-0.20 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Atomic fractional positional parameters are given in Table 1.* Bond lengths and angles are given in Table 2. The molecular structure and atomic numbering of potassium hydrogen diethylmalonate is illustrated in Fig. 1 (*PLUTO*; Motherwell & Clegg, 1978).

The C—C bond lengths and the C—C—C angles are in good agreement with the values found in our previous study (Dubourg *et al.*, 1988). However, the conformation of the potassium hydrogen diethylmalonatc around the atom C(1) is quite different from that of the acid. Indeed, in the acid salt, the carboxylic and carboxylate groups are in the same plane, nearly perpendicular [82.2 (5)°] to the chain plane (*XANADU*; Roberts & Sheldrick, 1975); moreover, we observed a mirror plane perpendicular to the carboxylic group that passes through the atom C(1). The C—O single and double bonds are exactly the same in the carboxyl and carboxylate groups (Table 2), as was found previously in the potassium hydrogen 1,1-cyclopropane malonate acid (Dubourg, Fabrègue, Maury & Declercq, 1990). Therefore, we concluded that these two acids salts, KH 1,1-cyclopropane dicarboxylate and KH diethylmalonate have a similar chelated ring with a short O—H···O intramolecular hydrogen bond. The crystals are also stabilized by two intermolecular hydrogen bonds (Table 3). K^+ is coordinated to eight O atoms at distances less than 3.10 Å as shown in Table 2. Six of the atoms, O(3^{i}), O(1^{iii}), O(w^{iii}), O(1^{iv}), O(3^{v}) and O(4^{v}), form a distorted trigonal prism; the other two O atoms, O(w^{ii}) and O(2^{iii}), face two of the lateral sides (Fig. 2) as in the anion complex [PtL_2H] (LH_2 = 5-oxoproline) (Viossat, Rodier, Nguyen-Huy & Guillard, 1986).

Table 3. *Hydrogen-bond parameters: distances* (Å) *and angles* (°)

H(O*w*)—O(*w*)	0.900 (5)	H(O*w*)···O(3')	1.98 (5)
H(O*w*)'—O(*w*)	0.951 (7)	O(2)···O(4)	2.39 (5)
H(O2)—O(2)	1.086 (14)	O(*w*)···O(2)	2.80 (5)
H(O2)···O(4)	1.66 (5)	O(*w*)···O(3')	2.75 (6)
H(O*w*)'···O(2)	1.95 (5)		
C(2)—O(1)—H(O2)	110.8 (8)	O(*w*)—H(O*w*)'···O(2)	149 (7)
H(O2)···O(4)—C(3)	105 (9)	O(*w*)—H(O*w*)···O(3')	142 (7)
O(2)—H(O2)···O(4)	119 (8)		

Symmetry: no code assymetric unit; (i) $1 + y$, $1 - x$, $0.75 + z$.

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54595 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Delarbre, J. L., Maury, L. & Bardet, L. (1985). *J. Raman Spectrosc.* **16**(1), 11–21.

Dubourg, A., Fabrègue, E., Maury, L. & Declercq, J.-P. (1990). *Acta Cryst.* C**46**, 1394–1396.

Dubourg, A., Rambaud, J., Delarbre, J. L., Maury, L. & Declercq, J.-P. (1988). *Acta Cryst.* C**44**, 1987–1989.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Roberts, P. & Sheldrick, G. M. (1975). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.

Rogers, D. (1981). *Acta Cryst.* A**37**, 734–741.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86*. In *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Kruger & R. Goddard, pp. 175–189. Oxford Univ. Press.

Viossat, B., Rodier, N., Nguyen-Huy, D. & Guillard, O. (1986). *Acta Cryst.* C**42**, 659–662.

