Synthesis and Magnetochemical, Spectroscopic, and Structural Studies of New Tris(*NN*-dialkyldiselenocarbamato)iron(IV) Tetrafluoroborate Complexes †

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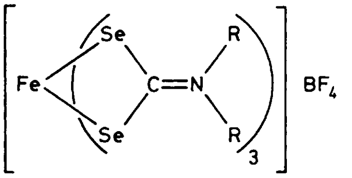
Four new $[Fe^{IV}(Se_2CNR_2)_3]^+$ complexes [R = C_2H_5 (1), R_2N = morpholino (2), R_2N = piperidino (3), and R = $CH_2C_6H_5$ (4)] have been prepared as BF_4^- salts, characterized by routine analytical and spectroscopic methods, and studied by variable-temperature magnetochemistry (100—300 K) and Mössbauer (120 K), e.s.r. (10—77 K), and *X*-ray photoelectron (300 K) spectroscopies. In addition, the molecular structure of (4) has been determined by *X*-ray crystallography with a = 33.213(18), b = 12.920(13), c = 10.748(10) Å, β = 90.26(4)°, Z = 4 and shown to possess D_3 macrosymmetry with the $FeSe_6$ core having six selenium donor atoms at the apexes of a co-ordination polyhedron which is intermediate between the idealized trigonal prismatic and trigonal antiprismatic geometries. Overall, the present study indicates these tris-diselenocarbamate complexes to be low-spin iron(IV) species, similar to their tris-dithiocarbamate counterparts.

Synthetic Fe^{IV} complexes are very uncommon, with the first reported examples apparently being of type $[Fe\{o\text{-}C_6H_4(AsMe_2)_2\}_2X_2]^{2+}$ ($X = Cl^-$ or Br^-) where spectroscopic and magnetochemical data indicated them to be pseudo-octahedral, low-spin d^4 complexes with large tetragonal distortions.[1] Subsequently, tris-dithiocarbamate [2,3] and tris-dithiolate [4] complexes of Fe^{IV} were also documented, with both species bearing FeS_6 cores. Magnetic and Mössbauer spectroscopy [3] and molecular structural determinations [4,5] for these FeS_6 complexes support a formal oxidation state at iron of (+4) in which the complex is distorted from an idealized octahedral geometry. Theoretically, a temperature-dependent magnetic moment of *ca.* 3.6 B.M. is expected for a low-spin d^4 case in O_h symmetry,[6] but experimental data for these $Fe^{IV}S_6$ species give magnetic moments considerably lower than predicted, perhaps due to their lower than O_h symmetry.[7]

In addition to the inherent novelty of Fe^{IV} species, the possible importance of Fe^{IV} chemistry in metalloprotein activity,[8] including peroxidases [9, 10] and cytochrome c oxidase,[11] has spurred recent interest in the inorganic biochemistry of Fe^{IV} systems in general. This interest has recently culminated in the identification of synthetic $Fe^{IV}{=}O$ ferryl complexes of metalloporphyrins,[12] the possible involvement of such ferryl and other related species in dehydrogenation reactions of alkanes,[13] and the utilization of $Fe^{IV}{=}O$ intermediates as precursors to novel mixed-metal ($Fe^{III}\text{–}O\text{–}Cu^{II}$) μ-oxo-species as model compounds for the active site of cytochrome c oxidase.[14]

In this paper we wish to contribute to the continuing study of Fe^{IV} complexes and report the variable-temperature magnetochemical properties, *X*-ray photoelectron spectra (x.p.s.), and Mössbauer spectral properties for four new tris(*NN*-dialkyldiselenocarbamato)iron(IV) tetrafluoroborate complexes (1)—(4) (see above).



(1) R = C_2H_5
(2) R_2N = NC_5H_{10}(piperidino)
(3) R_2N = NC_4H_8O(morpholino)
(4) R = $CH_2C_6H_5$

In addition, we report the crystal and molecular structure of (4) which serves to verify the general structure of this class of new compounds and provides some of the first detailed structural information about the nature of $FeSe_6$ co-ordination chemistry.

Experimental

The compounds were prepared by the method used previously [2] to synthesize the corresponding tris-dithiocarbamate derivatives, except that a 48% solution of $BF_3\text{–}Et_2O$ was used (with a stream of air bubbled through the solution) instead of BF_3. Elemental analyses were performed at the Istituto di Chimica degli Intermedi di Bologna, and the conductance measurements were carried out with a W.T.W. LBR type conductivity bridge.

