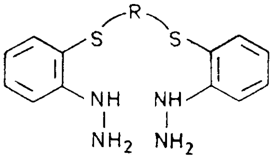
Reactions of Hydrazine Ligands. Part 2.[1] The *X*-Ray Structure Determination of {7-(3-Hydroxypropyl)-16,17-dihydro-15*H*-dibenzo[*f*,*m*][1,11,4,5,7,8]-dithiatetra-azacyclotetradecinato-N^5,N^9,S^{14},S^{18}}nickel(II) Perchlorate, an Unexpected Product for a Template Cyclization in Tetrahydrofuran

By **P. B. Donaldson**, **P. Haria**, and **Peter A. Tasker**,* Department of Chemistry, The Polytechnic of North London, Holloway, London N7 8DB

The reactions of 1,3-bis(2-hydrazinophenylthio)propane with a variety of ketones in tetrahydrofuran solutions of nickel(II) perchlorate have been investigated as part of a programme of study of the reactions of co-ordinated hydrazines. Many of these reactions give a crystalline by-product in low yield, which is shown to be the perchlorate salt of the macrocyclic monocation: {7-(3-hydroxypropyl)-16,17-dihydro-15*H*-dibenzo[*f*,*m*][1,11,4,5,7,8]dithia-tetra-azacyclotetradecinato-N^5,N^9,S^{14},S^{18}}nickel(II) perchlorate. Crystals are monoclinic, space group $P2_1/c$ with a = 9.973(8), b = 14.44(1), c = 17.83(1) Å, β = 124.3(1)°, and Z = 4. Structural refinement based on 2 180 two-circle diffractometer data converged at 0.067.

THE first paper [1] in this series described possible advantages of using dihydrazines such as (1)—(3) in metal-ion-template assisted cyclisations which depend upon the Schiff-base condensation and related reactions. It was shown that when compound (2) is treated with formaldehyde in the presence of nickel(II) perchlorate the macrocyclic complex (4a) is obtained.[1,2] The nickel salt appears to act as a ' kinetic ' template in this reaction, because co-ordination of the dihydrazine would give a particularly favourable alignment of the terminal NH_2 groups, thus allowing an intramolecular condensation with formaldehyde. The reaction is assumed to proceed as shown in the Scheme in which the intermediate macrocyclic complex (5a) is readily oxidised in air. In an attempt to isolate intermediate complexes of the type (5), the reactions of (2) with ketones in the presence of nickel(II) salts were examined because oxidation to give the anionic ring containing four nitrogen atoms could only occur in these cases by fission of a C–C bond. This paper reports an unexpected product which was observed in these reactions when they were carried out in tetrahydrofuran.



