Salts of the Tris(isonitrosomalonamido)ferrate(II) Ion: Crystal Structures and Anomalous Magnetism of the Potassium and Caesium Salts of the Tris(isonitrosomalonamido)ferrate(II) Anion

By **Colin L. Raston** and **Allan H. White,*** Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands 6009, Western Australia
Raymund M. Golding, School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, New South Wales

Complexes of the type $M[FeL_3]\cdot xH_2O$ [M^+ = alkali-metal cation, L^- = $NH_2\cdot COC(NO)^-\cdot CO\cdot NH_2$] have been prepared. The sodium and rubidium salts are diamagnetic; the potassium and caesium salts are paramagnetic, their room temperature magnetic moments being 2.1_6 and 2.6_6 B.M. respectively with only a slight temperature dependence. Mössbauer spectra are indicative of the presence of both singlet and quintet states.

The crystal structure of the potassium salt, $K[FeL_3]\cdot 2H_2O$, has been determined from diffractometer data and refined by least squares to *R* 0.040 for 3 981 observed reflections. Crystals are monoclinic, space group *C*2/*c*, a = 29.89(1), b = 9.780(2), c = 13.980(3) Å, β = 106.68(2)°, Z = 8. The cell contents comprise infinite zig-zag chains of K^+ cations and $[FeL_3]^-$ anions, the ligands co-ordinating through one of the amide oxygens and the nitrosyl nitrogen in a *fac*-configuration, interspersed by potassium cations, the co-ordination sphere of the latter being the three nitrosyl oxygens from one anion, and the three remaining amide oxygens from the next; the chains are parallel to *c*; mean distances: Fe–N 1.88_2, Fe–O 1.97_2 Å.

The crystal structure of $Cs[FeL_3]\cdot 2H_2O$ has also been determined by *X*-ray diffraction and refined by least squares to *R* 0.12 for 5 126 observed reflections. Crystals are monoclinic, space group *Aa*, a = 33.312(6), b = 24.792(5), c = 13.323(2) Å, β = 91.55(1)°, Z = 20 (for $Cs[FeL_3]$). As with $K[FeL_3]\cdot 2H_2O$, the cell contents comprise parallel independent chains of $[FeL_3]^-$ anions alternating with Cs cations, the chains being almost linear in this case; one of the chains is interrupted by a region of considerable disorder which adversely affects the accuracy of determination of the metal-atom geometries. Neither structure determination is helpful in understanding the anomalous magnetism of these two complexes.

THE few recent studies of complexes of ligands of the anionic isonitrosoketone type with transition-metal ions show the formation of a five-membered chelate ring co-ordinating with the metal by way of the carbonyl oxygen and nitrogen lone pair, the ligand disposition in tris(chelates) being *fac*.[1-3] Among the early literature of the subject, the work of Cambi and his school is particularly significant with regard to complexes of these ligands (A^-) with iron(II).[4,5] Salts of the type $FeA_2\cdot xH_2O$ were prepared for a variety of ligands and shown to exhibit a variety of magnetic behaviour, some derivatives being ' low-spin ', some ' high-spin ', and others intermediate and temperature dependent in the range 100—300 K. These results suggested that either the crystal-field properties of these ligands might lie about those required for a ' crossover ' situation (this has been demonstrated elsewhere for 8-hydroxyquinoline [6]) in complexes of iron(II), or that the ligands might be of a type peculiarly conducive to antiferromagnetic exchange or some similar mechanism. Accordingly, it was decided to embark on a detailed study of certain of these derivatives; the present paper describes the delineation of the magnetic and structural properties of a series of salts described by Cambi as $M_2[Fe_3L_8]\cdot xH_2O$, L^- being the ligand $NH_2\cdot COC(NO)^-\cdot CO\cdot NH_2$, the anion of isonitrosomalonamide, some of which were reported to have magnetic moments of intermediate spin. (Our studies have shown the stoicheiometry of these salts to be $M[FeL_3]\cdot xH_2O$.)

For the comparative purposes, the diamagnetic series of salts obtained with violuric acid, HV, and shown to be $M[FeV_3]\cdot xH_2O$ have recently been studied;[3] this series

---

[1] P. W. Carreck, J. Charalambous, M. J. Kensett, M. McPartlin, and R. Sims, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 749.

[2] S. Candeloro, D. Grdenić, N. Taylor, B. Thompson, M. Viswamitra, and D. Crowfoot Hodgkin, *Nature*, 1969, **224**, 589.

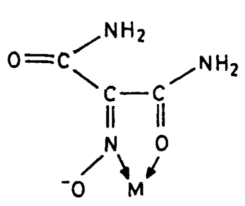
[3] C. L. Raston and A. H. White, *J.C.S. Dalton*, 1975, 1915.

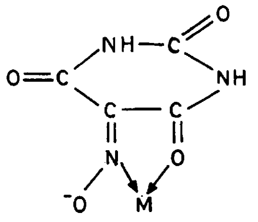
[4] L. Cambi, IXth Congress Internat. Quim. Pura Aplicada, 1934, **2**, 199.

[5] L. Cambi and A. Cagnasso, *Gazzetta*, 1933, **63**, 767.

[6] C. S. G. Phillips and R. J. P. Williams, ' Inorganic Chemistry,' vol. II, Oxford University Press, 1965, p. 313.

is diamagnetic, and the crystal structure of the ammonium salt has been reported. Chelation of L^- and V^- with iron(II) is as follows:


Isonitrosomalonamide


Violurate

EXPERIMENTAL

' Isonitrosomalonamide ' was prepared by the method of Whiteley[7] and aqueous solutions of the anionic ligand prepared by stoicheiometric reaction with solutions of MOH or M_2CO_3 ($M^+ = NH_4^+$, Li^+, Na^+, K^+, Rb^+, or Cs^+); the potassium salt was obtained from solution as an anhydrous solid K^+L^- (established by analysis) for the purpose of obtaining an accurate diamagnetic susceptibility correction for the ligand. $M[FeL_3]\cdot xH_2O$ are prepared as deep blue crystalline fine powders with a bronze sheen (very similar to $M[FeV_3]\cdot xH_2O$) by mixing a concentrated aqueous solution of the ligand salt with iron(II) sulphate; for the Na^+ and Li^+ derivatives iron(II) perchlorate in 1 : 1 water–ethanol was used because of their high solubility in water. Attempts to produce the NH_4^+ salt failed, however, producing $FeL_2\cdot 1\frac{1}{2}H_2O$, which was also produced if the solutions were too dilute or if precipitation of the salt were prolonged over a few hours. It is thus difficult to obtain crystals of any appreciable size for derivatives other than those of potassium; $FeL_2\cdot 1\frac{1}{2}H_2O$ is also prone to contaminate the $M[FeL_3]\cdot xH_2O$ samples, particularly the Li^+ and Na^+ derivatives. Consequently, all samples used in the magnetic work were checked immediately by analysis and microscopy for homogeneity and stoicheiometry. Analytical data (Table 1) suggest the following degrees of solvation of the derivatives: Li^+, $EtOH\cdot 2H_2O$; Na^+, $EtOH\cdot 2H_2O$ (doubtful in this case since preliminary X-ray data on a small crystal obtained from a sample prepared by the method used for the potassium salt shows it to be isomorphous with that derivative); K^+, $2H_2O$ (confirmed by subsequent X-ray work); Rb^+, $2H_2O$; Cs^+, $2H_2O$.

TABLE 1

Typical analyses for the derivatives in the text; calc. values are in parentheses

Compound	C	N	H	Fe	M
KL *	21.25	24.35	2.30		23.05
	(21.30)	(24.85)	(2.37)		(23.08)
KD	29.85	20.7	4.25		19.15
	(30.46)	(21.32)	(4.06)		(19.80)
$FeL_2\cdot 1\frac{1}{2}H_2O$	21.3	24.15	3.1	16.5	
	(21.01)	(24.50)	(3.23)	(16.28)	
$FeD_2\cdot 2H_2O$	29.4	20.5	5.0	13.45	
	(29.43)	(20.59)	(4.94)	(13.68)	
$Li[FeL_3]\cdot EtOH\cdot 2H_2O$	24.9	24.0	3.95	11.2	
	(24.67)	(23.55)	(4.14)	(10.45)	
$Na[FeL_3]\cdot EtOH\cdot 2H_2O$	23.65	22.9	3.45	10.3	3.85
	(23.98)	(22.87)	(4.02)	(10.13)	(4.17)
$K[FeL_3]\cdot 2H_2O$	20.9	24.2	2.85	11.2	
	(20.74)	(24.19)	(3.09)	(10.71)	
$Rb[FeL_3]\cdot 2H_2O$	19.2	21.7	2.85	9.9	
	(19.05)	(22.31)	(2.84)	(9.84)	
$Cs[FeL_3]\cdot 2H_2O$	17.3	20.5	2.75		21.25
	(17.58)	(20.50)	(2.67)		(21.61)

* $L^- = C_3H_4N_3O_3^-$ = isonitrosomalonamide anion; $D^- \equiv C_5H_8N_3O_3 \equiv$ *NN'*-dimethylisonitrosomalonamide anion.