U.v.-visible electronic spectral data were obtained using a Perkin-Elmer model 402 spectrophotometer. Infrared spectral data were recorded with a Perkin-Elmer model 325 spectrophotometer using KBr discs in the 4 000—450 cm^{-1} region and Nujol mulls in the 400—200 cm^{-1} region.

Variable-temperature (100—300 K) magnetic susceptibility

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† *Supplementary data available* (No. SUP 23438, 14 pp.): structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. units employed: 1 eV ≈ 1.60×10^{-19} J; 1 B.M. = 0.927×10^{-23} A m^2; c.g.s.u. = $10^6/4\pi$ S.I. unit.

Table 1. Final atomic co-ordinates (× 10^4) for complex (4) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Se(1)	348(2)	4 041(5)	8 775(5)	C(31)	2 199(11)	6 561(37)	7 609(45)
Se(2)	−65(2)	4 225(5)	6 294(5)	C(32)	2 552(11)	7 052(37)	7 991(45)
Se(3)	738(2)	6 034(4)	6 358(6)	C(33)	2 904(11)	6 937(37)	7 299(45)
Se(4)	1 284(2)	4 560(5)	7 706(6)	C(34)	2 902(11)	6 330(37)	6 226(45)
Se(5)	815(2)	3 757(5)	4 643(6)	C(35)	2 548(11)	5 839(37)	5 844(45)
Se(6)	789(2)	2 399(4)	6 922(6)	C(36)	2 197(11)	5 955(37)	6 536(45)
Fe	644(2)	4 226(6)	6 768(7)	C(41)	1 613(11)	8 216(30)	6 274(34)
N(1)	−487(12)	3 591(31)	8 459(37)	C(42)	1 925(11)	8 874(30)	6 631(34)
N(2)	1 453(14)	6 732(39)	7 510(40)	C(43)	2 180(11)	9 294(30)	5 734(34)
N(3)	1 145(12)	1 736(35)	4 639(41)	C(44)	2 122(11)	9 055(30)	4 480(34)
C(1A)	−156(14)	3 871(37)	7 906(43)	C(45)	1 809(11)	8 397(30)	4 124(34)
C(2A)	−528(17)	3 259(46)	9 751(53)	C(46)	1 554(11)	7 977(30)	5 021(34)
C(3A)	−861(13)	3 620(36)	7 637(41)	C(51)	904(10)	60(30)	5 317(43)
C(1B)	1 213(15)	5 943(44)	7 275(47)	C(52)	727(10)	−174(30)	6 456(43)
C(2B)	1 799(16)	6 542(41)	8 325(49)	C(53)	392(10)	−827(30)	6 498(43)
C(3B)	1 340(18)	7 777(50)	7 183(56)	C(54)	236(10)	−1 246(30)	5 402(43)
C(1C)	960(26)	2 552(72)	5 243(81)	C(55)	414(10)	−1 012(30)	4 263(43)
C(2C)	1 263(15)	761(42)	5 316(48)	C(56)	748(10)	−359(30)	4 220(43)
C(3C)	1 306(15)	1 903(39)	3 403(47)	C(61)	1 747(9)	2 124(30)	3 420(37)
C(11)	−186(8)	2 555(25)	10 201(30)	C(62)	2 012(9)	1 581(30)	2 659(37)
C(12)	25(8)	2 797(25)	11 287(30)	C(63)	2 419(9)	1 856(30)	2 630(37)
C(13)	348(8)	2 181(25)	11 667(30)	C(64)	2 559(9)	2 674(30)	3 360(37)
C(14)	460(8)	1 323(25)	10 960(30)	C(65)	2 293(9)	3 216(30)	4 121(37)
C(15)	249(8)	1 081(25)	9 873(30)	C(66)	1 887(9)	2 941(30)	4 151(37)
C(16)	−74(8)	1 697(25)	9 494(30)	B	−1 338(17)	900(51)	9 329(58)
C(21)	−1 157(12)	4 428(27)	8 143(36)	F(1)	−1 462(7)	58(21)	8 797(23)
C(22)	−992(12)	5 374(27)	8 506(36)	F(2)	−1 420(7)	1 809(20)	9 289(22)
C(23)	−1 241(12)	6 162(27)	8 942(36)	F(3)	−1 167(7)	466(19)	10 440(23)
C(24)	−1 656(12)	6 003(27)	9 016(36)	F(41)	−1 045(14)	952(40)	8 500(44)
C(25)	−1 821(12)	5 056(27)	8 652(36)	F(42)	−1 729(14)	899(38)	9 890(43)
C(26)	−1 571(12)	4 269(27)	8 216(36)				

data were obtained by the Gouy method using a Newport magnetometer. The sample chamber was operated under 1 atm (*ca.* 101 325 N m^{-2}) of N_2 and Hg[Co(NCS)$_4$] was used as the calibrant. The magnetic susceptibility data showed no appreciable field-strength dependence.

