for bond distances and angles. E.s.d.'s involving bonds to Cu are less than 0·004 Å and 0·2°.*

Discussion. The coordination geometry about Cu is of the 4 + 2 type. The major coordination plane is composed of *trans* chelated-ligand donor atoms, and the 'bite' distance across donor atoms is 2·838 (5) Å. The Cu–O(2) 'semi-coordinated' bond vector of 2·747 Å makes an angle of 86·4° to the major coordination plane. The next shortest contact between Cu and any ClO_4^- O atom is 3·77 Å.

Atoms in the pyridine ring have an average deviation from the best-fit plane through them of 0·009 (6) Å. The plane of the ring is inclined 53·4° to the major coordination plane. The Cu-coordinated O(1) atom is displaced by 0·04 Å from the best-fit ring plane, and the O(1)–N(1)–C(1)–C(6) torsion angle is 0·3 (6)°.

Two ClO_4^- O atoms are hydrogen-bonded to the amine H atom H(N2). An intramolecular hydrogen

bond to O(4) is present with a N(2)–O(4) distance of 3·087 Å and N(2)–H(N2)–O(4) angle of 146·7°, and a weaker intermolecular hydrogen bond to O(5) is also present with a N(2)–O(5) distance of 3·343 Å and N(2)–H(N2)–O(5) angle of 138·4°. It is noteworthy that the remaining ClO_4^- O atom O(3), which has no contacts to H(N2) under 3·0 Å, has the shortest O–Cl bond distance and largest temperature factor of any atom in the anion.

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The Structure of μ-Aqua-bis(μ-trifluoroacetato-*O,O'*)-bis[(*N,N,N',N'*-tetramethylethylenediamine)(trifluoroacetato)nickel(II)]

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Abstract. $[Ni_2(C_2F_3O_2)_4(C_6H_{16}N_2)_2H_2O]$, $C_{20}H_{34}F_{12}N_4Ni_2O_9$, $M_r = 819.9$, monoclinic, $P2_1/n$, $a = 17.183$ (5), $b = 13.879$ (5), $c = 15.509$ (5) Å, $\beta = 114.39$ (2)°, $Z = 4$, $D_c = 1.617$ Mg m^{-3}, μ(Mo $K\alpha$) = 1·24 mm^{-1}. Final $R = 0.071$ for 2012 reflections. The molecule is binuclear, with a Ni–Ni distance of 3·676 (3) Å. The central Ni atoms are octahedrally coordinated and bridged by a H_2O molecule and two carboxylate groups in *syn–syn* configuration. The noncoordinated O atoms of the unidentate carboxylate groups form intramolecular hydrogen bonds with the bridging H_2O molecule.

Introduction. The green crystals were obtained by slow evaporation of ethanol solution containing nickel(II) trifluoroacetate and *N,N,N',N'*-tetramethylethylenediamine. A single crystal of dimensions 0·25 × 0·30 × 0·35 mm was selected for the intensity measurements. Cell dimensions were determined by a least-squares treatment of 23 well-centered reflections on a Syntex $P2_1$ diffractometer. Intensities were collected (5 < 2θ < 50°) by the ω-scan method with a variable scan rate from 2·55 to 29·3° min^{-1} and graphite-monochromatized Mo $K\alpha$ radiation (λ = 0·71069 Å). Standards monitored about every 98 reflections showed

no significant systematic variation with time. Of the 5902 reflections collected, only 2012 had $F_o > 5\sigma(F_o)$ and these were used in subsequent calculations.