The ligand *NN'*-dimethylisonitrosomalonamide, HD (m.p. 152—153 °C), was also prepared from methylamine and methylammonium chloride instead of ammonia and ammonium chloride. K^+D^- crystallises as the dihydrate. Attempts to prepare salts of the type $M[FeD_3]\cdot xH_2O$ were unsuccessful; in all cases the product was $FeD_2\cdot 2H_2O$.

Magnetic susceptibilities were determined by the Gouy method over the temperature range 80—350 K; because of the very real possibility of contamination by $FeL_2\cdot 1\frac{1}{2}H_2O$, a number of independent samples of each derivative were made, run as duplicates, and subjected to independent analyses, it not being possible to recrystallise the derivatives without decomposition. [In the case of the potassium salt, when the X-ray structure analysis showed only one iron atom in the asymmetric unit, surrounded by what were thought to be bond lengths of an unlikely shortness, a batch of crystalline material was grown (up to 0.6 mm), and a number of crystals isomorphous with that used in the structure determination were handpicked and their bulk susceptibility and Mössbauer spectrum checked.] It is essential to run the magnetic data within days of the sample preparation; after a number of weeks the paramagnetic samples exhibit a gradual decrease in magnetic susceptibility; there appears to be no deterioration in other respects and analyses remain constant. Ligand diamagnetic correction terms ($-10^{12}\,\Delta$ m³ mol⁻¹) are: L^- 653 ± 20, $D^-\cdot 2H_2O$ 1 020 ± 50, and V^- 628 ± 20.

TABLE 2

Experimental molar magnetic susceptibility, χ_m', corrected for Δ, the diamagnetic correction term, and magnetic moment μ B.M. [calculated from $\mu = 797.5\sqrt{(\chi_m + \Delta)T}$] at temperatures T/K and field strength $H = 0.77$ tesla. Entries at each temperature are given in the order T, $10^9\,\chi_m'$, μ, the value of χ_m being appropriate to the molecular formula quoted. S.I. units for χ_m and Δ(m³ mol⁻¹). Diamagnetic correction terms for the cations were assumed to be ($-10^{12}\,\Delta$): Li^+, 7.5; Na^+, 63; K^+, 163; Rb^+, 250; Cs^+, 390; Fe^{2+}, 163; for H_2O, 163

(1) $Li[FeL_3]\cdot EtOH\cdot 2H_2O$ ($M = 535.2$, $-10^{12}\,\Delta = 2890$)

96, 38.6, 1.54; 117, 35.0, 1.61; 133, 32.3, 1.65; 160, 29.1, 1.72; 183, 26.9, 1.77; 214, 24.8, 1.84; 235, 23.5, 1.88; 300, 21.1, 2.00

(2) $K[FeL_3]\cdot 2H_2O$ (521.2, 2 610)

105, 53.3, 1.89; 129, 43.6, 1.89; 157, 36.9, 1.92; 171, 34.5, 1.94; 182, 32.7, 1.95; 213, 29.5, 2.00; 242, 27.4, 2.05; 268, 25.8, 2.10; 296, 24.7, 2.16

(3) $Cs[FeL_3]\cdot 2H_2O$ (615.0, 2 840)

95, 92.1, 2.36; 120, 74.3, 2.38; 132, 60.1, 2.25; 161, 56.2, 2.40; 187, 49.9, 2.44; 214, 45.3, 2.48; 265, 39,5. 2.58; 296, 37.7, 2.66

(4) $FeL_2\cdot 1\frac{1}{2}H_2O$ (352.1, 1 720)

100, 109.9, 2.64; 124, 90.9, 2.68; 142, 80.5, 2.70; 159, 73.6, 2.73; 186, 64.0, 2.75; 214, 58.8, 2.83; 242, 54.7, 2.90; 287, 47.9, 2.95

(5) $FeD_2\cdot 2H_2O$ (408.2, 2 010)

92, 106.2, 2.49; 114, 88.2, 2.53; 147, 69.9, 2.56; 159, 65.6, 2.58; 192, 56.3, 2.62; 221, 49.7, 2.64; 251, 44.9, 2.68; 281. 40.7, 2.70; 296, 39.8, 2.74; 308, 37.2, 2.70

Magnetic-moment data for the paramagnetic K^+ and Cs^+ salts are given in Table 2 for those samples we regard as

---

[7] M. A. Whiteley, *J. Chem. Soc.*, 1900, **77**, 1040; 1903, **83**, 24.

preparatively and analytically the best; Na^+ and Rb^+ salts are diamagnetic. [In view of the foregoing reservations, however, we are reluctant to place error limits on the data, those for the lithium salt being particularly suspect. Variations of up to 0.5 B.M. of the values shown have been obtained for all derivatives; while it is tempting to ascribe this to traces of $FeL_2 \cdot 1\frac{1}{2}H_2O$, the analytical purity of almost all samples studied suggests that the effect may be dependent to a considerable extent on the fine details of preparation and/or particle size.]

Mössbauer spectra were recorded with a scanned-velocity spectrometer operating in the time mode at 77, 195, and 295 K, by use of a 10 mCi Co^{57} sample in palladium foil. Samples were always powdered and supported in a 3 cm diameter Perspex holder such that the sample contained *ca.* 10 mg Fe cm^{-2}. Details of the spectra are given in Table 3; errors are typically ± 0.03 mm s^{-1} except where indicated otherwise.

TABLE 3

Isomer shifts and quadrupole spittings derived from the Mössbauer spectra (mm s^{-1})

T/K	298		195		72	
	ΔE_q	δ	ΔE_q	δ	ΔE_q	δ
$Li[FeL_3] \cdot EtOH \cdot 2H_2O$	0.27	0.50	0.34	0.56	0.36	0.57
$Na[FeL_3] \cdot EtOH \cdot 2H_2O$	0.36	0.53	0.40	0.57	0.45	0.57
$K[FeL_3] \cdot 2H_2O$		0.53	0.27	0.57	0.29	0.58
			3.6 *	1.7 *	3.7 *	1.7 *
$Rb[FeL_3] \cdot 2H_2O$	0.24	0.50	0.32	0.49	0.34	0.58
$Cs[FeL_3] \cdot 2H_2O$		0.47	0.22	0.51	0.28	0.55
	3.6 *	1.70 *	3.3 *	1.5 *	4.1 *	2.0 *
$FeL_2 \cdot 1\frac{1}{2}H_2O$		0.51	0.30	0.54	0.30	0.54
	4.1 *	1.7 *	4.1 *	1.7 *	4.5 *	2.0 *
$FeD_2 \cdot 2H_2O$	0.37	0.51	0.39	0.53	0.45	0.54
	3.9	1.6	4.1	1.8	4.3	1.90

* Error ± 0.3 mm s^{-1}; others ± 0.03 mm s^{-1}.

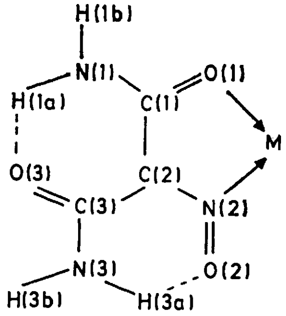
Crystallography

(*a*) *The Potassium Salt.*—Suitable crystals were obtained by slow diffusion of a freshly prepared aqueous iron(II) sulphate solution through a capillary into a concentrated solution of K^+L^- prepared as described previously. A crystal 0.28×0.15 (b) $\times$ 0.45 mm with a,c as section diagonals was used for the X-ray work. Unit-cell calibration was carried out by a least-squares fit of the angular parameters of 15 reflections centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer. A unique data set was gathered in the range $2\theta < 55°$ yielding 4 512 independent reflections, of which 3 981 with $I > 2\sigma(I)$ were considered observed and used in the structure solution and refinement after correction for absorption.

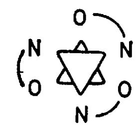
Crystal data. $KFeL_3 \cdot 2H_2O \equiv C_9H_{16}KN_9O_{11}$, $M = 520.7$, Monoclinic, $a = 29.89(1)$, $b = 9.780(2)$, $c = 13.980(3)$ Å, $\beta = 106.68(2)°$, $U = 3\,915(2)$ Å^3, $D_m = 1.75(1)$, $Z = 8$, $D_c = 1.77$ g cm^{-3}, $F(000) = 2\,128$. Monochromatic Mo-K_α radiation, $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 5.47 cm^{-1}. Space group $C2/c$ (C_{2h}^6, No. 15). Neutral atom scattering factors, those for all atoms except H corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[8-10]

The structure was solved by the heavy-atom method and refined by 9×9 block-diagonal least squares, all non-hydrogen atoms being refined with anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^2 + \ldots 2U_{23}klb^*c)^*]$. Refinement proceeded satisfactorily to R *ca.* 0.045. Regions of electron density in the difference map suggested that a disordered water molecule was present; its population in the various sites was estimated giving a total of 1 and the positional and anisotropic thermal parameters of the fragments refined. All hydrogen atoms except those associated with the disorder were located and refined isotropically. In order to approximate to a full-matrix treatment the parameters of all atoms about (and including) the iron and potassium atoms were refined as a single block in the final stages. Refinement was terminated with all non-hydrogen parameter shifts $< 0.2\sigma$, the final residual being 0.040, and R' $[= (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$ 0.053; a weighting scheme of the form $w = [\sigma^2(F_o) + n \times 10^{-4}(F_o)^2]^{-1}$ was found appropriate for $n = 6$.

