Iron(II) Complexes of a Potentially Quinquedentate Macrocyclic Ligand having an ' N_3S_2 ' Donor Set and the Crystal and Molecular Structures † of a High-spin (S = 2) Complex and a Low-spin (S = 0) Complex

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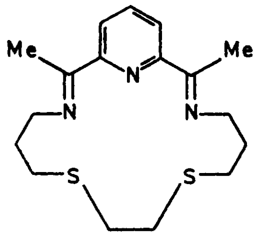
A series of iron(II) complexes of the 17-membered macrocyclic ligand L, having an ' N_3S_2 ' donor set, derived from the Schiff-base condensation of 2,6-diacetylpyridine with 4,7-dithiadecane-1,10-diamine, are described. Physical measurements (magnetic, Mössbauer) characterise the complexes as high-spin (S = 2) or low-spin (S = 0) depending on the nature of the associated unidentate ligands (halide, NCS^-, MeOH, MeCN, pyridine, or NH_3). Single-crystal *X*-ray structure determinations of two of the complexes reveal a versatility in the conformations and co-ordination modes of the macrocycle. Crystals of the low-spin complex [FeL(NCS)][BPh_4] (1) are monoclinic with a = 31.640(8), b = 11.019(8), c = 11.155(7) Å, β = 96.40(3)°, Z = 4, and space group $P2_1/a$. Crystals of the high-spin complex [FeLCl(HOMe)][ClO_4] (2) are monoclinic with a = 18.512(11), b = 18.279(12), c = 8.125(9) Å, β = 113.1(2)°, Z = 4, and space group $P2_1/a$. The two structures were solved by Patterson and Fourier methods from 2 548 and 1 772 reflections above background measured by diffractometer and refined by full-matrix least squares to R 0.047 and 0.102 respectively. In both (1) and (2), the co-ordination geometry of the metal ion is distorted octahedral. In (1), the macrocycle adopts a ' wrap-around ' conformation to occupy five of the octahedral sites [Fe–N 1.981(6), 1.870(6), 1.987(7); Fe–S 2.307(3), 2.258(3) Å], the sixth being filled by the nitrogen atom of the –NCS group [1.965(9) Å]. In (2), one sulphur atom of the macrocycle is not bonded to the metal while the other is only weakly co-ordinated [2.806(5) Å] *cis* to the trimethine nitrogens [Fe–N 2.205(11), 2.092(10), 2.200(12) Å]. The remaining two octahedral sites are occupied by the Cl^- ion (*trans* to the pyridine nitrogen) and the oxygen atom of the MeOH molecule [Fe–Cl 2.304(4), Fe–O 2.205(16) Å]. Possible structures for the remaining complexes of the series including three modifications of [$FeL(NCS)_2$] are considered.

WE have previously noted [1,2] the versatile co-ordinating properties of the 17-membered, potentially quinquedentate macrocycle L {2,15-dimethyl-7,10-dithia-3,14,20-triazabicyclo[14.3.1]icosa-1(20),2,14,16,18-pentaene} in combination with Ag^I, Cu^I, and Cu^{II}. The structures of the following complexes of L have been described:



L

[AgL][BPh_4]; [Cu^IL][ClO_4]; [$Cu^{II}L$][ClO_4]$_2$; and [$Cu^{II}L(NCS)$][ClO_4]$\cdot$0.5H_2O. In the first three the metal is five-co-ordinate being bonded to all five donor atoms of the macrocycle.[1,2] The geometry is variable, however, ranging from (approximate) square pyramidal to (approximate) trigonal bipyramidal with a wide range of bond lengths. The cation [$Cu^{II}L(NCS)$]$^+$ has a structure in which the metal atom is strongly bonded to the planar trimethine moiety of the macrocycle and to the nitrogen atom of the thiocyanate group to complete the square plane. In addition, one of the sulphur atoms in L is in an axial position at 2.745(5) Å while the other is not bonded.[2]

In continuation of our studies on the relationship between macrocycle size, flexibility, and the number and nature of the donor atoms, on the one hand, with the size and electronic configuration of the metal ion on the other, we now report on the structures and properties of some complexes of the macrocycle L with iron(II).

RESULTS AND DISCUSSION

Preparation and Properties of the Complexes.—The complexes examined are listed in Table 1 along with analytical and selected physical data. As is usual with this type of macrocyclic Schiff base, the present macrocycle is unstable in the uncomplexed state. It was therefore prepared by a template method using Ag^I as the template ion and isolated as [AgL]X (X = ClO_4 or BPh_4). Since neither iron(II) nor iron(III) ions proved effective as templates, the iron(II) complexes described in this paper were obtained from [AgL]$^+$ by transmetallation (see Experimental section).

Infrared spectra of the complexes (Table 2) are very similar except for variations attributable to the different anions or unidentate ligands. Most showed the expected imino- (C=N) and pyridine-ring vibrations at *ca.* 1 625 and 1 400—1 600 cm^{-1} respectively. In the perchlorate complexes both the ν_3 and ν_4 modes of the ClO_4^- ion occur as unsplit bands at *ca.* 1 090 and 620 cm^{-1}, consistent with their formulation as unco-ordinated anions, a conclusion in accord with the electrical conductances of their acetonitrile solutions (Table 1). A few of the complexes, those having S = 0 spin ground

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† Chloro{2,15-dimethyl-7,10-dithia-3,14,20-triazabicyclo-[14.3.1]icosa-1(20),2,14,16,18-pentaene-*NN'N''S*}(methanol)-iron(II) perchlorate and {2,15-dimethyl-7,10-dithia-3,14,20-triazabicyclo[14.3.1]icosa-1(20),2,14,16,18-pentaene-*NN'N''SS'*}-isocyanatoiron(II) tetraphenylborate, respectively.

TABLE 1

Analytical, magnetic, Mössbauer, and electrical conductance data for the complexes

Complex	Analysis (%) Found C	Found H	Found N	Calc. C	Calc. H	Calc. N	$\mu_{eff.}$ [a] B.M.	θ [b] K	δ/mm s^{-1} [c] 293 K	97 K	ΔE_Q/mm s^{-1} 293 K	97 K	Λ [d] S cm^2 mol^{-1}
$[FeLCl(HOMe)][ClO_4]$	39.1	5.4	7.4	38.7	5.2	7.5	5.20	0	0.96	1.07	2.15	2.81	171
$[FeLCl][ClO_4]$	38.5	5.0	7.5	38.8	4.8	8.0			0.83	0.94	1.23	2.09	
$[FeLCl][BPh_4]$	65.9	6.2	5.6	66.0	6.1	5.6	5.16	−8	0.93	1.05	2.23	2.76	122
$[FeLBr][ClO_4]$	35.5	4.4	7.2	35.8	4.4	7.4	5.30	−4	0.85	0.97	2.14	2.32	186
$[FeLI][ClO_4]$	33.0	4.1	6.6	33.1	4.1	6.8	0.60		0.28	0.37	1.50	1.49	285
$[FeL(NCS)][BPh_4]$	65.7	6.0	7.5	65.6	6.0	7.3	0.61		0.27	0.34	0.90	0.88	125
$[FeL(NCS)_2]$ (A)	45.0	5.1	13.7				5.25		0.32	0.38	0.58	0.57	
(B)	45.2	5.2	13.6	45.0	5.0	13.8	5.25	0	0.94	1.06	1.34	1.71	102
(C)	44.8	4.9	14.0				5.31	0	0.96		2.95		
$[FeL(HOMe)][BPh_4]_2$	74.2	6.5	3.7	74.7	6.6	4.0	5.60	−8	0.91	1.03	2.28	2.80	232
$[FeL(NCMe)][BPh_4]_2$	74.3	6.3	5.5	75.2	6.4	5.2	1.64		0.29	0.36	1.01	0.99	225
$[FeL(py)][BPh_4]_2$	76.3	6.7	5.0	75.8	6.4	5.1	1.37		0.31		0.94		231
$[FeL(NH_3)][BPh_4]_2$	73.9	5.5	5.2	74.6	6.6	5.4	1.72		0.28	0.37	0.87	0.88	234

