Seven-co-ordination in Metal Complexes of Quinquedentate Macrocyclic Ligands. Part II.[1] Synthesis, Properties, and Crystal and Molecular Structures of some Iron(III) Derivatives of Two ' N_5 ' Macrocycles

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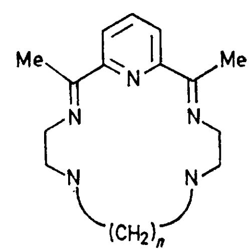
Template synthesis of the sixteen-membered, potentially quinquedentate, macrocycle formed by the Schiff-base condensation of 2,6-diacetylpyridine with 1,9-diamino-3,7-diazanonane (2,3,2-tet) in the presence of iron(II) salts yields a series of iron(III) complexes $[Fe(C)X_2]$ Y (C = macrocycle; X = Cl, Br, NCS, or N_3; and Y = ClO_4 PF_6, BPh_4, $FeCl_4$, or $FeBr_4$). Spectroscopic, magnetic, and electric conductance measurements characterise the complexes as having high-spin seven-co-ordinate structures similar to those of the previously prepared complexes of the fifteen-membered macrocycle (B) derived from 2,6-diacetylpyridine and 1,8-diamino-3,6-diazaoctane (2,2,2-tet). The crystal and molecular structure of $[Fe(C)(NCS)_2]ClO_4$ (II) has been determined and that of $[Fe(B)(NCS)_2]ClO_4$ (I) redetermined. Crystals of (I) are monoclinic, space group $P2_1/c$, $Z = 4$, with $a = 8.946(8)$, $b = 14.504(13)$, $c = 18.029(17)$ Å, $\beta = 92.66(9)°$. Crystals of (II) are monoclinic, space group $P2_1/a$, $Z = 4$, with $a = 17.349(13)$, $b = 12.151(10)$, $c = 12.295(12)$ Å, $\beta = 110.61(9)°$. The two structures were solved by Patterson and Fourier methods from 1 531 (I) and 1 473 (II) independent reflections collected by counter methods and refined to R 0.090 (I) and 0.077 (II). In both structures the metal atoms have distorted pentagonal bipyramidal environments with the isothiocyanate ligands in axial positions and the five nitrogen atoms of the macrocycle in equatorial positions. The Fe–N bond lengths and the conformation of the girdles are different in (I) and (II) as a consequence of the different ring sizes. The perchlorate anion in (I) is disordered.

IN Part I [1] the template synthesis of the first pentagonal bipyramidal complexes of iron(III) with a planar quinquedentate macrocyclic ligand (B) were described. The co-ordination geometry in the complexes $[Fe(B)X_2]ClO_4$ (X = halide or pseudohalide) was established on the basis of various physical properties [1,2] and confirmed in the case of one member of the series, $[Fe(B)(NCS)_2]$-ClO_4, by a preliminary single-crystal *X*-ray study.[3] This showed refinement to R 0.16 before an adequate model for the disordered perchlorate group had been obtained. However, the analysis was sufficient to establish the planarity of the macrocycle and the (approximate) local D_{5h} symmetry around the metal. More recently, Alcock *et al.*[4] and Lindoy and Busch [5] have reported a number of manganese(II), zinc(II), and cadmium(II) complexes of related quinquedentate complexes of related macrocycles having N_5,[4] N_3O_2,[4] or N_3S_2 [4,5] donor sets. From an *X*-ray structure determination the stereochemistry of one of these, $Mn(N_5)$-$(ClO_4)_2$, was also shown to be approximately pentagonal bipyramidal.[4] Wester and Palenik have determined the



(B) $n = 2$, (C) $n = 3$

structures of iron(II), cobalt(II), zinc(II), nickel(II), and copper(II) complexes with ligands having N_3O_2 donor sets and these are also pentagonal bipyramids with water molecules and/or chlorine atoms in axial positions.[6,7]

[1] Part I, S. M. Nelson and D. H. Busch, *Inorg. Chem.*, 1969, **8**, 1859.
[2] S. M. Nelson, P. Bryan, and D. H. Busch, *Chem. Comm.*, 1966, 641.
[3] E. Fleischer and S. Hawkinson, *J. Amer. Chem. Soc.*, 1967, **89**, 720.
[4] N. W. Alcock, D. C. Liles, M. McPartlin, and P. A. Tasker, *J.C.S. Chem. Comm.*, 1974, 727.
[5] L. F. Lindoy and D. H. Busch, *Inorg. Chem.*, 1974, **13**, 2494.
[6] D. Wester and G. J. Palenik, *J. Amer. Chem. Soc.*, 1973, **95**, 6505.
[7] D. Wester and G. J. Palenik, *J. Amer. Chem. Soc.*, 1974, **96**, 7565.

Complexes of this type are of interest, first, because of the rarity of seven-co-ordination in the first row of the transition metals, and secondly, because of the structural similarity to many naturally occurring macrocycles, yet with the difference that the equatorial macrocycle is quinque- rather than quadri-dentate. Aspects of particular interest to us are (i) the capacity of different metal ions to accommodate to a pentagonal bipyramidal geometry, (ii) the ways in which multidentate macrocycles of varying conformational flexibility may respond to the stereochemical preferences of different metal ions, and (iii) the consequence of unusual geometry for the physical and chemical properties of the metal.

We have recently extended the investigation to the synthesis of complexes of metal ions other than Fe^{3+} and to other potentially quinquedentate macrocycles varying in ring size, flexibility, and nature of donor atoms.[8] Among the new compounds prepared are the complexes $[Fe(C)X_2]Y$ of the 16-membered macrocycle (C) having one more methylene group than (B). These compounds were studied as part of an investigation of the effect of the nature of the central metal and ring size on macrocycle conformation. We now describe the properties of this series of complexes and show them to have structures similar to those of the (B) series. We also report the results of single-crystal *X*-ray structure determinations of (II) $[Fe(C)(NCS)_2]ClO_4$ and (I) $[Fe(B)(NCS)_2]ClO_4$.* A redetermination of the structure of the latter compound was considered necessary in order to permit a comparison of molecular dimensions with those of $[Fe(C)(NCS)_2]ClO_4$ and of the new pentagonal bipyramidal iron(II) complexes $[Fe(B)(NCS)_2]$ and $[Fe(C)(NCS)_2]$ [8] whose structures will be described in this series.

* Systematic names: (I) {2,13-dimethyl-3,6,9,12,18-penta-azabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene}di-isothiocyanatoiron(III) perchlorate: (II) {2,14-dimethyl-3,6,10,13,19-penta-azabicyclo[13.3.1]nonadeca-1(19),2,13,15,17-pentaene}di-isothiocyanatoiron(III) perchlorate.

RESULTS AND DISCUSSION

Synthesis and Properties of $[Fe(C)X_2]Y$ *Complexes*.—Analytical data are given in Table 1. The complexes were prepared by Schiff-base condensation in equimolar proportions of diacetylpyridine with 1,9-diamino-3,7-diazanonane in the presence of $FeCl_2,4H_2O$ in methanol. Digestion in air at 40 °C for at least 8 h, followed by treatment with concentrated HCl and $FeCl_3$, led to the isolation of $[Fe(C)Cl_2]FeCl_4$, the starting material for the preparation of most of the derivatives described here (see Experimental section). The complexes are stable in the solid state and in solution. They are only slowly attacked in acid solutions of moderate concentration. They are thermally very stable, melting with decomposition only at *ca.* ⩾ 200 °C. Depending on the nature of the anion they have varying solubility in 1,2-dichloroethane, acetone, nitromethane, acetonitrile, alcohols, and water.