Ligand numbering follows that used for the ammonium violurate analogue,[3] being as follows for each ligand:



The dotted contacts of *ca.* 2.0 Å represent hydrogen bonds. Where necessary atom numbers are prefixed by i, i being the ligand number [(1)—(3)]. O(i1) and N(i2) form the upper and lower triangles of the co-ordination polyhedron of C_3 symmetry about the metal:



Hydrogen atoms are labelled a or b as shown, prefixed by the nitrogen designation; the 'a' type hydrogen atoms are directed within the ligand and the 'b' type outwards. The unit cell is illustrated in Figure 1, and the anion in Figure 2.

(*b*) *The Caesium Salt.*—Crystals of this derivative are very difficult to obtain in any appreciable size; the crystal used in the present study was obtained as a thin leaf-like specimen $0.05 \times 0.09 \times 0.28$ mm by the slow addition of an aqueous solution of the caesium salt of the ligand to iron(II) sulphate solution at 80 °C. A unique data set was gathered by a conventional 2θ—θ scan within the range $2\theta < 100°$ yielding 5 611 reflections of which 5 126 with $I > 2\sigma(I)$ were considered observed and used in the structure solution and refinement, reflections being allocated weights of $[\sigma^2(F_o)]^{-1}$. Data were corrected for absorption.

Crystal data. $5Cs[Fe\{NH_2 \cdot CO \cdot C(NO) \cdot CO \cdot NH_2\}_3] \cdot 9H_2O \equiv C_{45}H_{78}Cs_5Fe_5N_{45}O_{54}$, $M = 3\,147$, Monoclinic, $a = 33.312(6)$, $b = 24.792(5)$, $c = 13.323(2)$ Å, $\beta = 91.55(1)°$, $U = 10\,999(4)$ Å^3, $D_m = 1.93(1)$, $Z = 4$, $D_c = 1.90$ g cm^{-3}, $F(000) = 6\,150$. Cu-K_α radiation (Ni-filtered), $\lambda = 1.5418$ Å; μ(Cu-K_α) = 191 cm^{-1}. Space group Aa (C_s^4, No. 9). Neutral-atom scattering factors, those for Cs and Fe being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[8-10]

---

[8] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[9] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

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

The structure was solved by the heavy-atom method, aided by foreknowledge of the solution of the potassium derivative, and refined by 9 × 9 block-diagonal least squares. Only the metal atoms could be refined significantly with anisotropic thermal motion, the form being as before. No hydrogen atoms were included in the refinement. The accuracy of the structure is severely vitiated by the occurrence of a large region of disorder of *ca.* 4 Å radius at about $(x,y,z) = (0.375, 0.15, 0.500)$; attempts to locate a meaningful disposition of atoms in this region failed. The periphery of the region of disorder at either end in the *a* direction is approximately coincident with the expected position of a caesium atom and, in fact, large regions of electron density found at these areas were represented by disordered caesium atoms Cs($3\alpha - \gamma$), the populations being fixed from a difference map to give a total of 1 rather than 2 since it appears that the expected $[\mathrm{FeL_3}]^-$ anion at the centre of the disorder is missing.* Refinement 'converged' with parameter shifts $<0.7\sigma$ at R 0.12, and R' 0.17. The atom numbering system within the ligand is as already defined, preceded by the number of the iron atom.

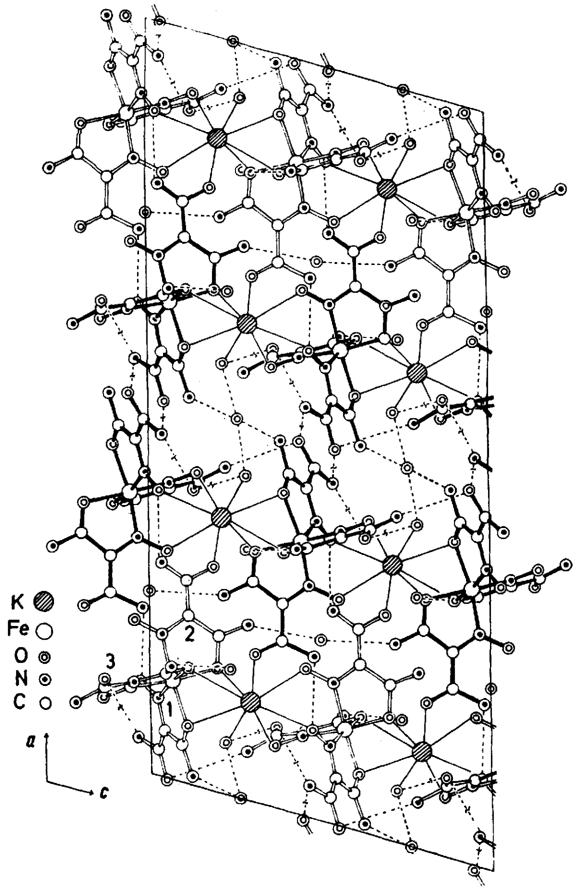


FIGURE 1 Unit-cell contents of the potassium salt projected down *b*; hydrogen bonds are shown as dotted lines. Ligand numbering is given

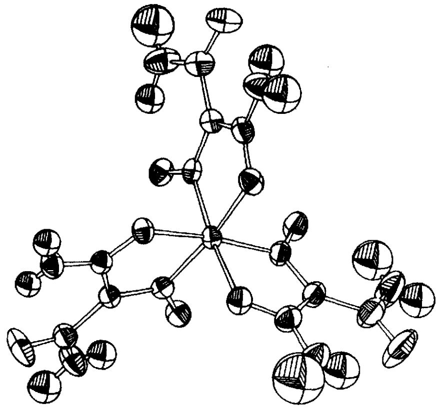


FIGURE 2 The anion of the potassium salt, showing 50% thermal ellipsoids

Computation was carried out by use of the '*X*-Ray System';[11] structure amplitudes for both salts, and bond distances and angles and least-squares planes for the caesium salt are deposited as Supplementary Publication No. SUP 21844 (48 pp., 1 microfiche).† Final positional and thermal parameters are listed in Table 4 for both salts.

DISCUSSION

(*a*) *Crystal Structure of the Potassium Salt.*—As expected, the crystal structure comprises potassium cations accompanied in a 1 : 1 proportion by complex $[\mathrm{FeL_3}]^-$ anions and associated lattice water molecules, one of which is disordered. The crystal packing is interesting, the lattice comprising infinite zig-zag chains made up of alternating anions and cations and lying parallel to *c*. Within each chain there are two anions per unit translation in *c*, spaced at $c/2$ (= 6.990 Å); the potassium ions lie midway between them in a plane parallel to *bc* and disposed with alternating positive and negative *y* co-ordinates giving rise to the zig-zag. Within each anion, the disposition of the three asymmetric bidentate ligands is *fac*, and the anion symmetry close to C_3 rather than the D_3 typical of symmetric bidentate ligands.

Whereas the two potassium ions about each iron atom are almost linearly disposed [K ··· Fe ··· K 178.2(1)°], the disposition of the irons about each potassium is angular [Fe ··· K ··· Fe 136.2(3)°]. The potassium ion is approached by the three (amide) O(1) type ligand atoms along the Fe ··· K axis which has essentially local threefold symmetry (no Fe–O–K angle deviates from the mean of 91.41° by more than 0.25° and the O–Fe–O and O–K–O angles are similarly closely equivalent). For this approach, the Fe ··· K distance is 3.488(1) Å. The next anion in the chain also approaches the potassium but along the other (nitrosyl) end of the three-fold co-ordination axis; the local symmetry as measured by the angles O(2)–K–O(2) and K–O(2)–N(2) is again very close to three-fold, with a larger K ··· Fe distance of 4.044(1) Å. Both approaches may be considered as co-ordination of the potassium ion by a pair of dissimilar

---

* A referee has raised the question as to whether the space group may not be centric and the 'disorder' an artefact of a wrong choice of space group compounded by subsequent malpositioning of the peripheral ligand atoms. We appreciate the considerations leading to this query but note that the density of the substance is consistent with the present model.

† For details see Notice to Authors, No. 7, *J.C.S. Dalton*, 1976, Index issue.

[11] 'The *X*-Ray System,' Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A., version of June 1972.