(1) R = $[CH_2]_2$

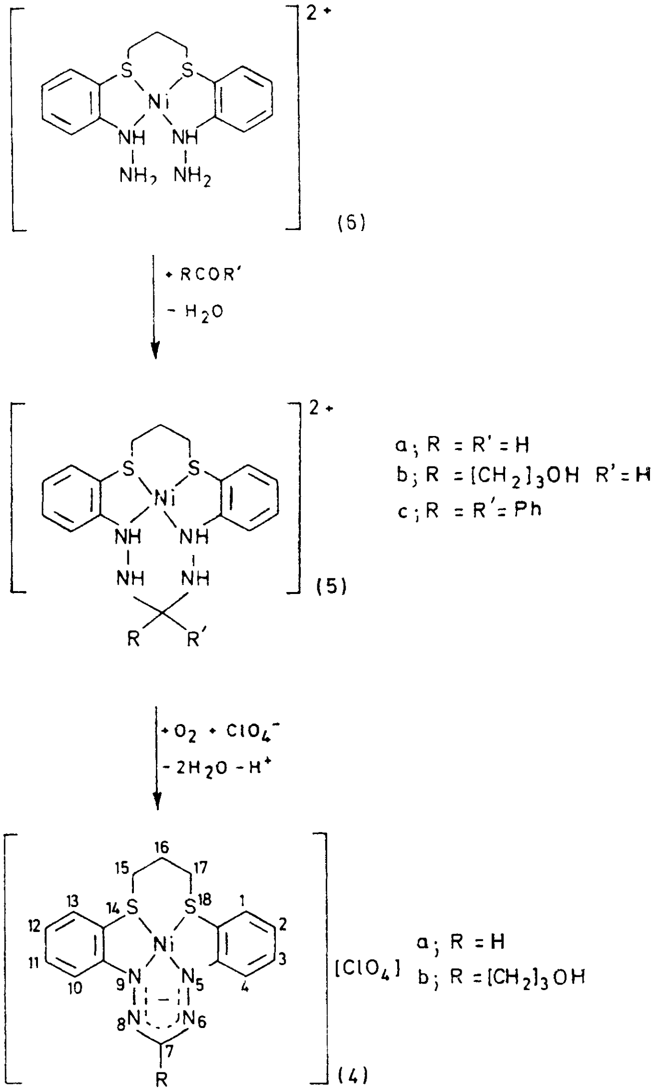
(2) R = $[CH_2]_3$

(3) R = $[CH_2]_4$

EXPERIMENTAL

General.—All chemicals were of reagent grade or equivalent. Magnetic susceptibility measurements were made by the Faraday method using $Hg[Co(NCS)_4]$ or $[Ni(en)_3][S_2O_3]$ as calibrants. I.r. spectra were recorded on a Perkin-Elmer 325 spectrophotometer at Royal Holloway College. Microanalyses were performed in the Bernhardt laboratories, Mülheim.

1,3-*Bis*(2-*hydrazinophenylthio*)*propane* (2).—This was prepared by the method reported previously.[1]



SCHEME

Reactions of 1,3-*Bis*(2-*hydrazinophenylthio*)*propane* (2) *with Nickel*(II) *Perchlorate in Tetrahydrofuran* (*thf*).—(*i*) *In the presence of benzophenone, using freshly distilled thf.* To a solution of compound (2) (320 mg, 1 mmol) and hydrated

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[1] Part I, P. B. Donaldson, P. A. Tasker, and N. W. Alcock, *J.C.S. Dalton*, 1976, 2262.

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

nickel(II) perchlorate (450 mg) in thf (15 cm^3, freshly distilled from $LiAlH_4$ under N_2) was added benzophenone (180 mg, 1 mmol). The solution developed a deep blue colour after several days and, when set aside in air to allow slow evaporation of solvent (to approximately half its volume), gave deep blue lustrous needles (2—5 mg) of the complex (4b) which were used in crystallographic studies; $\nu_{\max.}$ (Nujol and hexachlorobutadiene mulls), 3 560 (broad), 3 095, 3 075, 2 980, 2 950, 2 930, 2 840, 1 717, 1 575, 1 475, 1 455, 1 425, 1 364, 1 282, 1 239, 1 220, 1 196, 1 188, 1 172, 1 150, 1 090, and 1 070 cm^{-1}.

(*ii*) *In the presence of benzophenone, using reagent-grade thf in air.* Using undistilled reagent-grade thf, with no attempt to exclude air in procedure (*i*), gave compound (4b) in variable yields (25—35 mg, 5—6%) which was recrystallized from acetone (Found: C, 41.8; H, 3.9; N, 10.2; O, 14.8; S, 11.6. $C_{19}H_{21}ClN_4NiO_5S_2$ requires C, 42.0; H, 3.9; N, 10.3; O, 14.7; S, 11. 8%), $\lambda_{\max.}$ (recorded in acetone in range 350—800 nm, molar decadic absorptivities in parentheses) 418 (570), 564 (shoulder, 690), and 600 (990).

(*iii*) *In the presence of hexafluoroacetone, using reagent-grade thf in air.* A reaction on a 1 mmol scale, using conditions as in (*ii*), gave 20 mg (4%) of compound (4b).

(*iv*) *In the absence of ketones, using reagent-grade thf in air.* A solution of compound (2) (320 mg, 1 mmol) and hydrated nickel(II) perchlorate in reagent grade thf (15 cm^3) gave a dark blue microcrystalline material (30 mg), contaminated with a small quantity of white powder from which pure (4b) was obtained by recrystallization from acetone.

