydrazone-type compounds is generally weak or unobservable under normal operating conditions, and also with Abramvotich and Spenser [22] who were unable to find the ν(C=N) band in acetaldehyde phenylhydrazone.

The ligand-field electronic spectrum exhibited by powdered samples of the nickel complexes (4)—(10), together with their magnetic moments, support the six-co-ordinate nickel(II) configuration.[23] The two relatively intense absorption bands are assigned [24] as being derived from the $^3A_{2g}\rightarrow T_{2g}$ (ν_1, at lower frequency) and $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ (ν_2) transitions of octahedral Ni^{II} and show the usual ν_2/ν_1 quotient of 1.5—1.7.[24] The transition $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ was obscured by the onset of an intense charge-transfer band. Additionally, the two spin-forbidden transitions $^3A_{2g}\rightarrow{}^1E_g$ and $^3A_{2g}\rightarrow{}^1T_{2g}$ were within the expected frequency range as less-intense bands [25] (Table 4). A decrease in ligand-field strengths is seen for this series as the steric bulk of the terminal groups increases; this trend is paralleled by the magnetic

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[19] D. Y. Curtin, J. A. Gourse, W. H. Richardson, and K. L. Rinehart, *J. Org. Chem.*, 1959, **24**, 93.

[20] T. W. Milligan and B. C. Minor, *J. Org. Chem.*, 1962, 4663.

[21] J. Fabian, M. Legrand, and P. Poirier, *Bull. Soc. chim. France*, 1956, 1499.

[22] R. A. Abramvotich and J. D. Spenser, *J. Chem. Soc.*, 1957, 3767.

[23] C. J. Ballhausen, ' Introduction to Ligand Fields,' McGraw-Hill, New York, 1962, p. 261.

[24] L. Sacconi, *Transition Metal Chem.*, 1968, **4**, 199.

[25] D. Nicholls, ' Comprehensive Inorganic Chemistry,' vol. 3, eds. J. C. Bailar, H. J. Emeléus, R. S. Nyholm, and A. F. Trotman-Dickenson, Pergamon Press, Oxford, 1973, p. 1155.

moment for the more sterically hindered ketone derivatives and is consistent with nitrogen bond distances increasing along the series.

The electronic spectra of aqueous solutions of the nickel complexes (4)—(10) are more complex and showed several absorptions in the range 7 000—20 000 cm^{-1} superimposed on the spectrum derived from the same complex in the solid state. The origin of these additional absorption bands is uncertain. It has been verified from the spectrum of the corresponding zinc complexes [26] that none of the absorptions observed originates from within the ligand.

No imino stretching frequency was observed in the i.r. spectrum of the diaquated perchlorate complexes owing to masking by the δ(O–H) absorption. However, its presence is confirmed in the water-free dichloro-complex (11) where it occurs at 1 602 cm^{-1}.

Attempts to produce the macrocyclic complex (3) using more forcing conditions, for example reactions in a sealed tube at 150 °C for 48 h in the presence of zinc chloride, failed. The cyclisation reaction is a particular type of Aldol condensation which Curtis has shown to proceed by attack of a carbanion, derived from a free acetone molecule at the imino-carbon of a condensed acetone, followed by a second Schiff-base condensation.[5] In our case the lability of the terminal amines is high [4] leading to ready formation of the bis(hydrazone) in a reaction which is essentially irreversible. Thus the free terminal amine necessary for the second Schiff-base condensation is never available. By implication, suitable precursors for the Curtis cyclisation [5] should be either sufficiently kinetically non-labile, such that the Aldol condensation is faster than the irreversible blocking of the second amine site, or the imine-forming reaction must be readily reversible under the prevailing reaction conditions.

TABLE 4

Ligand-field spectra (±100 cm^{-1}) and magnetic moments of the nickel complexes

Complex	${}^3A_{2g}\rightarrow{}^3T_{2g}$ (ν_1)	${}^2A_{2g}\rightarrow{}^1E_g$	${}^3A_{2g}\rightarrow{}^3T_{1g}(F)$ (ν_2)	${}^3A_{2g}\rightarrow{}^1T_{2g}$	ν_2/ν_1	$\mu_{eff.}$ ±0.03 B.M.[a]
(2)	11 700	13 110	19 570	21 190	1.67	b
(4)	11 720	12 950	18 420	20 000	1.57	3.16
(5)	11 390	13 040	17 890	19 840	1.57	3.14
(6)	11 880	13 020	17 860	19 960	1.50	3.09
(7)	10 470	12 900	16 180	19 920	1.55	3.29
(8)	10 460	12 970	15 970	19 800	1.53	3.33
(9)	10 120	12 920	15 950	19 960	1.58	3.31
(10)	10 560	12 840	16 640	20 000	1.58	3.28