Acta Cryst. (1992). C**48**, 625–627

Adduct of Two 1,8-Naphthyridine Molecules (One Protonated) with Tetrachloroferrate(III)

By Pierluigi Barbaro, Claudio Bianchini, Marco Fochi, Dante Masi and Carlo Mealli

Istituo per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via J. Nardi 39, 50132 *Firenze, Italy*

(*Received* 20 *May* 1991; *accepted* 23 *September* 1991)

Abstract. 1,8-Naphthyridinium tetrachloroferrate(III)–1,8-naphthyridine (1/1), $C_8H_7N_2^+.FeCl_4^-.C_8H_6N_2$, $M_r = 458.9$, monoclinic, Cc, $a = 10.698$ (2), $b = 25.533$ (4), $c = 7.315$ (2) Å, $\beta = 101.83$ (1)°, $V = 1955.67$ (72) Å^3, $Z = 4$, $D_x = 1.5588$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 11.4$ mm^{-1}, $F(000) = 924$,

0108-2701/92/040625-03$03.00

room temperature, final $R = 0.0704$ for 929 reflections. The structure consists of discrete tetrahedral $FeCl_4^-$ anions, protonated $(NNH)^+$ and unprotonated (NN) 1,8-naphthyridine molecules.

Introduction. In the course of studies designed to synthesize model compounds for catechol 1,2-dioxygenase enzymes containing Fe as the cofactor (Que, 1983), the title compound has been found to be an active catalyst precursor for the oxidation of cathecols to *o*-quinones and muconic acids. The compound in question was obtained by adding a solution of 1,8-naphthyridine (0.26 g, 2 mmol) to anhydrous $FeCl_3$ (0.16 g, 1 mmol) dissolved in ethanol (10 mL) under nitrogen atmosphere. Recrystallization in the air from a THF (10 mL)/*n*-BuOH (5 mL) mixture gave yellow crystals in 73% yield.

Experimental. Philips PW 1100 diffractometer, lattice parameters determined using 20 reflections in the θ range 10–20°, scan rate $0.04° \text{ s}^{-1}$, scan width $(0.7 + 0.15\tan\theta)°$, 1126 measured reflections, $5 \leq 2\theta \leq 105°$, $-10 \leq h \leq 10$, $0 \leq k \leq 25$, $0 \leq l \leq 7$; 929 unique reflections with $I \geq 3\sigma(I)$; three standard reflections, no appreciable variation of their intensities; Lp correction, no absorption correction because of the small size of the crystal which had a prismatic shape with dimensions $0.1 \times 0.05 \times 0.2$ mm; scattering factors for non-H atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV) and for H atoms from Stewart, Davidson & Simpson (1965). Patterson and Fourier methods, full-matrix least-squares refinement, $\sum w(|F_o| - |F_c|)^2$ minimized, anisotropic thermal parameters for Fe and Cl atoms, isotropic for the remaining atoms. Final $R = 0.070$, $wR = 0.070$, $w = 1/\sigma(F_o)^2$; maximum shift/e.s.d. was < 1.0; maximum height in final ΔF map 0.19 e Å^{-3}. *SHELX76* (Sheldrick, 1976) and *PLUTO* (Motherwell, 1978) programs adapted for the HP Vectra 386/25 computer.

Table 1. *Atomic coordinates* ($\times 10^4$) *and thermal parameters* (Å$^2 \times 10^3$) *for the structure of* (NN)(NNH)$FeCl_4$

Equivalent isotropic thermal parameters for the Fe and Cl atoms: U_{eq} is defined as one third of the trace of the orthogonalized displacement tensor. Isotropic thermal parameters for N and C atoms.