When account is taken of the variations in the nature of the co-ordinated and unco-ordinated anions X and Y the i.r. spectra of the complexes (4 000—250 cm^{-1}) are virtually identical suggesting a common structural arrangement for them all. The spectra are also similar in important respects to those of the (B) series of com-

TABLE 1

Analytical data for the $[Fe(C)X_2]Y$ complexes

Complex	Colour	Found (%) C	H	N	Cl	Calc. (%) C	H	N	Cl
$[Fe(C)Cl_2]ClO_4$	Yellow	37.5	4.7	13.6		37.4	4.9	13.6	
$[Fe(C)Cl_2]PF_6$	Yellow	34.2	4.4	12.3	12.6	34.4	4.5	12.5	12.7
$[Fe(C)Cl_2]BPh_4$	Yellow	65.8	6.4	9.3	9.5	65.5	6.2	9.6	9.7
$[Fe(C)Cl_2]FeCl_4$	Yellow	31.4	4.1	11.4	34.6	31.4	4.1	11.5	34.8
$[Fe(C)Br_2]ClO_4$	Orange	31.9	4.1	11.5		31.9	4.2	11.6	
$[Fe(C)Br_2]FeBr_4$	Orange-red	21.6	2.9	8.0	54.7 [a]	21.9	2.9	8.0	54.6 [a]
$[Fe(C)(NCS)_2]ClO_4$	Red	38.7	4.6	17.3		38.7	4.5	17.6	
$[Fe(C)(N_3)_2]ClO_4$	Red	36.3	4.8	29.2		36.5	4.8	29.3	

[a] Br analysis.

TABLE 2

Magnetic, electric conductance, and i.r. spectral data for the $[Fe(C)X_2]Y$ complexes

Complex	μ/B.M.[a]	Λ/Ω⁻¹ cm² [b] MeNO₂	MeCN	H₂O	ν/cm⁻¹ N–H	C=N	Fe–X	Y
$[Fe(C)Cl_2]ClO_4$	5.92	103	165	446	3 260	1 662	319	1 085, 620
$[Fe(C)Cl_2]PF_6$					3 240	1 658	318	890, 560
$[Fe(C)Cl_2]BPh_4$		73			3 230	1 658	318	732, 705
$[Fe(C)Cl_2]FeCl_4$	5.92		161		3 240, 3 222	1 657	318	385
$[Fe(C)Br_2]ClO_4$	5.92	102	161	573	3 235	1 662	Below 250	1 085, 620
$[Fe(C)Br_2]FeBr_4$			149		3 230	1 659	Below 250	288
$[Fe(C)(NCS)_2]ClO_4$	5.92	101	167	351	3 275, 3 240	1 660	338 [c]	1 088, 622
$[Fe(C)(N_3)_2]ClO_4$	5.93	102	167	167	3 365, 3 300sp,[d] 3 240	1 658	410, 390 [c]	1 092, 622

[a] ±0.03 B.M., 85—300 K. [b] 10^{-3}M-solutions. [c] Fe–N stretch. [d] sp = sharp.

[8] M. G. B. Drew, A. H. bin Othman, W. E. Hill, P. D. A. McIlroy, and S. M. Nelson, *Inorg. Chim. Acta*, 1975, **12**, L25.

plexes.[1] The absence of any absorption at *ca.* 1 700 cm^{-1} attested to the absence of any unreacted keto-groups. Important features common to all the spectra are bands at 1 660s cm^{-1} attributable to the imino-linkages and at *ca.* 3 240m cm^{-1} to the secondary-amino-function. In two of the spectra two bands occur in the N–H stretch region while in another a third weak sharp band is present. In the absence of other information these observations might be considered evidence for the presence of unreacted primary-amino-groups. However

TABLE 3

Electronic spectra for the $[Fe(C)X_2]Y$ complexes

Complex	State	Band maxima in 10^3 cm^{-1}; (ε_M for solutions in parentheses)
$[Fe(C)Cl_2]ClO_4$	Mull	27.2
	$C_2H_4Cl_2$	25.2 (1 800)
	H_2O	46.7 (29 000), *ca.* 41.7sh, 36.1 (9 000)
$[Fe(C)Cl_2]PF_6$	Mull	27.1
$[Fe(C)Cl_2]FeCl_4$	Mull	*ca.* 27.0, 25.2
$[Fe(C)Br_2]ClO_4$	Mull	27.9, 21.6
	$C_2H_4Cl_2$	28.2sh, 21.6 (4 700)
	$MeNO_2$	21.5 (5 100)
	H_2O	46.7sh, *ca.* 41.7sh, 35.6 (10 400)
$[Fe(C)Br_2]FeBr_4$	Mull	*ca.* 28.0, *ca.* 24.5, 20.8
$[Fe(C)(NCS)_2]ClO_4$	Mull	19.2
	$C_2H_4Cl_2$	18.9 (12 800)
	$MeNO_2$	19.8 (14 600)
	H_2O	46.5 (34 200), *ca.* 41.7sh, 35.6 (10 200), 21.2 (2 500) [a]
$[Fe(C)(N_3)_2]ClO_4$	Mull	19.8
	$C_2H_4Cl_2$	19.7 (5 200)
	$MeNO_2$	20.2 (7 200)
	H_2O	46.7 (29 600), *ca.* 41.7sh, 35.6 (10 000), 21.1 (3 400) [a]

[a] These extinction coefficients are concentration-dependent; quoted values refer to 10^{-3}M-solutions; sh = shoulder.

this interpretation is untenable in the context of the other physical properties and of the crystal-structure determinations (see later). Variations in the spectra in this region are therefore attributed to variations in the nature and extent of hydrogen bonding of the secondary-amine groups. The i.r. bands assigned to X and Y (Table 2) are in accordance with the formulation of the complexes as complex salts, $[Fe(C)X_2]Y$. Thus, the number and positions of the spectral bands of ClO_4^-, PF_6^-, BPh_4^-, and $FeCl_4^-$ are precisely as expected from these ions in the unco-ordinated state.[9] A comparison of the different spectra, together with reference to spectra of related complexes,[10] allowed assignment of Fe–Cl, Fe–N(NCS), and Fe–N(N_3) to the medium intensity absorptions at **318** and **338**, and at **410** and **390** cm^{-1}. Terminal co-ordination of the azido-group is evidenced by the occurrence of $\nu_s(N_3)$ as a medium-to-strong band at 1 333 cm^{-1}, $\nu_{as}(N_3)$ occurring as a split band at 2 063 and 2 052 cm^{-1}.[11] The occurrence of ν_{as}(NCS) at 2 030 cm^{-1} is consistent with the nitrogen-co-ordination mode of this ion known from the structure determination. The symmetric (mainly C=S) stretch of the co-ordinated thiocyanate ion could not be assigned because of overlapping ligand absorption in the 750—850 cm^{-1} region.

The magnetic data (Table 2) characterise all the complexes as high spin. The measured moments are in remarkably good agreement with the spin-only value