[a] At 20 °C corrected for diamagnetism of ligands. 1 B.M. = 9.274×10^{-24} A m^2. [b] The Weiss constant, θ, is the negative intercept in the $\chi^{corr.}$ *vs.* T plot. [c] Relative to iron foil standard. [d] In 10^{-3} mol dm^{-3} CH_3CN solution at 25 °C; see W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81, for ranges of conductances of various electrolyte types.

states, did not exhibit the well defined ν(C=N) vibration at *ca.* 1 630 cm^{-1}. Instead these complexes showed broad weak absorption in this region. This is an often-noted feature of low-spin iron(II)–imine complexes which has been attributed to strong electron delocalization in the chelate ring.[3]

Three modifications of the complex of stoicheiometry $FeL(NCS)_2$, distinguishable on the basis of i.r. and Mössbauer spectra and magnetic properties, were obtained. As judged by electronic spectra all three have the same structure in acetonitrile solution. Some splitting of the $\nu_{asym.}$(NCS) mode in the 2 000—2 100 cm^{-1} region was discernible in all three cases. In the complex $[FeL(NCS)][BPh_4]$, the $\nu_{asym.}$(NCS) vibration occurs at 2 116 cm^{-1} an observation which at first suggested that the NCS group is either bridging or *S*-bonded. However, as revealed by an *X*-ray structure determination (see below) this is not the case.

TABLE 2

Infrared (cm^{-1}) and electronic spectral data for the complexes

Complex	ν(O–H) or ν(N–H)	$\nu_{asym.}$(NCS)	ν(C=N)	Electronic spectra (10^3 cm^{-1}) [a] Solid	MeCN
$[FeLCl(HOMe)][ClO_4]$	3 380 [b]		1 630	18.8, 16.3	20.4 (3 200), *ca.* 18.0 (sh)
$[FeLCl][BPh_4]$			1 628	19.7, 16.7	20.1 (1 600), 17.8 (sh)
$[FeLBr][ClO_4]$			1 632	18.5 (sh), 15.5	21.0 (3 900), *ca.* 18.0 (sh)
$[FeLI][ClO_4]$			*c*	18.6, 16.5 (sh)	21.0 (6 000), *ca.* 18.0 (sh)
$[FeL(NCS)][BPh_4]$		2 116, 2 060 (sh) [d]	*c*	19.9, 17.0 (sh)	20.2 (4 200), *ca.* 18.0 (sh)
$[FeL(NCS)_2]$ (A)		2 100, 2 060w	*c*	17.6, 14.8, 12.2 (sh)	20.3 (3 800), *ca.* 17.0 (sh)
(B)		2 070 (sh), 2 045	1 628		
(C)		2 050, 2 030	1 622		
$[FeL(HOMe)][BPh_4]_2$	3 436 [b]		1 615	17.8, *ca.* 11.0 (br)	20.6 (3 800), *ca.* 18.0 (sh)
$[FeL(NCMe)][BPh_4]_2$	*e*		*c*	21.0, 19.5 (sh), 18.0 (sh)	20.8 (4 900), *ca.* 18.0 (sh)
$[FeL(py)][BPh_4]_2$			*c*	20.0, 18.4 (sh), 17.0 (sh)	21.0 (4 500), *ca.* 18.0 (sh)
$[FeL(NH_3)][BPh_4]_2$	3 255 [f]		*c*	20.1, 18.5 (sh), 17.0 (sh)	21.0 (4 800), *ca.* 18.0 (sh)

[a] ϵ/dm^3 mol^{-1} cm^{-1} in parentheses. [b] ν(O–H). [c] Not observed. [d] sh = Shoulder, w = weak. [e] ν(C≡N) of MeCN occurs as a weak absorption at 2 290 cm^{-1}. [f] ν(N–H).

A number of lines of evidence combine to indicate that in $[FeLCl(HOMe)][ClO_4]$ and $[FeL(HOMe)][BPh_4]_2$ the molecule of MeOH is co-ordinated to the metal ion. The ν(OH) absorptions at 3 380 and 3 436 cm^{-1} respectively appear too sharp to be due to lattice MeOH. Also the MeOH molecule can be partially lost on storage (as in the former complex) or replaced by a molecule of MeCN, NH_3, or pyridine (as in the latter) to give new complexes having distinctly different magnetic properties and/or Mössbauer spectra (Table 1).

Magnetic susceptibilities were measured over the temperature range 93—298 K. The complexes fall into two groups according to whether they have high-spin ($S = 2$) or low-spin ($S = 0$) ground states (Table 1). Thus, while the complexes $[FeLX]^+$ are high-spin for X = Cl or Br, they are low-spin for X = I or NCS. Again, replacement of MeOH in the high-spin complex $[FeL(HOMe)][BPh_4]_2$ by MeCN, NH_3, or pyridine is accompanied by a spin-state changeover from $S = 2$ to $S = 0$. The small residual moments observed for the low-spin complexes presumably arise from the presence of small amounts of paramagnetic impurity, together with a contribution from the temperature-independent paramagnetism, although the presence of a low-lying quintet excited state cannot be excluded. Of the three modifications of $[FeL(NCS)_2]$ one is low-spin and two are high-spin.

The Mössbauer spectra (Table 1) of the complexes reinforce the conclusions derived from the magnetic measurements. Thus, those complexes shown to be high-spin have values of the isomer shift (δ) in the range 0.8—1.1 mm s^{-1} (relative to iron foil standard) and values of the quadrupole splitting (ΔE_Q) in the range 1.2—2.9 mm s^{-1}, characteristic of this class of iron(II) complex.[4] Corresponding ranges for the low-spin complexes are δ 0.2—0.4 mm s^{-1} and ΔE_Q 0.5—1.5 mm s^{-1}.

