

# The Crystal and Molecular Structure of $\mu$ -Aqua-bis( $\mu$ -dichloroacetato-*O,O'*)bis(dichloroacetato)bis(*N,N,N',N'*-tetramethylethylenediamine)dinickel(II), $\text{Ni}_2(\text{C}_6\text{H}_{16}\text{N}_2)_2(\text{Cl}_2\text{C}_2\text{HO}_2)_4\text{H}_2\text{O}$

MARKKU AHLGRÉN, URHO TURPEINEN and REIJO HÄMÄLÄINEN

Department of Inorganic Chemistry, University of Helsinki, SF-00100 Helsinki 10, Finland

The crystal and molecular structure of the title compound has been determined from three-dimensional X-ray data. The green crystals belong to the triclinic system with  $a = 9.713(7)$  Å,  $b = 11.795(21)$  Å,  $c = 16.823(9)$  Å,  $\alpha = 79.01(11)^\circ$ ,  $\beta = 105.19(5)^\circ$ ,  $\gamma = 95.34(11)^\circ$ ,  $Z = 2$ . The structure was solved by the heavy-atom method and refined by block-diagonal least-squares procedures to an  $R$  value of 0.044 for 4145 independent reflections. The complex molecule is binuclear, the nickel-nickel distance being 3.657(1) Å. The nickel(II) ions are joined by a bridging water molecule and two bridging carboxylate groups, with average bond lengths of Ni–O(water) 2.132 Å and Ni–O(carboxylate) 2.048 Å. The octahedral environment around each nickel(II) ion is completed by the nitrogen atoms of the diamine molecule and the carboxyl oxygen atom of the dichloroacetate ion, the average bond lengths being 2.164 and 2.092 Å, respectively. The two noncoordinated dichloroacetate oxygen atoms form strong intramolecular hydrogen bonds with the bridging water molecule, the average O···O interaction being 2.586 Å.

This work is part of a systematic investigation of dimeric nickel(II) complexes having the general formula  $\text{Ni}_2(\text{C}_6\text{H}_{16}\text{N}_2)_2(\text{carboxylate})_4\text{H}_2\text{O}$ . In previous papers five crystal and molecular structures were presented, where the carboxylate ions were acetate, chloroacetate, propionate, 2-chloropropionate or 3-chloropropionate.<sup>1</sup> In this paper the results of a three-dimensional X-ray structure analysis of  $\mu$ -aqua-bis( $\mu$ -dichloroacetato-*O,O'*)bis(dichloroacetato)bis(*N,N,N',N'*-tetramethylethylenediamine)dinickel(II) are reported.

## EXPERIMENTAL

*Preparation and analyses.*  $\text{Ni}_2(\text{C}_6\text{H}_{16}\text{N}_2)_2(\text{Cl}_2\text{C}_2\text{HO}_2)_4\text{H}_2\text{O}$  was prepared by adding 0.05 mol of *N,N,N',N'*-tetramethylethylenediamine (Fluka AG) to an ethanol solution containing 0.05 mol of nickel(II) dichloroacetate prepared from nickel(II) carbonate (J. T. Baker) and dichloroacetic acid (Fluka AG). After several days the green crystals were filtered off, washed with water and dried in air.

Nickel was analyzed gravimetrically as nickel dimethylglyoxime. Anal. Calc. for  $\text{Ni}_2(\text{C}_6\text{H}_{16}\text{N}_2)_2(\text{Cl}_2\text{C}_2\text{HO}_2)_4\text{H}_2\text{O}$ : Ni, 13.35%. Found: Ni, 13.34%. The density, 1.598 g/cm<sup>3</sup>, was measured by the flotation method using carbon tetrachloride and methyl iodide. The calculated value with  $Z = 2$  is 1.601 g/cm<sup>3</sup>.

*Space group, unit cell and intensity data.* Preliminary rotation and Weissenberg photographs taken with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418$  Å) showed that the crystals belong to the triclinic system, space group  $P1$  or  $P\bar{1}$ . The latter space group was chosen and subsequent refinement indicated that this choice was the correct one.