Table 4

Atomic fractional cell co-ordinates (x,y,z with preceding decimal omitted) and thermal parameters ($10^3\ U_{ij}$ Å^2) with least-squares estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(*a*) Potassium salt									
(i) Anion									
Fe	13 369(1)	00 555(4)	06 039(3)	22.5(2)	30.2(2)	25.7(2)	−3.0(2)	6.5(1)	−0.9(2)
Ligand (1)									
C(1)	05 078(9)	−0 651(3)	0 889(2)	26(1)	32(1)	24(1)	1(1)	6(1)	0(1)
C(2)	06 301(9)	−1 831(3)	0 378(2)	27(1)	29(1)	28(1)	−3(1)	8(1)	0(1)
C(3)	03 461(10)	−3 093(3)	0 175(2)	33(1)	34(1)	40(2)	−4(1)	12(1)	−2(1)
N(1)	01 214(9)	−0 634(3)	1 180(2)	31(1)	37(1)	45(1)	−3(1)	17(1)	−5(1)
N(2)	10 343(8)	−1 622(2)	0 163(2)	29(1)	29(1)	25(1)	2(1)	9(1)	1(1)
N(3)	04 539(12)	−4 041(3)	−0 385(2)	50(2)	39(2)	62(2)	−16(1)	28(2)	−17(1)
O(1)	07 798(6)	0 365(2)	1 058(1)	28(1)	33(1)	33(1)	−3(1)	11(1)	−6(1)
O(2)	12 038(7)	−2 547(2)	−0 296(2)	37(1)	33(1)	45(1)	0(1)	21(1)	−7(1)
O(3)	00 163(9)	−3 250(3)	0 545(2)	57(1)	48(1)	101(2)	−26(1)	50(2)	−27(1)
H(1a)	004(1)	012(4)	151(3)	41(9)					
H(1b)	−004(1)	−127(4)	105(3)	35(9)					
H(3a)	027(1)	−487(4)	−049(3)	60(12)					
H(3b)	067(1)	−395(4)	−055(3)	47(11)					
Ligand (2)									
C(1)	20 742(11)	−1 048(4)	1 994(2)	38(2)	50(2)	36(2)	2(1)	6(1)	9(1)
C(2)	22 427(10)	−0 876(4)	1 126(2)	28(1)	50(2)	37(2)	5(1)	8(1)	12(1)
C(3)	27 226(12)	−1 123(3)	1 123(3)	37(2)	78(3)	67(2)	18(2)	15(2)	28(2)
N(1)	23 421(14)	−1 570(5)	2 847(3)	52(2)	122(4)	49(2)	21(2)	8(2)	38(2)
N(2)	19 073(7)	−0 363(3)	0 352(2)	24(1)	39(1)	29(1)	0(1)	6(1)	5(1)
N(3)	28 353(12)	−1 110(5)	0 278(3)	39(2)	122(4)	81(3)	29(2)	30(2)	44(3)
O(1)	16 603(7)	−0 706(2)	1 932(1)	34(1)	52(1)	28(1)	0(1)	8(1)	4(1)
O(2)	19 860(7)	−0 141(3)	−0 492(2)	32(1)	64(2)	34(1)	5(1)	14(1)	13(1)
O(3)	30 067(10)	−1 627(4)	1 911(3)	48(2)	148(3)	79(2)	46(2)	18(1)	57(2)
H(1a)	225(2)	−168(7)	348(6)	150(27)					
H(1b)	257(2)	−178(5)	282(4)	77(12)					
H(3a)	307(2)	−135(5)	022(3)	69(14)					
H(3b)	265(2)	−068(6)	−021(4)	88(17)					
Ligand (3)									
C(1)	14 071(9)	2 801(3)	0 430(2)	30(1)	36(2)	42(2)	−7(1)	10(1)	−4(1)
C(2)	11 464(9)	2 362(3)	−0 564(2)	30(1)	32(1)	36(1)	−1(1)	9(1)	1(1)
C(3)	09 618(12)	3 314(3)	−1 399(2)	48(2)	37(2)	38(2)	5(1)	16(1)	2(1)
N(1)	14 857(14)	4 112(4)	0 675(3)	81(2)	37(2)	56(2)	−14(2)	1(2)	−2(2)
N(2)	10 770(7)	0 998(2)	−0 594(2)	19(1)	34(1)	29(1)	0(1)	7(1)	−4(1)
N(3)	06 621(12)	2 810(4)	−2 221(2)	70(2)	48(2)	40(2)	8(2)	4(1)	8(1)
O(1)	15 578(7)	1 896(2)	1 092(1)	36(1)	38(1)	32(1)	−9(1)	5(1)	−4(1)
O(2)	08 369(2)	0 419(2)	−1 400(1)	32(1)	40(1)	29(1)	−1(1)	1(1)	−6(1)
O(3)	10 792(10)	4 547(3)	−1 321(2)	73(2)	34(1)	57(2)	2(1)	19(1)	7(1)
H(1a)	165(2)	442(5)	142(4)	84(15)					
H(1b)	148(2)	449(5)	023(4)	69(16)					
H(3a)	053(2)	340(6)	−273(4)	101(19)					
H(3b)	063(1)	180(4)	−223(3)	47(10)					
(ii) Cation									
K	13 304(2)	1 432(8)	29 013(5)	42.0(4)	45.9(4)	31.5(3)	−9.6(3)	11.3(3)	−4.8(3)
(iii) Solvent water									
O(1)	0	1 706(5)	2 500(−)	58(3)	51(3)	83(3)	0(−)	15(2)	0(−)
H(1)	017(1)	219(4)	242(3)	45(11)					
O(2)	06 994(11)	3 549(3)	2 176(2)	71(2)	67(2)	73(2)	−2(2)	15(2)	−14(2)
H(2a)	085(2)	428(6)	243(4)	96(17)					
H(2b)	064(2)	358(5)	152(4)	94(10)					
O(3) *	2 500(−)	2 500(−)	0 000(−)	364(33)	73(10)	234(23)	−111(16)	272(26)	−87(13)
O(4) *	6 670(5)	0 968(13)	2 216(10)	181(13)	81(8)	113(10)	−51(9)	77(10)	−36(3)
* Population 0.33.									
(*b*) Caesium salt									
(i) Metal atoms ($x,y,z \times 10^4$)									
Cs(1)	3 691(2)	−0 147(1)	−0 082(4)	50(2)	46(2)	55(2)	0(2)	−2(1)	0(2)
Cs(2)	1 190(2)	−0 017(4)	−0 0071(7)	38(2)	155(4)	143(4)	0(2)	2(2)	−15(3)
Cs(3α) †	2 447(4)	1 449(6)	5 244(13)	87(7)	130(10)	179(12)	4(7)	−48(8)	−60(10)
Cs(3β) †	2 584(20)	1 705(32)	3 769(61)	85(41)	131(58)	153(60)	−60(40)	37(40)	75(50)
Cs(3γ) †	4 939(6)	1 439(17)	4 519(17)	61(11)	384(51)	116(15)	−6(17)	10(10)	61(22)
Cs(3δ) †	4 869(12)	1 713(15)	6 073(44)	56(23)	42(21)	191(49)	−39(18)	−44(2)	71(27)
Cs(4)	−0 052(2)	1 734(3)	4 955(4)	111(4)	110(4)	84(3)	−4(3)	−31(3)	2(3)
Cs(5)	7 464(2)	1 778(3)	4 848(4)	115(4)	116(4)	77(3)	31(3)	−17(3)	7(3)
Fe(1)	0 000(−)	0 126(4)	0 000(−)	41(5)	62(6)	37(4)	−3(4)	−2(3)	−8(4)
Fe(2)	2 358(2)	−0 157(2)	−0 134(4)	46(4)	14(3)	21(3)	−4(3)	1(3)	5(3)
Fe(3)	1 148(2)	1 608(3)	4 825(5)	53(5)	25(4)	42(4)	−1(3)	1(3)	−10(3)
Fe(4)	8 869(3)	1 888(4)	4 891(6)	76(6)	60(4)	36(4)	11(4)	−12(4)	−5(4)
Fe(5)	6 234(2)	1 669(3)	4 997(5)	63(5)	29(4)	29(4)	−6(3)	−10(3)	−1(3)

† Populations: α, 0.494; β, 0.080; γ, 0.323; δ, 0.103.