It remains to consider the structures of the various complexes. Previous studies[1,2] of complexes of the same macrocycle with other metal ions (Ag^I, Cu^I, and Cu^{II}) have shown that the ligand may use both sulphur atoms, one sulphur atom, or neither sulphur atom in five- and six-co-ordinate structures based on the pentagonal plane, the trigonal bipyramid, the square pyramid, and the octahedron. Infrared spectra of the different complexes did not reveal any clear pattern (*e.g.* in the C–S stretching region) that could reliably be associated with the co-ordination of the thioether groups. Electronic spectra (Table 2) were similarly unhelpful in assignment of co-ordination geometry since in all cases, whether low-spin or high-spin, the spectra are dominated by strong charge-transfer bands, attributable to d_π–p_π^* transitions of the co-ordinated trimethine moiety, which mask the weaker *d–d* transitions. The $S = 0$ ground state of several of the complexes strongly suggests that this group have six-co-ordinate (distorted octahedral) structures since a spin-singlet ground state is not readily reconciled with other possible co-ordination geometries. An implication is that in the group of low-spin complex cations, $[FeLX]^+$ (X = NCS, I, MeCN, NH_3, or pyridine), the macrocycle adopts a ' wrap around ' conformation occupying five octahedral sites with both thioether groups co-ordinated. For the high-spin complexes the situation is less clear. For example, for the complex $[FeLCl(HOMe)][ClO_4]$ for which there is evidence that both the chloride ion and the methanol molecule are co-ordinated, either a seven-co-ordinate structure (with both sulphur atoms co-ordinated) or a six-co-ordinate structure (with one sulphur atom co-ordinated) can be envisaged. To answer this specific problem and to assist generally in the assignment of structure to the other complexes, single-crystal *X*-ray analyses of high-spin $[FeLCl(HOMe)][ClO_4]$ (2) and of low-spin $[FeL(NCS)][BPh_4]$ (1) were undertaken.

Discussion of the Structures of (1) *and* (2).—Both (1) and (2) contain discrete cations and anions separated by the normal van der Waals distances. The cation in (1) is $[FeL(NCS)]^+$ and is illustrated, together with the atomic numbering scheme, in Figure 1. The metal atom is in a distorted octahedral environment being bonded to five donor atoms of the macrocycle [Fe–S(2) 2.307(3), Fe–N(6) 1.981(6), Fe–N(9) 1.870(6), Fe–N(12) 1.987(7), Fe–S(16) 2.258(3) Å] and to the nitrogen atom of the thiocyanate anion [Fe–N(100) 1.965(7) Å] which is *trans* to S(16).

The cation in (2) is $[FeLCl(HOMe)]^+$ and is illustrated in Figure 2 with the same atom-numbering scheme used for (1) in Figure 1. The metal atom in (2) is strongly bound to the trimethine moiety of the macrocycle [Fe–N(6) 2.205(11), Fe–N(9) 2.092(10), Fe–N(12) 2.200(12) Å]. The chlorine atom *trans* to N(9) [Fe–Cl 2.304(4) Å] completes an approximate square plane with the trimethine unit. The oxygen atom of the methanol molecule occupies one axial position at 2.205(16) Å while in the other the metal forms a long bond [Fe–S(2) 2.806(5) Å] with one sulphur atom of the macrocycle. The other sulphur atom is not co-ordinated. Thus, while both (1) and (2) have distorted octahedral structures they differ very markedly in the way the six-co-ordination is achieved.

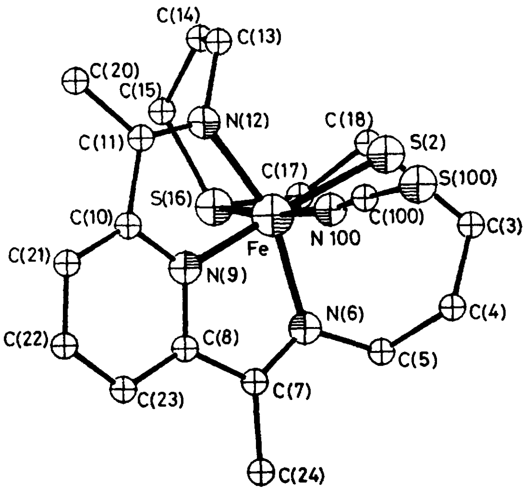

FIGURE 1 Structure of the cation of complex (1)

In considering the two structures, it is useful to place them in a wider perspective by comparing them (Table 3) with the structures of three other complexes containing the same macrocycle. Important factors in determining the co-ordination mode of the macrocycle are the electron configuration of the metal ion and the availability of other (unidentate) ligands. When only poorly co-ordinating donors other than the macrocycle are present,

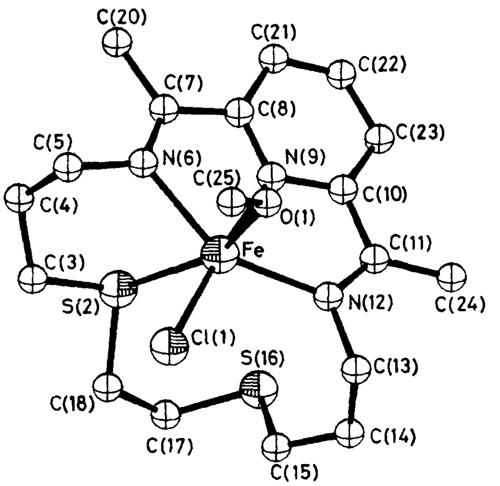

FIGURE 2 Structure of the cation of complex (2)

TABLE 3

Structures of molecules containing the macrocycle L; bond lengths are in Å

	$[AgL]^+$	$[CuL]^+$	$[CuL]^{2+}$	$[CuL(NCS)]^+$	$[FeL(NCS)]^+$	$[FeL(HOMe)Cl]^+$
M–N(6)	2.537(10)	2.519(25)	2.022(11)	2.074(16)	1.981(6)	2.205(11)
M–N(9)	2.317(9)	2.103(17)	1.930(11)	1.930(16)	1.870(6)	2.092(10)
M–N(12)	2.441(10)	2.279(22)	2.079(13)	2.033(12)	1.987(7)	2.200(12)
M–S(2)	2.555(4)	2.328(7)	2.470(4)	2.745(5)	2.307(3)	2.806(5)
M–S(16)	2.600(4)	2.324(8)	2.377(4)		2.258(3)	
Other bonds				N 1.854(19)	N 1.965(9)	Cl 2.304(4) O 2.205(16)
Co-ordination number *	5	5	5	4 + 1	6	5 + 1
Structure	Distorted trigonal prismatic		Distorted square pyramidal	Square planar	Octahedral	Square pyramidal
Ref.	1	1	2	2	This work	This work

* +1 indicates a weak M–S bond. The structure is described ignoring this ' bond.'

