Reactions of Hydrazine Ligands. Part I. Synthesis and X-Ray Structure Determination of a Nickel(II) Complex of a Novel Monoanionic Macrocyclic Ligand

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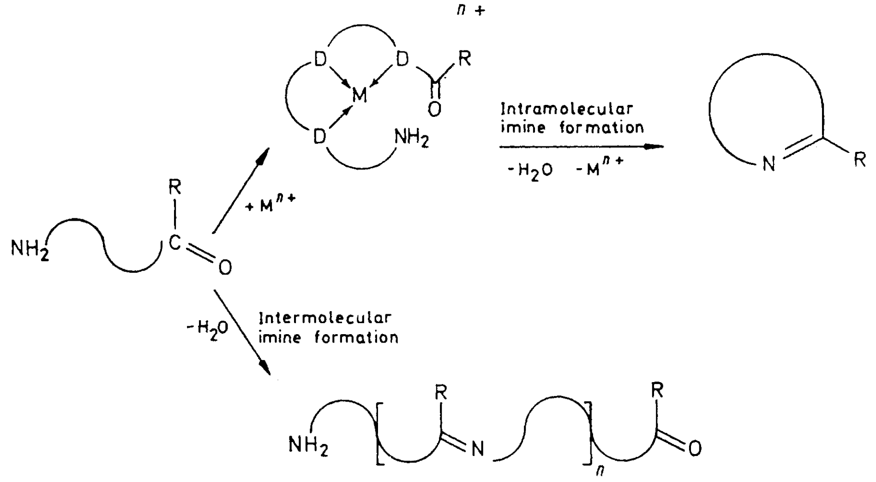
Reactions of 1,3-bis(2-hydrazinophenylthio)propane (2) with formaldehyde in the presence of nickel(II) salts are reported, the first of a study of metal-ion template control of condensation reactions of aromatic hydrazines. Complexes of an unusual macrocyclic ligand result, in which the two hydrazine groups have been ' bridged ' by the carbon atom of formaldehyde, and spontaneous aerial oxidation gives a novel monoanionic chelate ring containing four nitrogen atoms. (16,17-Dihydro-15*H*-dibenzo[*f,m*][1,11,4,5,7,8]dithiatetra-azacyclotetradecinato-N^5,N^9,S^{14},S^{18})-nickel(II) perchlorate (9) in an unsolvated monoclinic form, space group $P2_1/c$ with $a = 13.646(4)$, $b = 9.374(3)$, $c = 16.674(4)$ Å, $\beta = 96.02(4)°$, and $Z = 4$, allowed a more satisfactory X-ray structure determination (heavy-atom method, 2 299 diffractometer data, R 7.7%) than the triclinic methanol solvate previously examined.

The complex shows planar co-ordination geometry with the conjugated anionic chelate ring lying close to this plane. The perchlorate counter ion is well separated from the nickel ion in both crystalline modifications [shortest Ni • • • O contacts 3.51(2) and 3.51(6) Å].

THE Schiff-base condensation and related processes have frequently been applied[1] in studies where the stereochemical course of reaction is altered by the addition of co-ordinating metal ' template ' ions. In such reactions the role of the metal ion may be envisaged as either a ' kinetic ' or ' thermodynamic ' template, according to whether co-ordination to the metal lowers the free energy of the transition state or of the product in the desired reaction.[2] For the formation of macrocyclic ligands by Schiff-base formation these situations are presented schematically in Schemes 1 and 2.



SCHEME 1 Kinetic template control of the cyclization of a large molecule *via* imine formation

In many reactions of this type the co-ordination properties of the ligand in the transition state for the least favourable step in the intramolecular cyclization may closely resemble those of the macrocyclic ligand produced. Consequently co-ordination to the template ion may be involved in both. Under these circumstances the metal ion may have a dual role as both a ' kinetic ' and ' thermodynamic ' template in which it increases both the rate of formation and the yield of the macrocycle which results from the intramolecular reaction pathway.

Relatively few attempts to analyse the role of the metal ions have been reported for the large number of ligand syntheses which are apparently ' metal-ion template ' controlled. In many cases it is difficult to design control experiments and kinetic tests to distinguish between the ' kinetic ' and ' thermodynamic ' roles of the metal ions, especially where they operate simultaneously. However, the elucidation of kinetic template effects is of considerable interest since they relate closely to ' induced approximation effects '[3] in catalysis in which rate-enhancement is achieved by increasing the effective concentration of reacting functional groups, as well as inducing favourable orientation (rotamer distribution) for the desired reaction.

In template reactions leading to formation of cyclic imines one important factor is often overlooked, *i.e.* that under the conditions of pH usually employed the primary amine group cannot be co-ordinated to the metal

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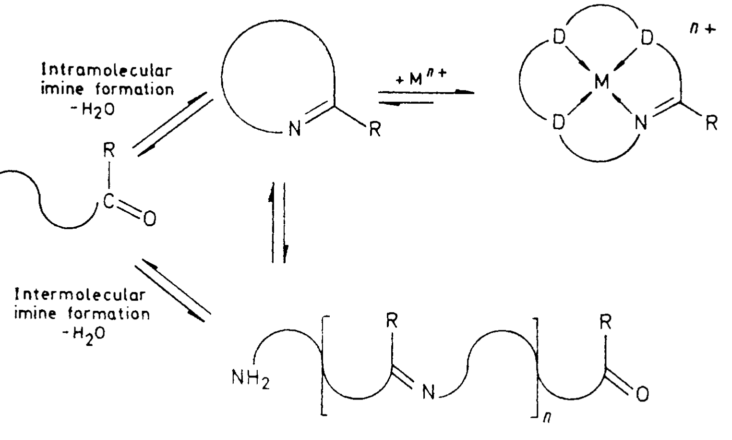
[1] L. F. Lindoy and D. H. Busch, *Pre. Inorg. Reactions*, 1970, **6**, 1; D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Adv. Chem.*, 1971, **100**, 44; D. St. C. Black and A. J. Hartshorn, *Co-ordination Chem. Rev.*, 1973, **9**, 219.