The structure was solved by Patterson and Fourier methods with programs of the XRAY 76 system (Stewart, 1976). For the non-hydrogen atoms scattering factors were from Cromer & Mann (1968) and for H atoms from Stewart, Davidson & Simpson (1965). The H atoms were geometrically positioned (C–H = 1·00, O–H = 0·95 Å and B = 5·5 Å²) and were not refined. A full-matrix refinement based on 2012

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq} (Å²)
Ni(1)	2255 (1)	3538 (1)	−464 (1)	3·1 (1)
Ni(2)	2632 (1)	6012 (1)	464 (1)	2·8 (1)
O(1)	2813 (6)	3509 (7)	−1445 (6)	4·0 (5)
O(2)	3797 (7)	4703 (8)	−952 (7)	6·0 (6)
O(3)	1426 (6)	4533 (8)	−1375 (6)	3·7 (5)
O(4)	1900 (6)	6040 (7)	−963 (6)	3·8 (5)
O(5)	1718 (6)	3690 (7)	503 (6)	3·7 (5)
O(6)	1707 (6)	5290 (7)	745 (6)	3·9 (6)
O(7)	3405 (6)	5903 (7)	1921 (6)	3·8 (5)
O(8)	3977 (6)	4422 (8)	2108 (7)	5·4 (6)
O(9)	3152 (5)	4654 (6)	286 (6)	3·3 (5)
N(1)	1313 (8)	2455 (9)	−1202 (8)	4·0 (7)
N(2)	3069 (8)	2335 (9)	289 (8)	4·0 (7)
N(3)	2060 (7)	7312 (9)	650 (8)	3·9 (7)
N(4)	3608 (7)	6934 (8)	343 (8)	3·5 (6)
F(1)	2599 (7)	4399 (10)	−3166 (6)	10·3 (8)
F(2)	3496 (8)	3296 (8)	−2758 (7)	9·0 (8)
F(3)	3935 (8)	4693 (9)	−2565 (7)	9·8 (8)
F(4)	1297 (7)	6036 (10)	−2964 (6)	10·0 (8)
F(5)	299 (9)	5095 (9)	−3015 (8)	14·0 (9)
F(6)	396 (6)	6480 (9)	−2487 (7)	8·4 (7)
F(7)	324 (6)	4782 (9)	1089 (8)	9·2 (8)
F(8)	825 (7)	3395 (8)	1472 (8)	8·4 (8)
F(9)	1481 (7)	4549 (9)	2297 (7)	9·0 (8)
F(10)	3677 (10)	5107 (13)	3803 (8)	15·3 (12)
F(11)	4343 (11)	6195 (8)	3741 (7)	14·7 (10)
F(12)	4826 (9)	4876 (13)	3923 (7)	16·3 (11)
C(1)	1652 (10)	1568 (13)	−670 (11)	4·8 (4)
C(2)	2606 (10)	1503 (12)	−323 (11)	5·0 (4)
C(3)	1236 (10)	2334 (12)	−2206 (12)	5·2 (4)
C(4)	440 (11)	2684 (13)	−1264 (12)	6·0 (4)
C(5)	3960 (11)	2381 (13)	395 (12)	6·0 (4)
C(6)	3095 (10)	2178 (12)	1268 (12)	5·2 (4)
C(7)	3307 (10)	4138 (12)	−1509 (10)	3·2 (3)
C(8)	3313 (11)	4134 (14)	−2523 (12)	4·5 (4)
C(9)	1452 (9)	5400 (13)	−1502 (10)	3·0 (3)
C(10)	823 (13)	5748 (15)	−2526 (13)	5·6 (4)
C(11)	2538 (10)	8089 (11)	442 (11)	4·8 (4)
C(12)	3485 (10)	7856 (12)	764 (11)	5·1 (4)
C(13)	2134 (9)	7418 (11)	1646 (10)	4·0 (3)
C(14)	1121 (10)	7409 (12)	4 (11)	4·7 (4)
C(15)	4476 (10)	6603 (12)	899 (11)	5·1 (4)
C(16)	3499 (10)	7083 (12)	−630 (12)	5·3 (4)
C(17)	3818 (9)	5182 (13)	2373 (10)	3·2 (3)
C(18)	4196 (13)	5381 (15)	3459 (13)	5·3 (4)
C(19)	1544 (9)	4444 (13)	838 (10)	3·1 (3)
C(20)	1032 (12)	4311 (14)	1420 (14)	5·2 (4)