as in $[AgL][BPh_4]$, $[CuL][ClO_4]$, and $[CuL][ClO_4]_2$, the metal is encapsulated within the macrocycle in such a way that all five donor atoms are co-ordinated. However as discussed elsewhere [1,2] there are considerable variations in the three five-co-ordinate geometries. For the two d^{10} metal ions, the co-ordination polyhedra are highly distorted trigonal bipyramids whereas for the copper(II) ion the arrangement of the five donor atoms approximates to that of a square pyramid. Where a strongly co-ordinating anion is present, in the case of Cu^{II} as in $[CuL(NCS)][ClO_4]\cdot0.5H_2O$, the square-pyramidal arrangement is retained, the nitrogen atom of the thiocyanate group displacing one sulphur atom from the square plane. In (2) the good co-ordinating anion Cl^- is available which also occupies the position *trans* to the pyridine nitrogen at 2.304(4) Å. The conformation of the macrocycle in (2) is therefore similar to that in $[CuL(NCS)]^+$ in that one sulphur atom is weakly bonded in an axial position at 2.806(5) Å, the other remaining unbonded. As can be seen from a comparison of the torsion angles in (2) and $[CuL(NCS)]^+$ (Table 4), the only significant differences are in those angles involving C(14) showing that in both complexes the macrocycle conformation is essentially strain free. In addition, a methanol oxygen atom is bonded to the iron(II) atom in (2), in an axial position *trans* to S(2) at 2.205(16) Å. The angles subtended by this oxygen atom at the metal with the equatorial atom are all within 2.0 of 90°. Least-squares planes (Table 5) show that the FeN_3Cl equatorial plane is planar within experimental error. The saturated six-membered chelate ring has an unstrained chair conformation (Plane 2, Table 5) with C(3), C(4), C(5) 1.49, 1.28, 1.19 Å from the Fe, S(2), N(6) plane.

TABLE 4

Torsion angles (°) in (1), (2), and $[CuL(NCS)]^+$

	(1)	(2)	$[CuL(NCS)]^+$
C(7)–N(6)–C(5)–C(4)	−128.4	82.7	92.7
N(6)–C(5)–C(4)–C(3)	−87.5	65.9	60.1
C(5)–C(4)–C(3)–S(2)	57.0	−70.5	−68.8
C(4)–C(3)–S(2)–C(18)	−114.5	−177.6	−172.7
C(3)–S(2)–C(18)–C(17)	97.7	169.4	172.8
S(2)–C(18)–C(17)–S(16)	37.4	51.4	57.3
C(18)–C(17)–S(16)–C(15)	75.2	71.8	70.4
C(17)–S(16)–C(15)–C(14)	−73.8	−172.8	−90.9
S(16)–C(15)–C(14)–C(13)	−56.8	84.5	−71.5
C(15)–C(14)–C(13)–N(12)	6.6	−56.9	76.0
C(14)–C(13)–N(12)–C(11)	−103.2	−79.9	−123.9

The structure of (1) is unique among the series of complexes of L in that the metal ion is strongly bound not only to all five macrocycle donor atoms but also to a thiocyanate nitrogen atom. In contrast to the structures discussed above, the thiocyanate is not *trans* to the pyridine nitrogen but axial to the plane containing the trimethine moiety. This, of course, is an inevitable consequence of the bonding of both macrocycle sulphur atoms which must be mutually *cis*. Thus S(2) is *trans* to the pyridine nitrogen at 2.308(3) Å with S(16) and the NCS group in axial positions [Fe–S(16) 2.258(3), Fe–N(100) 1.965(7) Å]. As is apparent from torsion angles in Table 4 and as discussed below, this conformation is not achieved without considerable strain.

TABLE 5

Least-squares planes for (1) and (2). Distances of atoms from the planes are given in Å. Atoms not contributing to the plane are marked with an asterisk

(*a*) For (1)

Plane 1: Fe 0.04, N(6) −0.03, C(7) 0.03, C(8) −0.01, N(9) 0.02, C(10) −0.01, C(11) −0.01, N(12) −0.03, C(21) −0.05, C(22) 0.02, C(23) 0.03, C(13) * −0.11, C(5) * 0.10

Plane 2: Fe −0.09, N(100) −0.22, N(6) 0.25, N(12) 0.26

Plane 3: Fe 0.02, N(100) −0.06, S(2) 0.05, N(9) 0.05, S(16) −0.05

Plane 4: Fe −0.04, N(6) 0.03, N(9) −0.01, N(12) 0.03

Plane 5: Fe, S(2), N(6) 0.00, C(3) * −0.66, C(4) * −1.11, C(5) * −0.01

Plane 6: Fe, N(12), S(16) 0.00, C(13) * −1.18, C(14) * −1.43, C(15) * −0.41

Plane 7: Fe, S(2), S(16) 0.00, C(17) * 0.64, C(18) * 0.15

(*b*) For (2)

Plane 1: Fe 0.01, N(16) −0.03, N(9) 0.04, N(12) −0.04, Cl 0.02

Plane 2: Fe, N(6), S(2) 0.00, C(3) * 1.49, C(4) * 1.28, C(5) * 1.19

The Fe–N distances in the metal–trimethine unit [Fe–N(6) 1.981(6), Fe–N(9) 1.870(6), Fe–N(12) 1.987(7) Å] are *ca.* 0.06 Å shorter than those in $[CuL(NCS)]^+$, comparable to the difference in ionic radii between Cu^{2+} and low-spin Fe^{2+}. As is often found, the Fe–N(pyridine) bond is the shortest of the three. The Fe atoms and the atoms of the trimethine unit are closely planar (Plane 1, Table 5). The positioning of S(2) *trans* to N(9), with a displacement of only -0.22 Å from Plane 1, is achieved without difficulty *via* torsion angles of -128.4, -87.5, and 57.0° for the C–C, C–C, and C–S bonds respectively.

The linkage from N(12) to S(16), however, is much more highly strained as is apparent from the remarkably small torsion angle of 6.6° for N(12)–C(13)–C(14)–C(15). As is clear from Figure 1, this leaves N(12) and C(15) almost eclipsed. The strain is a consequence of the need to bring S(16) into an axial bonding position. Angles between S(16) and the four equatorial donor atoms range between 86.3 and 95.3°. Somewhat surprisingly the Fe–S(16) bond [2.258(3) Å] is shorter than the equatorial Fe–S(2) bond [2.307(3) Å]. The linkage between S(2) and S(16) is also strained with a S–C–C–S torsion angle of 37.4°.

It is also probable that the substantial macrocycle strain in (1) is compensated by the crystal-field stabilisation energy derived from the low-spin state of the iron(II) ion. The regularity of the octahedron is shown by the Planes 3, 4, and 5 (Table 5) which show little distortion from the equatorial planes. It is important to note that it is only the relatively small size of the (low-spin) iron(II) ion that permits this conformation for L. The N–Fe–N angles in the trimethine unit are *ca.* 80° compared to 74° in (2) thus allowing S(2) and S(16) to approach their respective equatorial and axial positions *via* the six-membered rings more closely. The metal –NCS bond [1.965(9) Å] is longer than in $[CuL(NCS)]^+$ [1.854(19) Å]. This may be due to the former bond being in a more sterically strained axial position.

In (1) there are no intermolecular contacts between non-hydrogen atoms less than 3.5 Å. In (2) there are many, all involving an oxygen atom of the perchlorate anion and an atom of the cation. Several of these are less than 3 Å [minima 2.79 Å for both O(15) $\cdots$ C(24) and O(11) $\cdots$ O(1) ($\frac{1}{2} + x$, $\frac{1}{2} - y$, z)] but in view of the disorder in the perchlorates we cannot attach any significance to these values.