Crystal Data.—$C_{19}H_{21}ClN_4NiO_5S_2$, $M = 544$, Monoclinic, $a = 9.973(8)$, $b = 14.44(1)$, $c = 17.83(1)$ Å, $\beta = 124.2(1)°$, $U = 2\,121$ Å^3, $D_m = 1.72$ g cm^{-3}, $Z = 4$, $D_c = 1.70$ g cm^{-3}, $F(000) = 1\,120$. Mo-K_α radiation (graphite monochromated), $\lambda = 0.7107$ Å. Space group $P2_1/c$ is indicated unambiguously from the absences $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$. Data were collected on a crystal having faces of the forms {100}, {011} and dimensions 0.13 × 0.12 × 0.12 mm which was cut from a needle-shaped crystal with *a* parallel to the needle axis, and was mounted with the *b* axis coincident with the rotation axis of a Stoe-Weissenberg two-circle diffractometer. Unit-cell parameters were obtained from the reflecting positions of high-angle reflections with standard deviations estimated from the observed and calculated values. 4 930 Reflections were measured in 12 layers using the ω-scan technique, scan widths varying from 1.20° to 1.60° and a scan rate of 1° min^{-1}. 169 Reflections in 2 layers of the crossing axis *a* were used to merge the data after the method of Rae.[3a] No decomposition of the crystal was observed. Lorentz and polarisation corrections were applied to give 2 180 independent, statistically significant reflections using the criterion $I \leqslant 3\sigma(I)$ for rejection.

Structure Solution and Refinement.—A three-dimensional Patterson map yielded the approximate co-ordinates of the nickel and the two sulphur atoms. These atoms were included in a least-squares refinement and the positions of the remaining atoms found from subsequent electron-density difference maps. The scattering factors used for all atoms except hydrogen were those of Cromer and Mann [3b] and included both real and imaginary corrections for anomalous dispersion.[4] Hydrogen atoms were included at their calculated positions with carbon–hydrogen bond lengths of 1.0 Å and isotropic thermal parameters 10% greater than those of the attached carbon atoms. The hydrogen scattering factors were those of Stewart *et al.*[5] The perchlorate anion exhibits a large degree of thermal motion but no resolvable disorder. As the existence of the chain C(10)–C(23)–C(24)–C(25)–O(26) was unexpected this region of the electron-density difference maps was closely examined. A least-squares refinement of the final model with the nickel and sulphur atoms and the atoms of the chain and the perchlorate group assigned anisotropic thermal parameters converged at R 0.067; R' 0.70: average shift/σ, 0.068; maximum shift/σ, 0.21; where

$$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|},\ R' = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w(|F_o|)^2}\right]^{\frac{1}{2}} \quad \text{and } w = 1/\sigma^2(F_o)$$

A model assigning the atoms in the chain attached to C(10) as shown in Figure 1 was preferred at more than 99% confidence level [6] over other models in which the carbon atoms C(23), C(24), and C(25) were tested as oxygen atoms by the introduction of oxygen scattering factors. Furthermore, the thermal parameters of these atoms assumed physically impossible values when tested in turn as oxygen atoms. A final electron-density difference map showed no substantial peaks remaining, with the largest positive and negative peaks (+0.09 and −0.5 *cf.* carbon 3.0 eÅ^{-3}) being situated in the region of the perchlorate anion. Programs used were those of the ' *X*-Ray '74 ' crystallographic package.[7]

DISCUSSION

In an attempt to isolate the nickel(II) complex (5c) from a reaction mixture containing 1,3-bis(2-hydrazinophenylthio)propane (2), nickel(II) perchlorate, and benzophenone in tetrahydrofuran, the solution was set aside for several days in a stoppered flask and then allowed to evaporate slowly in air. A small quantity of deep-blue crystalline needles separated. The absence of N–H stretching bands in the i.r. spectrum and the intensity of bands in the visible spectrum suggested that this product was not the desired material (5c). In view of the low yield, the structure of this material was investigated by single-crystal *X*-ray diffraction without further chemical analysis.

The ' heavy-atom method ' allowed a straightforward solution of the structure, and at an early stage revealed the presence of a macrocyclic nickel cation, well separated from a perchlorate counter ion. Refinement of the structure showed that the inner ring surrounding the nickel atom was very similar to that observed [1,2] in an earlier structure complex (4a). After five cycles of least-squares refinement, including all atoms of the 14-membered macrocycle, the fused benzene rings, and the perchlorate group with isotropic thermal parameters, a conventional R of 0.14 was obtained. At this stage a careful examination of electron-density difference maps revealed a four-atom chain attached to the six-membered chelate ring derived from the hydrazine groups. Various

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[3] (*a*) A. D. Rae, *Acta Cryst.*, 1965, **19**, 683; (*b*) D. Cromer and J. Mann, *ibid.*, 1968, **A24**, 321.