Table 2. *Interatomic distances* (Å) *with e.s.d.'s in parentheses*

Ni(1)–N(1)	2·158 (12)	Ni(2)–N(3)	2·131 (13)
Ni(1)–N(2)	2·182 (12)	Ni(2)–N(4)	2·178 (13)
Ni(1)–O(1)	2·107 (12)	Ni(2)–O(7)	2·100 (8)
Ni(1)–O(3)	2·066 (9)	Ni(2)–O(6)	2·072 (12)
Ni(1)–O(5)	2·072 (12)	Ni(2)–O(4)	2·046 (8)
Ni(1)–O(9)	2·156 (8)	Ni(2)–O(9)	2·153 (9)
N(1)–C(3)	1·52 (2)	N(3)–C(13)	1·50 (2)
N(1)–C(4)	1·50 (2)	N(3)–C(14)	1·51 (2)
N(1)–C(1)	1·46 (2)	N(3)–C(11)	1·47 (2)
C(1)–C(2)	1·50 (2)	C(11)–C(12)	1·53 (2)
C(2)–N(2)	1·50 (2)	C(12)–N(4)	1·49 (2)
N(2)–C(5)	1·47 (2)	N(4)–C(15)	1·45 (2)
N(2)–C(6)	1·52 (2)	N(4)–C(16)	1·46 (2)
O(1)–C(7)	1·25 (2)	O(7)–C(17)	1·26 (2)
O(2)–C(7)	1·21 (2)	O(8)–C(17)	1·20 (2)
C(7)–C(8)	1·58 (3)	C(17)–C(18)	1·56 (2)
C(8)–F(1)	1·27 (2)	C(18)–F(10)	1·27 (3)
C(8)–F(2)	1·30 (2)	C(18)–F(11)	1·20 (2)
C(8)–F(3)	1·34 (2)	C(18)–F(12)	1·24 (2)
O(3)–C(9)	1·22 (2)	O(6)–C(19)	1·23 (2)
O(4)–C(9)	1·24 (2)	O(5)–C(19)	1·26 (2)
C(9)–C(10)	1·58 (2)	C(19)–C(20)	1·51 (3)
C(10)–F(4)	1·32 (3)	C(20)–F(8)	1·33 (2)
C(10)–F(5)	1·28 (2)	C(20)–F(9)	1·30 (2)
C(10)–F(6)	1·27 (2)	C(20)–F(7)	1·29 (2)
O(2)···O(9)	2·584 (17)	Ni(1)···Ni(2)	3·676 (3)
O(8)···O(9)	2·606 (12)		

independent reflections and 325 variables with anisotropic thermal parameters for Ni, F, O and N atoms and isotropic thermal parameters for C and H atoms and minimizing the function $\sum w(|F_o| - |F_c|)^2$ gave $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.071$. Anomalous-dispersion corrections for Ni were taken from *International Tables for X-ray Crystallography* (1974). The weights were given by $w = 1/\sigma^2(F_o)$. The average shift/error ratio in the last cycle was 0·03. A difference Fourier map showed no electron density greater than 0·58 e Å⁻³.

Final positional and isotropic thermal parameters are given in Table 1, interatomic distances and angles in Tables 2 and 3, respectively.*

Discussion. The structure consists of discrete binuclear molecules possessing pseudo C_2 symmetry (Figs. 1 and 2). The shortest intermolecular contacts (> 3.06 Å) are between fluorine atoms of the trifluoroacetate groups and they are comparable to those found in trifluoroacetic acid (Nahringbauer, Lundgren & Andersen, 1979).