Mössbauer spectra were obtained using an instrument previously described [15] and computer fitted by the program of Chrisman and Tumolillo.[16] Sodium nitroprusside was used as the reference compound, and the temperature was monitored by a copper *vs.* constantan thermocouple embedded in the sample. The computer-generated plots of the spectra were obtained using a CALCOMP plotting program.

X-Ray photoelectron spectra were recorded using a DuPont model 650 spectrophotometer equipped with a multi-channel analyzer. The binding energies were referenced to the C 1*s* photoelectron line of contaminant carbon, using a value of 285.0 eV as previously described.[17,18] The powdered samples were dusted onto a double-sided sticky tape attached to the sample probe tip and then introduced into the vacuum chamber of the spectrometer.

Collection of electron spin resonance (e.s.r.) spectral data was attempted using a Varian model E-6 spectrophotometer equipped with Air Products liquid helium cryogenics. Spectra were attempted at 77 K and 10 K on chloroform glasses 10^{-3} mol l^{-1} in iron complex.

X-*Ray Crystal Structure Analysis.*—*Crystal data.* $C_{45}H_{42}BF_4FeN_3Se_6$, $M = 1\,241.257$, Monoclinic, $a = 33.213(18)$, $b = 12.920(13)$, $c = 10.748(10)$ Å, $\beta = 90.26(4)°$, $U = 4\,612(7)$ Å^3, $D_m = 1.78$, $Z = 4$, $D_c = 1.79$ g cm^{-3}, $F(000) = 2\,416$, Mo-$K_{\alpha 1}$ radiation ($\lambda = 0.709\,26$ Å), μ(Mo-$K_{\alpha 1}$) = 50.66 cm^{-1}, space group $P2_1/n$ (from systematic absences). Preliminary unit-cell parameters were determined from rotation and Weissenberg photographs and refined by a least-squares procedure applied to the θ values of 23 reflections carefully measured on a Siemens AED single-crystal diffractometer.

Intensity data. Intensity data were collected on the same diffractometer, by use of niobium-filtered Mo-$K_{\alpha 1}$ radiation and the θ—2θ scan technique. A dark blue twinned platelet of dimensions 0.14 × 0.01 × 0.21 mm was aligned with its *c* axis along the φ axis of the diffractometer and all the reflections with θ in the range 3—22° were measured. Of a total of 5 688 independent reflections, 1 564 having $I > 2\sigma(I)$ were considered observed and used in the analysis. The intensities were corrected for Lorentz and polarization effects, but no absorption correction was made. The first absolute scaling and the overall isotropic thermal parameter were obtained by Wilson's method.[19]

Structure determination and refinement. The structure was solved by Patterson and Fourier methods and refined by least-squares blocked full-matrix cycles using the SHELX system of computer programs [20] with initially isotropic thermal parameters, then anisotropic thermal parameters only for the heavy atoms. All the phenyl groups were refined as rigid bodies with C–C = 1.395 Å and free thermal parameters. The function minimized was $\Sigma w|\Delta F|^2$, with $w = 0.1717/\sigma_2(F_o) + 0.086\,793\,(F_o)^2$.

The difference electron-density map was not valuable in locating the hydrogen atoms. The final *R* was 0.091 (observed reflections only).

The atomic scattering factors used (corrected for the anomalous dispersion) were those of Cromer and Mann.[21] Table 1 shows the positional parameters with their estimated standard deviations. A fluorine atom of the BF_4^- anion was disordered with a 50—50 occupancy deduced from the electron density and the refinement of the site occupation factor. All calculations were performed on a CYBER 7600 computer of the Consorzio per la Gestione del Centro di

Table 2. Analytical data (%) for the tris(diselenocarbamato)iron(IV) tetrafluoroborate compounds [a]

Compound	C	H	N
(1) [b]	20.6 (20.75)	3.7 (3.50)	4.8 (4.85)
(2)	19.5 (19.80)	3.1 (2.65)	4.5 (4.60)
(3)	23.5 (23.90)	3.1 (3.35)	4.6 (4.65)
(4)	43.6 (43.55)	4.0 (3.40)	3.1 (3.40)

[a] Calculated values in parentheses. [b] Equivalent conductance $\Lambda_{eq.}$ = 86.5 Ω^{-1} cm^2 mol^{-1} for a 10^{-3} mol dm^{-3} CH_3NO_2 solution at 25 °C, indicating uni-univalent electrolyte behaviour.