[2] E. Ochiai, *Co-ordination Chem. Rev.*, 1968, **3**, 49; M. Green, J. Smith, and P. A. Tasker, *Inorg. Chim. Acta*, 1971, **5**, 17.

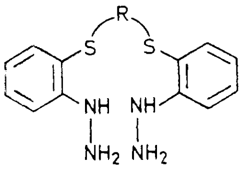
[3] W. P. Jencks, ' Catalysis in Chemistry and Enzymology,' McGraw-Hill, New York, 1969, p. 7.

ion at the stage where attack at the carbonyl is required. Consequently, a severe limitation is placed on the use of a kinetic template ion to orientate the reacting amino group relative to the carbonyl group. Indeed, for this reason, many of the template reactions involving the formation of imine groups may well involve a thermodynamic template effect rather than the kinetic template effect which is often assumed.

This limitation does not apply to reactions of hydrazines because two lone pairs of electrons are present in this functional group. Consequently we have chosen to study applications of dihydrazines such as (1)—(3) to template syntheses of complexes of macrocyclic ligands in the hope that it may prove easier to achieve effective stereochemical control of the reaction pathways by making use of kinetic template effects. A preliminary account of this work has appeared.[4]



SCHEME 2 Thermodynamic template control of the cyclization of a large molecule *via* imine formation

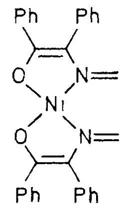


R

(1) $[CH_2]_2$

(2) $[CH_2]_3$

(3) $[CH_2]_4$



(4)

Many of the principles outlined may apply equally to the reactions of co-ordinated hydrazones. Thus the reaction of benzil hydrazone with various ketones R^1R^2CO in the presence of nickel(II) allows [5] convenient synthesis of the complexes (4). Since the commencement of this work a number of syntheses of macrocyclic ligands from dihydrazones have been reported,[6] by both template and non-template methods.

EXPERIMENTAL

Methods and Materials.—Analytical-grade formaldehyde solution (40%) (B.D.H.) was used as supplied. All other chemicals were of reagent grade or equivalent.

Magnetic susceptibility measurements were made by the Faraday method using $Hg[Co(NCS)_4]$ or $[Ni(en)_3][S_2O_3]$ (en = ethylenediamine) as calibrants. ^1H n.m.r. spectra were recorded at 60 MHz on a Perkin-Elmer 12B spectrometer operating at 35 °C with tetramethylsilane as internal standard. Mass spectra were determined with an A.E.I. MS 902 operating at 70 eV. Microanalysis data were obtained on a Perkin-Elmer Elemental Analyzer 240 and from Bernhardt laboratories, Mulheim.

Preparations.—1,2-Bis(2-aminophenylthio)ethane was prepared by the method of ref. 7.

1,3-*Bis*(2-*aminophenylthio*)*propane*. Commercial *o*-aminobenzenethiol was purified by extraction into NaOH solution, followed by neutralization with aqueous hydrochloric acid and extraction into diethyl ether.

To a solution of clean sodium (10.4 g) in absolute ethanol (200 cm^3) was added slowly with stirring a solution of *o*-aminobenzenethiol (56 g) in ethanol (200 cm^3). After 10 min 1,3-dibromopropane (40 g) in ethanol (100 cm^3) was added, and the mixture refluxed under nitrogen for 6 h, filtered, reduced to 100 cm^3 by evaporation under reduced pressure, and then added to water (250 cm^3). The resulting oil was extracted with diethyl ether (4 × 50 cm^3) and the extracts washed with 5% sodium carbonate solution and water, and then dried (Na_2SO_4). Evaporation gave 1,3-bis(2-aminophenylthio)propane (49 g, 85%) as a pale yellow oil (Found: C, 61.6; H, 6.1; N, 9.3. $C_{15}H_{18}N_2S_2$ requires C, 62.0; H, 6.2; N, 9.6%); δ ($CDCl_3$), 1.70 (q, *J* 12 Hz, SCH_2CH_2), 2.76 (t, *J* 12 Hz, SCH_2), 4.20 (s, NH_2), and 6.4—7.5 p.p.m. (m, 4 × aryl H); $\nu_{max.}$ 3 460, 3 360, 3 180, 1 615, 1 480, 1 445, 1 304, 1 250, and 1 242 cm^{-1}.

1,4-*Bis*(2-*aminophenylthio*)*butane*. A similar procedure gave an oil which crystallized slowly when set aside at

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[4] N. W. Alcock and P. A. Tasker, *J.C.S. Chem. Comm.*, 1972, 1239.

[5] C. M. Kerwin and G. A. Melson, *Inorg. Chem.*, 1972, **11**, 726; D. B. Bonfoey and G. A. Melson, *ibid.*, 1975, **14**, 309.

[6] J. E. Baldwin, R. H. Holm, R. W. Harper, J. Huff, S. Koch, and T. J. Truex, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 393; V. L. Goedken and Shie-Ming Peng, *J.C.S. Chem. Comm.*, 1973, 62.