The central Ni atoms are bridged by a H_2O and two carboxylate groups, with average bond lengths of

$[Ni_2(C_2F_3O_2)_4(C_6H_{16}N_2)_2H_2O]$

Table 3. *Interatomic angles* (°) *with e.s.d.'s in parentheses*

N(1)–Ni(1)–N(2)	85·8 (4)	N(3)–Ni(2)–N(4)	85·9 (5)
N(1)–Ni(1)–O(1)	94·0 (5)	N(3)–Ni(2)–O(7)	92·2 (4)
N(1)–Ni(1)–O(3)	87·1 (4)	N(3)–Ni(2)–O(6)	86·8 (5)
N(1)–Ni(1)–O(5)	89·7 (5)	N(3)–Ni(2)–O(4)	91·0 (4)
N(1)–Ni(1)–O(9)	177·4 (5)	N(3)–Ni(2)–O(9)	176·7 (5)
N(2)–Ni(1)–O(1)	89·4 (5)	N(4)–Ni(2)–O(7)	88·2 (4)
N(2)–Ni(1)–O(3)	170·4 (4)	N(4)–Ni(2)–O(6)	170·8 (4)
N(2)–Ni(1)–O(5)	94·0 (5)	N(4)–Ni(2)–O(4)	92·7 (4)
N(2)–Ni(1)–O(9)	95·9 (4)	N(4)–Ni(2)–O(9)	97·4 (4)
O(1)–Ni(1)–O(3)	84·9 (4)	O(7)–Ni(2)–O(6)	86·4 (4)
O(1)–Ni(1)–O(5)	175·2 (4)	O(7)–Ni(2)–O(4)	176·7 (4)
O(1)–Ni(1)–O(9)	88·1 (4)	O(7)–Ni(2)–O(9)	87·9 (3)
O(3)–Ni(1)–O(5)	92·2 (4)	O(6)–Ni(2)–O(4)	93·1 (4)
O(3)–Ni(1)–O(9)	91·5 (3)	O(6)–Ni(2)–O(9)	89·9 (4)
O(5)–Ni(1)–O(9)	88·2 (4)	O(4)–Ni(2)–O(9)	88·9 (4)
Ni(1)–N(1)–C(1)	104·5 (8)	Ni(2)–N(3)–C(11)	105·1 (10)
Ni(1)–N(1)–C(3)	110·5 (10)	Ni(2)–N(3)–C(13)	111·9 (8)
Ni(1)–N(1)–C(4)	113·5 (10)	Ni(2)–N(3)–C(14)	114·3 (9)
C(1)–N(1)–C(3)	109·3 (13)	C(11)–N(3)–C(13)	109·6 (11)
C(1)–N(1)–C(4)	111·7 (14)	C(11)–N(3)–C(14)	109·2 (11)
C(3)–N(1)–C(4)	107·3 (11)	C(13)–N(3)–C(14)	106·7 (13)
N(1)–C(1)–C(2)	112·0 (15)	N(3)–C(11)–C(12)	113·0 (12)
C(1)–C(2)–N(2)	113·4 (14)	C(11)–C(12)–N(4)	111·2 (12)
C(2)–N(2)–C(5)	111·2 (13)	C(12)–N(4)–C(15)	107·9 (10)
C(2)–N(2)–C(6)	108·1 (12)	C(12)–N(4)–C(16)	110·5 (12)
C(5)–N(2)–C(6)	107·2 (11)	C(15)–N(4)–C(16)	108·7 (14)
Ni(1)–N(2)–C(2)	101·2 (7)	Ni(2)–N(4)–C(12)	102·3 (10)
Ni(1)–N(2)–C(5)	115·7 (10)	Ni(2)–N(4)–C(15)	113·6 (10)
Ni(1)–N(2)–C(6)	113·2 (10)	Ni(2)–N(4)–C(16)	113·5 (8)
Ni(1)–O(1)–C(7)	124·8 (10)	Ni(2)–O(7)–C(17)	128·1 (9)
O(1)–C(7)–O(2)	133·6 (16)	O(7)–C(17)–O(8)	131·4 (14)
O(1)–C(7)–C(8)	111·1 (12)	O(7)–C(17)–C(18)	110·4 (15)
O(2)–C(7)–C(8)	115·2 (16)	O(8)–C(17)–C(18)	118·1 (14)
C(7)–C(8)–F(1)	112·3 (17)	C(17)–C(18)–F(10)	110·4 (15)
C(7)–C(8)–F(2)	112·7 (15)	C(17)–C(18)–F(11)	119·5 (17)
C(7)–C(8)–F(3)	112·2 (13)	C(17)–C(18)–F(12)	113·7 (18)
F(1)–C(8)–F(2)	107·8 (14)	F(10)–C(18)–F(11)	101·9 (21)
F(1)–C(8)–F(3)	108·9 (15)	F(10)–C(18)–F(12)	100·5 (18)
F(2)–C(8)–F(3)	102·4 (17)	F(11)–C(18)–F(12)	108·6 (16)
Ni(1)–O(3)–C(9)	135·0 (8)	Ni(2)–O(6)–C(19)	135·9 (11)
Ni(2)–O(4)–C(9)	130·3 (10)	Ni(1)–O(5)–C(19)	129·6 (11)
O(3)–C(9)–O(4)	130·4 (12)	O(6)–C(19)–O(5)	129·9 (17)
O(3)–C(9)–C(10)	113·9 (13)	O(6)–C(19)–C(20)	113·9 (16)
O(4)–C(9)–C(10)	115·6 (15)	O(5)–C(19)–C(20)	116·2 (16)
C(9)–C(10)–F(4)	107·4 (15)	C(19)–C(20)–F(8)	112·9 (18)
C(9)–C(10)–F(5)	113·6 (16)	C(19)–C(20)–F(9)	110·8 (15)
C(9)–C(10)–F(6)	111·4 (16)	C(19)–C(20)–F(7)	112·8 (16)
F(4)–C(10)–F(5)	109·9 (18)	F(8)–C(20)–F(9)	103·7 (15)
F(4)–C(10)–F(6)	105·8 (17)	F(8)–C(20)–F(7)	106·1 (16)
F(5)–C(10)–F(6)	108·4 (17)	F(9)–C(20)–F(7)	110·0 (18)
Ni(1)–O(9)–Ni(2)	117·2 (4)		