TABLE 4 (*Continued*)

(ii) Ligand ($x,y,z \times 10^3$)

Atom	x	y	z	U
Ligand (11)				
O(1)	040(1)	031(1)	107(2)	33(7)
N(1)	049(2)	085(2)	248(4)	83(16)
C(1)	030(1)	072(2)	160(3)	26(9)
O(2)	−049(1)	101(1)	−004(3)	54(9)
N(2)	−020(1)	081(1)	037(2)	23(7)
C(2)	−006(1)	104(2)	119(3)	33(10)
O(3)	−005(1)	167(2)	253(4)	87(13)
N(3)	−046(2)	186(3)	112(5)	102(20)
C(3)	−019(1)	152(2)	170(3)	26(9)
Ligand (13)				
O(1)	038(1)	−051(1)	−028(2)	45(8)
N(1)	042(2)	−137(2)	023(4)	74(14)
C(1)	018(1)	−090(2)	028(3)	18(8)
O(2)	−058(1)	−015(1)	134(2)	47(8)
N(2)	−028(1)	−038(2)	075(3)	40(9)
C(2)	−015(2)	−079(2)	085(4)	58(14)
O(3)	−012(2)	−170(3)	149(5)	122(19)
N(3)	−065(1)	−115(2)	191(3)	39(9)
C(3)	−031(2)	−124(2)	132(4)	56(14)
Ligand (22)				
O(1)	202(1)	−030(1)	−134(2)	49(8)
N(1)	195(1)	−084(1)	−270(3)	33(8)
C(1)	215(2)	−069(3)	−182(4)	62(15)
O(2)	293(1)	−101(1)	−003(3)	52(9)
N(2)	263(1)	−076(2)	−062(4)	63(12)
C(2)	246(1)	−096(2)	−146(3)	28(10)
O(3)	246(1)	−168(2)	−270(3)	57(9)
N(3)	293(7)	−176(2)	−151(4)	61(12)
C(3)	266(2)	−147(3)	−199(3)	89(21)
Ligand (31)				
O(1)	091(1)	198(2)	364(3)	72(11)
N(1)	088(1)	201(2)	200(3)	55(11)
C(1)	105(1)	183(2)	282(3)	39(11)
O(2)	179(1)	103(1)	395(2)	42(8)
N(2)	149(1)	133(1)	381(2)	20(7)
C(2)	138(2)	147(2)	279(4)	57(14)
O(3)	142(1)	133(2)	112(3)	68(11)
N(3)	185(1)	090(2)	204(3)	52(11)
C(3)	153(1)	130(2)	201(3)	41(11)
Ligand (33)				
O(1)	082(1)	202(1)	585(2)	38(7)
N(1)	079(1)	275(2)	683(3)	39(9)
C(1)	094(1)	245(2)	610(4)	43(12)
O(2)	184(1)	236(2)	458(3)	58(9)
N(2)	146(1)	226(2)	499(3)	40(9)
C(2)	131(1)	262(2)	571(3)	29(10)
O(3)	138(1)	347(1)	646(2)	48(8)
N(3)	178(2)	332(3)	535(4)	88(17)
C(3)	149(1)	314(2)	588(4)	61(15)
Ligand (42)				
O(1)	923(2)	241(2)	424(4)	93(14)
N(1)	931(1)	335(2)	411(3)	54(11)
C(1)	912(2)	292(2)	440(4)	54(14)
O(2)	825(1)	250(1)	571(2)	49(8)
N(2)	859(1)	251(2)	528(3)	44(10)
C(2)	866(2)	298(2)	489(5)	57(13)
O(3)	875(2)	391(2)	474(5)	114(18)
N(3)	824(1)	358(2)	559(4)	61(12)
C(3)	861(2)	351(3)	513(6)	90(21)
Ligand (51)				
O(1)	655(1)	196(1)	613(2)	28(6)
N(1)	653(1)	206(2)	795(4)	63(12)
C(1)	640(1)	185(2)	693(4)	47(12)
O(2)	567(1)	101(2)	582(3)	68(11)
N(2)	596(2)	137(2)	598(4)	76(14)
C(2)	606(1)	145(2)	696(3)	25(9)
O(3)	598(2)	142(2)	874(4)	102(16)
N(3)	553(2)	086(2)	776(4)	71(14)
C(3)	585(2)	119(2)	785(4)	48(12)
Ligand (53)				
O(1)	661(1)	102(1)	505(2)	38(7)
N(1)	668(1)	015(2)	441(3)	40(9)
C(1)	651(1)	068(2)	450(4)	46(12)
O(2)	572(1)	142(1)	344(2)	37(7)
N(2)	603(1)	125(1)	395(2)	29(8)
C(2)	620(1)	076(2)	377(3)	30(9)
O(3)	619(1)	−010(2)	288(3)	70(11)
N(3)	573(2)	048(2)	243(4)	78(15)
C(3)	600(1)	037(2)	312(3)	39(11)
Ligand (12)				
O(1)	041(1)	056(1)	−097(2)	47(8)
N(1)	041(2)	086(2)	−248(4)	85(16)
C(1)	029(1)	061(2)	−180(3)	35(10)
O(2)	−056(1)	−028(2)	−126(3)	71(11)
N(2)	−026(1)	007(1)	−131(3)	30(8)
C(2)	−014(1)	022(2)	−202(3)	18(8)
O(3)	−017(1)	051(2)	−374(3)	68(11)
N(3)	−062(2)	001(2)	−319(4)	78(15)
C(3)	−030(1)	023(2)	−307(2)	26(9)
Ligand (21)				
O(1)	206(1)	−055(1)	072(2)	26(6)
N(1)	197(1)	−086(1)	235(2)	24(7)
C(1)	220(1)	−056(1)	163(3)	24(9)
O(2)	303(1)	022(1)	111(2)	46(8)
N(2)	270(1)	−005(2)	099(3)	37(9)
C(2)	252(1)	−035(2)	193(4)	44(12)
O(3)	258(1)	−062(2)	362(4)	87(13)
N(3)	312(2)	001(3)	303(5)	90(17)
C(3)	273(2)	−040(3)	296(6)	92(22)
Ligand (23)				
O(1)	210(1)	052(1)	004(2)	35(7)
N(1)	205(1)	142(2)	−035(3)	55(11)
C(1)	219(2)	090(2)	−041(4)	49(12)
O(2)	299(1)	018(2)	−144(3)	78(12)
N(2)	264(1)	030(1)	−098(3)	32(8)
C(2)	253(1)	084(2)	−109(3)	26(9)
O(3)	260(2)	174(2)	−164(4)	102(15)
N(3)	308(2)	111(3)	−231(3)	111(12)
C(3)	274(2)	124(3)	−186(5)	78(18)
Ligand (32)				
O(1)	079(1)	099(1)	481(3)	55(9)
N(1)	071(2)	015(2)	533(4)	71(14)
C(1)	092(1)	059(2)	542(3)	39(11)
O(2)	170(1)	143(2)	647(3)	71(11)
N(2)	143(1)	125(1)	585(2)	25(8)
C(2)	127(1)	075(2)	606(3)	29(9)
O(3)	131(1)	−010(1)	678(2)	41(8)
N(3)	175(1)	057(2)	739(3)	48(10)
C(3)	141(1)	038(2)	686(3)	39(11)
Ligand (41)				
O(1)	921(1)	195(1)	615(2)	45(8)
N(1)	932(2)	154(2)	770(4)	79(15)
C(1)	911(1)	161(2)	685(3)	33(10)
O(2)	825(1)	125(1)	538(3)	80(12)
N(2)	860(1)	140(2)	568(3)	50(11)
C(2)	874(1)	138(2)	674(3)	30(10)
O(3)	875(1)	088(2)	817(3)	73(11)
N(3)	818(1)	070(2)	683(4)	68(13)
C(3)	858(2)	095(3)	734(4)	65(16)
Ligand (43)				
O(1)	917(1)	117(1)	443(2)	42(8)
N(1)	921(1)	071(2)	283(4)	76(14)
C(1)	907(1)	108(2)	353(3)	39(11)
O(2)	826(1)	199(2)	353(3)	84(13)
N(2)	860(1)	175(2)	373(3)	42(10)
C(2)	873(1)	133(2)	321(4)	43(12)
O(3)	873(1)	099(2)	150(3)	64(10)
N(3)	816(2)	145(2)	187(4)	73(14)
C(3)	855(2)	123(2)	209(4)	55(14)
Ligand (52)				
O(1)	660(1)	200(1)	413(2)	36(7)
N(1)	663(1)	274(2)	308(3)	52(11)
C(1)	643(1)	249(1)	377(3)	15(8)
O(2)	561(1)	231(1)	522(3)	53(9)
N(2)	591(1)	226(2)	484(3)	40(9)
C(2)	607(1)	264(2)	433(3)	42(12)
O(3)	607(1)	350(2)	338(3)	69(11)
N(3)	553(1)	329(2)	448(3)	53(11)
C(3)	590(2)	320(2)	401(4)	48(12)
Water molecules				
O(1)	515(1)	229(2)	829(3)	84(13)
O(2)	749(2)	014(2)	550(4)	101(15)
O(3)	−016(2)	018(3)	434(6)	146(24)
O(4)	732(3)	275(5)	689(8)	200(39)
O(5)	499(2)	263(3)	278(5)	131(21)
O(6)	741(1)	234(2)	238(3)	75(11)
O(7)	863(2)	014(3)	491(6)	128(20)
O(8)	867(2)	176(2)	−015(6)	114(16)
O(9)	391(2)	210(2)	262(4)	97(15)

TABLE 5

Interatomic distances (Å) and angles (°) (potassium salt only), with least-squares estimated standard deviations in parentheses