Measurements of the unit cell parameters and reflection intensities were carried out on a Syntex  $\text{P2}_1$  automatic diffractometer using graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069$  Å). The crystal selected for the intensity measurements was approximately  $0.25 \times 0.50 \times 0.70$  mm<sup>3</sup>. Intensity data were collected ( $5^\circ < 2\theta < 48^\circ$ ) at room temperature using the  $\omega$ -scan technique and a scan rate varying from 2.55 to 29.3° min<sup>-1</sup> depending upon the peak intensity. The intensity of one standard reflection, recorded after every 99 measurements to monitor the crystal stability, remained essentially constant throughout the data collection. Out of 5716 measured intensities 4145 were considered as ob-

served on the basis of  $I > 3\sigma(I)$ . The data were corrected for Lorentz and polarization effects and for absorption from  $\phi$ -scan data. The following crystal data were obtained:

$$\begin{aligned} a &= 9.713(7) \text{ \AA} & \alpha &= 79.01(11)^\circ \\ b &= 11.795(21) \text{ \AA} & \beta &= 105.19(5)^\circ \\ c &= 16.823(9) \text{ \AA} & \gamma &= 95.34(11)^\circ \\ V &= 1824.0 \text{ \AA}^3 & Z &= 2 \\ D_m &= 1.598 \text{ g/cm}^3 & D_c &= 1.601 \text{ g/cm}^3 \\ \mu(\text{MoK}\alpha) &= 16.6 \text{ cm}^{-1} & \text{Space group} &: P\bar{1} \end{aligned}$$

Table 1. Fractional atomic coordinates ( $\times 10^4$ , except Ni  $\times 10^5$ ) and anisotropic thermal parameters<sup>a</sup> ( $\times 10^3$ , except Ni  $\times 10^4$ ) for non-hydrogen atoms. Estimated standard deviations are given in parentheses.