[7] R. D. Cannon, B. Chiswell, and L. M. Venanzi, *J. Chem. Soc.* (*A*), 1967, 1277.

0 °C, and was recrystallized from ethanol as pale grey needles m.p. 43—46 °C, yield 85%. (Found: C, 62.5; H, 7.0; N, 9.0. $C_{16}H_{20}N_2S_2$ requires C, 63.1; H, 6.6; N, 9.2%); δ ($CDCl_3$) 1.5 (m, CH_2CH_2S), 2.6 (m, SCH_2), 4.19 (s, NH_2), and 6.4—7.5 p.p.m. (m, 4 × aryl H); $\nu_{max.}$ (Nujol and hexachlorobutadiene mulls) 3 560, 3 365, 3 175, 2 920, 2 851, 1 612, 1 560, 1 478, 1 441, 1 419, 1 306, 1 300, 1 280, and 1 249 cm^{-1}.

1,2-*Bis*(2-*hydrazinophenylthio*)*ethane*, (1). *Diazotization of* 1,2-*bis*(2-*aminophenylthio*)*ethane*. A suspension of the hydrochloride of the diamine was prepared by slow addition of 6 g to concentrated hydrochloric acid (100 cm^3) in water (100 cm^3) at 0 °C. A cooled solution of $NaNO_2$ (4 g) in water (20 cm^3) was added with vigorous stirring.

Addition of a portion of the resulting bright yellow solution to a solution of sodium tetrafluoroborate gave bright yellow needles of the fluoroborate of the bisdiazonium dication (Found: C, 36.2; H, 2.8; N, 11.2. $C_{14}H_{12}B_2F_8N_4S_2$ requires C, 35.5; H, 2.6; N, 11.8%).

Reduction of the diazonium salt. Tin(II) chloride (34 g) in concentrated hydrochloric acid (25 cm^3) was added to the yellow solution of the bisdiazonium chloride at 0 °C and the resulting thick paste diluted with a little water and stirred at room temperature for 2 h. A tin complex of the desired dihydrazine was washed with a little dilute hydrochloric acid, suspended in water (100 cm^3), and H_2S was passed through the stirred suspension for 2 h. Bis(2-hydrazinophenylthio)ethane was obtained after filtration and neutralization of the filtrate with dilute sodium hydroxide solution, as a white powder, which became discoloured on drying or when set aside in air (yield 1.8 g); $\nu_{max.}$ (Nujol and hexachlorobutadiene mulls) 3 300, 3 065, 1 615, 1 586, 1 510, 1 485, 1 420, 1 370, 1 295, and 1 250 cm^{-1}.

Benzaldehyde hydrazone derivative. A suspension of (1) (200 mg) in methanol (10 cm^3) containing benzaldehyde (400 mg) was heated under reflux for 30 min. The dihydrazone was obtained as white needles on cooling, m.p. 161—162 °C after recrystallization from chloroform–methanol (Found: C, 69.4; H, 5.8; N, 11.5. $C_{28}H_{26}N_4S_2$ requires C, 69.7; H, 5.4; N, 11.6%). Mass spectrum: calc. for $^{12}C_{28}{}^{1}H_{26}{}^{14}N_4{}^{32}S_2$ parent ion *m/e* 482.159 8; found *m/e* 482.159 3; δ ($CDCl_3$) 2.82 (s, CH_2), 6.5—7.9 (m, 9 × aryl H), and 8.82 p.p.m. (s, CH:N).

1,3-*Bis*(2-*hydrazinophenylthio*)*propane*, (2). Diazotization as already described was applied to 1,3-bis(2-aminophenylthio)propane, but less reproducibly since there is a tendency for the hydrochloride of the diamine to separate as an oil during the diazotization. (2) was obtained by a reduction and isolation procedure analogous to that for (1) as a white powder which became discoloured on drying or when set aside in air (yields 0—45%). No satisfactory solvents for recrystallization were found (Found: C, 56.8; H, 6.4; N, 17.6. $C_{15}H_{20}N_4S_2$ requires C, 56.2; H, 6.3; N, 17.5%); $\nu_{max.}$ (Nujol mull) 3 300, 3 060, 1 585, 1 490, 1 415, 1 345, 1 315, 1 290, 1 268, and 1 250 cm^{-1}.

1,4-*Bis*(2-*hydrozinophenylthio*)*butane*, (3). A similar procedure gave (3) as a cream powder (40%), which again could not be satisfactorily recrystallized (Found: C, 57.1; H, 6.5; N, 16.4. $C_{16}H_{22}N_4S_2$ requires C, 57.5; H 6.6; N, 16.7%); $\nu_{max.}$ (Nujol) 3 320, 3 200, 1 615, 1 587, 1 515, 1 487, 1 320, 1 300, and 1 210 cm^{-1}.