Table 3. Selected i.r. spectral data for the tris(diselenocarbamato)iron(IV) tetrafluoroborate compounds

Compound	ν(C=N)/cm^{-1}	ν(Fe–Se)/cm^{-1}
(1)	1 525vs *	249s
(2)	1 520vs *	245s
(3)	1 535vs *	250s
(4)	1 510vs *	252s

* For comparison purposes, corresponding very strong bands in the neutral tris(diselenocarbamato)iron(III) complexes occur at 1 490, 1 480, 1 480, and 1 475 cm^{-1}, respectively.

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Results and Discussion

Analytical and conductivity data for compounds (1)—(4) are given in Table 2 and are consistent with a $[Fe(Se_2CNR_2)_3]BF_4$ formulation for all of the derivatives.

Infrared Spectra.—All of the compounds show a broad band centred at 1 070 cm^{-1} and a doublet at 532—521 cm^{-1} which is characteristic of the BF_4^- anion. As shown in Table 3, a single, strong band near 1 500 cm^{-1} is assigned to a ν(C=N) vibrational mode associated with the symmetrically bonded $R_2N{=}CSe_2^-$ ligand.[22] A positive shift in ν(C=N) of *ca.* 35—40 cm^{-1} (see Table 3) for (1)—(4), relative to the values found in the corresponding tris(diselenocarbamato)iron(III) derivatives, is consistent with greater C=N double bond character in going from the Fe^{III} to Fe^{IV}. This observation, in turn, suggests that a ligand resonance form of the type $R_2N{=}\overset{+}{C}{<}^{Se^-}_{Se^-}$ makes a greater contribution to the electronic structure in the Fe^{IV} derivatives. This is consistent with the increase in oxidation state at iron in (1)—(4) relative to their Fe^{III} analogues and also with the increase in ligand-field strength to give only low-spin species (see below) as opposed to spin-equilibrium compounds in the case of Fe^{III}.[23,24]

For all the Fe^{IV} compounds, the strong i.r. band near 250 cm^{-1} in Table 3 is attributable to a ν(Fe–Se) stretching mode.[23]

U.v.-visible Spectra.—The absorption bands in the solution electronic spectrum of compounds (1)—(4) are documented in Table 4. In all cases the relatively large intensity of the bands indicates them to be charge transfer in origin, with the metal-centered *d–d* transitions being obscured.

Table 4. U.v.-visible electronic spectral data for the tris(diselenocarbamato)iron(IV) tetrafluoroborate compounds

Compound	Absorption bands in CH_2Cl_2 (10^3 cm^{-1})*
(1)	37.5 (4.46), 34.2 (4.48), 30.3 (4.30), 28.6 (4.21), 25.8 (sh), 21.0 (sh), 19.0 (3.93)
(2)	37.7 (sh), 34.1 (4.55), 30.3 (sh), 29.0 (sh), 25.8 (3.90), 21.0 (sh), 18.9 (3.88)
(3)	37.3 (sh), 33.9 (4.52), 30.3 (sh), 29.2 (sh), 25.8 (3.93), 21.0 (sh), 18.9 (3.98)
(4)	37.2 (sh), 33.2 (4.58), 30.3 (sh), 28.7 (sh), 25.6 (sh), 21.0 (sh), 18.9 (3.98)

* Values of log (ε/dm^3 mol^{-1} cm^{-1}) are in parentheses.

Table 5. Variable-temperature reciprocal magnetic susceptibility data (χ_M corr./c.g.s.u.)$^{-1}$ [a,b]

	Compound			
T/K	(1)	(2)	(3)	(4)
101	72.2	87.6	71.9	59.7
120	99.9	99.9	83.4	72.9
138	113.7	110.0	98.4	84.0
157	127.5	129.5	112.3	95.4
175	144.5	142.8	131.4	106.5
194	164.5	161.2	140.3	118.0
212	187.6	168.9	157.0	129.0
231	200.0	183.3	172.4	140.6
250	214.9	194.3	191.4	152.2
269	230.4	206.0	205.9	163.8
288	255.4	221.8	223.3	175.4
307	256.6	235.6	239.1	193.3

[a] Diamagnetic corrections in 10^6 c.g.s.u. per mol: (1) −369.8, (2) −355.1, (3) −377.0, and (4) −492.5. [b] Magnetic moments: (1) 3.0, (2) 3.3, (3) 3.1, and (4) 3.6 B.M.