(*a*) Cation environment

K–O(2)	2.788(3)	O(11)–K–O(22$^{\mathrm{I}}$)	130.53(7)
K–O(11)	2.829(2)	O(11)–K–O(32$^{\mathrm{I}}$)	81.15(6)
K–O(21)	2.820(3)	O(11)–K–O(23$^{\mathrm{II}}$)	124.51(9)
K–O(31)	2.838(3)	O(21)–K–O(31)	58.92(7)
K–O(12$^{\mathrm{I}}$)	2.870(3)	O(21)–K–O(12$^{\mathrm{I}}$)	148.97(6)
K–O(22$^{\mathrm{I}}$)	2.820(2)	O(21)–K–O(22$^{\mathrm{I}}$)	77.98(7)
K–O(32$^{\mathrm{I}}$)	2.690(2)	O(21)–K–O(32$^{\mathrm{I}}$)	88.83(7)
K–O(23$^{\mathrm{II}}$)	2.702(4)	O(21)–K–O(23$^{\mathrm{II}}$)	102.70(10)
O(2)–K–O(11)	77.69(8)	O(31)–K–O(12$^{\mathrm{I}}$)	148.01(7)
O(2)–K–O(21)	132.01(8)	O(31)–K–O(22$^{\mathrm{I}}$)	119.47(7)
O(2)–K–O(31)	82.38(9)	O(31)–K–O(32$^{\mathrm{I}}$)	136.72(7)
O(2)–K–O(12$^{\mathrm{I}}$)	77.91(8)	O(31)–K–O(23$^{\mathrm{II}}$)	67.53(9)
O(2)–K–O(22$^{\mathrm{I}}$)	149.89(8)	O(12$^{\mathrm{I}}$)–K–O(22$^{\mathrm{I}}$)	73.02(7)
O(2)–K–O(32$^{\mathrm{I}}$)	104.31(9)	O(12$^{\mathrm{I}}$)–K–O(32$^{\mathrm{I}}$)	73.24(7)
O(2)–K–O(23$^{\mathrm{II}}$)	85.11(11)	O(12$^{\mathrm{I}}$)–K–O(23$^{\mathrm{II}}$)	85.78(9)
O(11)–K–O(21)	58.72(6)	O(22$^{\mathrm{I}}$)–K–O(32$^{\mathrm{I}}$)	74.80(7)
O(11)–K–O(31)	58.18(6)	O(22$^{\mathrm{I}}$)–K–O(23$^{\mathrm{II}}$)	85.09(9)
O(11)–K–O(12$^{\mathrm{I}}$)	138.65(7)	O(32$^{\mathrm{I}}$)–K–O(23$^{\mathrm{II}}$)	154.28(9)
K · · · Fe	3.488(1)	K · · · Fe$^{\mathrm{I}}$	4.044(1)
K–O(11)–Fe	91.47(7)	K–O(21)–Fe	91.59(9)
K–O(31)–Fe	91.17(8)	K–O(12$^{\mathrm{I}}$)–N(12$^{\mathrm{I}}$)	100.8(2)
K–O(22)–N(22$^{\mathrm{I}}$)	112.7(2)	K–O(32$^{\mathrm{I}}$)–N(32$^{\mathrm{I}}$)	112.9(2)
K · · · Fe · · · K$^{\mathrm{I}}$	178.29(2)	Fe · · · K · · · Fe$^{\mathrm{I}}$	136.20(3)

(*b*) Anion: (i) iron environment

O(11)–Fe–O(21)	89.2(1)	N(12)–Fe–N(22)	97.1(1)
O(11)–Fe–O(31)	88.8(1)	N(12)–Fe–N(32)	95.6(1)
O(21)–Fe–O(31)	89.7(1)	N(22)–Fe–N(22)	96.0(1)
O(11)–Fe–N(12)	82.4(1)	O(11)–Fe–N(32)	92.3(1)
O(21)–Fe–N(22)	82.5(1)	O(21)–Fe–N(12)	92.2(1)
O(31)–Fe–N(32)	82.6(1)	O(31)–Fe–N(22)	91.8(1)
		O(11)–Fe–N(22)	171.6(1)
		O(21)–Fe–N(32)	172.1(1)
		O(31)–Fe–N(12)	171.0(1)

(ii) Ligand geometries

Ligand	(1)	(2)	(3)	Mean
Fe–O(1)	1.969(2)	1.976(2)	1.971(2)	1.972
Fe–N(2)	1.889(2)	1.883(3)	1.873(2)	1.882
O(1)–Fe–N(2)	82.5(1)	82.5(1)	82.6(1)	82.5
O(1)–C(1)	1.263(3)	1.262(4)	1.266(4)	1.264
Fe–O(1)–C(1)	112.2(2)	111.8(2)	111.8(2)	112.0
C(1)–N(1)	1.330(4)	1.332(5)	1.331(5)	1.331
C(1)–C(2)	1.458(4)	1.450(5)	1.449(4)	1.452
O(1)–C(1)–N(1)	120.1(3)	119.3(4)	119.1(3)	119.5
O(1)–C(1)–C(2)	118.4(3)	118.7(3)	118.4(3)	118.5
C(2)–C(1)–N(1)	121.5(3)	122.1(3)	122.6(3)	122.1
C(2)–N(2)	1.342(4)	1.344(3)	1.349(4)	1.345
C(2)–C(3)	1.478(4)	1.478(5)	1.471(4)	1.476
Fe–N(2)–C(2)	115.9(2)	115.9(2)	116.0(2)	115.9
N(2)–O(2)	1.292(3)	1.286(4)	1.282(3)	1.287
Fe–N(2)–O(2)	123.5(2)	123.3(2)	123.5(2)	123.4
C(2)–N(2)–O(2)	120.6(2)	120.8(3)	120.4(2)	120.6
C(1)–C(2)–N(2)	111.0(2)	111.1(3)	110.9(2)	111.0
C(1)–C(2)–C(3)	122.9(3)	123.0(3)	123.4(3)	123.1
N(2)–C(2)–C(3)	126.1(3)	125.9(3)	125.6(2)	125.9
C(3)–O(3)	1.247(5)	1.244(5)	1.252(4)	1.248
C(3)–N(3)	1.312(5)	1.324(7)	1.333(4)	1.323
C(2)–C(3)–O(3)	120.2(3)	119.2(4)	120.6(3)	120.0
C(2)–C(3)–N(2)	118.6(3)	118.5(3)	117.2(3)	118.1
O(3)–C(3)–N(3)	121.3(3)	122.3(4)	122.3(3)	122.0
N(1)–H(1a)	0.94(4)	1.00(8)	1.07(5)	1.00
N(1)–H(1b)	0.76(4)	0.74(6)	0.72(5)	0.74
H(1a) · · · O(3)	2.09(4)	2.06(6)	2.16(5)	2.10
N(1)–H(1b) · · · O(3)	137(4)	142(5)	138(5)	139
N(3)–H(3a)	0.96(4)	0.76(5)	0.92(5)	0.88
N(3)–H(3b)	0.75(4)	0.85(5)	0.99(5)	0.86
H(3a) · · · O(2)	2.05(4)	1.99(5)	1.78(4)	1.94
N(3)–H(3a) · · · O(2)	136(4)	132(6)	137(3)	135

(*c*) Hydrogen bonding (i) About O(1)

O(1)–H(1)	0.72(4)	H(1)–O(1)–H(1$^{\mathrm{III}}$)	98(5)
O(1) · · · H(1a)	2.10(4)	H(1a) · · · O(1) · · · H(1a$^{\mathrm{III}}$)	85(1)
H(1)–O · · · H(1a)	102(4)	H(1)–O · · · H(1a$^{\mathrm{III}}$)	139(3)
H(1) · · · O(2)	2.17(4)	O(1)–H(1) · · · O(2)	177(4)

TABLE 5 (*Continued*)

(ii) About O(2)

O(2)–H(2a)	0.86(5)	H(2a)–O–H(2b)	109(5)
O(2)–H(2b)	0.89(5)	H(2a)–O · · · H(1)	139(4)
O(2) · · · H(1)	2.17(4)	H(2b)–O · · · H(1)	104(3)

(*d*) Interligand hydrogen bonds (<2.3 Å)

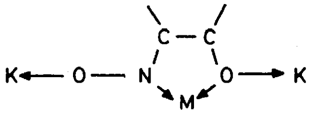
H(2a) · · · O(33$^{\mathrm{IV}}$)	2.04(5)	H(13a) · · · O(13$^{\mathrm{V}}$)	2.03(4)

Roman numerals denote the following transformations of the asymmetric unit at x,y,z

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

' tripod ' ligands; since the angle between them is essentially the Fe · · · K · · · Fe angle of 136.2°, there is ample space for ' co-ordination ' by other atoms about the centre of the Fe · · · K · · · Fe reflex angle, and in fact we find two further co-ordination positions occupied by a water molecule [O(2)] and an amide O(3) type oxygen from ligand (2) of one of the anions in the adjacent chain, so that each potassium is eight-co-ordinate. In addition to the intra-chain contacts, adjacent chains are linked by interligand hydrogen bonds (Table 5). Lattice interstices are occupied by water molecules O(1)—(4) of which O(1) and O(3) are on special positions and O(3) and O(4) are partially occupied sites, totalling two water molecules in all.