(16,17-*Dihydro*-15H-*dibenzo*[f,m][1,11,4,5,7,8]*dithiatetraazacyclotetradecinato*-N^5,N^9S^{14},S^{18})*nickel*(II) *Perchlorate*, (9). Hydrated nickel(II) perchlorate (450 mg) in a small volume of methanol was added to a solution of (2) (320 mg) in tetrahydrofuran (10 cm^3) in a stoppered flask. Addition of aqueous formaldehyde (100 mg, 36% solution) gave an immediate brown colouration. Red-violet triclinic crystals of (9) separated as the methanol solvate when set aside for 24 h. These (40 mg) were collected, and further quantities obtained from the mother liquid after exposure to air (total 160 mg, 31%) (Found: C, 40.2; H, 3.7; N, 10.4. $C_{17}H_{19}ClN_4NiO_5S_2$ requires C, 39.5; H, 3.7; N, 10.8%); $\nu_{max.}$ (Nujol and hexachlorobutadiene mulls) 3 400br (MeOH), 3 080, 3 060 2 925, 1 585br, 1 470, 1 448, 1 425, 1 380, 1 367, 1 315, 1 300, 1 262, 1 222, and 1 085 (ClO_4) cm^{-1}. An unsolvated monoclinic form of (9) was obtained as red-purple crystals on recrystallization from aqueous tetrahydrofuran, $\nu_{max.}$ (Nujol and hexachlorobutadiene mulls) 3 085, 3 062, 2 950, 2 925, 1 580, 1 570, 1 545, 1 467, 1 450, 1 442, 1 425, 1 393, 1 362, 1 340, 1 305, 1 295, 1 230, 1 215, and 1 075 (ClO_4) cm^{-1}.

X-*Ray Crystallography*

Crystal Data.—(*a*) *Triclinic form of* (9). $M = 517$, Triclinic, $a = 11.38$ (1), $b = 14.27$ (1), $c = 7.572$ (6) Å, $\alpha = 106.3$ (1), $\beta = 83.1$ (1), $\gamma = 114.3$ (1)°, $U = 1\,076$ Å^3, $D_m = 1.599$, $Z = 2$, $D_c = 1.595$, $F(000) = 532$.

(*b*) *Monoclinic form of* (9). $M = 485$, Monoclinic, $a = 13.646$ (4), $b = 9.374$ (3), $c = 16.674$ (4) Å, $\beta = 96.02$ (4)°, $U = 2\,123$ Å^3, $D_m = 1.522$, $Z = 4$, $D_c = 1.518$, $F(000) = 1\,000$. Space group $P2_1/c$.

A crystal of the monoclinic form of dimensions 0.12 × 0.11 × 0.12 mm and having faces of the forms {100}, {010}, {011} was mounted on a Philips PW 1100 four-circle diffractometer with the crystal *c* axis approximately coincident with the diffractometer ϕ axis. Data were collected using the coupled ω—2θ method, at a scan speed of 0.0250 ° s^{-1} and variable scan width of $1.0 + 0.1 \tan \theta$°. Mo-$K_{\bar{\alpha}}$ radiation was used with a graphite monochromator and counter equipped with peak-height analyser tuned to accept 95% of the Mo-$K_{\bar{\alpha}}$ peak. Single scans were made of all reflections.

Peaks having $I < 2\sigma(I)$ were rejected on a preliminary test and not collected. Three reference reflections measured at 6 h intervals showed no evidence of decomposition. Of a total of 5 889 reflections examined below 2θ 54°, 2 579 were collected after the preliminary significance tests. These reflections were corrected for Lorentz and polarization effects and 2 294 reflections were found to be statistically reliable, having $I > 3\sigma(I)$. Structure-factor amplitudes and their standard deviations were calculated using an uncertainty factor of 0.04.[8]

Structure Solution and Refinement for the Monoclinic Form of (9).—The structure was solved by conventional heavy-atom methods. The nickel, sulphur, and perchlorate atoms were assigned anisotropic thermal parameters and the least-squares refinement converged at R 0.097, R' 0.132 {where $R' = [(\Sigma w||F_o| - |F_c||^2)/\Sigma w|F_o|^2]^{\frac{1}{2}}$} and $w = 1/\sigma^2|F_o|$.

Scattering factors used for all atoms except hydrogen were those of ref. 9 and included both real and imaginary contributions to anomalous scattering.[10] The hydrogen atoms were assigned isotropic thermal parameters 10%

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[8] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

[9] D. Cromer and J. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[10] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

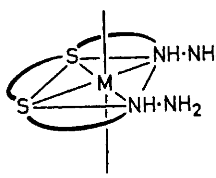
greater than those of the carbon atoms to which they were attached and the scattering factors used were those of ref. 11.

Poor agreement of F_o and F_c was observed for the 44 lowest-angle reflections which were collected with θ values close to and below the minimum value (3°) recommended for the instrument. These were excluded from a final 4 cycles of least-squares refinement which converged at R 0.077 and R' 0.103; mean shift-to-σ, 0.06, maximum shift to-σ 0.28.

A final electron-density difference map showed no systematic residual peaks, with the largest positive and negative peaks being 0.8 and -0.5 eÅ^{-3} respectively (*cf.* carbon 3 eÅ^{-3}). Major programmes used in these studies were taken from ref. 12.

RESULTS AND DISCUSSION

Examination of molecular models reveals that complexes of the dihydrazines (1)—(3) may exist in forms in which the hydrazino-groups occupy either adjacent or opposed octahedral co-ordination positions in the isomers (5), (6), or (7). For the purpose of effecting a cyclization of the molecule by a condensation involving the terminal NH_2 groups of the dihydrazine, the isomers (5) and (6) would appear to be more promising on the grounds of the induced approximation[3] of the amino-groups by complex formation with the metal ion. Under such circumstances the geometrical disposition of the NH_2 groups [particularly in (5)] is not unlike that in 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (8) which is known[13] to react rapidly with aldehydes, giving the cyclization shown in Scheme 3. It was therefore proposed to examine the reactions of the dihydrazines (1)—(3) with various aldehydes in the presence of metal ions which might induce approximation of the terminal NH_2 groups and promote a similar reaction. This paper reports results with formaldehyde in the presence of nickel(II) ' template ' ions. When a solution of (2) was treated with nickel(II) perchlorate and aqueous formaldehyde in a stoppered flask, a deep purple colouration developed rapidly and crystals separated when the solution was set aside. Further crops of crystals could only be obtained by exposing the solution to air.