Fig. 1. Perspective view of the molecule.
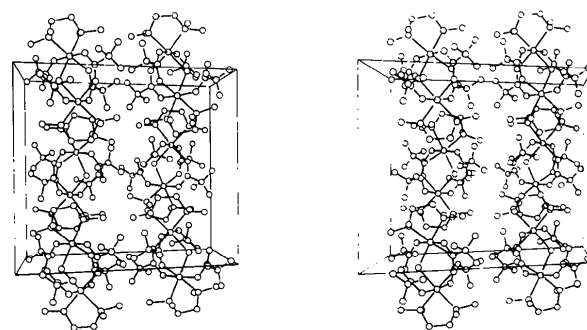
Fig. 2. Stereoview of the packing of molecules in the unit cell.

Ni–O(water) 2·154 (9) Å and Ni–O(μ-carboxylate) 2·064 (10) Å. The octahedral environment around each Ni atom is completed by the N atoms of the diamine molecule and the O atom of the unidentate carboxylate group. The Ni–N distances range from 2·131 (13) to 2·182 (13) Å, the shorter distances being *trans* to the bridging H_2O molecule. This is consistent with the values reported earlier for other similar dimeric nickel(II) carboxylates with N,N,N',N'-tetramethyl-ethylenediamine (Ahlgrén, Turpeinen & Hämäläinen, 1978) where the Ni–N distances *trans* to H_2O are on average about 3σ shorter than the other two. The Ni–O(carboxylate) distances are about 0·04 Å longer than the Ni–O(μ-carboxylate) distances, in agreement with earlier observations, too.
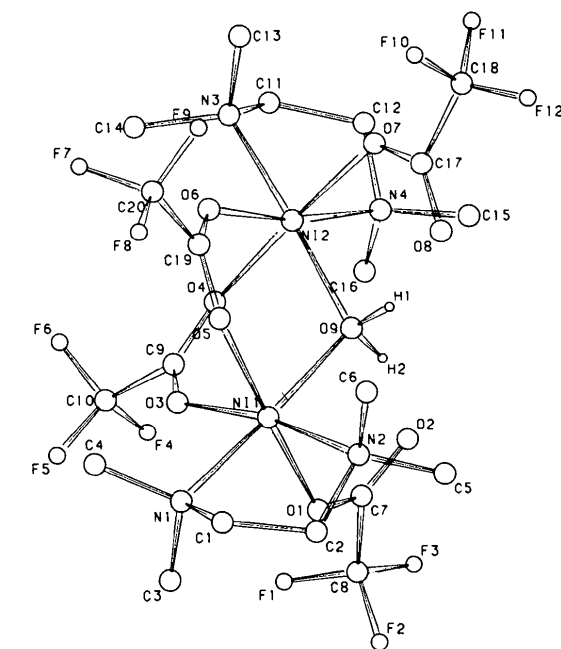
The dimensions of the N,N,N',N'-tetramethyl-ethylenediamine ligands are as expected and the diamine chelate rings are in normal unsymmetric *gauche* configuration. The CCO_2 groups are planar within experimental error but the Ni atoms deviate 0·24–0·70 Å from these planes. The large anisotropy among the fluorine thermal parameters suggests a slight disorder for the $-CF_3$ groups. This appears to be a relatively common phenomenon.