TABLE 4

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

Atom	*x*	*y*	*z*
Fe	2 506(3)	2 291(2)	4 338(1)
S(1)	6 261(6)	3 058(4)	6 156(3)
S(2)	−0 951(9)	1 199(4)	2 505(3)
N(1)	4 262(16)	2 536(9)	5 021(9)
N(2)	0 746(16)	2 007(10)	3 644(7)
C(1)	5 087(19)	2 775(12)	5 474(10)
C(2)	0 085(21)	1 691(11)	3 170(9)
N(3)	3 607(15)	3 086(10)	3 470(8)
N(6)	3 783(15)	1 297(9)	3 640(6)
N(9)	2 402(14)	0 895(9)	4 807(7)
N(12)	1 129(15)	2 287(11)	5 349(7)
N(15)	1 622(17)	3 710(9)	4 481(8)
C(4)	3 741(23)	2 590(15)	2 791(11)
C(5)	4 463(20)	1 675(13)	2 986(9)
C(7)	3 899(18)	0 452(12)	3 828(9)
C(8)	3 101(18)	0 179(10)	4 470(9)
C(10)	1 661(18)	0 776(11)	5 423(8)
C(11)	0 886(18)	1 553(12)	5 732(8)
C(13)	0 467(22)	3 189(13)	5 579(10)
C(14)	1 437(23)	3 941(12)	5 235(10)
C(16)	2 573(22)	4 376(14)	4 080(14)
C(18)	2 855(25)	4 022(14)	3 358(13)
C(20)	4 740(24)	−0 257(14)	3 377(12)
C(21)	3 036(25)	−0 708(12)	4 790(12)
C(22)	2 291(25)	−0 838(15)	5 392(12)
C(23)	1 509(22)	−0 124(15)	5 718(11)
C(24)	0 043(21)	1 501(14)	6 419(10)
Cl	7 572(6)	3 933(4)	3 489(3)
O(1A)	7 001(38)	3 043(24)	3 731(20)
O(2A)	8 678(56)	4 060(36)	4 071(29)
O(3A)	6 689(42)	4 750(27)	3 382(21)
O(4A)	8 554(69)	3 986(43)	2 941(35)
O(1B)	7 550(36)	3 417(21)	4 214(17)
O(2B)	6 314(40)	4 420(25)	3 607(20)
O(3B)	7 452(36)	3 481(21)	2 794(17)
O(4B)	8 994(27)	4 263(17)	3 509(16)
H(3)	4 595	3 165	3 690
H(41)	2 670	2 440	2 569
H(42)	4 413	2 973	2 445
H(51)	4 430	1 236	2 545
H(52)	5 704	1 833	3 147
H(131)	−0 665	3 198	5 364
H(132)	0 501	3 192	6 180
H(141)	0 840	4 590	5 304
H(142)	2 494	3 988	5 565
H(15)	0 695	3 699	0 775
H(161)	2 025	5 058	4 087
H(162)	3 645	4 510	4 443
H(181)	1 763	3 950	3 092
H(182)	3 527	4 493	3 085
H(21)	3 517	−1 312	4 501
H(22)	2 286	−1 515	5 656
H(23)	0 786	−0 215	6 186

of 5.92 B.M. Moreover, they are temperature inde pendent over the range 80—300 K as required for high-spin d^5 compounds having orbitally non-degenerate ground states.[12]

Electrical conductance measurements in different solvents confirm the conclusions derived from the i.r. spectra, *viz.* that the X^- anions are co-ordinated and the Y^- anions are not. In 10^{-3}M-solutions of nitromethane

[9] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091; K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' Wiley Interscience, New York, 1963.

[10] D. M. Adams, 'Metal–Ligand and Related Vibrations,' Arnold, London, 1967.

[11] S. M. Nelson and J. Nelson, *J. Chem. Soc. (A)*, 1969, 1557.

[12] B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, 1964, **6**, 37.

and acetonitrile, the molar conductances fall towards the higher end of the ranges expected[13] for univalent electrolyte behaviour in these solvents (Table 2). Measurements on more dilute solutions of selected complexes suggested some ionic dissociation of the complex cation. On the other hand, data for 10^{-3}-M aqueous solutions indicate extensive dissociation.

Good agreement between the solid-state spectra and spectra of solutions in nitromethane and/or 1,2-dichloroethane was observed for most of the compounds (Table 3). Where slight discrepancies occur these can be accounted for in terms of a small degree of ionic dissociation. In the case of aqueous solutions, however, the 'colour' band is virtually absent in the spectra of the chloro- and bromo-complexes and present only in diminished intensity in the spectra of the thiocyanate and azide. All of these spectra displayed a common spectrum in the u.v. region. Addition of NaX to these solutions partially restored the 'colour' band. These observations are consistent with the occurrence of the dissociation equilibrium:

$$[Fe(C)X_2]^+ + 2H_2O \rightleftharpoons [Fe(C)(H_2O)_2]^{3+} + 2X^-$$

The high intensities and the relative positions of the colour bands as the nature of X is varied point to a ligand-to-metal charge transfer origin. They occur at slightly lower energies than in corresponding complexes of macrocycle (B).[1]

Mössbauer spectra of the complexes are currently being studied and have so far been shown to display temperature-dependent paramagnetic relaxation effects similar to those previously found[14] for the (B) series of complexes.

The foregoing data point to a common seven-co-ordinate structure for all the complexes of macrocycle (C). The *X*-ray structure determination of the complex $[Fe(C)(NCS)_2]ClO_4$ (II) further defines the structure as being approximately pentagonal bipyramidal.

CRYSTAL AND MOLECULAR STRUCTURE DETERMINATIONS

Crystal Data.—(*a*) For $[Fe(B)(NCS)_2]ClO_4$, $[C_{17}H_{23}N_7S_2ClO_4Fe$, complex (I)]. $M = 544.8$, Monoclinic, $a = 8.946(8)$, $b = 14.504(13)$, $c = 18.029(17)$ Å, $\beta = 92.66(9)°$, $D_c = 1.55$, $Z = 4$, $D_m = 1.53(2)$, $U = 2\,336.8$ Å^3. $F(000) = 1\,124$. Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ-(Mo-K_α) = 9.6 cm.$^{-1}$ Space group $P2_1/c$ from systematic absences: $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$.

(*b*) For $[FeC(NCS)_2]ClO_4$ $[C_{18}H_{25}N_7S_2ClO_4Fe$, complex (II)]. $M = 558.8$, Monoclinic, $a = 17.349(13)$, $b = 12.151(10)$, $c = 12.295(12)$ Å, $\beta = 110.61(9)°$, $D_c = 1.53$, $Z = 4$, $D_m = 1.50(2)$, $U = 2\,426.1$ Å^3. $F(000) = 1\,156$. μ(Mo-K_α) = 9.4 cm^{-1}. Space group $P2_1/a$ from systematic absences: $h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$.

Crystals with dimensions *ca.* 0.15 × 0.20 × 1.0 mm (I) and 0.15 × 0.30 × 1.00 mm (II) were mounted with the a^* (I) and the b axis (II) parallel to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and dimensions. It was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered molybdenum *X*-radiation was used, and the stationary-crystal–

TABLE 5

Anisotropic thermal parameters (× 10^3) for (I), with estimated standard deviations in parentheses [a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	48.6(14)	33.2(11)	36.7(12)	02.0(13)	−09.2(10)	−00.3(12)
S(1)	76(4)	68(3)	61(3)	−07(3)	−18(3)	−19(3)
S(2)	174(7)	87(4)	41(3)	−54(4)	−28(3)	08(3)
N(1)	62(10)	47(10)	77(10)	−05(7)	−29(8)	01(8)
N(2)	81(11)	67(10)	29(7)	−15(8)	−13(7)	05(7)
C(1)	46(11)	42(10)	58(11)	11(9)	01(9)	11(9)
C(2)	87(14)	31(10)	31(9)	−16(10)	−11(10)	06(7)
N(3)	52(9)	68(10)	66(10)	8(7)	−04(7)	19(8)
N(6)	65(10)	46(8)	40(7)	8(7)	−1(7)	−1(7)
N(9)	63(8)	44(8)	48(8)	1(7)	−27(7)	5(7)
N(12)	59(9)	84(10)	34(7)	10(8)	4(6)	−3(8)
N(15)	76(10)	47(9)	62(9)	05(8)	−10(8)	−00(7)
C(4)	88(15)	83(16)	64(12)	23(13)	32(11)	25(11)
C(5)	71(13)	71(14)	36(11)	06(11)	18(9)	−09(9)
C(7)	45(11)	59(11)	43(10)	03(9)	−08(8)	−05(9)
C(8)	60(12)	30(9)	41(10)	09(8)	−12(8)	−09(8)
C(10)	52(11)	41(10)	34(9)	−05(9)	−05(8)	12(8)
C(11)	54(12)	60(12)	28(8)	11(9)	−10(8)	02(8)
C(13)	86(14)	58(13)	56(12)	31(12)	−14(10)	−05(10)
C(14)	88(15)	39(12)	61(12)	20(10)	−24(11)	−09(9)
C(16)	66(14)	57(14)	119(20)	13(12)	−02(14)	35(13)
C(18)	101(18)	54(14)	88(16)	00(12)	03(14)	38(12)
C(20)	93(17)	72(15)	86(15)	26(12)	−03(13)	−39(13)
C(21)	109(18)	28(10)	72(14)	10(11)	−35(13)	−06(10)
C(22)	87(16)	58(14)	64(14)	−11(12)	−23(13)	12(11)
C(23)	66(14)	73(15)	75(14)	−17(12)	−11(11)	25(12)
C(24)	69(14)	96(16)	50(11)	−06(12)	07(10)	−03(11)
Cl	52(3)	93(4)	110(4)	06(3)	−17(3)	−31(4)

[a] Isotropic temperature factors for oxygen atoms: O(1A) 109(11), O(2A) 167(17), O(3A) 108(13), O(4A) 211(23); O(1B) 221(24), O(2B) 97(12), O(3B) 94(9), O(4B) 62(7).