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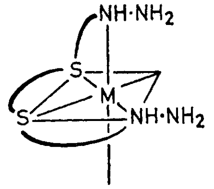

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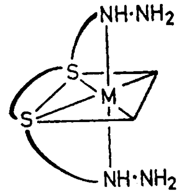

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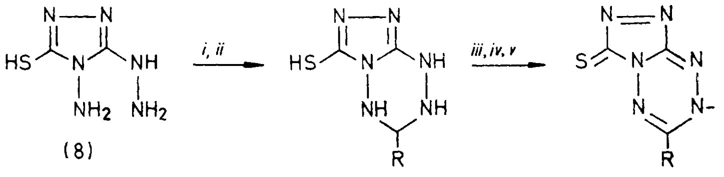
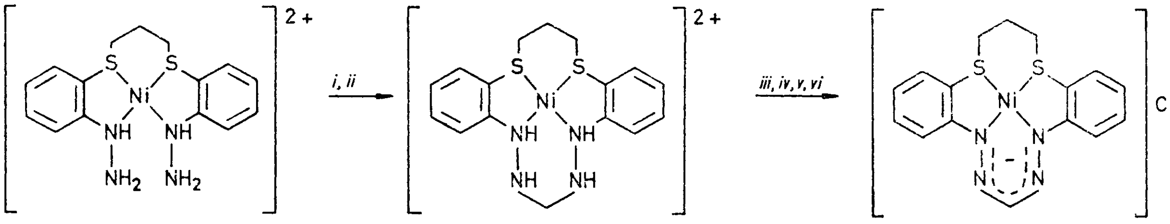


(11)

SCHEME 3 Reagents: *i*, RCHO; *ii*, $-H_2O$; *iii*, O_2, *iv*, $-2H_2O$; *v*, $-H^+$



(10) (9)

SCHEME 4 Reagents: *i*, CH_2O; *ii*, $-H_2O$; *iii*, O_2; *iv*, ClO_4^-; *v*, $-2H_2O$; *vi*, $-H^+$

The i.r. spectrum of (9) indicated that the reaction resulted in complete destruction of the N–H bonds originally present in the dihydrazine, and thus suggested that the oxidation of the presumed intermediate (10) in the reaction sequence shown in Scheme 4 had proceeded to completion. The diamagnetism of the complex and the absence of any splitting in the strong $[ClO_4]^-$ band at 1 085 (ν_3 for T_d symmetry) were consistent with the planar, approximately square, arrangement of donors of the macrocyclic ligand about the nickel(II) ion. A weak broad absorption centred around 3 400 cm^{-1} supported the presence of one mole of methanol of crystallization per complex unit which was suggested by analytical data and subsequent crystallographic molecular-weight

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[11] R. F. Stewart, E. Davidson, and W. Simpson, *J. Chem. Phys.*, 1968, **42**, 3175.

[12] J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, ' *X*-Ray ' program system, Technical Report TR 192 of the Computer Science Centre, 1972, University of Maryland.

[13] R. G. Dickinson and N. W. Jacobsen, *Chem. Comm.*, 1970, 1719.

determination. These preliminary observations suggested that the reaction had indeed proceeded by the sequence outlined in Scheme 4 in a manner entirely analogous to the synthesis of the heterocycle (11) (Scheme 3).

When the reaction was attempted under identical conditions in the absence of nickel(II) salts an intractable oil was obtained, which when digested with solutions of nickel(II) perchlorate gave no detectable quantity of (9). This implies that the nickel(II) ion indeed acts as a template in the reaction, and that possibly the role is as a ' kinetic ' template (*vide supra*), since in the absence of the metal ions an undesired product is formed irreversibly.

TABLE 1

Refined atomic positional and isotropic thermal parameters *

	x	y	z	B/Å^2
Ni(1)	0.143 3(1)	0.034 9(1)	0.105 8(1)	
S(1)	0.206 4(2)	−0.112 8(3)	0.197 5(2)	
C(2)	0.202 7(8)	−0.003(1)	0.288 4(6)	
C(3)	0.095 5(8)	0.012(1)	0.309 2(6)	
C(4)	0.028 7(7)	0.102(1)	0.251 1(6)	
S(5)	0.002 7(2)	0.005 8(2)	0.154 5(2)	
C(6)	−0.067 2(8)	0.130(1)	0.092 8(6)	5.8(3)
C(7)	−0.017 1(8)	0.200(1)	0.034 5(6)	6.2(3)
N(8)	0.083 6(7)	0.162 8(9)	0.032 5(5)	
N(9)	0.121 9(8)	0.225(1)	−0.023 2(6)	
C(10)	0.218(1)	0.204(1)	−0.033 3(7)	
N(11)	0.288 6(8)	0.132(1)	0.009 3(9)	
N(12)	0.266 0(7)	0.057(1)	0.071 6(6)	
C(13)	0.350 8(9)	−0.009(1)	0.115 9(7)	6.9(3)
C(14)	0.331 4(8)	−0.096(1)	0.179 3(7)	6.7(3)
C(15)	−0.167 2(8)	0.150(1)	0.099 6(7)	6.4(3)
C(16)	−0.216 4(8)	0.248(1)	0.047 3(7)	7.3(3)
C(17)	−0.170 2(9)	0.323(1)	−0.009 1(8)	7.7(3)
C(18)	−0.071 0(9)	0.299(1)	−0.015 2(7)	7.2(3)
C(19)	0.448(1)	0.010(1)	0.099 3(8)	8.6(4)
C(20)	0.520(1)	−0.061(2)	0.147 3(9)	9.9(4)
C(21)	0.502(1)	−0.146(2)	0.211 0(9)	9.5(4)
C(22)	0.405(1)	−0.168(1)	0.227 4(8)	8.7(4)
Cl(1)	0.225 7(2)	0.413 3(3)	0.199 2(2)	
O(1)	0.128 2(6)	0.412(1)	0.158 2(7)	
O(2)	0.259(1)	0.550(1)	0.211 8(9)	
O(3)	0.230(1)	0.355(2)	0.276 1(8)	
O(4)	0.285 9(8)	0.340(2)	0.155(1)	