Magnetochemical Measurements.—As previously reported, the $[Fe^{III}(Se_2NCR_2)_3]$ complexes are $^6A \rightleftharpoons {}^2T$ spin-equilibrium compounds, with the position of the equilibrium dependent on temperature and the nature of the R substituent.[23,24] For the present low-spin Fe^{IV} compounds, in a field of O_h symmetry, the ground state is $^3T_1$ and a spin-only magnetic moment of 2.83 B.M. with a temperature-dependent orbital contribution is expected. In fact, using the results of Kotani [6] and a single-electron spin-orbit coupling constant of 475 cm^{-1} for the Fe^{IV} ion,[1] a theoretical value for the magnetic moment as high as 3.6 B.M. can be calculated. The variable-temperature (100—300 K) magnetic susceptibility data for complexes (1)—(4) are shown in Table 5, where it can be seen that the plots of (χ_M corr.)$^{-1}$ *vs.* T are essentially Curie–Weiss in nature, with the $\mu_{eff.}$ values of 3.0—3.6 B.M. falling in a range somewhat lower than predicted by theory. This slight lowering of the magnetic moments toward the spin-only value seems reasonable in view of the fact that the molecular structure of the $[Fe^{IV}(Se_2NCR_2)_3]^+$ cation (see below) is significantly distorted from cubic symmetry which would tend to quench any orbital moment contribution.[7] In addition, extensive metal–ligand(π) delocalization involving the Fe^{IV} *d* electrons would also produce a reduction in the orbital contribution.[23] In fact, in view of the lower than O_h symmetry and the probable existence of appreciable Fe–ligand(π) bonding in (1)—(4), it is somewhat surprising that the magnetic moments approximate to the theoretical value as well as they do. In any event, it is clear that, as for their $[Fe^{IV}(S_2CNR_2)_3]^+$ analogues, the $[Fe^{IV}(Se_2CNR_2)_3]^+$ cations are all low-spin species possessing a $S = 1$ ground state.

Mössbauer Spectra.—As reported earlier for the $[Fe^{III}(Se_2CNR_2)_3]$ species, no spectrum of (1) was obtained at all using only naturally abundant ^{57}Fe (2%) in the synthetic scheme, presumably due to a selenium edge absorption at 12.6 keV or to effective γ-ray scattering by the selenium

Table 6. Selected shortest contacts (Å) for complex (4)

(*a*) Intramolecular contacts

Ligand	C(phenyl) ··· C(phenyl)		Se ··· C(phenyl)		N ··· C(phenyl)		C(methylene) ··· C(phenyl)	
A			Se(1) ··· C(11)	3.03(3)	N(1) ··· C(16)	3.02(5)	C(2A) ··· C(21)	3.10(7)
			Se(1) ··· C(12)	3.32(3)	N(1) ··· C(22)	2.85(5)		
			Se(1) ··· C(16)	3.43(3)				
B	C(31) ··· C(41)	3.22(6)			N(2) ··· C(36)	2.87(6)	C(2B) ··· C(41)	3.15(6)
	C(31) ··· C(42)	3.29(6)			N(2) ··· C(46)	3.14(6)	C(3B) ··· C(31)	3.29(7)
C			Se(6) ··· C(52)	3.37(4)	N(3) ··· C(56)	3.04(6)	C(2C) ··· C(61)	3.14(6)
					N(3) ··· C(66)	2.96(5)	C(3C) ··· C(51)	3.42(7)

(*b*) Intermolecular contacts

C(15) ··· C(15$^{\text{III}}$)	3.26(4)	C(65) ··· C(32$^{\text{II}}$)	3.49(6)	Se(2) ··· Se(2$^{\text{V}}$)	3.456(9)
C(51) ··· C(41$^{\text{I}}$)	3.50(5)	F(1) ··· C(62$^{\text{IV}}$)	3.20(4)	Se(3) ··· Se(2$^{\text{V}}$)	3.630(9)
C(51) ··· C(46$^{\text{I}}$)	3.47(5)	F(41) ··· C(56$^{\text{IV}}$)	3.18(7)	Se(5) ··· Se(2$^{\text{V}}$)	3.741(9)
C(52) ··· C(3B$^{\text{I}}$)	3.43(7)				

Key to symmetry operations: I $x, -1 + y, z$; II $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$; III $-x, -y, 2 - z$; IV $-x, -y, 1 - z$; V $-x, 1 - y, 1 - z$.