[13] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.
[14] F. A. Deeney and S. M. Nelson, *J. Phys. Chem. Solids*, 1973, **34**, 277.

stationary-counter method employed to measure 3 259 (I) and 2 428 (II) independent reflections with $2\theta \leqslant 45°$ (I) and $\leqslant 40°$ (II); backgrounds were taken for those reflections whose counts were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of 2θ. Several standard reflections monitored during the course of both experiments showed no significant changes in intensity. No absorption or extinction corrections were applied. The standard deviation $\sigma(I)$ of the reflections was taken to be $[I + 2E + (0.03I^2)]^{\frac{1}{2}}$, where E is the estimated background of the reflection. 1 537 (I) and 1 473 (II) reflections with $I > \sigma(I)$ were used in subsequent calculations.

The positions of the iron atoms were determined from a Patterson function and Fourier syntheses were then calculated to determine the positions of the remaining atoms. Both structures were refined by full-matrix least-squares, but with three blocks of approximately equal size. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of F_o, and $\sin\theta/\lambda$ was $\sqrt{w} = 1$ for $F_o < F^*$ and $\sqrt{w} = F^*/F_o$ for $F_o > F^*$. F^* was 60 in (I) and 65 in (II). Calculations were made on a CDC 7 600 computer at the University of London Computer Centre using the programs described in ref. 15. Atomic scattering factors for iron, sulphur, carbon, nitrogen, chlorine, and oxygen were taken from ref. 16 as were the corrections for the real and imaginary part of the anomalous dispersion for iron and sulphur atoms. Hydrogen atom scattering factors were taken from ref. 17. The anisotropic thermal parameters are defined as $\exp -2\pi^2 \sum_i \sum_j h_i h_j b_i b_j U_{ij}$; $i, j = 1, 2, 3$ where b_i is the i^{th} reciprocal cell parameter. The isotropic thermal parameter is $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)$. In both (I) and (II) non-methyl hydrogen atom positions were calculated assuming tetrahedral or trigonal positions; these corresponded to positive regions in the difference-Fourier map and were included in the structure-factor calculation but not refined. In (I) a difference Fourier showed that the perchlorate ion was disordered, as is so often found for this anion. The chlorine atom was ordered but was surrounded by eight peaks, some of which were quite broad, representing two different tetrahedra of oxygen atoms. These eight oxygen positions were given half-occupancy and included in the refinement with isotropic thermal parameters. The O–Cl–O angles ranged between 95 and 125° and with Cl–O bond lengths in the expected region, and this was therefore considered to be a successful treatment of the disorder, although the large spread of thermal parameters suggest that it is not ideal. All other atoms were refined anisotropically to R 0.090 for the 1 531 observed reflections. In (II), the perchlorate anion was ordered and refinement with all atoms anisotropic gave R 0.077 for 1 473 non-zero reflections. For both (I) and (II), subsequent difference-Fourier maps showed no significant peaks; in the final cycles of refinement no shift was $>0.12\sigma$. The reflections given zero weight showed no large discrepancies. Final positional and thermal parameters for (I) are given in Tables 4 and 5. Final positional and thermal parameters for (II) are given in Tables 6 and 7. Molecular dimensions for the two structures are compared in Table 8 while Table 9 summarises the dihedral angles in the three saturated chelate rings of the complexes. Observed and calculated structure factors for (I) and (II) together with lists of shortest intermolecular contacts are listed in Supplementary Publication No. SUP 21 448 (14 pp., 1 microfiche).*

TABLE 6

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

Atom	x	y	z
Fe	2 169(1)	1 371(2)	2 634(2)
S(1)	2 137(3)	1 707(4)	−1 025(4)
S(2)	0 865(3)	1 394(5)	5 212(5)
N(1)	2 335(7)	0 884(11)	1 158(12)
N(2)	1 932(8)	1 836(10)	4 041(11)
C(1)	2 247(9)	1 230(12)	0 201(14)
C(2)	1 467(11)	1 663(13)	4 575(13)
N(3)	3 148(8)	0 065(10)	3 559(10)
N(6)	1 440(8)	−0 109(10)	2 766(11)
N(9)	0 832(6)	1 547(9)	1 523(8)
N(12)	1 948(7)	3 025(9)	1 800(10)
N(15)	3 351(17)	2 335(17)	3 466(10)
C(4)	2 724(12)	−1 042(13)	3 382(14)
C(5)	1 942(12)	−0 941(12)	3 602(14)
C(7)	0 651(10)	−0 146(15)	2 295(14)
C(8)	0 306(9)	0 773(13)	1 562(12)
C(10)	0 619(9)	2 450(13)	0 864(12)
C(11)	1 297(9)	3 271(13)	0 972(13)
C(13)	2 636(10)	3 785(13)	2 095(14)
C(14)	3 154(9)	3 511(14)	3 308(14)
C(16)	4 021(11)	2 063(15)	3 029(15)
C(17)	4 429(10)	0 967(17)	3 549(15)
C(18)	3 862(11)	0 012(17)	3 176(16)
C(20)	0 107(12)	−0 997(15)	2 553(19)
C(21)	−0 507(10)	0 858(17)	0 796(17)
C(22)	−0 778(11)	1 733(21)	0 092(15)
C(23)	−0 220(12)	2 567(18)	0 092(15)
C(24)	1 121(12)	4 269(14)	0 213(15)
Cl	3 814(3)	0 843(4)	6 843(4)
O(1)	3 423(9)	−0 097(13)	6 221(13)
O(2)	4 516(9)	0 547(14)	7 761(11)
O(3)	3 292(9)	1 386(14)	7 288(13)
O(4)	4 040(8)	1 500(11)	6 067(12)
H(3)	3 314	0 250	4 347
H(41)	3 124	−1 658	3 958
H(42)	2 600	−1 337	2 482
H(51)	2 102	−0 643	4 476
H(52)	1 646	−1 708	3 483
H(131)	2 441	4 642	2 013
H(132)	3 003	3 671	1 526
H(141)	2 850	3 795	3 894
H(142)	3 749	3 991	3 559
H(15)	3 510	2 119	4 256
H(161)	4 475	2 735	3 254
H(162)	3 779	2 005	2 076
H(171)	4 649	1 041	4 490
H(172)	4 972	0 837	3 295
H(181)	4 223	−0 729	3 545
H(182)	3 663	−0 041	2 242
H(21)	−0 959	0 185	0 747
H(22)	−1 396	1 767	−0 533
H(23)	−0 418	3 282	−0 497

DISCUSSION

The structures of the cation of both complexes (I) and (II) are shown in Figures 1 and 2 together with the atomic numbering scheme; unit-cell contents are illustrated in Figures 3 and 4. Both cations are numbered in an equivalent manner with (II) having an additional $-CH_2-$ group at C(17). The geometry of the co-ordination spheres of both cations is pentagonal bipyramidal

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[15] ' *X*-Ray ' system of programs, ed. J. M. Stewart, University of Maryland Technical Report, TR 67 58, 1972.

[16] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

[17] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

with the five macrocycle nitrogen atoms lying approximately in the equatorial plane and the thiocyanate nitrogen atoms occupying axial positions. The axial Fe^{III}–N distances are equivalent in (I) [1.982(15) and 2.008(14)] and in (II) [2.023(16) and 1.996(16) Å].