The Ni–Ni distance is 3·676 (3) Å and slightly longer than the distances 3·497 (1)–3·665 (1) Å measured in corresponding dimeric nickel(II) carboxylate complexes (Ahlgrén, Turpeinen & Hämäläinen, 1978). The difference supports the generalization that the Ni–Ni distance is elongated as the acid strength increases. It should be noted, however, that steric factors also play a role in determining the Ni–Ni distance. The major structural changes in these dimeric compounds accompanying the elongation of the metal–

metal distance are the shortening of the average Ni–N distance from 2·19 Å in the propionate compound to 2·16 Å in the present compound and the elongation of the Ni–O(water) distance from 2·07 Å in the propionate compound to 2·16 (1) Å in the present compound. Other structural parameters show no discernible trends.

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Furanne-2,5-dicarboxylate Acide de Potassium

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Abstract. $C_6H_3O_5^-.K^+$, monoclinic, $B2/b$, $a = 9.759$ (2), $b = 6.6952$ (9), $c = 11.193$ (2) Å, $\gamma = 114.49$ (1)°, $Z = 4$, $d_o = 1.95$ (1), $d_c = 1.94$ Mg m^{-3}. The structure has been solved by the heavy-atom method and refined by least-squares procedures to a final R value of 0·0486 for 1057 reflexions. K^+ is surrounded by seven O atoms. $C_6H_3O_5^-$ anions lying along twofold axes are linked into infinite chains by very short hydrogen bonds of length O···H···O = 2·459 (2) Å. The two carboxylic groups are slightly twisted out of the furan ring plane.

Introduction. Cette étude porte sur le sel monopotassique de l'acide furanne-2,5-dicarboxylique.
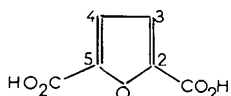
La plupart des anions de type HOOC–*R*–COO⁻ (dérivés des diacides HOOC–*R*–COOH) sont à l'état cristallin liés entre eux en chaînes infinies par des liaisons hydrogène intermoléculaires plus ou moins fortes, et plus ou moins symétriques.

Speakman (1972) distingue deux types de structures: les sels acides de type A_2 dans lesquels les groupements carboxyliques et carboxylates sont 'équivalents' et où la liaison hydrogène est symétrique, et les sels acides de type B_2 où la liaison n'est pas symétrique, les distances C–O étant différentes pour les groupements COOH et COO⁻.

L'étude des spectres infrarouge et Raman (Cassanas & Bardet, 1981) du sel acide cristallisé étudié montre que cette liaison hydrogène est forte et symétrique et que l'atome d'hydrogène de la liaison O···H···O est situé sur un élément de symétrie de la structure (axe binaire, centre de symétrie ou miroir plan). Les résultats