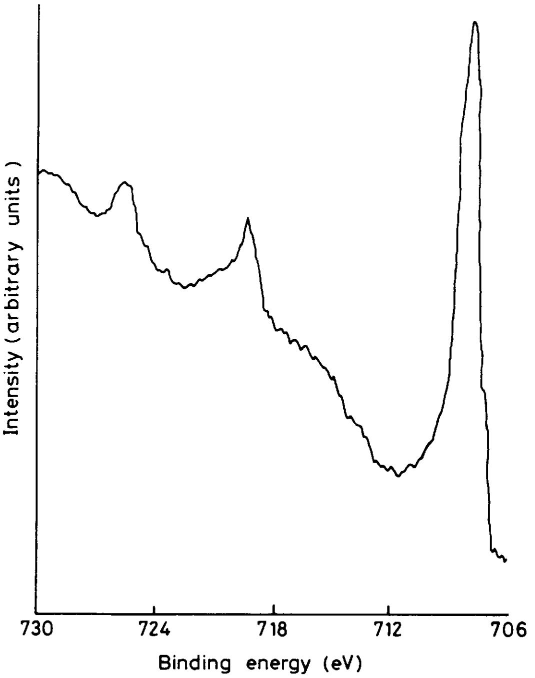


Figure 1. Iron $2p$ *X*-ray photoelectron spectrum of [Fe{Se$_2$CN(C$_2$H$_5$)$_2$}$_3$]BF$_4$ (1) at room temperature

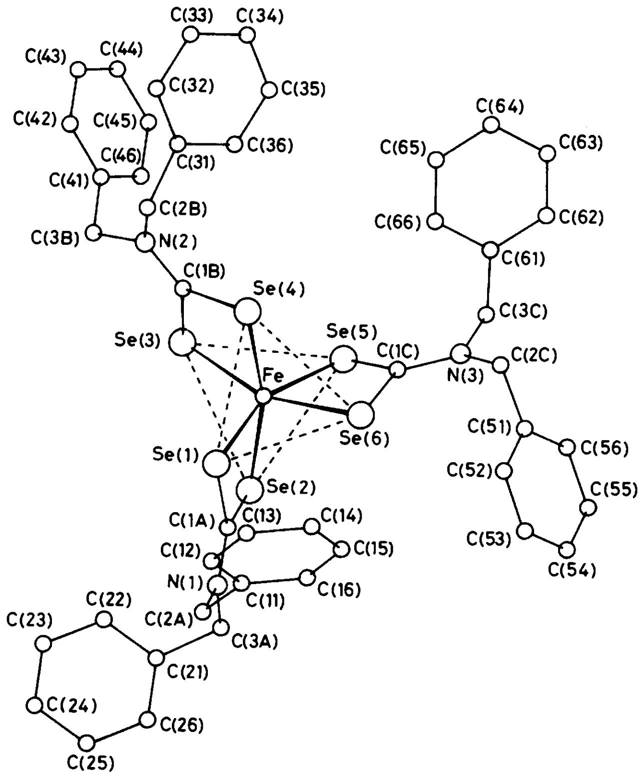


Figure 2. Perspective view of the cation in [Fe{Se$_2$CN(CH$_2$C$_6$H$_5$)$_2$}$_3$]BF$_4$ (4) looking down the three-fold axis

atoms.[24] However, enrichment of *ca.* 25% in ^{57}Fe for (1) and (4) produced the appearance of a spectrum over a 42 h collection time using a 10 mCi (1 Ci = 3.7 × 10^{10} Bq) source. Even under these conditions, the spectrum is not of high quality, but computer fitting of the data results in a quadrupole splitting (ΔE_Q) of 2.02 ± 0.06 mm s^{-1} in general agreement with that obtained previously for the tris(dithiocarbamato)iron(IV) compounds.[3] On the other hand, the isomer shift (δ) of 0.87 ± 0.04 mm s^{-1} (sodium nitroprusside as reference) is considerably greater than the value of *ca.* 0.56 mm s^{-1} obtained for the tris(dithiocarbamato)iron(IV) species at a similar temperature.[3] Therefore, the validity, significance, and interpretation of the present Mössbauer data will have to await a more systematic Mössbauer study, probably one employing greater ^{57}Fe enrichment and/or a more active source.