TABLE 7

Anisotropic thermal parameters ($\times 10^3$) for (II), with estimated standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	44.9(13)	37.2(13)	38.6(13)	02.9(11)	08.9(10)	02.1(11)
S(1)	101(4)	83(4)	51(3)	−12(3)	24(3)	04(3)
S(2)	83(4)	99(4)	105(4)	9(4)	59(3)	6(4)
N(1)	52(8)	60(9)	64(9)	9(7)	4(7)	−9(8)
N(2)	65(9)	51(9)	59(9)	5(7)	4(7)	2(7)
C(1)	50(10)	34(9)	41(11)	13(8)	7(8)	−6(8)
C(2)	56(11)	53(12)	36(10)	−13(9)	−2(8)	−8(8)
N(3)	78(8)	55(8)	54(8)	10(7)	−4(6)	13(7)
N(6)	82(9)	46(8)	74(8)	−2(7)	32(7)	−3(7)
N(9)	59(8)	56(8)	31(6)	11(6)	12(6)	7(6)
N(12)	60(8)	36(7)	55(8)	3(6)	−1(6)	−1(6)
N(15)	50(8)	56(9)	67(9)	6(7)	14(7)	−9(7)
C(4)	115(16)	38(1)	53(11)	33(11)	21(11)	18(8)
C(5)	101(15)	30(10)	66(12)	8(10)	25(11)	9(9)
C(7)	61(11)	70(13)	52(11)	−12(10)	12(8)	−1(10)
C(8)	49(10)	57(11)	41(9)	−14(9)	16(8)	−1(9)
C(10)	53(10)	55(10)	37(9)	15(9)	9(8)	−2(8)
C(11)	57(11)	34(9)	50(10)	7(8)	10(8)	−1(7)
C(13)	75(12)	40(11)	71(13)	−3(9)	19(10)	6(9)
C(14)	54(11)	52(12)	69(12)	−5(9)	9(9)	−17(10)
C(16)	59(13)	62(13)	78(13)	−0(10)	19(10)	02(10)
C(17)	49(11)	99(17)	66(12)	26(12)	14(9)	00(11)
C(18)	68(13)	88(17)	77(13)	30(12)	23(11)	06(11)
C(20)	91(14)	65(14)	136(18)	−41(12)	63(13)	03(12)
C(21)	47(11)	79(14)	96(15)	08(11)	31(11)	−21(12)
C(22)	39(11)	103(19)	102(17)	08(12)	09(11)	−21(14)
C(23)	65(14)	103(17)	55(12)	46(13)	−3(10)	05(11)
C(24)	108(16)	54(12)	70(13)	15(11)	10(11)	26(10)
Cl	57(3)	60(3)	52(3)	05(3)	16(2)	−2(2)
O(1)	130(13)	116(12)	120(12)	−56(11)	34(10)	−51(11)
O(2)	115(12)	147(14)	65(9)	34(10)	−10(8)	06(9)
O(3)	132(12)	134(13)	132(13)	41(11)	91(11)	31(11)
O(4)	115(10)	79(9)	104(10)	−28(8)	65(8)	−12(8)

There is a striking difference in the remaining dimensions of the thiocyanate ions, Fe–N–C angles being 167.2(14) and 159.1(15)° in (I) and 139.7(12) and 142.4(11)° in (II). Variations in M–N–C angles between

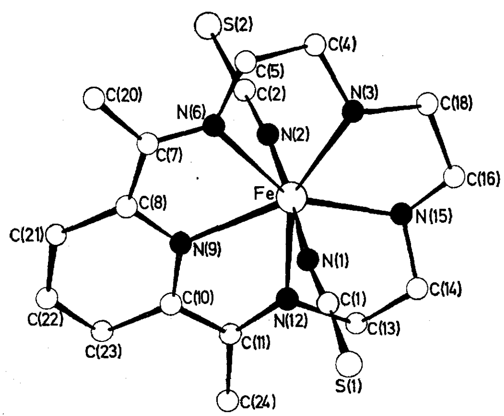


FIGURE 1 Complex (I)

140 and 180° are often found in metal isothiocyanates [18] but the *ca.* 140° found in (II) is among the smallest angles found, comparable with Ni–N–C 140° in Ni(ethylenediamine)$_2$(NCS)$_2$,[19] but larger than the value of 129° found in Cu(*NN'*-dimethylethylenediamine)$_2$(NCS)$_2$.[20] These latter molecules have crystallographically imposed centres of symmetry so it is noteworthy that in (II) the two M–N–C angles are similar, since they have different environments. It has been suggested [21,22] that inter-

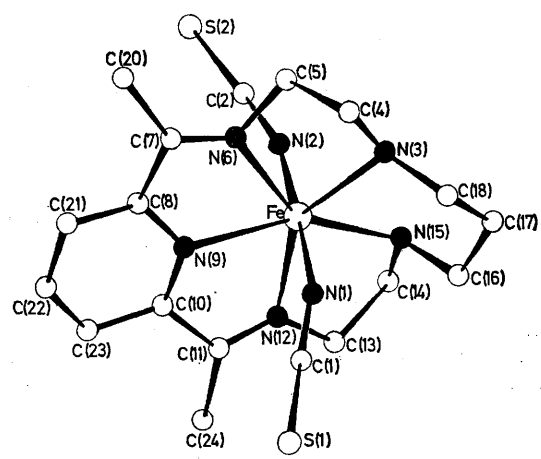


FIGURE 2 Complex (II)

molecular forces affect the M–N–C bond angles in some structures, but this is often difficult to prove, as in the

[18] A. C. Hazell, *J. Chem. Soc.*, 1963, 5745.
[19] B. W. Brown and E. C. Lingafelter, *Acta Cryst.*, 1963, **16**, 753.
[20] J. Korvenranta and A. Pajunen, *Suomen Kem.*, 1970, **B43**, 119.
[21] J. R. Knox and K. Eriks, *Inorg. Chem.*, 1968, **7**, 84.
[22] D. V. Naik and W. R. Scheidt, *Inorg. Chem.*, 1973, **12**, 272.

TABLE 8

Molecular dimensions for (I) and (II), with estimated standard deviations in parentheses

(a) Distances (Å)	(I)	(II)
Fe–N(1)	1.982(15)	2.023(16)
Fe–N(2)	2.008(14)	1.996(16)
Fe–N(3)	2.212(15)	2.309(12)
Fe–N(6)	2.259(13)	2.237(13)
Fe–N(9)	2.198(13)	2.251(10)
Fe–N(12)	2.248(13)	2.228(11)
Fe–N(15)	2.224(15)	2.268(12)
N(1)–C(1)	1.13(2)	1.21(2)
N(2)–C(2)	1.12(2)	1.22(2)
C(1)–S(1)	1.63(2)	1.56(2)
C(2)–S(2)	1.64(2)	1.55(2)
N(3)–C(4)	1.43(3)	1.51(2)
C(4)–C(5)	1.51(3)	1.48(3)
C(5)–N(6)	1.46(2)	1.49(2)
N(6)–C(7)	1.27(2)	1.29(2)
C(7)–C(20)	1.53(3)	1.51(3)
C(7)–C(8)	1.44(2)	1.43(2)
C(8)–N(9)	1.37(2)	1.32(2)
N(9)–C(10)	1.33(2)	1.34(2)
C(8)–C(21)	1.41(2)	1.40(2)
C(21)–C(22)	1.31(3)	1.35(2)
C(22)–C(23)	1.40(3)	1.40(3)
C(23)–C(10)	1.42(3)	1.44(2)
C(10)–C(11)	1.45(2)	1.41(2)
C(11)–C(24)	1.48(2)	1.49(2)
C(11)–N(12)	1.29(2)	1.26(2)
N(12)–C(13)	1.50(2)	1.45(2)
C(13)–C(14)	1.54(3)	1.48(2)
C(14)–N(15)	1.42(2)	1.47(2)
N(15)–C(16)	1.50(3)	1.48(3)
C(16)–C(17)		1.54(3)
C(16)–C(18)	1.43(3)	
C(17)–C(18)		1.48(3)
C(18)–N(3)	1.52(3)	1.47(3)