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Ni1	10996(7)	18875(6)	25059(4)	350(4)	259(3)	330(4)	52(3)	117(3)	-54(3)
Ni2	29137(7)	47515(6)	23908(4)	327(4)	263(3)	290(4)	52(3)	98(3)	-33(3)
N1	766(5)	271(4)	3284(3)	47(3)	35(3)	42(3)	7(2)	14(2)	-6(2)
C1	-800(7)	41(6)	3080(5)	49(4)	49(4)	77(5)	0(3)	26(4)	4(4)
C2	-1428(8)	387(6)	2160(5)	48(4)	44(4)	84(6)	-5(3)	2(4)	-7(4)
C3	1297(9)	299(6)	4200(4)	100(6)	45(4)	43(4)	13(4)	24(4)	3(3)
C4	1489(8)	-677(5)	3119(4)	69(5)	29(3)	59(4)	13(3)	22(4)	0(3)
C5	-2091(7)	2349(7)	2076(5)	42(4)	61(5)	90(6)	15(3)	18(4)	-12(4)
C6	-1371(8)	1822(7)	936(5)	56(5)	85(6)	51(4)	1(4)	-6(4)	-17(4)
N2	-1117(5)	1627(4)	1872(3)	39(3)	37(3)	52(3)	6(2)	9(2)	-9(2)
N3	4237(5)	6042(4)	3045(3)	41(3)	37(3)	34(3)	6(2)	7(2)	-8(2)
C7	5294(7)	6461(5)	2556(4)	45(4)	42(4)	57(4)	-10(3)	21(3)	-14(3)
C8	4599(7)	6551(5)	1626(4)	60(4)	42(4)	44(4)	-12(3)	29(3)	-2(3)
C9	4974(8)	5555(6)	3918(4)	61(4)	57(4)	36(4)	5(3)	-6(3)	-10(3)
C10	3406(7)	7019(6)	3079(4)	56(4)	42(4)	49(4)	-2(3)	9(3)	-21(3)
C11	5212(8)	4682(6)	1424(5)	57(4)	55(4)	67(5)	7(3)	35(4)	-15(3)
C12	3094(8)	5563(6)	561(4)	81(5)	59(4)	29(3)	7(4)	12(3)	4(3)
N4	4033(5)	5410(4)	1419(3)	46(3)	33(3)	34(3)	4(2)	13(2)	-3(2)
O1	3188(4)	1847(3)	3155(3)	41(2)	35(2)	52(3)	5(2)	4(2)	4(2)
O2	4411(4)	3551(3)	2960(3)	40(2)	31(2)	46(2)	9(2)	9(2)	4(2)
C13	4266(6)	2502(5)	3245(3)	36(3)	38(3)	29(3)	9(2)	10(2)	-4(2)
C14	5659(7)	1968(5)	3813(4)	41(3)	40(3)	43(4)	14(3)	4(3)	-1(3)
C11	5765(3)	2171(2)	4847(1)	109(2)	107(2)	37(1)	39(1)	-4(1)	-12(1)
C12	5812(2)	524(2)	3776(1)	70(1)	49(1)	93(1)	30(1)	5(1)	-10(1)
O3	562(5)	2755(3)	3329(3)	58(3)	40(2)	47(2)	-3(2)	26(2)	-17(2)
O4	1950(5)	4389(4)	3365(3)	51(3)	46(3)	49(3)	-10(2)	28(2)	-18(2)
C15	1059(6)	3660(5)	3585(4)	43(3)	31(3)	44(3)	-1(3)	18(3)	-15(3)
C16	516(9)	3978(6)	4294(5)	78(5)	57(4)	63(5)	-24(4)	42(4)	-35(4)
C13	782(6)	2901(3)	5172(2)	343(6)	97(2)	74(2)	8(3)	112(3)	-6(2)
C14	-1333(3)	4263(3)	3914(2)	82(2)	186(3)	195(3)	3(2)	62(2)	-124(3)
O5	1700(4)	1070(3)	1639(3)	53(3)	32(2)	47(2)	5(2)	27(2)	-6(2)
O6	2591(5)	2556(3)	845(3)	87(3)	28(2)	60(3)	6(2)	42(3)	-7(2)
C17	2399(6)	1519(5)	1115(3)	44(3)	32(3)	33(3)	7(3)	9(3)	-5(2)
C18	2997(7)	612(5)	762(4)	51(4)	43(4)	52(4)	10(3)	24(3)	-11(3)
C15	4210(3)	-232(2)	1569(1)	103(2)	77(1)	79(1)	58(1)	40(1)	21(1)
C16	3777(3)	1205(2)	-62(1)	114(2)	81(1)	75(1)	46(1)	62(1)	12(1)
O7	1399(4)	5962(3)	1808(3)	37(2)	35(2)	56(3)	8(2)	1(2)	-11(2)
O8	-516(5)	4975(4)	1172(3)	47(3)	33(2)	82(3)	7(2)	-13(2)	-19(2)
C19	126(6)	5851(5)	1409(4)	41(3)	31(3)	40(3)	9(2)	7(3)	-8(2)
C20	-780(6)	6922(5)	1220(4)	41(3)	33(3)	50(4)	5(3)	7(3)	-9(3)
C17	-1334(2)	7004(2)	2129(1)	69(1)	69(1)	91(1)	5(1)	48(1)	-19(1)
C18	188(2)	8218(1)	934(1)	67(1)	34(1)	67(1)	4(1)	20(1)	2(1)
O9	1507(4)	3508(3)	1775(2)	42(2)	30(2)	31(2)	9(2)	10(2)	-7(2)

<sup>a</sup> The anisotropic thermal parameters are of the form  $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12} + \dots)]$ .

**Structure determination and refinement.** The structure was solved by the heavy-atom method. All computations in the structure determination were performed on a Univac 1108 computer using programs of the *X-Ray 72* system.<sup>2</sup> The approximate positions of the nickel atoms were deduced from a three-dimensional Patterson map, and positions of other non-hydrogen atoms were located by three-dimensional Fourier syntheses.

Block-diagonal least-squares refinement was carried out on  $F$ . The function minimized was  $\Sigma w[|F_o| - |F_c|]^2$  with the weighting scheme  $w = 1/[45.0 + |F_o| + 0.005|F_o|^2]$ . Scattering factors for Ni, Cl, O, N and C were taken from Cromer and Mann<sup>3</sup> and those for H atoms from Stewart, Davidson and Simpson.<sup>4</sup> Corrections for anomalous dispersion<sup>5</sup> were applied to the nickel and chlorine atoms.