* Standard deviations of the significant digit(s) are expressed in parentheses here and in subsequent tables.

Nickel(II) halides appeared to give similar products, but these had a much lower solubility in common solvents, and therefore were studied less extensively.

The single-crystal X-ray structure determination of (9) was undertaken to confirm the presence of the novel monoanionic macrocyclic ligand.

Crystals obtained directly from the template reaction as a methanol solvate in a triclinic form allowed the gross features of the structure to be established.[4] Unfortunately the quality of the data and serious disorder of the methanol molecule and the perchlorate counter ion prevented satisfactory refinement of the structure and it was considered necessary to examine another crystalline modification to obtain reliable bond lengths and angles in the complex unit. Attempts to crystallize the complex with other anions were hampered by its very low solubility. However, the triclinic form of (9) could be converted into an unsolvated monoclinic form by recrystallization from aqueous tetrahydrofuran. Data for this form were obtained on a four-circle instrument (Phillips PW 1100) and the structure was refined satisfactorily, although the perchlorate counter ion showed signs of disorder, as witnessed by the high thermal parameters for the oxygen atoms.

Both crystalline modifications of (9) contain one complex cation and one perchlorate anion per asymmetric unit. In the following discussion only parameters for the more reliable structure determination are quoted. Atomic positional and isotropic thermal parameters are listed in Table 1, selected bond lengths, angles, and intramolecular contacts in Tables 2—4. Molecular least squares planes, anisotropic thermal parameters, and structure factors are listed in Supplementary Publication No. SUP 21812 (17 pp., 1 microfiche).* The atom numbering system used is shown in Figure 1.

TABLE 2

Selected interatomic bond lengths (Å)

Ni(1)–S(1)	2.173(3)	C(10)–N(11)	1.32(2)
Ni(1)–S(5)	2.177(3)	N(11)–N(12)	1.30(2)
Ni(1)–N(8)	1.840(9)	N(12)–C(13)	1.44(2)
Ni(1)–N(2)	1.836(10)	C(13)–C(14)	1.39(2)
S(1)–C(2)	1.84(1)	C(13)–C(19)	1.39(2)
S(1)–C(14)	1.77(1)	C(14)–C(22)	1.39(2)
C(2)–C(3)	1.54(1)	C(15)–C(16)	1.39(2)
C(3)–C(4)	1.52(1)	C(16)–C(17)	1.38(2)
C(4)–S(5)	1.85(1)	C(17)–C(18)	1.39(2)
S(5)–C(6)	1.77(1)	C(19)–C(20)	1.37(2)
C(6)–C(7)	1.40(2)	C(20)–C(21)	1.37(2)
C(6)–C(15)	1.39(2)	C(21)–C(22)	1.38(2)
C(7)–N(8)	1.42(1)	Cl(1)–O(1)	1.43(1)
C(7)–C(18)	1.40(2)	Cl(1)–O(2)	1.37(2)
N(8)–N(9)	1.26(2)	Cl(1)–O(3)	1.39(2)
N(9)–C(10)	1.36(2)	Cl(1)–O(4)	1.35(2)

TABLE 3

Selected interatomic angles (°)

S(1)–Ni(1)–S(5)	87.5(1)	N(9)–C(10)–N(11)	132(1)
S(1)–Ni(1)–N(8)	176.2(5)	C(10)–N(11)–N(12)	119(1)
S(1)–Ni(1)–N(12)	89.0(3)	Ni(1)–N(12)–N(11)	127.0(8)
S(5)–Ni(1)–N(8)	89.0(3)	Ni(1)–N(12)–C(13)	120.2(8)
S(5)–Ni(1)–N(2)	176.1(6)	N(11)–N(12)–C(13)	113(1)
N(8)–Ni(1)–N(12)	94.3(4)	N(12)–C(13)–C(14)	116(1)
Ni(1)–S(1)–C(2)	100.4(3)	N(12)–C(13)–C(19)	125(1)
Ni(1)–S(1)–C(14)	98.0(4)	C(14)–C(13)–C(19)	119(1)
C(2)–S(1)–C(14)	101.6(5)	S(1)–C(14)–C(13)	117(1)
S(1)–C(2)–C(3)	110.1(7)	S(1)–C(14)–C(22)	121(1)
C(2)–C(3)–C(4)	115.4(8)	C(13)–C(14)–C(22)	123(1)
C(3)–C(4)–S(5)	109.5(7)	C(6)–C(15)–C(16)	117(1)
Ni(1)–S(5)–C(4)	99.7(3)	C(15)–C(16)–C(17)	123(1)
Ni(1)–S(5)–C(6)	98.2(4)	C(16)–C(17)–C(18)	119(1)
C(4)–S(5)–C(6)	103.2(5)	C(7)–C(18)–C(17)	122(1)
S(5)–C(6)–C(7)	116.0(8)	C(13)–C(19)–C(20)	118(1)
S(5)–C(6)–C(15)	120.8(8)	C(19)–C(20)–C(21)	124(1)
C(7)–C(6)–C(15)	123.1(9)	C(20)–C(21)–C(22)	120(1)
C(6)–C(7)–N(8)	116.3(9)	C(14)–C(22)–C(21)	117(1)
C(6)–C(7)–C(18)	117(1)	O(1)–Cl(1)–O(2)	111(1)
N(8)–C(7)–C(18)	127(1)	O(1)–Cl(1)–O(3)	113(1)
Ni(1)–N(8)–C(7)	120.4(7)	O(1)–Cl(1)–O(4)	109(1)
Ni(1)–N(8)–N(9)	127.2(8)	O(2)–Cl(1)–O(4)	110(1)
C(7)–N(8)–N(9)	112.3(9)	O(3)–Cl(1)–O(4)	110(1)
N(8)–N(9)–C(10)	120(1)		