Since the complexes $[FeLX]^+$ (X = I, MeCN, NH_3, or pyridine) all have $S = 0$ ground states, it may safely be concluded that they have the same distorted octahedral structure found for $[FeL(NCS)]^+$ (this has been confirmed for $[FeLI][ClO_4]$ by *X*-ray analysis). It is surprising that $[FeLCl][BPh_4]$ and $[FeLBr][ClO_4]$ are high-spin when viewed against the relative ligand-field strengths of Cl^-, Br^-, and I^-. It may be therefore that the chloro- and bromo-complexes have a pentagonal-pyramidal structure as found for some manganese(II), cadmium(II), and mercury(II) complexes of the corresponding 'N_5' macrocycle (L^1) having the same number of member atoms.[5,6]

On the evidence available we are unable to make firm structural assignments to the three modifications of $[FeL(NCS)_2]$. The low-spin nature of the most stable form (A) indicates an octahedrally based structure. The occurrence of one of the two $\nu_{asym.}$(NCS) features at 2 100 cm^{-1} might argue for a bridging mode for one of the two NCS groups. On this basis, a di-μ-thiocyanato-dimeric structure, in which none of the macrocycle thioether groups is co-ordinated, may be envisaged. However assignment of the i.r. band at 2 100 cm^{-1} in these systems to bridging NCS may be unwise since it has been shown that in $[FeL(NCS)][BPh_4]$ the $\nu_{asym.}$ vibration of the terminally *N*-bonded NCS group occurs at 2 116 cm^{-1}. Modification C shows the same $\nu_{asym.}$(NCS) splitting pattern (Table 2) as $[MnL^1(NCS)_2]$ (L^1 the same 17-membered 'N_5' macrocycle referred to above) known to have a distorted pentagonal-bipyramidal geometry in which the macrocycle is appreciably folded.[6] The Mössbauer spectrum of modification C is also very similar to that of the high-spin complex $[FeL^2(NCS)_2]$ where L^2 is a 16-membered 'N_3S_2' analogue of L.[7] Since L^2 is incapable of folding so as to occupy five octahedral sites, $[FeL^2(NCS)_2]$ is believed to be pentagonal bipyramidal. We therefore tentatively assign a distorted pentagonal-bipyramidal structure to modification C. Whatever the structures of the three forms of $[FeL(NCS)_2]$, it is clear that different conformations of the macrocycle must be involved, reflecting, once again, the versatile co-ordinating capabilities of this macrocyclic ligand.

EXPERIMENTAL

Preparation of the Complexes.—$[FeLCl(HOMe)][ClO_4]$. To a solution of $[AgL][ClO_4]$ (1 mmol) in dry MeOH (150 cm^3) under a N_2 atmosphere was added a solution of $FeCl_2$ (1 mmol) in dry MeOH (25 cm^3). The yellow solution changed immediately on mixing to dark purple and AgCl was precipitated. The mixture was refluxed for 10 min and filtered under N_2. Concentration of the purple filtrate by rotary evaporation followed by cooling overnight at 0 °C gave dark blue crystals of the desired product in 61% yield.

$[FeLBr][ClO_4]$. To a refluxing solution of $[AgL][ClO_4]$ (1 mmol) in dry MeOH (150 cm^3) under N_2 was added $Fe[ClO_4]_2$ (1 mmol) followed by LiBr (3 mmol). On addition of the bromide the colour changed to a dark purple with precipitation of AgBr. The mixture was refluxed for another 10 min and filtered under N_2. The dark blue product was obtained in 65% yield on concentration of the filtrate.

$[FeLI][ClO_4]$. This complex was prepared in a similar manner to the bromide perchlorate except that NaI was used instead of LiBr. The product was isolated as dark purple needles in 55% yield.

$[FeL(HOMe)][BPh_4]_2$. To a solution of $[FeLCl(HOMe)][ClO_4]$ (1 mmol) in dry oxygen-free MeOH (250 cm^3) was added $Na[BPh_4]$ (2 mmol). The bright pink product separated almost immediately in 81% yield.

$[FeLCl][BPh_4]$. To a refluxing suspension of $[FeL(HOMe)][BPh_4]_2$ (1 mmol) in dry oxygen-free MeOH (150 cm^3) was added LiCl (2 mmol). The red colour slowly darkened to deep blue. The mixture was refluxed for 1 h, filtered under N_2, and the fitrate concentrated to yield blue needles of the product in 65% yield.

$[FeL(NCMe)][BPh_4]_2$. The above complex was dissolved in methanol–acetonitrile (2 : 1). Concentration by rotary evaporation gave the product as a red-brown powder in 80% yield.

$[FeL(py)][BPh_4]_2$. The complex $[FeL(HOMe)][BPh_4]_2$ (1 mmol) was suspended in dry methanol (100 cm^3) under an atmosphere of N_2. Pyridine (py) was added dropwise to the stirred suspension until the suspended solid had all dissolved to give a dark purple solution. This solution was stirred for another 15 min, filtered under N_2, then reduced in volume to *ca.* 25 cm^3 when a dark purple solid separated in 79% yield.

$[FeL(NH_3)][BPh_4]_2$. This complex was prepared by reaction between powdered $[FeL(HOMe)][BPh_4]_2$ and NH_3 vapour over a period of 5 h. A fresh surface of the solid was exposed every 30 min. The colour of the solid gradually changed from red to purple. The course of the reaction was monitored by periodically recording the i.r. spectrum of small samples.

$[FeL(NCS)][BPh_4]$. This complex was prepared as described for the chloride tetraphenylborate except that Na[NCS] was used in place of LiCl.

$[FeL(NCS)_2]$. To a refluxing solution of $[FeLCl(HOMe)][ClO_4]$ (1 mmol) in dry oxygen-free methanol (150 cm^3) was added dropwise a two-fold excess of Na[NCS] in dry methanol (25 cm^3). The purple solution darkened slightly and was refluxed for *ca.* 30 min. After filtering the solution under N_2 and concentrating the filtrate to *ca.* 50 cm^3 deep purple crystals separated in 60% yield. This is modification A.

Recrystallisation of this product from acetonitrile gave modification B. When form B was dissolved in dry methanol and the solution refluxed under N_2 for 1 h, partial conversion into modification C occurred. All these modifications are deep purple. Both forms B and C are spontaneously converted to form A in the solid state over a period of 1—2 d, the changes being conveniently monitored by Mössbauer spectroscopy.

Physical measurements were carried out as described previously.[8]

Crystal Data.—(1). $[FeL(NCS)][BPh_4]$, $C_{42}H_{45}BFeN_4S_3$, $M = 768.2$, Monoclinic, $a = 31.640(8)$, $b = 11.019(8)$, $c = 11.155(7)$ Å, $\beta = 96.40(3)°$, $U = 3\,864.7$ Å^3, $F(000) = 1\,616$, $D_m = 1.32$, $Z = 4$, $D_c = 1.32$ g cm^{-3}, $\mu = 5.94$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, space group $P2_1/a$ from systematic absences $h0l$, $h = 2n + 1$, $0k0$, $k = 2n + 1$.