X-Ray Photoelectron Spectra.—Attempts to corroborate the existence of the iron(IV) in compound (1) by x.p.s. proved unsuccessful. As is the case with numerous other inorganic compounds involving a metal centre in a ' high ' oxidation state, photoreduction of the complex apparently occurs during the experiment.[25] The photoelectron spectrum at room temperature of (1) (Figure 1) in the Fe $2p$ region revealed an Fe $2p_{\frac{3}{2}}$ binding energy of 708.1 eV. This is a typical binding energy for a Fe$^{\text{II}}$ species [26] rather than one involving Fe$^{\text{IV}}$; also, the satellite structure at ~6.6 eV to the high binding energy side of the Fe $2p_{\frac{3}{2}}$ line is in good agreement with those reported for another Fe$^{\text{II}}$ system.[27]

Table 7. Deviations (Å), with e.s.d.s in parentheses, from the weighted least-squares planes through the atoms marked with an asterisk

Plane 1		Plane 2		Plane 3	
Se(1) *	−0.002(7)	Se(3) *	0.000(7)	Se(5) *	0.000(7)
Se(2) *	0.002(7)	Se(4) *	0.000(7)	Se(6) *	−0.001(7)
C(1A) *	0.03(5)	C(1B) *	0.01(5)	C(1C) *	−0.01(9)
N(1) *	0.02(4)	N(2) *	0.06(4)	N(3) *	0.07(4)
C(2A) *	0.13(6)	C(2B) *	−0.04(5)	C(2C) *	−0.01(5)
C(3A) *	−0.11(5)	C(3B) *	−0.03(6)	C(3C) *	−0.07(5)
Fe	0.410(8)	Fe	−0.194(8)	Fe	−0.451(7)
C(11)	1.15(3)	C(31)	1.29(5)	C(51)	1.38(4)
C(21)	−1.43(4)	C(41)	1.18(4)	C(61)	−1.45(3)

Table 8. Bond distances (Å) and angles (°) with e.s.d.s in parentheses for complex (4)

(*a*) Co-ordination polyhedron

Se(1)-Fe	2.387(10)	Se(3)-Fe	2.398(10)	Se(5)-Fe	2.443(10)
Se(2)-Fe	2.407(10)	Se(4)-Fe	2.388(10)	Se(6)-Fe	2.415(10)

Se(1)-Fe-Se(2)	77.6(3)	Se(2)-Fe-Se(3)	95.2(3)	Se(3)-Fe-Se(5)	92.2(4)
Se(1)-Fe-Se(3)	108.6(4)	Se(2)-Fe-Se(4)	163.3(4)	Se(3)-Fe-Se(6)	159.9(4)
Se(1)-Fe-Se(4)	90.4(4)	Se(2)-Fe-Se(5)	91.9(3)	Se(4)-Fe-Se(5)	103.3(4)
Se(1)-Fe-Se(5)	157.3(4)	Se(2)-Fe-Se(6)	102.0(4)	Se(4)-Fe-Se(6)	88.3(3)
Se(1)-Fe-Se(6)	85.6(3)	Se(3)-Fe-Se(4)	77.6(3)	Se(5)-Fe-Se(6)	76.9(3)

(*b*) Ligands

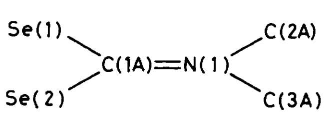
Se(1)-C(1A)	1.93(5)	C(1B)-N(2)	1.32(7)	C(3C)-N(3)	1.45(7)
Se(2)-C(1A)	1.82(5)	C(1C)-N(3)	1.38(10)	C(2A)-C(11)	1.53(6)
Se(3)-C(1B)	1.86(5)	C(2A)-N(1)	1.46(7)	C(3A)-C(21)	1.54(6)
Se(4)-C(1B)	1.86(6)	C(3A)-N(1)	1.52(6)	C(2B)-C(31)	1.54(7)
Se(5)-C(1C)	1.75(9)	C(2B)-N(2)	1.46(7)	C(3B)-C(41)	1.45(7)
Se(6)-C(1C)	1.90(9)	C(3B)-N(2)	1.44(8)	C(2C)-C(51)	1.50(6)
C(1A)-N(1)	1.30(6)	C(2C)-N(3)	1.51(7)	C(3C)-C(61)	1.49(6)