[4] ' International Tables for *X*-ray Crystallography,' vol. III, Kynoch Press, Birmingham, England, 1962.

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

[6] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

[7] J. M. Stewart, G. I. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, ' The *X*-ray System,' University of Maryland, 1974.

models were tested for this chain (see Experimental section) but by far the most successful was a 3-hydroxypropyl group, and with this assignment the structure refined satisfactorily, although the perchlorate counter ion showed signs of disorder, as witnessed by the high thermal parameters for the oxygen atoms.

TABLE 1

Refined atomic positional parameters, thermal parameters (B/Å^2), and anisotropic thermal parameters (U/Å^2 × 10^2) with standard deviations in parentheses

	x	y	z	B
Ni(1)	0.807 8(2)	0.547 3(1)	0.424 8(1)	*
S(1)	0.774 5(2)	0.433 4(2)	0.491 5(2)	*
C(2)	0.555(1)	0.431(1)	0.430 1(8)	4.6(3)
C(3)	0.480(1)	0.394(1)	0.333 3(9)	4.8(3)
C(4)	0.494(1)	0.456(1)	0.272 4(9)	5.3(3)
S(5)	0.701 5(2)	0.460 4(2)	0.305 5(2)	*
C(6)	0.701(1)	0.542 5(9)	0.233 1(7)	4.1(2)
C(7)	0.770(1)	0.627 9(9)	0.271 6(7)	3.9(2)
N(8)	0.823(1)	0.642 3(7)	0.361 9(6)	3.6(2)
N(9)	0.873(1)	0.726 1(8)	0.388 2(6)	4.2(2)
C(10)	0.926(1)	0.754(1)	0.473 7(8)	4.6(3)
N(11)	0.935(1)	0.700 2(7)	0.538 8(6)	3.9(2)
N(12)	0.890 1(9)	0.617 6(7)	0.526 6(6)	3.3(2)
C(13)	0.900(1)	0.579 7(9)	0.603 0(7)	3.6(2)
C(14)	0.841(1)	0.490 3(9)	0.593 6(8)	4.2(3)
C(15)	0.648(1)	0.520(1)	0.145 3(8)	4.9(3)
C(16)	0.662(2)	0.587(1)	0.094(1)	6.0(3)
C(17)	0.727(2)	0.670(1)	0.129 8(9)	5.5(3)
C(18)	0.785(2)	0.692(1)	0.220 0(9)	5.4(3)
C(19)	0.973(1)	0.624(1)	0.684 8(8)	4.6(3)
C(20)	0.979(1)	0.580(1)	0.754 9(9)	4.9(3)
C(21)	0.918(2)	0.496(1)	0.746(1)	6.2(4)
C(22)	0.847(1)	0.448(1)	0.663 0(8)	4.9(3)
C(23)	0.974(2)	0.853(1)	0.493(1)	*
C(24)	1.147(3)	0.868(2)	0.572(1)	*
C(25)	1.259(2)	0.836(2)	0.554(2)	*
O(26)	1.240(2)	0.885(1)	0.478(1)	*
Cl(1)	0.5418(4)	0.240(3)	0.131 2(2)	*
O(1)	0.437(1)	0.314(1)	0.108 6(9)	*
O(2)	0.469(2)	0.168(1)	0.074(1)	*
O(3)	0.669(2)	0.270(1)	0.130(2)	*
O(4)	0.593(3)	0.213(2)	0.215(1)	*

* The anisotropic temperature-factor expression is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}kha^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni(1)	3.17(6)	3.97(9)	3.84(6)	0.02(6)	2.26(5)	−0.07(6)
S(1)	4.0(1)	4.5(2)	5.0(1)	0.4(1)	2.8(1)	0.4(1)
S(5)	3.8(1)	4.1(2)	4.5(1)	−0.3(1)	2.5(1)	−0.6(1)
C(23)	7.2(9)	6(1)	6.6(9)	−1.2(8)	3.8(8)	11.7(8)
C(24)	10(1)	9(2)	9(1)	13(1)	5(1)	−1(1)
C(25)	7(1)	9(2)	11(1)	0(1)	4(1)	2(1)
O(26)	9(1)	10(1)	10(1)	−1(1)	4(1)	−1(1)
Cl(1)	5.1(2)	4.9(2)	5.9(2)	−0.6(1)	2.5(1)	−0.6(2)
O(1)	9.0(8)	6.4(9)	10.9(9)	1.2(6)	5.4(8)	−0.6(7)
O(2)	8.5(9)	9(1)	12(1)	−1.9(7)	7(1)	−6(1)
O(3)	11(1)	9(1)	11(1)	−2(1)	6(1)	−1(1)
O(4)	13(1)	12(2)	10(1)	2(1)	6(1)	1(1)