(2). $[FeCl(HOMe)][ClO_4]$, $C_{18}H_{28}Cl_2FeO_5S_2$, $M = 557.1$, Monoclinic, $a = 18.512(11)$, $b = 18.279(12)$, $c = 8.125(9)$ Å, $\beta = 113.1(2)°$, $U = 2\,529.7$ Å^3, $D_m = 1.46$, $Z = 4$, $D_c = 1.46$ g cm^{-3}, $\mu = 10.1$ cm^{-1}, $F(000) = 1\,156$, space group $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å, $P2_1/a$ from systematic absences $h0l$, $h = 2n + 1$, $0k0$, $k = 2n + 1$.

For (1) 4 874 reflections with $2\theta < 50$ were collected on an Enraf–Nonius CAD-4 diffractometer using the variable ω scan method. 2 548 Independent reflections with $I > 2\sigma(I)$ were used in subsequent calculations. For (2) the crystal decayed rapidly in the X-ray beam and five crystals were used to collect the data. All crystals were mounted with the (101) planes perpendicular to the instrument axis of a General Electric XRD5 diffractometer. In all, 2 586 reflections were measured with $2\theta < 40°$ by the stationary crystal-stationary-counter method with each crystal being used for *ca.* 20% of the data collection. Of these, 1 772 reflections with $I > 2\sigma(I)$ were used in subsequent refinement. For both structures, neither extinction nor absorption corrections were deemed necessary.

The positions of the iron atoms were obtained from the Patterson functions and subsequent Fourier maps enabled the positions of all other non-hydrogen atoms to be obtained in a straightforward manner. There was only one problem, the positions of the perchlorate oxygens in (2). From a difference-Fourier map it was tempting to assume that the oxygen atoms were distributed spherically around the chlorine atom. However certain peaks were observable and eventually the electron density was described in terms of five ideal tetrahedra with occupancy factors of 0.22, 0.30, 0.18, 0.18, and 0.12 respectively. Three of these tetrahedra shared a common atom. For both structures the hydrogen atoms were included in fixed trigonal or tetrahedral positions at 1.08 Å from the carbon atom to which they were bonded. Thermal parameters were allowed to refine in (1). In the cation, thermal factors of hydrogen atoms bonded to the same carbon were constrained to be equivalent and in the anion, those in the same phenyl group were similarly constrained. In (2), thermal parameters were fixed at a value equivalent to that of the carbon atom to which they are bonded. In (1) all atoms bar hydrogen were refined anisotropically. In (2) only Fe, Cl, and S

TABLE 6

Atomic co-ordinates for (1) ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Fe(1)	755(0)	1 018(1)	2 564(1)
S(100)	−23(1)	−2 643(3)	2 135(2)
N(100)	450(2)	−539(8)	2 489(6)
C(100)	262(3)	−1 407(11)	2 320(7)
S(2)	125(1)	1 835(3)	1 675(2)
C(3)	−271(3)	1 824(10)	2 754(8)
C(4)	−119(2)	1 271(10)	3 982(7)
C(5)	279(3)	1 876(9)	4 639(7)
N(6)	661(2)	1 307(7)	4 267(5)
C(7)	960(2)	907(9)	5 066(6)
C(8)	1 299(2)	272(8)	4 547(6)
N(9)	1 245(2)	280(6)	3 331(5)
C(10)	1 514(3)	−274(9)	2 675(7)
C(11)	1 388(3)	−63(10)	1 369(7)
N(12)	1 050(2)	559(7)	1 149(5)
C(13)	921(3)	1 056(12)	−64(7)
C(14)	1 015(3)	2 398(13)	−118(7)
C(15)	1 260(3)	2 988(10)	976(7)
S(16)	1 053(1)	2 866(3)	2 419(2)
C(17)	599(4)	3 913(11)	2 278(11)
C(18)	209(4)	3 438(12)	1 501(11)
C(20)	985(3)	1 088(11)	6 416(6)
C(21)	1 649(3)	−333(9)	5 142(7)
C(22)	1 925(3)	−932(10)	4 472(9)
C(23)	1 856(3)	−915(9)	3 228(9)
C(24)	1 691(4)	−466(11)	492(9)
B(1)	3 345(3)	634(10)	2 110(7)
C(41)	2 959(2)	1 593(10)	2 291(6)
C(42)	2 975(4)	2 770(12)	1 884(8)
C(43)	2 668(4)	3 623(11)	2 010(8)
C(44)	2 322(3)	3 339(13)	2 590(9)
C(45)	2 291(3)	2 194(13)	3 021(10)
C(46)	2 603(3)	1 318(9)	2 874(8)
C(51)	3 733(2)	787(8)	3 185(6)
C(52)	3 739(3)	1 670(9)	4 089(6)
C(53)	4 071(3)	1 761(10)	5 034(7)
C(54)	4 409(3)	980(11)	5 093(8)
C(55)	4 421(3)	109(11)	4 202(9)
C(56)	4 089(3)	29(9)	3 289(7)
C(61)	3 515(2)	917(8)	797(6)
C(62)	3 229(3)	939(9)	−274(6)
C(63)	3 358(3)	1 238(9)	−1 378(7)
C(64)	3 769(4)	1 587(9)	−1 465(8)
C(65)	4 062(3)	1 603(10)	−445(8)
C(66)	3 931(3)	1 252(9)	653(7)
C(71)	3 161(2)	−740(10)	2 234(7)
C(72)	3 139(3)	−1 258(11)	3 382(9)
C(73)	2 956(4)	−2 363(15)	3 545(13)
C(74)	2 794(4)	−3 056(13)	2 599(18)
C(75)	2 814(3)	−2 608(14)	1 441(13)
C(76)	2 994(3)	−1 466(11)	1 272(9)

atoms were refined anisotropically, the rest isotropically. For both structures, weighting schemes were chosen such that $w\Delta^2$ was constant over ranges of F_o and $(\sin\theta)/\lambda$. For (1) unit weights achieved this, while for (2) the scheme was $\sqrt{w} = 1$ for $F_o < 70$ and $70/F_o$ for $F_o > 70$. Final R values were 0.047 (1) and 0.102 (2). In the final cycles of refinement all shifts were <0.1 and the difference-Fourier maps showed no significant peaks. All calculations were done using SHELX 76 [9] and the University of Manchester Computer Centre. Scattering factors and dispersion correactions were taken from International Tables.[10]

Atomic co-ordinates are given in Tables 6 and 7 for (1) and (2) respectively. Bond lengths and angles are in Table 8. Thermal parameters and observed and calculated structure factors are deposited in Supplementary Publication No. SUP 23091 (30 pp.).*