(b) Angles (°)	(I)	(II)
N(1)–Fe–N(2)	178.4(6)	176.5(5)
N(1)–Fe–N(3)	88.8(6)	85.9(5)
N(1)–Fe–N(6)	93.1(5)	95.3(5)
N(1)–Fe–N(9)	88.5(5)	85.7(4)
N(1)–Fe–N(12)	86.9(6)	84.7(5)
N(1)–Fe–N(15)	92.2(5)	99.5(5)
N(2)–Fe–N(3)	91.6(5)	96.2(5)
N(2)–Fe–N(6)	85.6(5)	82.5(5)
N(2)–Fe–N(9)	90.3(5)	90.9(5)
N(2)–Fe–N(12)	93.5(4)	95.1(5)
N(2)–Fe–N(15)	89.4(6)	83.8(5)
N(3)–Fe–N(6)	71.6(5)	75.5(4)
N(3)–Fe–N(9)	141.3(5)	141.9(4)
N(3)–Fe–N(12)	148.7(6)	145.5(5)
N(3)–Fe–N(15)	76.8(5)	75.0(4)
N(6)–Fe–N(9)	70.0(5)	68.4(4)
N(6)–Fe–N(12)	139.6(5)	138.5(4)
N(6)–Fe–N(15)	147.9(5)	145.8(4)
N(9)–Fe–N(12)	69.6(5)	70.2(4)
N(9)–Fe–N(15)	141.8(4)	143.1(4)
N(12)–Fe–N(15)	72.4(6)	73.9(4)
Fe–N(1)–C(1)	167.4(14)	139.7(12)
Fe–N(2)–C(2)	159.1(15)	142.4(11)
N(1)–C(1)–S(1)	176.4(16)	178.6(14)
N(2)–C(2)–S(2)	176.7(17)	177.2(14)
Fe–N(3)–C(4)	113.6(12)	107.7(9)
Fe–N(3)–C(18)	110.5(11)	115.3(10)
C(4)–N(3)–C(18)	112.9(15)	109.7(14)
N(3)–C(4)–C(5)	107.1(15)	109.4(14)
C(4)–C(5)–N(6)	109.2(15)	106.4(15)
Fe–N(6)–C(5)	116.8(10)	112.8(10)
Fe–N(6)–C(7)	120.1(10)	122.4(11)
C(5)–N(6)–C(7)	123.1(14)	124.0(15)
N(6)–C(7)–C(8)	116.1(15)	113.5(15)
N(6)–C(7)–C(20)	122.7(15)	125.2(15)
C(8)–C(7)–C(20)	121.0(15)	121.0(14)
C(7)–C(8)–C(21)	127.5(16)	125.6(16)

TABLE 8 Continued)

(b) Angles (°)	(I)	(II)
C(7)–C(8)–N(9)	113.7(14)	116.0(12)
N(9)–C(8)–C(21)	118.7(15)	117.9(14)
Fe–N(9)–C(10)	118.2(10)	116.8(9)
Fe–N(9)–C(8)	119.9(10)	119.1(8)
C(10)–N(9)–C(8)	121.8(13)	124.0(11)
N(9)–C(10)–C(23)	119.5(15)	116.6(15)
C(11)–C(10)–C(23)	121.1(15)	124.6(15)
N(9)–C(10)–C(11)	119.1(15)	116.6(15)
C(8)–C(21)–C(22)	120.1(18)	122.2(18)
C(21)–C(22)–C(23)	121.6(18)	119.0(16)
C(22)–C(23)–C(10)	117.8(17)	117.9(17)
C(10)–C(11)–N(12)	109.9(14)	111.3(13)
C(10)–C(11)–C(24)	123.6(15)	119.9(12)
N(12)–C(11)–C(24)	126.4(16)	128.6(14)
Fe–N(12)–C(11)	123.2(12)	123.0(10)
Fe–N(12)–C(13)	117.3(11)	117.8(8)
C(11)–N(12)–C(13)	119.5(14)	118.4(12)
N(12)–C(13)–C(14)	105.6(15)	105.2(14)
C(13)–C(14)–N(15)	108.2(14)	112.5(13)
C(14)–N(15)–C(16)	113.9(15)	110.2(14)
Fe–N(15)–C(16)	109.2(11)	114.9(9)
Fe–N(15)–C(14)	112.8(11)	108.2(8)
N(15)–C(16)–C(1x) *	109.6(17)	110.3(16)
N(3)–C(18)–C(1x) †	107.1(17)	114.0(17)
C(16)–C(17)–C(18)		112.9(13)

* x is 8 in (I) and 7 in (II). † x is 6 in (I) and 7 in (II).

(c) Perchlorate geometry	$(I)_A$	$(I)_B$	(II)
Cl–O(1)	1.46(4)	1.42(3)	1.409(16)
Cl–O(2)	1.41(5)	1.51(7)	1.385(13)
Cl–O(3)	1.43(4)	1.35(4)	1.380(19)
Cl–O(4)	1.35(6)	1.36(3)	1.401(16)
O(1)–Cl–O(2)	98(2)	122(3)	110.5(9)
O(1)–Cl–O(3)	125(2)	111(2)	110.2(10)
O(1)–Cl–O(4)	121(3)	103(2)	106.8(9)
O(2)–Cl–O(3)	111(3)	94(3)	108.2(9)
O(2)–Cl–O(4)	94(3)	102(3)	109.1(9)
O(3)–Cl–O(4)	103(3)	127(3)	112.2(10)

TABLE 9

Dihedral angles (°) in the three saturated rings of (I) and (II)

	(I)	(II)
Fe–N(6)–C(5)–C(4)	−18.1	−44.1
N(6)–C(5)–C(4)–N(3)	43.6	59.2
C(5)–C(4)–N(3)–Fe	−51.8	−45.4
C(4)–N(3)–Fe–N(6)	32.1	15.8
N(3)–Fe–N(6)–C(5)	−6.2	15.1
Fe–N(12)–C(13)–C(14)	−22.3	−30.8
N(12)–C(13)–C(14)–N(15)	47.4	51.4
C(13)–C(14)–N(15)–Fe	−53.7	−47.9
C(14)–N(15)–Fe–N(12)	31.0	21.7
N(15)–Fe–N(12)–C(13)	−2.7	5.6
Fe–N(15)–C(16)–C(1x) *	45.3	−76.7
N(15)–C(16)–C(17)–C(18)		64.8
N(15)–C(16)–C(18)–N(3)	−57.8	
C(16)–C(17)–C(18)–N(3)		−63.2
C(1x)†–C(18)–N(3)–Fe	42.4	71.2
C(18)–N(3)–Fe–N(15)	−13.7	−58.9
N(3)–Fe–N(15)–C(16)	−15.6	62.7

* x is 8 in (I) and 7 in (II).
† x is 6 in (I) and (7) in (II).

present case. Consideration of intra- and inter-molecular contacts for the –NCS groups in (II) leads to no definite conclusion. Decreases of M–N–C angles from 180° are usually concomitant with decreases in C–S bond length and the data for (I) and (II) are consistent with this.

In (I) the macrocycle is approximately planar. The ten *cis*-angles involving N(1) and N(2) are all within 4.4

of 90° and least-squares planes calculations (Table 10) show that the maximum deviation of a contributing atom from the FeN_5 least-squares plane is 0.11 Å. The deviations from the plane of all atoms in the macrocycle N(3) and N(15) are respectively 0.11 and −0.10 Å from the plane. The nine carbon atoms numbered 7, 8, 10, 11, 20—24 are also close to the plane.