Table 1 contains the refined atomic positional and isotropic thermal parameters and the anisotropic thermal parameters. The scheme for labelling of atoms is shown in Figure 1. Other Tables give selected interatomic bond lengths and angles (Table 2), non-bonded contacts (Tables 3 and, 4), and least-squares planes (Table 5). Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21833 (7 pp., 1 microfiche).*

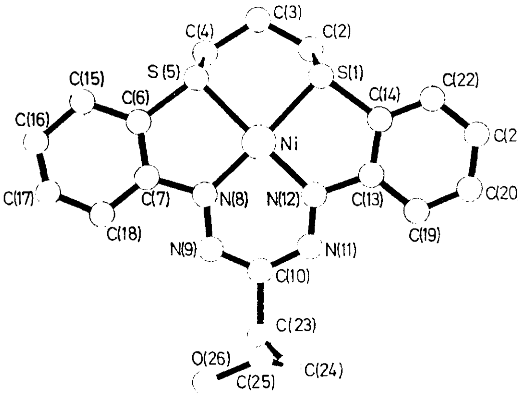

FIGURE 1 The cation of (4b) showing the atom labelling scheme used in the Tables

TABLE 2

Selected interatomic bond lengths (Å) and interatomic angles (°) with standard deviations in parentheses

(a) Distances

Ni(1)–S(1)	2.162(4)	N(11)–N(12)	1.28(2)
Ni(1)–S(2)	2.164(3)	N(12)–C(13)	1.42(2)
Ni(1)–N(8)	1.83(1)	C(13)–C(14)	1.39(2)
Ni(1)–N(2)	1.82(1)	C(13)–C(19)	1.37(2)
S(1)–C(2)	1.81(1)	C(14)–C(22)	1.35(2)
S(1)–C(14)	1.75(1)	C(15)–C(16)	1.39(2)
C(2)–C(3)	1.54(2)	C(16)–C(17)	1.35(2)
C(3)–C(4)	1.47(2)	C(17)–C(18)	1.40(2)
C(4)–S(5)	1.80(1)	C(19)–C(20)	1.37(2)
S(5)–C(6)	1.75(1)	C(20)–C(21)	1.31(2)
C(6)–C(7)	1.39(2)	C(21)–C(22)	1.41(2)
C(6)–C(15)	1.38(2)	C(23)–C(24)	1.51(2)
C(7)–N(8)	1.40(2)	C(24)–C(25)	1.40(4)
C(7)–C(18)	1.37(2)	C(25)–O(26)	1.44(4)
N(8)–N(9)	1.29(1)	Cl(1)–O(1)	1.39(2)
N(9)–C(10)	1.36(2)	Cl(1)–O(2)	1.35(2)
C(10)–N(11)	1.34(2)	Cl(1)–O(3)	1.35(3)
C(10)–C(23)	1.49(2)	Cl(1)–O(4)	1.33(2)

(b) Angles (°)