TABLE 7

Atomic co-ordinates for (2) ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Fe(1)	635(1)	2 111(1)	1 658(3)
C(3)	382(9)	245(8)	2 730(22)
C(4)	1 233(10)	103(9)	3 034(23)
C(5)	1 590(10)	610(9)	2 050(22)
N(6)	1 635(7)	1 349(6)	2 738(16)
C(7)	2 211(9)	1 560(8)	4 190(21)
C(8)	2 162(9)	2 305(8)	4 819(20)
N(9)	1 478(7)	2 638(6)	3 861(15)
C(10)	1 329(9)	3 347(8)	4 287(20)
C(11)	564(9)	3 635(8)	3 075(19)
N(12)	167(7)	3 205(6)	1 798(16)
C(13)	−594(10)	3 458(10)	433(23)
C(14)	−1 292(12)	3 408(11)	1 069(27)
C(15)	−1 453(12)	2 689(10)	1 643(25)
S(16)	−827(3)	2 498(3)	4 009(6)
C(17)	−1 088(10)	1 558(8)	4 136(22)
C(18)	−784(10)	1 005(9)	3 178(23)
S(2)	265(2)	1 094(2)	3 796(6)
C(20)	2 924(11)	1 094(10)	5 243(24)
C(21)	2 725(10)	2 664(9)	6 253(22)
C(22)	2 565(11)	3 326(9)	6 757(24)
C(23)	1 885(10)	3 691(9)	5 806(22)
C(24)	368(12)	4 403(11)	3 441(25)
O(1)	1 196(8)	2 587(7)	−40(17)
C(25)	1 192(15)	2 250(14)	−1 678(33)
Cl(2)	6 888(3)	473(3)	368(8)
O(11)	7 177(13)	1 195(9)	623(3)
O(12)	6 918(27)	163(22)	−1 204(41)
O(13)	6 090(16)	485(30)	177(67)
O(14)	7 334(26)	19(21)	1 850(52)
O(15)	6 116(21)	302(21)	1 128(50)
O(16)	7 544(21)	−22(21)	1 284(54)
O(17)	6 582(23)	207(21)	−1 425(32)
O(18)	7 342(31)	47(27)	−297(70)
O(19)	6 923(31)	205(31)	2 027(46)
O(20)	6 097(19)	480(37)	−874(68)
O(21)	7 482(23)	391(26)	−310(55)
O(22)	7 064(32)	1 151(22)	1 431(60)
O(23)	6 159(22)	661(37)	−1 126(59)
O(24)	6 777(33)	−81(24)	1 331(59)
O(25)	7 205(41)	260(40)	2 161(48)
O(26)	7 427(30)	997(29)	81(66)
O(27)	6 161(27)	844(39)	−39(77)
O(28)	6 776(42)	−77(28)	−902(65)
Cl(1)	−360(2)	1 604(2)	−776(5)

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TABLE 8

Molecular dimensions in (1) and (2): [a] distances (Å), angles (°)

(*a*) Co-ordination sphere in (1)

N(100)–Fe(1)	1.965(7)	N(9)–Fe(1)	1.870(6)
S(2)–Fe(1)	2.307(3)	N(12)–Fe(1)	1.987(7)
N(6)–Fe(1)	1.981(6)	S(16)–Fe(1)	2.258(3)
N(100)–Fe(1)–S(2)	85.8(2)	N(6)–Fe(1)–N(12)	159.5(3)
N(100)–Fe(1)–N(6)	93.2(3)	N(9)–Fe(1)–N(12)	79.3(3)
S(2)–Fe(1)–N(6)	97.8(2)	N(100)–Fe(1)–S(16)	172.4(2)
N(100)–Fe(1)–N(9)	91.1(3)	S(2)–Fe(1)–S(16)	88.0(1)
S(2)–Fe(1)–N(9)	176.3(2)	N(6)–Fe(1)–S(16)	91.8(2)
N(6)–Fe(1)–N(9)	80.6(3)	N(9)–Fe(1)–S(16)	95.3(2)
N(100)–Fe(1)–N(12)	90.9(3)	N(12)–Fe(1)–S(16)	86.3(2)
S(2)–Fe(1)–N(12)	102.5(2)		

(*b*) Co-ordination sphere in (2)

Cl(1)–Fe(1)	2.304(4)	N(9)–Fe(1)	2.092(10)
S(2)–Fe(1)	2.806(5)	N(12)–Fe(1)	2.200(12)
N(6)–Fe(1)	2.205(11)	O(1)–Fe(1)	2.205(16)
Cl(1)–Fe(1)–S(2)	87.6(2)	N(6)–Fe(1)–N(12)	147.1(4)
Cl(1)–Fe(1)–N(6)	110.6(3)	N(9)–Fe(1)–N(12)	73.4(4)
S(2)–Fe(1)–N(6)	72.9(4)	Cl(1)–Fe(1)–O(1)	92.0(3)
Cl(1)–Fe(1)–N(9)	175.5(4)	S(2)–Fe(1)–O(1)	159.7(4)
S(2)–Fe(1)–N(9)	93.2(4)	N(6)–Fe(1)–O(1)	88.3(5)
N(6)–Fe(1)–N(9)	73.9(3)	N(9)–Fe(1)–O(1)	88.7(5)
Cl(1)–Fe(1)–N(12)	102.2(3)	N(12)–Fe(1)–O(1)	88.0(5)
S(2)–Fe(1)–N(12)	111.9(4)		

(*c*) Macrocycle dimensions in the two structures

	(1)	(2)
C(3)–S(2)	1.832(10)	1.83(2)
C(18)–S(2)	1.800(13)	1.81(2)
C(4)–C(3)	1.527(12)	1.52(3)
C(5)–C(4)	1.537(11)	1.53(3)
N(6)–C(5)	1.463(11)	1.45(2)
C(7)–N(6)	1.302(9)	1.30(2)
C(8)–C(7)	1.454(12)	1.47(2)
C(20)–C(7)	1.513(10)	1.52(2)
N(9)–C(8)	1.349(9)	1.34(2)
C(21)–C(8)	1.394(11)	1.39(2)
C(10)–N(9)	1.333(11)	1.40(2)
C(11)–C(10)	1.485(11)	1.47(2)
C(23)–C(10)	1.379(12)	1.41(2)
N(12)–C(11)	1.272(12)	1.28(2)
C(24)–C(11)	1.511(15)	1.51(3)
C(13)–N(12)	1.474(10)	1.49(2)
C(14)–C(13)	1.511(19)	1.57(3)
C(15)–C(14)	1.518(13)	1.46(3)
S(16)–C(15)	1.809(9)	1.85(2)
C(17)–S(16)	1.836(12)	1.80(2)
C(18)–C(17)	1.519(16)	1.51(3)
C(22)–C(21)	1.381(13)	1.35(3)
C(23)–C(22)	1.381(13)	1.37(3)
Fe(1)–S(2)–C(3)	109.6(3)	99.5(6)
Fe(1)–S(2)–C(18)	107.4(4)	112.5(6)
C(3)–S(2)–C(18)	101.4(6)	96.0(8)
S(2)–C(3)–C(4)	115.0(6)	112.0(10)
C(3)–C(4)–C(5)	114.4(8)	116.3(13)
C(4)–C(5)–N(6)	109.8(7)	109.5(16)
Fe(1)–N(6)–C(5)	123.9(4)	121.4(8)
Fe(1)–N(6)–C(7)	115.3(5)	115.8(10)
C(5)–N(6)–C(7)	120.7(6)	121.9(12)
N(6)–C(7)–C(8)	113.7(6)	116.7(12)
N(6)–C(7)–C(20)	126.2(8)	124.5(14)
C(8)–C(7)–C(20)	120.0(7)	118.8(12)
C(7)–C(8)–N(9)	112.3(6)	113.0(11)
C(7)–C(8)–C(21)	128.5(7)	127.0(13)
N(9)–C(8)–C(21)	119.2(7)	120.0(14)
Fe(1)–N(9)–C(8)	118.0(5)	120.3(9)
Fe(1)–N(9)–C(10)	119.8(5)	119.1(8)
C(8)–N(9)–C(10)	122.1(6)	120.6(11)
N(9)–C(10)–C(11)	110.4(7)	113.5(11)
N(9)–C(10)–C(23)	120.5(8)	118.9(13)
C(11)–C(10)–C(23)	129.1(9)	127.5(14)
C(10)–C(11)–N(12)	113.7(8)	114.8(13)
C(10)–C(11)–C(24)	117.9(8)	118.9(13)