	x	*y*	*z*	*U* or U_{eq}
Fe(1)	5971 (0)	1608 (1)	2120 (0)	48 (1)
Cl(1)	7418 (4)	2118 (2)	3715 (8)	68 (3)
Cl(2)	5338 (5)	1961 (2)	−651 (8)	80 (3)
Cl(3)	6758 (5)	826 (2)	1855 (8)	72 (3)
Cl(4)	4382 (5)	1504 (2)	3543 (10)	98 (4)
N(1)	10768 (12)	1263 (6)	10558 (21)	62 (4)
N(2)	9670 (11)	545 (5)	9314 (17)	48 (3)
N(3)	1660 (12)	5 (5)	6026 (18)	54 (3)
N(4)	380 (12)	677 (5)	4983 (17)	51 (3)
C(1)	10835 (20)	1774 (9)	10776 (29)	77 (5)
C(2)	9844 (18)	2127 (8)	10031 (26)	76 (6)
C(3)	8787 (21)	1945 (8)	8903 (28)	79 (5)
C(4)	8666 (17)	1393 (8)	8599 (26)	66 (5)
C(5)	7604 (16)	1134 (7)	7426 (23)	61 (4)
C(6)	7610 (17)	603 (8)	7300 (25)	71 (5)
C(7)	8654 (16)	339 (7)	8234 (23)	57 (4)
C(8)	9699 (14)	1077 (6)	9495 (19)	45 (3)
C(9)	195 (18)	1209 (7)	4871 (25)	68 (5)
C(10)	1116 (17)	1567 (7)	5750 (25)	66 (5)
C(11)	2244 (17)	1415 (7)	6664 (24)	64 (4)
C(12)	2503 (17)	870 (7)	6763 (25)	62 (4)
C(13)	3672 (17)	640 (7)	7620 (23)	66 (5)
C(14)	3790 (17)	115 (8)	7724 (25)	69 (5)
C(15)	2758 (16)	−200 (8)	6934 (26)	69 (5)
C(16)	1524 (14)	534 (6)	5958 (21)	50 (4)

Table 2. *Selected bond distances* (Å) *and angles* (°) *for the structure of* (NN)(NNH)$FeCl_4$

Fe(1)—Cl(1)	2.170 (4)	N(2)—C(7)	1.32 (2)
Fe(1)—Cl(2)	2.194 (6)	N(2)—C(8)	1.36 (2)
Fe(1)—Cl(3)	2.192 (5)	N(3)—C(15)	1.33 (2)
Fe(1)—Cl(4)	2.183 (7)	N(3)—C(16)	1.36 (2)
N(1)—C(1)	1.31 (3)	N(4)—C(9)	1.37 (2)
N(1)—C(8)	1.33 (2)	N(4)—C(16)	1.34 (2)
Cl(3)—Fe(1)—Cl(4)	106.4 (2)	N(1)—C(1)—C(2)	125 (2)
Cl(2)—Fe(1)—Cl(4)	111.6 (2)	N(1)—C(8)—C(4)	124 (3)
Cl(2)—Fe(1)—Cl(3)	110.1 (2)	N(1)—C(8)—N(2)	114 (1)
Cl(1)—Fe(1)—Cl(4)	110.8 (2)	N(2)—C(7)—C(6)	127 (2)
Cl(1)—Fe(1)—Cl(3)	110.5 (2)	N(2)—C(8)—C(4)	121 (1)
Cl(1)—Fe(1)—Cl(2)	107.5 (2)	N(3)—C(15)—C(14)	122 (2)
C(1)—N(1)—C(8)	116 (2)	N(3)—C(16)—C(12)	112 (2)
C(7)—N(2)—C(8)	117 (1)	N(3)—C(16)—N(4)	112 (1)
C(15)—N(3)—C(16)	119 (1)	N(4)—C(9)—C(10)	123 (2)
C(9)—N(4)—C(16)	114 (1)	N(4)—C(16)—C(12)	126 (1)

Discussion. Atomic parameters for the compound (NN)(NNH)$FeCl_4$ are given in Table 1* and a selection of bond distances and angles is reported in Table 2. Fig. 1 shows the contents of the unit cell. The oxidation state +3 of the metal is consistent with the magnetic moment of the complex (μ = 5.9 BM), corresponding to five unpaired spins. An analysis of the structural parameters confirms this point and allows the NN protonated molecule to be distinguished from the unprotonated one. The tetrachloroferrate group is known to exist either as a monoanion or as a dianion and both structures have been reported (Lauher & Ibers, 1975). A comparison leads to the conclusion that the title compound contains the monoanion $FeCl_4^-$. In fact, the average Fe—Cl distance is 2.185 (9) Å, a value *ca* 0.14 Å shorter than that found for the $FeCl_4^{2-}$ group.