Refinement of a model including all non-hydrogen atoms with individual isotropic thermal parameters led to an  $R$  value of 0.136 [ $R = \Sigma |F_o| - |F_c| / \Sigma |F_o|$ ]. Further refinement with anisotropic thermal parameters reduced the  $R$  factor to 0.057. At this point all of the 38 hydrogen atoms were located from a difference Fourier map. Also the water hydrogen atoms were found clearly, the peaks of maximum density being 0.51 and 0.40  $e^-/\text{\AA}^3$ . The peaks of this height are very probably significant, since they are considerably larger than the random "noise" in the final difference Fourier map. Three more least-squares cycles were then computed with the non-

hydrogen atoms assigned anisotropic and the hydrogen atoms isotropic thermal parameters. After the last cycle the final  $R$  value for 4145 observed reflections was 0.044. The C-H and the two O-H bonds thus obtained were of reasonable length (0.85–1.27  $\text{\AA}$ ), the mean value being 1.00  $\text{\AA}$ .

The final atomic coordinates and thermal parameters together with their estimated standard deviations are given for the non-hydrogen atoms in Table 1 and for the hydrogen atoms in Table 2. A list of the observed and calculated structure factors is obtainable on request from the authors.

## RESULTS AND DISCUSSION

The interatomic distances and angles together with their standard deviations are given in Table 3. The structure of the complex molecule, as shown in Fig. 1, is composed of two nickel(II) ions joined by one bridging water molecule and two bridging dichloroacetate ions. The octahedral environment around each nickel(II) ion is completed by the nitrogen atoms of the diamine molecule and the carboxyl oxygen atom of the monodentate dichloroacetate ion. The strong intramolecular hydrogen bonds  $\text{O6}\cdots\text{H1}-\text{O9}$  [ $\text{O6}\cdots\text{O9} = 2.564(7) \text{\AA}$ ,  $\text{O9}-\text{H1} = 0.98(8) \text{\AA}$ ,  $\text{O6}\cdots\text{H1} = 1.63(8) \text{\AA}$ ,  $\text{O6}\cdots\text{H1}-\text{O9} = 159(6)^\circ$ ] and  $\text{O8}\cdots\text{H2}-\text{O9}$  [ $\text{O8}\cdots\text{O9} = 2.608(6) \text{\AA}$ ,  $\text{O9}-\text{H2} = 0.85(8) \text{\AA}$ ,  $\text{O8}\cdots\text{H2} = 1.80(8) \text{\AA}$ ,  $\text{O8}\cdots\text{H2}-$

Table 2. Fractional atomic coordinates ( $\times 10^3$ ) and isotropic temperature factors ( $\times 10^2$ ) with their standard deviations for hydrogen atoms.

Atom	x	y	z	U	Atom	x	y	z	U
H1(C1)	-127(8)	56(6)	338(4)	7(2)	H2(C8)	525(6)	683(5)	138(3)	3(2)
H2(C1)	-113(9)	-73(7)	327(5)	9(3)	H1(C9)	426(8)	519(7)	427(5)	9(3)
H1(C2)	-251(8)	18(6)	202(4)	7(2)	H2(C9)	571(8)	617(6)	418(5)	8(2)
H2(C2)	-120(10)	-15(8)	187(6)	11(3)	H3(C9)	548(7)	493(6)	393(4)	6(2)
H1(C3)	115(6)	-54(5)	455(4)	5(2)	H1(C10)	411(6)	747(5)	342(4)	4(2)
H2(C3)	237(10)	64(8)	438(6)	13(3)	H2(C10)	255(9)	664(7)	336(5)	9(3)
H3(C3)	93(7)	96(5)	432(4)	5(2)	H3(C10)	295(5)	740(4)	256(3)	2(1)
H1(C4)	137(6)	-136(5)	349(3)	3(1)	H1(C11)	586(8)	466(6)	193(4)	8(2)
H2(C4)	265(6)	-41(5)	326(4)	5(2)	H2(C11)	488(7)	395(6)	130(4)	5(2)
H3(C4)	107(7)	-86(5)	256(4)	5(2)	H3(C11)	584(8)	500(7)	100(5)	8(2)
H1(C5)	-187(7)	227(6)	274(4)	6(2)	H1(C12)	244(8)	611(6)	50(5)	8(2)
H2(C5)	-312(7)	220(6)	176(4)	6(2)	H2(C12)	266(8)	486(6)	41(5)	7(2)
H3(C5)	-190(7)	306(6)	182(4)	5(2)	H3(C12)	347(7)	590(6)	15(4)	6(2)
H1(C6)	-73(7)	129(6)	80(4)	6(2)	H(C14)	646(7)	243(6)	371(4)	6(2)
H2(C6)	-111(10)	290(8)	79(6)	13(3)	H(C16)	101(7)	472(5)	451(4)	5(2)
H3(C6)	-240(8)	158(6)	69(5)	8(2)	H(C18)	220(8)	6(7)	51(5)	8(3)
H1(C7)	599(5)	581(4)	267(3)	2(1)	H(C20)	-165(8)	688(6)	74(5)	8(2)
H2(C7)	573(7)	722(5)	270(4)	5(2)	H1(O9)	197(7)	333(6)	137(4)	6(2)
H1(C8)	366(6)	707(5)	146(4)	5(2)	H2(O9)	71(9)	382(7)	157(5)	8(3)