S(1)–Ni(1)–S(5)	87.5(1)	C(10)–N(11)–N(12)	122(1)
S(1)–Ni(1)–N(8)	176.4(3)	Ni(1)–N(12)–N(11)	128.4(8)
S(1)–Ni(1)–N(12)	89.9(4)	Ni(1)–N(12)–C(13)	119.3(7)
S(5)–Ni(1)–N(8)	89.8(3)	N(11)–N(12)–C(13)	112(1)
S(5)–Ni(1)–N(12)	176.9(4)	N(12)–C(13)–C(14)	116(1)
N(8)–Ni(1)–N(12)	92.6(4)	N(12)–C(13)–C(19)	123(1)
Ni(1)–S(1)–C(2)	100.9(5)	C(14)–C(13)–C(19)	120(1)
Ni(1)–S(1)–C(14)	97.4(5)	S(1)–C(14)–C(13)	116(1)
C(2)–S(1)–C(14)	105.0(7)	S(1)–C(14)–C(22)	122(1)
S(1)–C(2)–C(3)	110(1)	C(6)–C(15)–C(16)	118(1)
C(2)–C(3)–C(4)	115(1)	C(15)–C(16)–C(17)	121(1)
C(3)–C(4)–S(5)	110.4(8)	C(16)–C(17)–C(18)	122(2)
Ni(1)–S(5)–C(4)	100.3(5)	C(7)–C(18)–C(17)	119(1)
Ni(1)–S(5)–C(6)	97.3(4)	C(13)–C(19)–C(20)	119(1)
C(4)–S(5)–C(6)	104.9(6)	C(19)–C(20)–C(21)	122(1)
S(5)–C(6)–C(7)	116.2(9)	C(20)–C(21)–C(22)	120(2)
S(5)–C(6)–C(15)	121(1)	C(14)–C(22)–C(21)	118(1)
C(7)–C(6)–C(15)	122(1)	C(10)–C(23)–C(24)	114(1)
C(6)–C(7)–N(8)	118(1)	C(23)–C(24)–C(25)	112(2)
C(6)–C(7)–C(18)	119(1)	C(24)–C(25)–O(26)	110(2)
N(8)–C(7)–C(18)	124(1)	O(1)–Cl(1)–O(2)	112.4(8)
Ni(1)–N(8)–C(7)	118.9(8)	O(1)–Cl(1)–O(3)	108(1)
Ni(1)–N(8)–N(9)	128.9(9)	O(1)–Cl(1)–O(4)	108(1)
C(7)–N(8)–N(9)	112(1)	O(2)–Cl(1)–O(3)	110(1)
N(8)–N(9)–C(10)	121(1)	O(2)–Cl(1)–O(4)	108(1)
N(9)–C(10)–N(11)	127(1)	O(3)–Cl(1)–O(4)	110(1)
N(9)–C(10)–C(23)	115(1)		
N(11)–C(10)–C(23)	118(1)		

A 3-hydroxypropyl substituent on the macrocyclic ligand [see (4b)] would be expected if 4-hydroxybutanal, which is a possible product of the oxidation of

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

tetrahydrofuran, were included in the reaction sequence shown in the Scheme (R = $[CH_2]_3OH$, R′ = H). Alternatively, other possible products of the oxygenation of tetrahydrofuran in which the 5-membered ring remains intact, *e.g.* tetrahydrofuran-2-one or 2-hydroperoxytetrahydrofuran, may be susceptible to nucleophilic attack by the hydrazine complex (8) with subsequent ring opening giving (5b) which is then spontaneously oxidised to (4b). No attempts have been made to discover the effects of adding tetrahydrofuran-2-one, 2-hydroperoxytetrahydrofuran, or 4-hydroxybutanal on the yields of (4b).

It seems unlikely that the nickel complex (6) would serve to promote the oxygenation of tetrahydrofuran since the few known[8] transition-metal catalysts for oxygenation *in vitro* contain metals in very different environments and formal oxidation states. A nitrogenation of tetrahydrofuran which involves a dinitrogen metal complex has been reported recently.[9]

The postulate that oxygenation of tetrahydrofuran is required for the isolation of (4b) is supported by the observation that appreciably higher yields are obtained both when reagent-grade tetrahydrofuran is used without distillation and when the reaction is performed in air throughout. Benzophenone was shown not to be essential to the reaction since (4b) was also obtained in the presence of other ketones or in the absence of any added ketone (see Experimental section). Isolation of larger quantities of material from these modified syntheses allowed a confirmation of the nature of the side chain [R in (4)] by microanalysis data.

The *X*-ray structure determination reveals a planar co-ordination geometry in the macrocyclic cation, with the nickel ion being insignificantly displaced from the best plane defined by the 'N_2S_2' donor set (see Table 5). The bond lengths and angles in the co-ordination sphere are similar to those determined and discussed[1,2] for complex (4a).