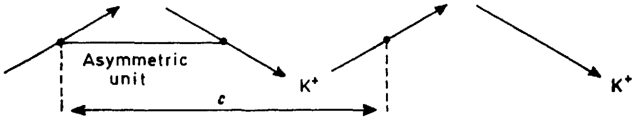
O(1) is tetrahedrally co-ordinated by its own hydrogen atoms, which hydrogen-bond to O(2), and an adjacent anionic ligand hydrogen so that it also spans adjacent chains since it lies on a two-fold axis. A similar array of two tripod ligands of a very similar type about a potassium ion has been reported in potassium tris-(4-chloro-2-nitrosophenolato)nickelate(II),[1] the system being derived from the similar nucleus of:



In this case, however, the potassium salt is seven- rather than eight-co-ordinate.

The co-ordination geometry about the metal atom is similar to that found in the tris(violurato)ferrate(II) species:[3] the bond lengths Fe–N(2) and Fe–O(1) are not significantly different and the difference in O(1)–Fe–N(2) angles is only trivial (82.5 *vs.* 83.8°). The geometry of the remainder of the ligand in the two species is compared in Figure 3; significant and non-trivial differences are found as a consequence of ring closure and consequent extension of the conjugation resulting in changes in the angles in the chelate ring.

(*b*) *Crystal Structure of the Caesium Salt.*—As in the potassium analogue, the structure is comprised of alkali-metal cations accompanied in a 1 : 1 proportion by complex $[FeL_3]^-$ anions and lattice water molecules (Figure 4). The quality of the structure is affected by factors militating against geometrical accuracy, *viz.* the gross disorder occurring in the present structure and, less important, the unsatisfactory crystal habit. As a result the anion geometries in the present structure are so inaccurate as to be meaningless and cast no light on the possible existence of low- and high-spin forms among the anions insofar as co-ordination disparities are concerned; we simply note that the mean anion geometry agrees well with that of the anion in the potassium salt. The structure itself is again of considerable interest, however. As in the potassium salt, the lattice is again centred monoclinic and the dominant feature of the lattice is chains of zig-zag arrays of alternating cations and anions. In the present case, by contrast, the chains run parallel to the long axis of the cell, *a*, rather than the short axis *c* as was the case in the potassium salt, although it should be noted that the lattice in the present case is defined as *A* rather than *C* as in the potassium salt. As in the potassium salt, the anionic generator of the first chain lies centred at (0,*y*,0) where *y* is quite small; however, in the caesium salt the generator comprises a double unit, the generator at the origin being accompanied by an independent anion centred close to ($\frac{1}{4}$,0,0); the second anion, moreover, is the enantiomer of the first, being related by a pseudo-inversion centre close to ($\frac{1}{8}$,0,0) near Cs(2). The remainder of the first chain is created along *a* by the ($x + \frac{1}{2},\bar{y},z$) glide acting on the above dimeric unit, a further false C_2 symmetry element resulting at ($\frac{3}{8}$,0,0) near Cs(1). Although the Fe–Cs–Fe–Cs chain is zig-zag as in the potassium salt, the angle at both Cs ions does not differ significantly from 180° (*cf.* the angle at K^+ of *ca.* 136°), whereas the angle at the iron atom in the present case is *ca.* 171° (*cf.* 78.2° in the potassium salt). If the anionic array of ligands is considered as having a head (comprising the three nitrosyl oxygens) and a tail (comprising the three co-ordinated amide oxygens), then, as in the case of the potassium salt, the cation is 'co-ordinated' by the tripod-like heads and tails of the anions on either side. In the case of the potassium salt, the disposition in both chains is:



so that each potassium ion is co-ordinated by the tripod 'head' of one ligand and the tripod 'tail' of the next; the eight-co-ordination of the potassium is made up by a pair of water molecules approaching at the reflex angle.

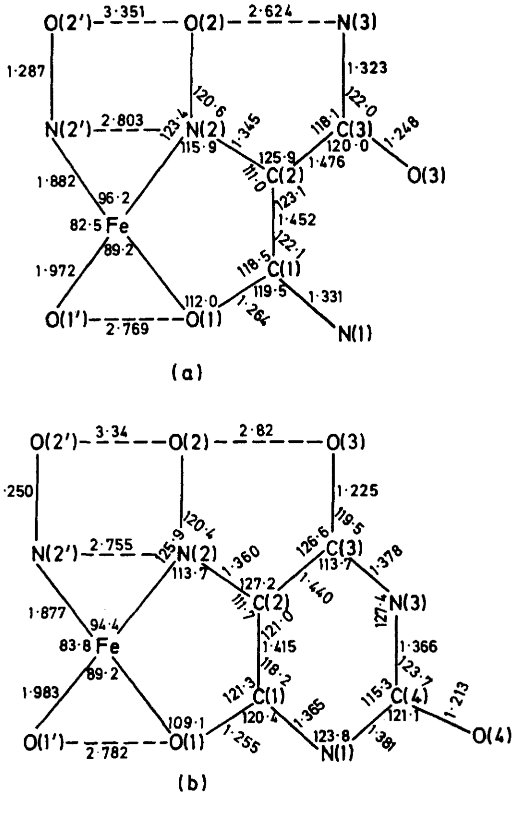


FIGURE 3 Comparison of the mean ligand geometries in (a) the tris(isonitrosomalonamido)- and (b) tris(violurato)-ferrate(II) species

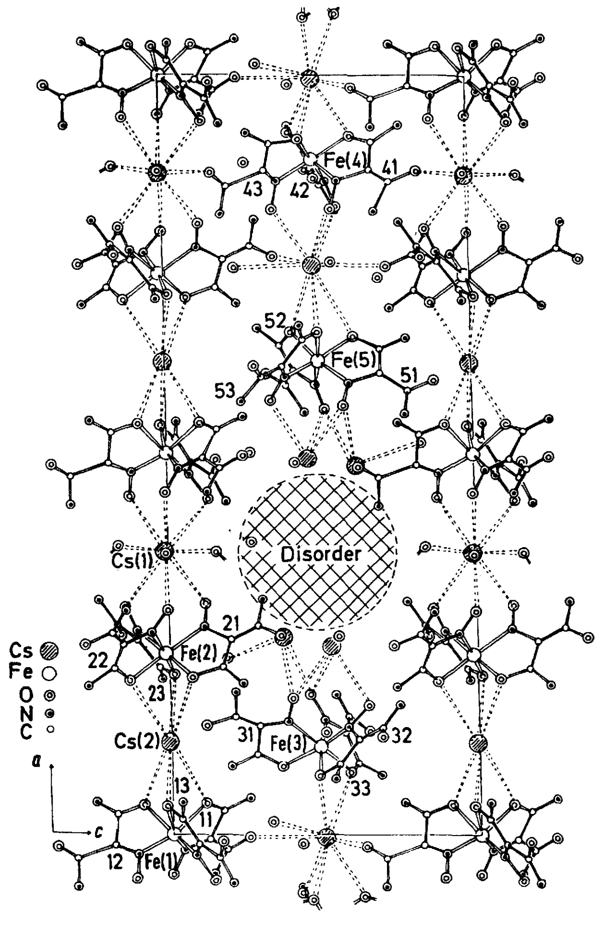
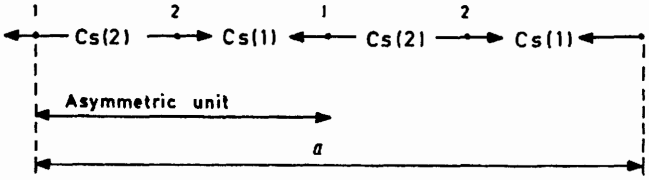


FIGURE 4 The lower half of the cell of the caesium salt projected down *b*, showing the asymmetric unit and chain structure of the lattice, the metal atom co-ordination spheres, and the region of disorder. Ligand numbering is shown

In the first chain in the caesium salt, the co-ordination is different:



Cs(1) is co-ordinated by a pair of ' heads ' and Cs(2) by a pair of ' tails '. The co-ordination geometries are quite different for the two caesium ions, Cs(1) being irregularly nine-co-ordinated by the two ' axially opposed ' tripod ligand heads and three O(3) oxygen atoms from the second chain, while Cs(2) is only six-co-ordinate by the two tripod ligand tails in a very elongated irregular pseudo-trigonal antiprism. About Cs(1), the ligand heads are arranged eclipsed in a trigonal prismatic array with the three additional equatorial atoms occupying staggered positions between them. Because of this disposition with the false symmetry elements in the chain, we find that the ligand planes in anion (2) are almost coplanar with those of anion (1) (Table 3). Nearly all Cs–O contacts are at distances greater than the sum of the ionic radii (*ca.* 3.10 Å).