The X-ray diffraction results confirm the postulated structure in which the formaldehyde carbon atom has ' bridged ' the terminal nitrogen atoms of the hydrazine groups in (2) giving the macrocyclic ligand (10) and sub-

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

sequent oxidation results in the conjugated anionic chelate ring in (9).

TABLE 4

Selected intramolecular contacts and shortest intermolecular contacts (Å)

(*a*) Intramolecular contacts

S(1) · · · S(5)	3.016(6)	N(8) · · · N(12)	2.77(2)
S(1) · · · N(12)	2.80(1)	N(9) · · · N(11)	2.48(2)
S(5) · · · N(8)	2.85(1)		

(*b*) Shortest intermolecular contacts (excluding H · · · H contacts)

O(4) · · · $H(21^{I})$	2.58(2)	O(2) · · · $H(15^{II})$	2.68(2)
O(1) · · · $H(4^{II})$ *	2.58(2)	N(9) · · · $H(3^{III})$ †	2.69(1)
O(3) · · · $H(15^{II})$	2.59(2)		

Hydrogen atoms are numbered according to the carbon to which they are attached.

* One of two hydrogens attached to C(4). † One of two hydrogens attached to C(3).

Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x, y, z:

I $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$ III $x, \frac{1}{2} - y, -\frac{1}{2} + z$
II $-x, \frac{1}{2} + y, \frac{1}{2} - z$

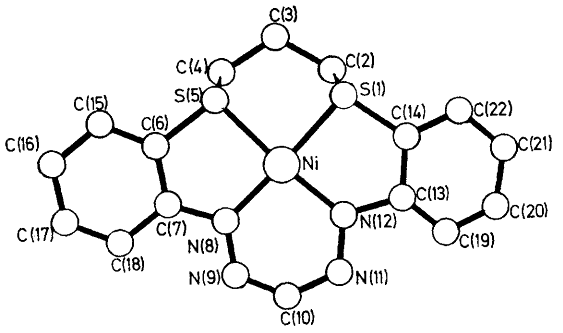


FIGURE 1 The cation of (9), showing the atom labelling scheme used

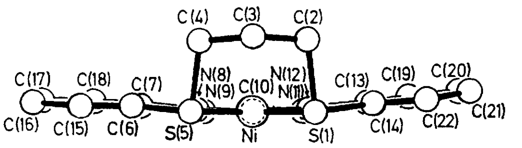


FIGURE 2 The cation of (9), showing atom deviations from the co-ordination plane

Planar co-ordination geometry is observed with the nickel ion being insignificantly displaced from the best plane defined by the atoms S(1), S(5), N(8), and N(12). The trapezoidal arrangement of the four donor atoms (Table 4) is a consequence of the longer nickel bonds to sulphur than to nitrogen.[14]

The three unsaturated chelate rings in the macrocycle lie close to the nickel(II) co-ordination plane (see Figure 2), but the aliphatic bridge between the two sulphur donors bends considerably from this plane, assuming a somewhat flattened chair-conformation for the six-membered ring containing the nickel ion. The bond lengths and angles in this chelate ring are similar to those in the comparable ring of the 1,4,8,11-tetrathiacyclotetradecanenickel(II) cation.[15]

The anionic six-membered chelate ring derived from the hydrazine groups lies close to the nickel(II) co-ordination plane and the equivalence of bond lengths and angles in the two halves of the ring suggests extensive delocalization of the negative charge in a similar manner to that observed in co-ordinated acetylacetonate. Table 5 compares bond lengths in related six-membered rings. With the more rigid porphyrin and corrin ligands longer Ni–N distances are observed. These can be partially ascribed to the larger number of atoms in the macrocycle producing a 'hole' for the complexed ion which is larger than that required for an 'ideal' Ni–N bond. Indeed for the macrocycles included in Table 5 there is a monotonic increase in mean Ni–N length with increasing number of atoms in the macrocycles. An elegant demonstration of similar effects of ring size in

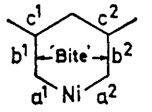
TABLE 5

Bond lengths (Å) in selected six-membered chelate rings

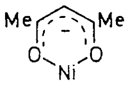
Chelate ring	Atoms in macrocycle	Mean σ a	b	c	'Bite'
(I) †		2.02 [a]	1.27	1.41	2.92 [b]
(II)		1.87	1.29	1.37	2.68 [c]
(III)	13	1.83	1.34	1.41	2.80 [d]
(IV)	14	1.85	1.34	1.41	2.75 [e]
(V)	14	1.84	1.28	1.34	2.70 [f]
(VI)					
A/D-Secocorrin		1.88	1.36	1.39	2.70 [g]
C/D-Secocorrin		1.86	1.34	1.41	2.70 [h]
Corrin	15	1.87	1.34	1.39	2.74 [i]
Porphyrin	16	1.96	1.40	1.40	2.77 [j]
Porphyrin	16	1.96	1.38	1.38	2.77 [k]
Porphyrin	16	1.93	1.39	1.37	2.73 [l]
Porphyrin	16	1.96	1.38	1.37	2.77 [m]
Porphyrin	16	2.04 [a]	1.35	1.40	2.86 [n]