[a] At 295 K. 1 B.M. ≈ 9.27×10^{-24} A m^2. [b] Diamagnetic.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on a Varian HA 100 instrument using $SiMe_4$ as lock, and ^{13}C n.m.r. on a Varian XL 100 FT using the solvent ($CDCl_3$) deuterium as lock. Infrared spectra were measured as Nujol mulls using a Perkin-Elmer 237 spectrometer. Conductance data were obtained using a Wayne–Kerr universal bridge. Magnetic moments were determined on a Newport Gouy balance and were corrected for ligand and inner-core diamagnetism using Pascal's constants.[27] Electronic spectra were recorded on a Unicam SP 700A u.v. and visible spectrometer. Melting points were determined in a Koffler block and are uncorrected. Microanalyses were by the University Chemical Laboratory Microanalytical Department. Molecular weights of neutral compounds were determined by mass spectrometry using an A.E.I. MS12 spectrometer. All such compounds showed molecular-ion peaks and the expected fragmentation pattern.

6,6′-Dibromo-2,2′-bipyridyl was prepared according to the procedure of Burstall.[28] All the aldehydes and ketones were obtained commercially and were distilled before use. Commercial hydrazine hydrate ('99—100%') was used without further purification.

6,6′-Dihydrazino-2,2′-bipyridyl.—Hydrazine hydrate (100 cm^3) was heated under reflux for 10 min in a stream of nitrogen. 6,6′-Dibromo-2,2′-bipyridyl (8.0 g) was then added and the mixture refluxed for 3 h. At the conclusion of this period all the dibromide had dissolved. The solution was refluxed for another hour before allowing it to cool to room temperature, whereupon the crude product crystallised. The crystals were collected by filtration and recrystallised once from water (600 cm^3) to yield the pure product as yellow needles (5.3 g, 96%), m.p. 208 °C (Found: C, 55.2; H, 5.6; N, 38.9. Calc. for $C_{10}H_{12}N_6$: C, 55.5; H, 5.6; N, 38.9%).

6,6′-Dihydrazino-2,2′-bipyridylnickel(II) *Perchlorate*, (2).—**CAUTION**: This complex detonates violently on heating, but is quite stable to shock treatment. 6,6′-Dihydrazino-2,2′-bipyridyl (1.0 g) was dissolved in refluxing ethanol (200 cm^3). To the refluxing solution hexa-aquanickel(II) perchlorate (1.7 g) dissolved in ethanol (15 cm^3) was added dropwise over a period of 10 min. The fine yellow crystals which precipitated were collected by filtration and dried *in vacuo* to give the pure product (1.6 g, 72%) (Found: C, 25.7; H, 2.7; N, 17.5. Calc. for $C_{10}H_{12}Cl_2N_6NiO_8$: C, 25.4; H, 2.6; N, 17.7%).

Diaqua[*6,6′-dihydrazino-2,2′-bipyridyl*]*nickel*(II) *Perchlorate Complexes*, (4)—(10).—6,6′-Dihydrazino-2,2′-bipyridylnickel(II) perchlorate was suspended in the appropriate aldehyde or ketone and the mixture brought to reflux. Sufficient water was then added to render the solvent 10% aqueous, resulting in rapid dissolution of the solid. The solution was heated under reflux for another 10 min before evaporating it to dryness under reduced pressure. Recrystallisation from acetone–diethyl ether gave the pure product. Yields were essentially quantitative.

[*6,6′-Bis*(N′-*isopropylidenehydrazino*)-*2,2′-bipyridyl*]-*nickel*(II) *Chloride*, (11).—6,6′-Dihydrazino-2,2′-bipyridyl-

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[26] J. Lewis and K. P. Wainwright, unpublished work.

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

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

nickel(II) perchlorate (0.24 g) and zinc(II) chloride (0.5 g) were dissolved in a mixture of methanol (60 cm^3) and acetone (3 cm^3) and allowed to stand for 3 d. The yellow crystals which formed were collected by filtration, washed with methanol, and dried *in vacuo*, yielding the pure product (0.18 g, 84%).

6,6′-Dihydrazino-2,2′-bipyridyl Ligands, (12)—(18).—The appropriate 6,6′-dihydrazino-2,2′-bipyridylnickel(II) perchlorate complex (1 mmol) was dissolved in methanol (30 cm^3) and brought to reflux. Sodium cyanide (4 mmol) was added and refluxing continued for another 15 min. The volume of methanol was then reduced to *ca.* 5 cm^3 at decreased pressure. In one case, (15), the free ligand precipitated at this point; it was collected by filtration and recrystallised from methanol to give the pure product. In general, the solution was applied to a 30-cm alumina column packed in chloroform. Elution with chloroform gave a single yellow band which was collected, dried with magnesium sulphate, filtered, and diluted with light petroleum to a point where precipitation commenced. The fine crystals so formed were collected by filtration and recrystallised from a mixture of chloroform and light petroleum. Typically, the yield was *ca.* 70%.

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