The Fe–N equatorial bond lengths are in the range

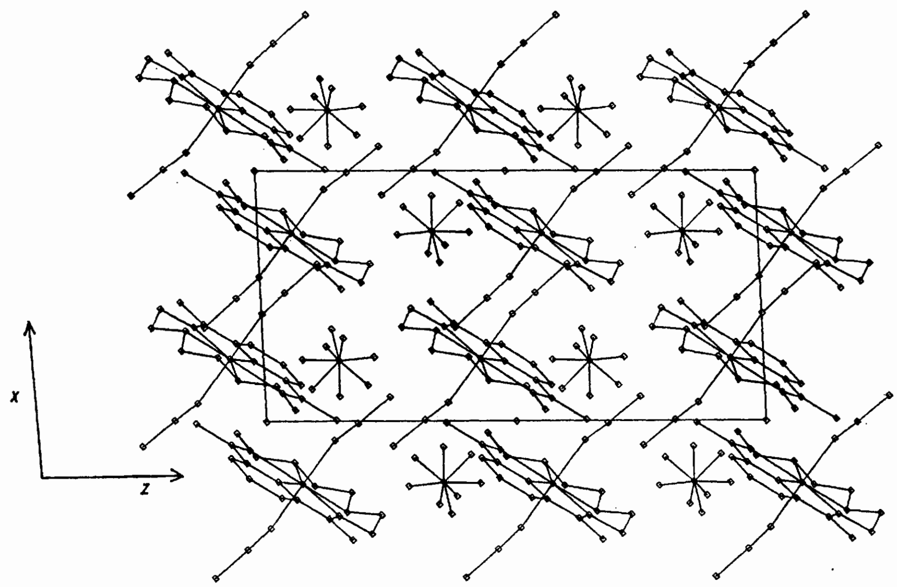


FIGURE 3 The unit cell of (I) in the *b* projection

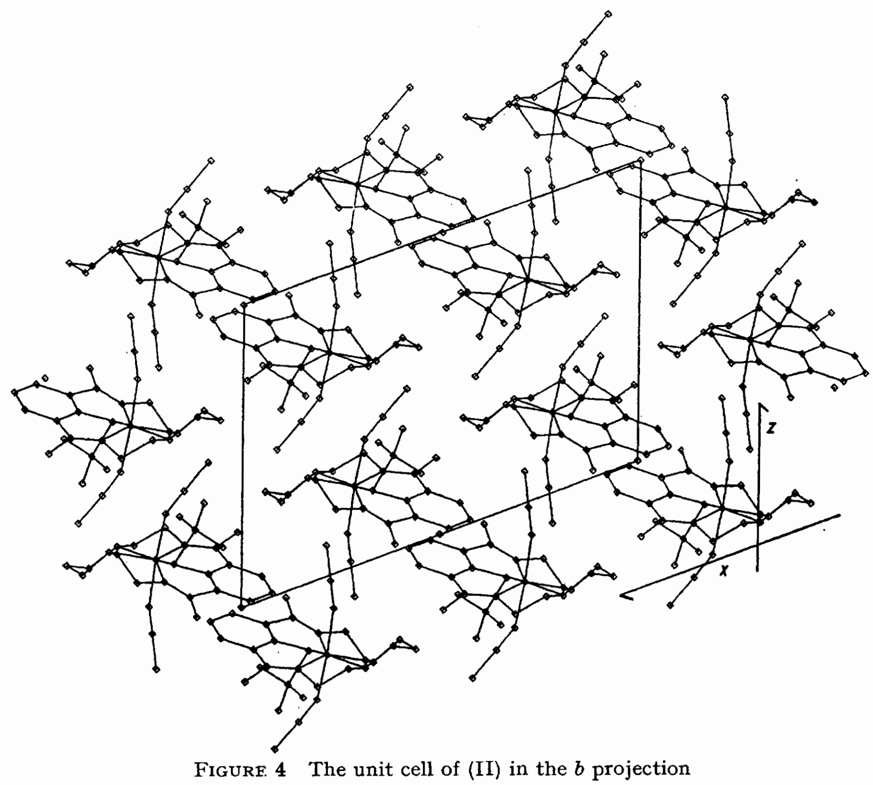


FIGURE 4 The unit cell of (II) in the *b* projection

follow a C_2 distortion, a well known way for the pentagonal bipyramid to accommodate bulky ligands.[23] The two-fold axis is coincident with the Fe–N(9) bond and the midpoint of the C(16)–C(18) bond. Thus 2.198(13)—2.257(13) Å, much longer than the Fe–N axial bonds as is usually found for pentagonal bipyramidal structures.[23] These lengths are much longer than the 2.06 (ref. 24) and 2.07 Å (ref. 25) found for

[23] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1974, 1579.
[24] D. F. Koenig, *Acta Cryst.*, 1965, **18**, 663.
[25] J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *J. Amer. Chem. Soc.*, 1965, **87**, 2312.

high-spin Fe^{III}–N bonds in porphyrins. However in these structures steric effects are reduced by the iron atom being 0.48 and 0.49 Å out of the porphyrin plane. This is not possible for (I) and (II) and the Fe–N bonds are longer. In (I) bond lengths follow the pattern Fe–N(9) < Fe–N(3),N(15) < Fe–N(6),N(12).

TABLE 10

Least-squares planes calculations for (I) and (II). Equations are in the form $Ax + By + Cz = D$, where x, y, z are the crystallographic fractional co-ordinates of the atoms. Distances (Å) of the relevant atoms from each plane are given in square brackets. Values for (I) precede those for (II)

Plane (1): Fe, N(1), C(1), S(1)

A	*B*	*C*	*D*
1.25	12.86	−8.06	−0.24
15.06	4.30	0.25	3.92

[Fe 0.00, −0.00; N(1) −0.02, 0.00; C(1) 0.03, −0.00; S(1) −0.01, 0.00; (I): N(6) −0.56, C(13) −0.10, C(5) 0.54, C(14) 1.27; (II): N(3) 0.93, N(12) 0.36, C(4) −0.18, C(11) −0.54]

Plane (2): Fe, N(2), C(2), S(2)

A	*B*	*C*	*D*
−3.08	−10.02	11.74	2.02
−8.14	8.48	−4.20	−1.71

[Fe −0.00, 0.00; N(2) −0.01, −0.00; C(2) 0.02, 0.00; S(2) −0.01, −0.00; (I): N(6) 0.22, C(7) −0.81, C(14) 0.27, C(13) −1.19]; (II): C(7) 0.09, C(14) 0.73, N(6) −0.72, N(15) −0.49]

Angles between planes (1)—(2) (I) 19.4, (II) 69.6°

Plane (3): Fe, N(3), N(6), N(9), N(12), N(15)

A	*B*	*C*	*D*
6.99	2.70	10.07	6.74
−8.73	3.76	11.46	1.65

[Fe 0.00, −0.01; N(3) −0.11, −0.29; N(6) 0.08, 0.22; N(9) −0.02, −0.05; N(12) −0.05, −0.15; N(15) 0.10, 0.28; C(7) 0.04, 0.36; C(8) 0.02, 0.16; C(10) −0.09, −0.28; C(11) −0.07, −0.44; C(20) 0.09, 0.81; C(21) −0.01, 0.03; C(22) −0.06, −0.21; C(23) −0.04, −0.39; C(24) −0.16, −0.78; C(4) 0.62, −0.54; C(5) 0.16, 0.43; C(13) −0.06, −0.13; C(14) −0.60, 0.71; C(16) −0.35, −0.91; (II), C(17) −1.08, C(18) 0.28, −1.38]

Plane (4): N(9), C(8), C(10), C(21)—(23)

A	*B*	*C*	*D*
7.16	2.68	9.62	6.58
−7.95	5.34	9.50	1.63

[N(9) −0.00, −0.02; C(8) −0.02, 0.02; C(10) 0.03, 0.01; C(21) 0.01, −0.01; C(22) −0.02, 0.00; C(23) −0.04, 0.00]

Angles between (3)—(4) (I) 1.7, (II) 11.2°

Plane (5): Fe, N(12), N(15)

A	*B*	*C*	*D*
7.04	3.42	9.60	6.71
10.89	−4.00	−10.83	−1.04

[C(13) 0.06, −0.12; C(14) 0.67, 0.51]

Plane (6): Fe, N(3), N(6)

A	*B*	*C*	*D*
6.99	1.67	10.40	6.65
−5.80	3.90	11.64	2.34

[C(4) −0.69, −0.39; C(5) −0.14, 0.36]

Plane (7): Fe, N(3), N(15)

A	*B*	*C*	*D*
6.56	2.97	11.06	7.12
−9.48	1.33	11.91	1.26

[C(16) 0.38, −1.19; C(18) −0.34, −1.14; (II) C(17) −1.11]

The macrocycle in (II) is much more severely distorted than in (I), and while the distortion still maintains some elements of the C_2 distortion found in (I) cannot be quite so exact because of the six-membered ring in macrocycle (C). Thus while in (I), H(3) and H(15) are alternatively above and below the plane, in (II) both hydrogen atoms are on the same side of it, thus ensuring that the six-membered ring can be accommodated in the chair formation (Figure 2).