Se(1)-C(1A)-Se(2)	107(2)	Se(6)-C(1C)-N(3)	120(6)	C(2B)-N(2)-C(3B)	120(5)
Se(1)-C(1A)-N(1)	123(3)	C(1A)-N(1)-C(2A)	127(4)	N(2)-C(2B)-C(31)	112(4)
Se(2)-C(1A)-N(1)	130(4)	C(1A)-N(1)-C(3A)	115(4)	N(2)-C(3B)-C(41)	112(5)
Se(3)-C(1B)-Se(4)	107(3)	C(2A)-N(1)-C(3A)	119(4)	C(1C)-N(3)-C(2C)	122(5)
Se(3)-C(1B)-N(2)	124(4)	N(1)-C(2A)-C(11)	114(4)	C(1C)-N(3)-C(3C)	119(5)
Se(4)-C(1B)-N(2)	128(4)	N(1)-C(3A)-C(21)	109(3)	C(2C)-N(3)-C(3C)	118(4)
Se(5)-C(1C)-Se(6)	111(5)	C(1B)-N(2)-C(2B)	117(5)	N(3)-C(2C)-C(51)	108(4)
Se(5)-C(1C)-N(3)	129(6)	C(1B)-N(2)-C(3B)	121(5)	N(3)-C(3C)-C(61)	113(4)

(*c*) BF_4^- anion

B-F(1)	1.30(7)	B-F(3)	1.43(7)	B-F(42)	1.43(7)
B-F(2)	1.21(7)	B-F(41)	1.32(8)		

F(1)-B-F(2)	137(5)	F(2)-B-F(3)	120(5)	F(3)-B-F(41)	107(5)
F(1)-B-F(3)	99(4)	F(2)-B-F(41)	95(5)	F(3)-B-F(42)	90(4)
F(1)-B-F(41)	89(5)	F(2)-B-F(42)	79(4)	F(41)-B-F(42)	162(6)
F(1)-B-F(42)	84(4)				



Electron Spin Resonance Spectra.—In keeping with species possessing an even spin ground state (*i.e.*, $S = 1$), compounds (1)—(4) proved to be e.s.r. silent under the conditions outlined in the Experimental section.

Crystal and Molecular Structure.—The crystal structure of (4) is composed of discrete $[Fe\{Se_2CN(CH_2C_6H_5)_2\}_3]^+$ cations (Figure 2) and BF_4^- anions held together at van der Waals contact distances (Table 6). The Fe^{IV} cation is bonded to six selenium atoms, forming a co-ordination polyhedron intermediate between a trigonal prism and an idealized trigonal antiprism, with approximate D_3 macrosymmetry. The mean angular twist, 2θ,[28] adopts a value of 36°. All of the four-membered chelated rings are puckered and the dihedral angles between the FeSeSe and SeSeC(1) planes are 165.8(3), 174.4(5), and 165.7(5)° for the first, the second, and the third ring, respectively. The ligand fragment is not planar (Table 7) with the maximum derivations being 0.13(6) and −0.11(5) Å for the C(2A) and C(3A) atoms, respectively. The phenyl groups are on the same side with respect to the SeSeC(1)NC(2)C(3) plane in ligand B, while they are on the opposite side in the other two ligands (Table 7). Consequently, each ligand molecule can form intramolecular contacts (Table 6) of type: (*a*) C(phenyl) • • • C(phenyl) as in ligand B; (*b*) Se • • • C(phenyl) as in the ligands A and C owing to the torsion angles being less than 90° [C(1A)-N(1)-C(2A)-

C(11) = −41(7) and C(1C)–N(3)–C(2C)–C(51) = 86(6)°]; (*c*) N · · · C(phenyl) as in all the ligands and as observed in the tris(*NN*-dibenzyldithiocarbamato)iron(III) derivative;[29] and (*d*) C(methylene) · · · C(phenyl) as observed in the above mentioned dithiocarbamate compound and in the present one only when the torsion angle is not significantly smaller than 90°.

Bond distances and angles involving both the cation and the anion are listed in Table 8. Those observed in the diselenocarbamato-fragments agree substantially with those reported earlier for similar compounds. The distances Fe–Se (see Table 8) lie in the range (2.327—2.440 Å), reported in the literature.[30–32]

The BF_4^- anion is disorderly distributed and its geometry is due to a deep penetration of two tetrahedra sharing the B atom. It was not possible to split the two images of each F atom of the common base.

A comparison of the molecular structure of $[Fe\{Se_2CN(CH_2C_6H_5)_2\}_3]BF_4$ with those reported for the other Fe^{IV} complexes containing FeS_6 cores shows that the deviation from octahedral symmetry is very similar with the averaged projected twist angle of the two triangular faces of the $FeSe_6$ polyhedron being $2\theta = 36°$, as compared to 36 and 38° for the FeS_6 core.[4,9] Moreover, a comparison with other structural parameters like bond distances and internal angles reveals that the values in compound (4) are very similar to those found in $Fe^{IV}S_6$ compounds, demonstrating once again the rather remarkable similarities between sulphur and selenium in these novel Fe^{IV} species.

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