Because of the change in relative proportions of the cell axes the disposition of the chains within the cell is considerably altered with respect to that of the potassium salt. In the latter, the chains run parallel to the short non-unique axis, whereas in the caesium salt the length of the asymmetric unit is doubled in chain (1) so that the chain is parallel to the long non-unique axis. Because of the short *b* axis and the fact that the *y* co-ordinate of the iron atom is close to zero in the potassium salt, the chains lie ' side-by-side ' along *a*. In the caesium salt, the *b* axis is considerably longer and the *y* co-ordinates of the iron atoms in the second chain are considerably different from zero. The result is that the second chain lies below rather than beside the first chain transposed by the $(0,\frac{1}{2},\frac{1}{2})$ centring operation, so that stacking of the two types of chain occurs up *b*. The non-zero value of *b* has further consequences for the second chain in that its second half within the cell along *a* is not the result of the glide operation on the first half as in the potassium salt, but is an entirely independent entity. Thus, whereas the first chain comprises two symmetry-related fragments within the cell, the second chain is independent throughout the cell length in *a*, the glide operation generating a new and independent chain. The constitution of the second chain is of interest, since it is not a complete chain but comprises a very considerable region of disorder. The disposition of the anions in the second chain appears to be controlled by hydrogen bonding and anion–cation interactions dictated by the ordering with the first chain. Thus we find that the head–tail cation disposition is much less regular than in the first chain, being of the type:

i.e. both chains in the potassium salt have the potassium ions co-ordinated by head–tail combinations oriented in the same direction; the first chain in the caesium salt has head–head, tail–tail sequences, but the second chain is a mixture of both types. Whereas Cs(5) has a fairly regular nine-co-ordination of the type observed in the first chain, but with one of the equatorial oxygen atoms missing, the co-ordination of Cs(4) is much less regular owing to the fact that anion (3) does not pack as symmetrically (*i.e.* as a pseudo-three-fold axis) about the *a* direction as the remainder and co-ordinates Cs(4) by only two of the three possible tail atoms, so that Cs(4) is seven-co-ordinate; two of the co-ordination positions being filled by water molecules, are at a very long distance.

In both the potassium and caesium salts of $[FeL_3]^-$ (and possibly also the lithium salt) it is clear that considerable paramagnetism exists although the confidence limits are somewhat indefinite as a result of the preparative difficulties. Typically, the magnetic moments are slightly >2 B.M. and only slightly temperature-dependent, suggesting the presence of a low-spin–high-spin ' crossover ' situation, exchange, or independent lattice sites in different environments. In view of the relative insensitivity to temperature change, the first two possibilites seem unlikely, a hypothesis reinforced by the fact that the magnetic moment of the caesium salt has been shown to change very little at liquid-helium temperatures.[12]

The Mössbauer spectroscopic properties of the potassium and caesium isonitrosomalonamideiron(II) derivatives are also indicative of the presence of a high-spin component not present in the sodium and rubidium analogues. The Mössbauer spectrum of all compounds is basically an intense sharp doublet with a very small and almost temperature-independent quadrupole splitting, corresponding to the expected Mössbauer spectrum for iron(II) in the low-spin state with a small asymmetric bonding to the ligands. In the potassium and caesium salts, and in $FeL_2{\cdot}1\frac{1}{2}H_2O$ and $FeD_2{\cdot}2H_2O$, a weaker doublet with a very large slightly temperature-dependent quadrupole splitting is observed. Both peaks of this doublet are very broad, indicating a much shorter relaxation time than that giving rise to the relatively sharp low-spin doublet, and the isomer shift and large quadrupole splitting correspond to the expected Mössbauer spectrum for high-spin iron(II) in an environment well-distorted from octahedral symmetry. The relative intensities of the two doublets appear to be temperature-independent, suggesting that there are two iron sites rather than a thermally dependent ' crossover ' equilibrium between high- and low-spin forms. From the relative intensities the very approximate ratio of high- to low-spin iron(II) in $Cs[FeL_3]{\cdot}2H_2O$ and $FeL_2{\cdot}2H_2O$ is 1 : 2; in the case of $K[FeL_3]{\cdot}2H_2O$, the ratio is *ca.* 1 : 3. These populations are consistent with the observed magnetic susceptibility results and confirm that there are two types of iron(II) species present and suggest that

---

[12] B. N. Figgis and J. Baker, personal communication.

the temperature-dependence of the magnetic moment may be more typical of the high-spin iron(II) component in an environment well-distorted from octahedral symmetry rather than a ' crossover ' equilibrium.

The magnetic susceptibility results for the lithium salt suggest a small amount of high-spin iron to be present but less than for the potassium and caesium salts; such an iron species could not be confirmed from the Mössbauer spectrum.

Considering these properties in the light of the determined structure, the possibility of different spin states in different lattice sites is unattractive in the case of the potassium salt since the foregoing structure determination has shown the existence of only one type of lattice site (the caesium salt, however, has a much larger cell, with more than one iron atom in the asymmetric unit, and this possibility is not ruled out in that case). The structure determination is similarly unhelpful in that the metal–ligand geometry is very similar to that found in the low-spin violurate analogue, although in the present case the magnetic moment is not so high as to suggest that a substantial difference would be expected. It is also relevant that we have shown the diamagnetic sodium analogue to be isomorphous with the potassium salt by single-crystal photography; however, it has not been possible to grow crystals of a size comparable to those of the potassium salt for comparative accurate structural purposes. This latter observation, however, suggests that it is rather unlikely that an exchange mechanism is responsible for the anomalous magnetism; any such mechanism would need to be sought in an interaction between anions within the chains or more form of overlap between parallel ligand π systems. The closest approach between ligands in adjacent chains occurs between ligands of type (2) which will be approximately normal to b and are separated by *ca.* $b/2$ ($= 4.9$ Å), seemingly too large for significant interaction. About the potassium ions, ligands (2) from anions in the same chain are approximately parallel, and the same is true of ligands (3); for these ligands the closest approach between different anions is *ca.* 3.3 Å, again probably too large to permit an interaction of the necessary magnitude. A further possibility is suggested by the observation that it is the ligand p_π orbitals which ' co-ordinate ' the potassium; it is possible but improbable that interligand π interaction might occur *via* overlap with potassium d orbitals, a possibility made even more remote by the fact that the sodium analogue was observed to be diamagnetic and not *vice versa*. It thus seems unlikely that exchange is responsible for the anomaly.

A further possibility is that the preparation produces two compounds or phases, whose ratios vary with the derivative. Certainly the preparations can produce impurities, notably $FeL_2 \cdot 1\frac{1}{2}H_2O$, if considerable care is not taken, and it was not possible to purify the products by recrystallization without decomposition. Nevertheless, it will be seen from the Experimental section that extreme precautions have been taken to assure sample homogeneity, even to the extent of handpicking the crystalline sample in the potassium case, and it seems unlikely also that impurities are responsible.

Of further interest are the compounds $FeL_2 \cdot 2H_2O$ and $FeL_2 \cdot 2py$ reported earlier by Cambi, exemplified in the present study by $FeD_2 \cdot 2H_2O$. It is clear that considerable paramagnetism also exists in these derivatives and the most likely explanation in this case would appear to lie in the probable low symmetry of the central metal-atom environment, yielding a triplet ground-state, if the substituents are octahedral and ***trans***, or, less likely, a mixing of low-lying paramagnetic ground states with the diamagnetic term. It is possible also that in the $[FeL_3]^-$ species, already clearly C_3 in the crystal field about the iron, that distortion imposed both by the ligand and by crystal packing may render such paramagnetic states accessible. Further studies are in progress on these systems.

TABLE 6

Least-squares planes (K salt only) through the $C_3N_3O_3$ ligand skeletons in the form $pX + qY + rZ = s$ where $X = ax + cz \cos\beta$, $Y = by$, $Z = cz \sin\beta$. σ/Å is the estimated standard deviation of the defining atoms. Atom deviations are in Å; associated iron deviations are also given

Plane	(1)	(2)	(3)
10^4p	2 941	2 252	9 544
10^4q	−3 844	9 297	−1 215
10^4r	8 751	2 914	−2 729
s	1.6542	1.0464	3.3716
σ	0.08	0.04	0.09
χ^2	7 040	789	7 084
O(1)	0.01	0.01	0.03
N(1)	−0.07	−0.04	−0.13
C(1)	−0.03	−0.01	−0.01
O(2)	0.05	0.01	0.01
N(2)	0.04	0.01	0.03
C(2)	−0.01	0.00	0.04
O(3)	0.16	0.07	0.16
N(3)	−0.14	−0.06	−0.15
C(3)	0.00	0.00	0.03
Fe	0.14	0.08	−0.02

Angles between planes: (1)–(2) 87.9, (1)–(3) 84.9, (2)–(3) 88.7°.

[6/051 *Received, 8th January*, 1976]