The maximum deviation of a contributing atom from the FeN_5 least-squares plane is 0.29 Å and the *cis*-angles involving N(1) and N(2) have deviations of up to 9.5 from 90°. The distortions from a pentagonal bipyramid follow to some extent the same pattern as in (I) although the deviations from the girdle of the five nitrogen atoms are about three times those in the macrocycle (B). The deviations of the nine carbon atoms which are almost coplanar in (I) are much larger (⩽ 0.81 Å) (Table 10).

The Fe–N bond lengths in (II) follow the pattern Fe–N(6),N(12) < Fe–N(9) < Fe–N(15) < Fe–N(3). The increase in the Fe–N(9) bond length between (I) and (II) is possibly due to the weakening of overlap by the twist in the pyridine ring by 11° from the girdle plane. It is logical that the Fe–N(3) and Fe–N(15) bond lengths are increased in (II) to fit the six-membered ring into the girdle. The fact that the bond to N(3) is increased by more than that to N(15) is also thought to be significant since the C(16)—(18) segment of the six-membered ring is on the same side of the girdle as is N(3). The Fe–N(6) and Fe–N(12) bonds are little different in the two compounds, being smaller if anything for (II), suggesting that the six-membered ring has no effect on this part of the molecule.

Of the five angles subtended at Fe by pairs of atoms in the girdle, N(6)–Fe–N(9) and N(9)–Fe–N(12) at *ca.* 70° are equivalent in (I) and (II). The N(3)–Fe–N(6) and N(12)–Fe–N(15) angles are increased in (II) presumably as N(3) and N(15) are pulled out of the girdle plane to fit into the six-membered ring. Dihedral angles for the three saturated rings are given in Table 9. In (I), the two rings either side of the two-fold axis both have the asymmetric puckered conformation,[26] while the N(3)–Fe–N(15) ring has the symmetric puckered conformation. In (II) the N(3)–Fe–N(6) ring has the symmetric puckered conformation while the N(12)–Fe–N(15) ring has the asymmetric puckered conformation, the difference presumably having the same cause as the Fe–N(3) bond-lengthening, *i.e.* the steric effects of the six-membered ring in the chair conformation.

In this six-membered ring the dihedral angles of the type Fe–N–C–C are >70°. The Fe–N(15)–C(14) and Fe–N(3)–C(4) angles have decreased by *ca.* 5° from (I) to (II). Similarly Fe–N(3)–C(18) and Fe–N(15)–C(16) are increased by *ca.* 5° while C(14)–N(15)–C(16) and C(4)–N(3)–C(18) are decreased by *ca.* 3°. Other angles in the macrocycles are equivalent in both molecules. Bond lengths for N–C and C–C are as expected. The N(6)–C(7) and N(12)–C(11) distances correspond to C=N double bonds [1.262—1.293 Å]; N(9)–C(8) and N(9)–C(10) are slightly longer [1.322—1.368 Å] and are comparable with values usually found for a pyridine group so bonded. There are no significant differences between the dimensions of the two ligands.

The bending of the six-membered ring below the equatorial plane in (II) restricts the positions of the thiocyanate group (1) on that side of the plane. The plane of the $Fe–(NCS)_1$ group is however not markedly

[26] J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, 1969, **5**, 1168.

along the Fe $\cdots$ N(9) vector, as might have been thought, but falls half-way along the C(11)–N(12) bond (see Table 10). The Fe–$(NCS)_2$ group is roughly coplanar with C(7). The two thiocyanate planes intersect each other at 69.6° [19.4° in (I)]. There are no significantly short contacts between the thiocyanate groups and the remainder of the molecule in either structure.

The closest intermolecular contacts in both (I) and (II) are listed in the Supplementary Publication. There are several contacts between the perchlorate oxygen atoms and atoms in the macrocycle of *ca.* 3.20 Å, but none are significantly shorter than the sum of van der Waals radii.

EXPERIMENTAL

Preparation of the Complexes.—2,6-Diacetylpyridine (Emmanuel) was used without further purification. The tetramine 1,9-diamino-3,7-diazanonane was prepared by the method of Alphen [27] as modified by Brubaker and Schaefer.[28]

(*a*) $[Fe(C)Cl_2]FeCl_4$, *Complex* (III). 2,6-Diacetylpyridine (0.01 mol) in methanol (50 ml) was added to $FeCl_2,4H_2O$ (0.01 mol) in methanol (50 ml). This blue solution was then added slowly to a solution of the tetramine (0.01 mol) in methanol (100 ml), when it turned brown. It was then digested at *ca.* 40 °C, with stirring, for at least 8 h. A solution in methanol (30 ml) of $FeCl_3$ (0.01 mol) and concentrated hydrochloric acid (5 ml) was then added. The brown solid which separated was extracted with acetone and evaporated nearly to dryness to give the crude *complex* as a yellow solid. This was washed with ethanol and recrystallised from acetone–ethanol (yield variable, 40—60%).

(*b*) $[Fe(C)Cl_2]ClO_4$. An excess of $NaClO_4,H_2O$ in acetone was added to a solution of (III) in acetone, and the solution set aside. The yellow *product* which separated was recrystallised from ethanol–water (70%).

(*c*) $[Fe(C)Cl_2]PF_6$. An aqueous solution of (III) was added to a concentrated aqueous solution of KPF_6 and the mixture set aside. The yellow *precipitate* which separated was recrystallised from water (55%).

(*d*) $[Fe(C)Cl_2]BPh_4$. An aqueous solution of (III) was added to an excess of $NaBPh_4$ in water. The orange solid which separated immediately was washed with water, and dried and dissolved in acetone which deposited a *yellow-orange solid* on evaporation to near dryness. It was recrystallised from acetone–water (80%).

(*e*) $[Fe(C)(NCS)_2]ClO_4$ *and* $[Fe(C)(N_3)]ClO_4$. To a hot aqueous solution of $[Fe(C)Cl_2]ClO_4$ was added an aqueous solution of NaNCS (NaN_3) containing also some added $NaClO_4,H_2O$ and the solution set aside and cooled. The *red crystals* which separated were washed with cold water and recrystallised from warm aqueous methanol (*ca.* 60%).

(*f*) $[Fe(C)Br_2]FeBr_4$. This was prepared as for compound (III) with substitution of $FeBr_2$ and HBr for $FeCl_2$ and HCl (*ca.* 50%).

(*g*) $[Fe(C)Br_2]ClO_4$. This was prepared either as for $[Fe(C)Cl_2]ClO_4$ starting from $[Fe(C)Br_2]FeBr_4$, or alternatively by addition of excess of NaBr to a warm aqueous solution of $[Fe(C)Cl_2]ClO_4$. It was recrystallised from ethanol–water (40—60%).

Physical Measurements.—I.r. spectra were recorded for KBr pellets and Nujol mulls in the range 4 000—250 cm^{-1} by use of a Perkin-Elmer 457 grating spectrophotometer. Magnetic measurements were made by the Gouy method on a Newport Instruments variable-temperature magnetic balance. Electric conductivities were measured at 1 000 Hz by use of a resistance–capacitances bridge with magic-eye detector in a Pt electrode cell of cell constant 0.038. Electronic spectra were recorded on a Unicam SP 700 spectrophotometer.

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27 J. van Alphen, *Rec. Trav. chim.*, 1936, **55**, 835.
28 G. R. Brubaker and D. P. Schaefer, *Inorg. Chem.*, 1971, **10**, 811.