Table 3. Bond lengths (Å) and angles (°) with standard deviations for non-hydrogen atoms.

The nickel environments					
Ni1 – N1	2.146(5)	N1 – Ni1 – N2	84.4(2)	N2 – Ni1 – O3	91.7(2)
Ni1 – N2	2.160(5)	N1 – Ni1 – O3	89.8(2)	N2 – Ni1 – O5	89.5(2)
Ni1 – O1	2.037(4)	N1 – Ni1 – O5	92.8(2)	N2 – Ni1 – O9	97.9(2)
Ni1 – O3	2.063(5)	O3 – Ni1 – O9	89.3(2)	N2 – Ni1 – O1	170.6(2)
Ni1 – O5	2.118(5)	O5 – Ni1 – O9	88.2(2)	O1 – Ni1 – N1	87.3(2)
Ni1 – O9	2.130(4)	N1 – Ni1 – O9	177.6(1)	O1 – Ni1 – O3	92.4(2)
		O3 – Ni1 – O5	177.3(2)	O1 – Ni1 – O5	86.8(2)
		Ni1 – O9 – Ni2	118.1(2)	O1 – Ni1 – O9	90.6(1)
Ni2 – N3	2.171(5)	N3 – Ni2 – N4	84.4(2)	N4 – Ni2 – O2	91.4(2)
Ni2 – N4	2.179(5)	N3 – Ni2 – O2	90.4(2)	N4 – Ni2 – O7	88.3(2)
Ni2 – O2	2.042(4)	N3 – Ni2 – O7	89.8(2)	N4 – Ni2 – O9	98.3(2)
Ni2 – O4	2.051(5)	O2 – Ni2 – O9	91.8(1)	N4 – Ni2 – O4	170.7(2)
Ni2 – O7	2.066(4)	O7 – Ni2 – O9	88.0(1)	O4 – Ni2 – N3	87.0(2)
Ni2 – O9	2.135(4)	N3 – Ni2 – O9	176.5(2)	O4 – Ni2 – O2	92.2(2)
		O2 – Ni2 – O7	179.6(2)	O4 – Ni2 – O7	88.0(2)
				O4 – Ni2 – O9	90.2(2)
The diamine ligand molecules					
N1 – C1	1.480(9)	Ni1 – N1 – C1	105.2(3)	Ni1 – N2 – C2	103.4(4)
N1 – C3	1.498(9)	Ni1 – N1 – C3	113.5(4)	Ni1 – N2 – C5	113.9(4)
N1 – C4	1.480(10)	Ni1 – N1 – C4	112.0(4)	Ni1 – N2 – C6	113.0(4)
C1 – C2	1.498(11)	C1 – N1 – C3	109.1(6)	C2 – N2 – C5	110.7(6)
N2 – C2	1.479(8)	C1 – N1 – C4	110.6(5)	C2 – N2 – C6	107.9(6)
N2 – C5	1.472(11)	C3 – N1 – C4	106.5(5)	C5 – N2 – C6	107.9(5)
N2 – C6	1.504(9)	N1 – C1 – C2	110.3(6)	N2 – C2 – C1	111.5(6)
N3 – C7	1.472(9)	Ni2 – N3 – C7	104.6(4)	Ni2 – N4 – C8	102.0(4)
N3 – C9	1.485(7)	Ni2 – N3 – C9	112.5(4)	Ni2 – N4 – C11	114.1(1)