TABLE 3

Selected intramolecular non-bonded contacts (Å) with standard deviations in parentheses

S(1) · · · S(5)	2.993(5)	N(8) · · · N(12)	2.64(1)
S(1) · · · N(12)	2.83(1)	N(9) · · · N(11)	2.42(2)
S(5) · · · N(8)	2.83(1)		

TABLE 4

Shortest intermolecular contacts * (Å)

Atoms	Symmetry operation (on second atom)	Distance/Å
H(20) · · · O(26)	$x, \frac{3}{2} - y, \frac{1}{2} + z$	2.38(2)
H(2a) · · · O(2)	$x, \frac{1}{2} - y, \frac{1}{2} + z$	2.41(2)
H(2b) · · · O(2)	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$	2.42(2)
H(22) · · · O(3)	$x, \frac{1}{2} - y, \frac{1}{2} + z$	2.42(2)
H(24a) · · · O(4)	$2 - z, 1 - y, -z$	2.51(2)
H(16) · · · O(1)	$1 - x, 1 - y, -z$	2.67(2)
H(18) · · · C(20)	$x, \frac{3}{2} - y, -\frac{1}{2} + z$	2.68(2)

* Excluding hydrogen–hydrogen contacts; hydrogen atoms are given the number of the carbon to which they are attached.

The three unsaturated chelate rings in (4b) lie close to the co-ordination plane (see Figure 2 and Table 5), 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 atom. Chemically equivalent bonds in the two halves of the molecule were found to have the same lengths within estimated errors with only one exception [C(2)–C(3) 1.47(2) and C(3)–C(4) 1.54(2)].

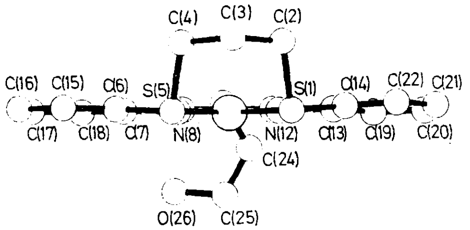

FIGURE 2 The cation of (4b), showing atom deviations from the co-ordination plane

TABLE 5

Least squares planes in direct space, for (4a) and (4b), in the form $Px + Qy + Rz = S$. Atom deviations in Å. Values for (4b) in parentheses

Plane 1, defined by S(1), S(5), N(8), and N(12)

(4a) * $1.908x + 7.071y + 10.39z = 1.650$
(4b) $8.874x - 4.705y - 4.226z = 2.762$

[Atom deviations S(1) −0.001 (0.005), S(5) 0.001 (−0.005), N(8) −0.002 (0.006), N(12) 0.002 (−0.006), Ni(1) −0.030 (−0.037), C(2) 1.71 (1.68), C(3) 1.83 (1.77), C(4) 1.73 (1.67), C(6) 0.11 (0.08), C(7) 0.09 (0.03), N(9) −0.07 (0.07), C(10) −0.14 (0.09), N(11) −0.07 (0.04), C(13) 0.17 (0.05), C(14) 0.17 (0.11)]

Plane 2, defined by Ni(1), N(8), N(9), C(10), N(11), and N(12)

(4a) * $2.104x + 7.242y + 9.943z = 1.647$
(4b) $8.997x - 4.144y - 4.308z = 3.178$

[Atom deviations Ni(1) −0.041 (0.008), N(8) 0.031 (−0.009), N(9) 0.010 (0.002), C(10) −0.040 (0.008), N(11) 0.007 (−0.006), N(12) 0.033 (−0.003)]

Plane 3, defined by C(6), C(7), C(15), C(16), C(17), and C(18)

(4a) * $2.286x + 6.837y + 10.71z = 1.715$
(4b) $8.770x - 5.149y - 4.180z = 2.389$

[Atom deviations C(6) 0.018 (0.005), C(7) −0.015 (0.004), C(15) −0.007 (−0.008), C(16) −0.007 (0.001), C(17) 0.008 (0.009), C(18) 0.002 (−0.011)]

Plane 4, defined by C(13), C(14), C(19), C(20), C(21), and C(22)

(4a) $0.3165x + 7.349y + 10.25z = 1.236$
(4b) $8.683x - 5.639y - 4.332z = 1.953$

[Atom deviations C(13) 0.005 (0.020), C(14) 0.002 (−0.014), C(19) −0.003 (−0.009), C(20) −0.006 (−0.008), C(21) 0.013 (0.014), C(22) −0.011 (−0.003)]

Angles between planes (°)

Planes	(4a) *	(4b)
1 and 2	2.0	2.3
1 and 3	2.5	1.9
1 and 4	7.0	4.0
2 and 3	3.7	4.2
2 and 4	7.5	6.3
3 and 4	9.2	4.5

* The monoclinic modification with $a = 13.64$, $b = 9.374$, $c = 16.67$ Å, $\beta = 96.02°$; see ref. 1.