Concerning the nature of the two naphthyridine molecules in the asymmetric unit, there is only indirect evidence that one of them is protonated. In fact, it was not possible to locate with precision all of the H atoms in the structure and only those attached

---

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54669 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GE0274]

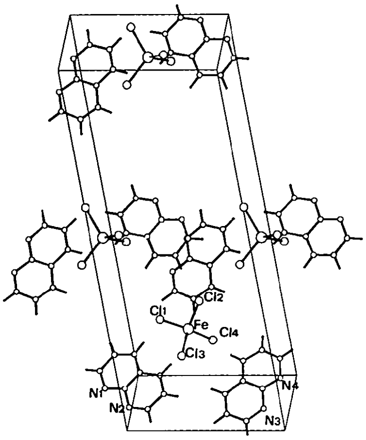

Fig. 1. A perspective view (down the *c* axis) of the contents of the unit cell.

to the C atoms were introduced at calculated positions. It has been proposed (Bacci, Dei & Morassi, 1973) that in protonated naphthyridine the proton could be symmetrically bridging between the two N atoms, but this is unlikely on account of the unfavourable energy predicted by molecular orbital calculations (Pacinotti, 1981). Thus, it is likely that only one of the two N atoms is protonated. The location of the proton is suggested from a comparison of all of the C—N—C angles in the title compound and in the structure of the free NN molecule at 163 K (Dapporto, Ghilardi, Mealli, Orlandini & Pacinotti, 1984): the average C—N—C angle is 117.0 (2)° in the latter case. The angle in question should increase if the N atom is bound to an acid (either a proton or a metal atom in a donor–acceptor relationship). This is normally observed for pyridine molecules as well. In the title compound, the angles at N(1) and N(2) of the first NN molecule are 116 (1) and 117 (1)°, respectively, while those at N(3) and N(4) of the second NN molecule are 119 (1) and 114 (1)°; N(3) is therefore the most probable host site for the proton.

References

BACCI, M., DEI, A. & MORASSI, R. (1973). *Inorg. Chim. Acta*, **7**, 209–214.
DAPPORTO, P., GHILARDI, C. A., MEALLI, C., ORLANDINI, A. & PACINOTTI, S. (1984). *Acta Cryst.* C**40**, 891–894.
LAUHER, J. W. & IBERS, J. A. (1975). *Inorg. Chem.* **14**, 348–351.
MOTHERWELL, W. D. S. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
QUE, L. JR (1983). *Adv. Inorg. Biochem.* **5**, 167–199.
PACINOTTI, S. (1981). PhD thesis, Univ. of Firenze, Italy.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1992). C**48**, 627–629

Structure of Di(*n*-butyl)bis(*N*,*N*-dipropyldithiocarbamato)tin(IV)

BY V. VRÁBEL,* J. LOKAJ, E. KELLÖ AND V. RATTAY

Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinského 9, 812 37 *Bratislava, Czechoslovakia*

AND A. C. BATSANOV AND YU. T. STRUCHKOV

A. N. Nesmeyanov Institute of Organoelement Compounds, USSR Academy of Sciences, 28 *Vavilov Street, Moscow* 117813, *USSR*

(*Received* 20 *April* 1991; *accepted* 25 *September* 1991)

Abstract. [$Sn(C_4H_9)_2(C_7H_{14}NS_2)_2$], $M_r = 585.6$, triclinic, $P\bar{1}$, $a = 9.7836$ (7), $b = 12.3437$ (6), $c = 13.2950$ (8) Å, $\alpha = 101.750$ (4), $\beta = 103.606$ (5), $\gamma = 94.872$ (5)°, $V = 1512.9$ (2) Å^3, $Z = 2$, $D_m = 1.28$, $D_x = 1.29$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 1.12$ mm^{-1}, $F(000) = 612$, room temperature, final $R = 0.044$ for 5055 unique observed reflections. The dithiocarbamate (dtc) ligands are anisobidentately chelated to tin(IV), with one longer and one shorter Sn—S bond. The overall geometry at the Sn atom is highly distorted from *trans* octahedral. Four S atoms are nearly coplanar but are greatly distorted from square-planar geometry (*cis* S—Sn—S angles range from 63.9 to 148.6°).

Introduction. Crystallographic studies of organotin dithiocarbamato complexes have revealed a variety of coordination geometries around the Sn atom.

---

* To whom correspondence should be addressed.

0108-2701/92/040627-03$03.00