N3 – C10	1.484(9)	Ni2 – N3 – C10	112.4(3)	Ni2 – N4 – C12	113.9(4)
C7 – C8	1.521(9)	C7 – N3 – C9	110.0(5)	C8 – N4 – C11	110.9(5)
N4 – C8	1.475(8)	C7 – N3 – C10	109.9(5)	C8 – N4 – C12	109.3(5)
N4 – C11	1.491(10)	C9 – N3 – C10	107.4(5)	C11 – N4 – C12	106.6(6)
N4 – C12	1.480(7)	N3 – C7 – C8	110.4(5)	N4 – C8 – C7	110.9(5)
The dichloroacetate ligand ions					
C13 – O1	1.236(7)	Ni1 – O1 – C13	138.7(4)	C13 – C14 – C11	107.3(5)
C13 – O2	1.249(7)	Ni2 – O2 – C13	130.4(4)	C13 – C14 – C12	114.6(4)
C13 – C14	1.547(8)	O1 – C13 – O2	130.0(5)	C11 – C14 – C12	111.3(3)
C14 – C11	1.776(7)	O1 – C13 – C14	116.3(5)		
C14 – C12	1.737(7)	O2 – C13 – C14	113.8(5)		
C15 – O3	1.236(7)	Ni1 – O3 – C15	131.6(5)	C15 – C16 – C13	112.3(5)
C15 – O4	1.238(7)	Ni2 – O4 – C15	136.5(4)	C15 – C16 – C14	109.0(5)
C15 – C16	1.542(11)	O3 – C15 – O4	130.5(7)	C13 – C16 – C14	110.2(5)
C16 – C13	1.734(7)	O3 – C15 – C16	117.4(6)		
C16 – C14	1.782(8)	O4 – C15 – C16	112.1(6)		
C17 – O5	1.260(8)	Ni1 – O5 – C17	127.2(4)	C17 – C18 – C15	110.0(4)
C17 – O6	1.237(7)	O5 – C17 – O6	128.1(6)	C17 – C18 – C16	113.7(4)
C17 – C18	1.540(10)	O5 – C17 – C18	112.7(5)	C15 – C18 – C16	110.7(4)
C18 – C15	1.757(6)	O6 – C17 – C18	119.1(6)		
C18 – C16	1.752(8)				
C19 – O7	1.252(7)	Ni2 – O7 – C19	131.2(4)	C19 – C20 – C17	108.2(4)
C19 – O8	1.233(7)	O7 – C19 – O8	128.1(6)	C19 – C20 – C18	112.2(4)
C19 – C20	1.542(9)	O7 – C19 – C20	116.4(5)	C17 – C20 – C18	109.2(4)
C20 – C17	1.772(8)	O8 – C19 – C20	115.5(5)		
C20 – C18	1.772(6)				

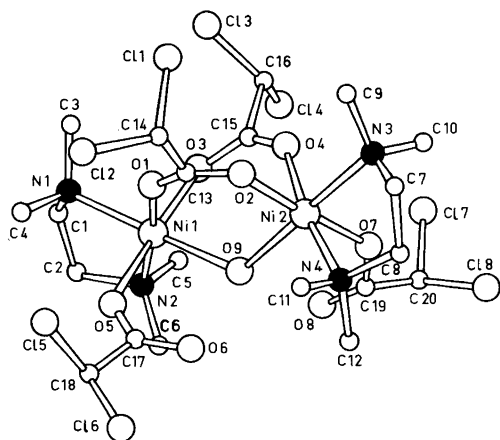


Fig. 1. Molecular structure and atom labeling scheme.