[a] High-spin, pseudo-octahedral nickel(II) complexes. [b] H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, 1964, **17**, 1481. [c] B. L. Holian and R. E. Marsh, *ibid.*, 1970, **B26**, 1049. [d] M. R. Richardson and R. E. Sievers, *J. Amer. Chem. Soc.*, 1972, **94**, 4134. [e] F. Hanic, M. Handlovic, and O. Lindgren, *Coll. Czech. Chem. Comm.*, 1972, **37**, 2119. [f] This work. [g] M. Currie and J. D. Dunitz, *Helv. Chim. Acta*, 1971, **54**, 98. [h] M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 1971, **54**, 90. [i] J. D. Dunitz and E. F. Meyer, *Helv. Chim. Acta*, 1971, **54**, 77. [j] E. B. Fleischer, *J. Amer. Chem.* Soc., 1965, **87**, 146. [k] T. A. Hamor, W. S. Caughey, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1965, **87**, 2305. [l] E. F. Meyer, *Acta Cryst.*, 1972, **B28**, 2162. [m] D. L. Cullen and E. F. Meyer, *J. Amer. Chem. Soc.*, 1974, **96**, 2095. [n] J. F. Kirner, J. Garafalo, and W. R. Scheidt, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 107.

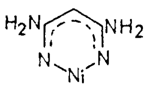
* Numbering system for bonds:



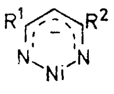
† Key to formula:



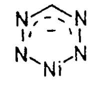
(I)



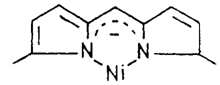
(II)



	R^1	R^2
(III)	Me	Me
(IV)	H	Me



(V)



(VI)

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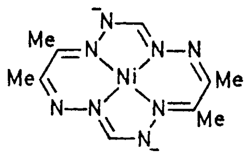
[14] L. Sacconi, *Transition Metal Chem.*, 1968, **4**, 199.

[15] P. H. Davis, L. K. White, and R. L. Belford, *Inorg. Chem.*, 1975, **14**, 1753.

determining ligand-field splitting parameters observed in macrocyclic complexes has been reported recently.[16]

For the two high-spin nickel(II) complexes in Table 5, which are pseudo-octahedral, the nickel–donor distances are significantly longer.

Other bonds within the tetra-aza-chelate ring of (9) are shorter than in analogous complexes, but despite this the ' bite ' developed is similar (see Table 5). As a consequence, the angle N(9)–C(10)–N(11) is more obtuse, having the unusually high values of 132 and 134° respectively in the monoclinic and triclinic forms. A similar tetra-aza-chelate ring may also be present[17] in molecular nickel(II) complexes of 3,4,10,11-tetramethyl-1,2,5,6,8,9,12,13-octa-aza[14]annulene but, significantly, the most stable isomer of this complex has been shown to have a structure as in (12), in which no more than three nitrogen atoms exist in any chelate ring. Longer N–N bonds are observed in (12) and the ligand has an alternating double-bond structure which is best described by a distribution of bonds as in (12).



(12)

In both crystalline modifications of (9) the benzene rings bend away slightly from the co-ordination plane towards the side containing the $[CH_2]_3$ bridge. This ' tilting ' of the rings is more regular for the triclinic (8 and 8°) than for the monoclinic modification (2.5 and 7.0°), but the differences are small and can probably be ascribed to optimization of packing forces.

The dihydrazines (1) and (3), with longer and shorter bridges between the sulphur donors, were also tested as substrates in comparable reactions to those those outlined in Scheme 4. Intractable mixtures of products have been obtained in such reactions, and although the formation of monoanionic complexes comparable to (9) cannot be excluded, it is clear that they are present in lower yields. A possible explanation for this observation may be made in terms of the geometries of the suggested intermediate nickel(II) complexes of the dihydrazines. The most desirable geometric isomer for the cyclization reaction is (5) (*vide supra*). Molecular models reveal that the dihydrazine (1) would be unlikely to adopt such a configuration, since strain in the ligand is greatly reduced in the alternative isomers (6) or (7). Consequently the reaction with formaldehyde under conditions when the nickel is required as a ' kinetic template ' is unlikely to result in formation of macrocycles comparable to (9) or (10).

The dihydrazines (2) and (3) may readily adopt both configurations (5) and (6), and a prediction of relative stabilities of these configurations may not be made by use of simple molecular models. It is thus possible that, in the presence of nickel(II) salts, both (2) and (3) may undergo reaction with formaldehyde to give (10) and its homologue. However, the oxidation of the resulting macrocycle derived from (3) is unlikely to occur because the anionic ligand comparable to that in (9) experiences severe strain as a result of the crowding of methylene groups between the sulphur donors.

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[5/2166 *Received, 7th November,* 1975]

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[16] L. Y. Martin, L. J. DeHayes, L. J. Zompa, and D. H. Busch, *J. Amer. Chem. Soc.*, 1974, **96**, 4046.

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