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

TABLE 8 (*continued*)

(*c*) Macrocycle dimensions in the two structures (*continued*)

	(1)	(2)
N(12)–C(11)–C(24)	127.9(8)	128.7(13)
Fe(1)–N(12)–C(11)	116.3(5)	119.2(8)
Fe(1)–N(12)–C(13)	121.9(6)	121.5(9)
C(11)–N(12)–C(13)	121.2(7)	119.3(13)
N(12)–C(13)–C(14)	111.4(7)	119.3(13)
C(13)–C(14)–C(15)	118.2(8)	117.0(18)
C(14)–C(15)–S(16)	118.7(7)	112.2(12)
Fe(1)–S(16)–C(15)	109.0(4)	
Fe(1)–S(16)–C(17)	104.1(4)	
C(15)–S(16)–C(17)	103.6(5)	99.6(8)
S(16)–C(17)–C(18)	114.3(8)	116.5(14)
S(2)–C(18)–C(17)	113.3(8)	111.8(11)
C(8)–C(21)–C(22)	119.2(8)	119.9(25)
C(21)–C(22)–C(23)	119.9(8)	122.0(15)
C(10)–C(23)–C(22)	119.0(9)	118.2(15)

(*d*) Thiocyanate dimensions in (1)

C(100)–S(100)	1.634(11)
C(100)–N(100)	1.130(14)
Fe(1)–N(100)–C(100)	172.7(7)
S(100)–C(100)–N(100)	177.0(8)

(*e*) Methanoate dimensions in (2)

O(1)–C(25)	1.46(3)
Fe–O(1)–C(25)	124.5(13)

(*f*) Tetraphenylborate dimensions in (1) [b]

C(41)–B(1)	1.644(13)	C(55)--C(54)	1.385(15)
C(51)–B(1)	1.626(11)	C(56)–C(55)	1.382(12)
C(61)–B(1)	1.645(11)	C(62)–C(61)	1.415(10)
C(71)–B(1)	1.633(15)	C(66)–C(61)	1.392(11)
C(42)–C(41)	1.378(17)	C(63)–C(62)	1.379(12)
C(46)–C(41)	1.395(12)	C(64)–C(63)	1.370(15)
C(43)–C(42)	1.371(17)	C(65)–C(64)	1.386(12)
C(44)–C(43)	1.368(15)	C(66)–C(65)	1.391(12)
C(45)–C(44)	1.358(19)	C(72)–C(71)	1.411(13)
C(46)–C(45)	1.404(15)	C(76)–C(71)	1.395(13)
C(52)–C(51)	1.399(12)	C(73)–C(72)	1.368(20)
C(56)–C(51)	1.396(12)	C(74)–C(73)	1.357(22)
C(53)–C(52)	1.406(11)	C(75)–C(74)	1.390(24)
C(54)–C(53)	1.369(14)	C(76)–C(75)	1.403(19)
C(41)–B(1)–C(51)	110.6(7)	C(53)–C(54)–C(55)	119.0(8)
C(41)–B(1)–C(61)	107.9(7)	C(54)–C(55)–C(56)	119.6(9)
C(51)–B(1)–C(61)	110.1(6)	C(51)–C(56)–C(55)	124.3(9)
C(41)–B(1)–C(71)	107.9(7)	B(1)–C(61)–C(62)	120.9(6)
C(51)–B(1)–C(71)	106.3(7)	B(1)–C(61)–C(66)	124.0(6)
C(61)–B(1)–C(71)	113.9(7)	C(62)–C(61)–C(66)	114.9(7)
B(1)–C(41)–C(42)	120.6(8)	C(61)–C(62)–C(63)	122.2(8)

TABLE 8 (*continued*)

(*f*) Tetraphenylborate dimensions in (1) [b]

B(1)–C(41)–C(46)	124.6(9)	C(62)–C(63)–C(64)	120.5(8)
C(42)–C(41)–C(46)	114.8(9)	C(63)–C(64)–C(65)	119.9(9)
C(41)–C(42)–C(43)	124.0(10)	C(64)–C(65)–C(66)	118.8(8)
C(42)–C(43)–C(44)	120.4(11)	C(61)–C(66)–C(65)	123.6(7)
C(43)–C(44)–C(45)	118.3(11)	B(1)–C(71)–C(72)	120.4(8)
C(44)–C(45)–C(46)	121.2(10)	B(1)–C(71)–C(76)	125.1(8)
C(41)–C(46)–C(45)	121.4(10)	C(72)–C(71)–C(76)	114.4(10)
B(1)–C(51)–C(52)	123.6(7)	C(71)–C(72)–C(73)	123.1(10)
B(1)–C(51)–C(56)	122.3(7)	C(72)–C(73)–C(74)	121.7(14)
C(52)–C(51)–C(56)	114.1(7)	C(73)–C(74)–C(75)	118.1(14)
C(51)–C(52)–C(53)	122.7(8)	C(74)–C(75)–C(76)	120.3(12)
C(52)–C(53)–C(54)	120.4(9)	C(71)–C(76)–C(75)	122.4(10)

[a] Perchlorate dimensions in (2) were fixed in the refinement. Tetrahedra are made up of the following atoms: (1) O(11),-O(12),O(13),O(14) [0.22]; (2) O(11),O(15),O(16),O(17) [0.30]; (3) O(11),O(18),O(19),O(20) [0.18]; (4) O(21),O(22),O(23),O(24) [0.18]; (5) O(25),O(26),O(27),O(28) [0.12]. The value in square brackets is the population parameter. [b] Angles(°) between phenyl rings: 4—5 85.06; 4—6 71.78; 4—7 77.47; 5—6 67.95; 5—7 76.79; 6—7 49.93. Ring 4 is C(41)—C(46); ring, 5, C(51)—C(56); ring 6, C(61)—C(66); and ring 7 C(71)—C(76).

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