The majority of the bond lengths and angles in (4b) agree closely with those found previously[1,2] for (4a). Some interesting differences were found in the anionic

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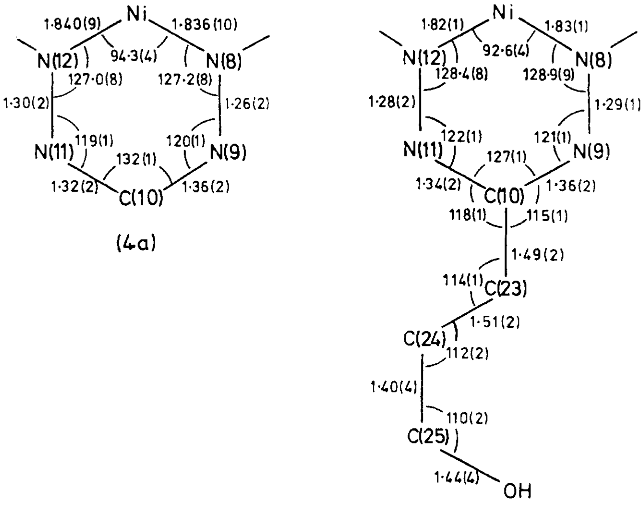
[8] G. Henrici-Olive and S. Olive, *Angew. Chem. Internat. Edn.*, 1974, **13**, 29 and refs. therein; A. Nishinaga, T. Tojo, and T. Matsuura, *J.C.S. Chem. Comm.*, 1974, 896; G. D. Mercer, J. Shing Shu, T. B. Rauchfuss, and D. M. Roundhill, *J. Amer. Chem. Soc.*, 1975, **97**, 1967.

[9] A. A. Diamantis, J. Chatt, G. A. Heath, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1975, 28.

chelate rings derived from the hydrazine groups (see Figure 3). In the 3-hydroxypropyl derivative (4b) the angle N(9)–C(10)–N(11) at the substituted carbon assumes a more normal value [127(1)°] for an sp^2 hybridised atom than in (4a). The anionic chelate develops a smaller 'bite' in (4b) [2.64(1) Å] than in (4a) [2.70(1) Å], and the N(8)–Ni–N(12) bond angle observed in (4b) is also smaller. Such differences would be expected to affect the energies of multicentre π orbitals associated with this region of the molecule, and would partially explain the differences in the positions and intensities of the charge-transfer bands in the visible spectra of (4a) and (4b) (see Figure 4).



(4a)

(4b)

FIGURE 3 Bond lengths and angles in the anionic chelate rings of (4a) and (4b)

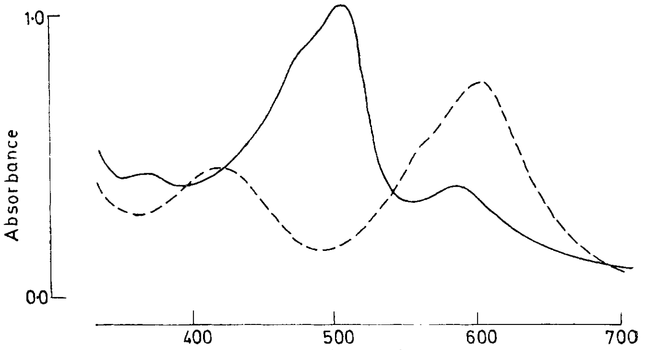


FIGURE 4 Visible spectra of acetone solutions (10^{-2}m path-length) of (4a) and (4b); —— (4a) (1.24×10^{-4} mol dm^{-3}), – – – (4b) (7.54×10^{-5} mol dm^{-3})

The shortest intermolecular contacts (Table 4) involve the oxygen atoms of the perchlorate anion. There is no evidence for hydrogen bonding between the hydroxy-group and the perchlorate oxygens, which is in accordance with the position of the OH stretching frequency in the i.r. spectrum.

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