$\text{O9} = 158(8)^\circ$ ] formed between the bridging water molecule and the uncoordinated carboxyl oxygen atoms stabilize the complex molecule.

The complex molecules possess approximately a diad axis passing through O9 and are held in the crystal lattice by van der Waals forces. The intermolecular distances below 3.6 Å are between the atoms  $\text{O6} \cdots \text{C20}^{\text{I}}$  [3.423(7) Å],  $\text{O8} \cdots \text{C12}^{\text{I}}$  [3.428(8) Å],  $\text{C4} \cdots \text{C10}^{\text{II}}$  [3.454(10) Å] and  $\text{C7} \cdots \text{C17}^{\text{III}}$  [3.510(8) Å] where the equivalent position I =  $(-x, 1-y, -z)$ , II =  $(x, y-1, z)$  and III =  $(1+x, y, z)$ . Also these shortest C–C and C–Cl intermolecular interactions are consistent with van der Waals contact distances calculated by Bondi.<sup>6</sup> The structure is similar to the

structures of dimeric nickel(II) carboxylate complexes with  $N,N,N',N'$ -tetramethylethylenediamine examined earlier by us, and selected relevant structural parameters for these complexes are presented in Table 4.

The nickel–oxygen distances of the bridging dichloroacetate ions fall within the range 2.037–2.063 Å. They are somewhat shorter than the corresponding distances of 2.066 and 2.118 Å for the nonbridging dichloroacetate ions and 2.130 and 2.135 Å for the bridging water molecule. The same trend has been found in the compared structures, as can be seen from Table 4.

The nickel–nitrogen distances vary from 2.146 to 2.179 Å, the mean value being 2.164 Å. These values are in the same range as in the compared complexes. Although the mean values seem to increase slightly with increasing basicity of the carboxylate ion, the trend is not clear-cut.

The nickel–nickel distance of 3.657 Å is about 0.1 Å greater than in the other nickel(II) dimers. This difference may be due in part to the decreased basicity of the carboxylate ligand and the steric interactions within the complex molecule. Our failure to prepare the corresponding trichloroacetate crystals in stable form is largely explained by these properties.

In dimeric copper(II) carboxylates there appears to be a slight opening of the O–C–O angle in the case of haloacetates.<sup>7</sup> This trend is also observable in the dimeric nickel(II) complexes. Moreover, in the present compound the O–C–O angles of the bridging dichloroacetate ions are slightly greater than those of the nonbridging ones.

Table 4. Selected relevant structural parameters<sup>a</sup> for  $\text{Ni}_2(\text{C}_6\text{H}_{16}\text{N}_2)_2(\text{carboxylate})_4\text{H}_2\text{O}$ .

Carboxylate		Acetate	Chloroacetate	Dichloroacetate	Propionate	2-Chloropropionate	3-Chloropropionate
Ni–Ni	Å	3.563(1)	3.567(3)	3.657(1)	3.497(1)	3.566(3)	3.549(3)
Ni–N	Å	2.192(7)	2.172(12)	2.164(5)	2.191(6)	2.164(11)	2.174(15)
Ni–O(bridg. RCOO)	Å	2.037(6)	2.040(9)	2.048(5)	2.035(4)	2.028(9)	2.038(13)
Ni–O(nonbridg. RCOO)	Å	2.072(6)	2.117(9)	2.092(5)	2.109(4)	2.076(9)	2.062(13)
Ni–O(water)	Å	2.088(4)	2.088(9)	2.133(4)	2.073(4)	2.112(7)	2.109(10)
N–Ni–N	degr.	83.4(2)	84.1(4)	84.4(2)	83.8(2)	84.2(4)	84.4(5)
Ni–O(water)–Ni	degr.	117.2(2)	117.4(4)	118.1(2)	115.0(2)	114.6(5)	115.2(4)
Dihedral angle <sup>b</sup>	degr.	78.3	64.9	66.9	63.0	64.0	64.1
O–C–O	degr.	126.0(7)	127.7(11)	129.2(6)	126.7(6)	128.8(13)	128.1(17)

<sup>a</sup> When more than one chemically equivalent distance or angle is present, the mean value is tabulated. The estimated standard deviations in the parentheses are average e.s.d.'s for an individual distance or angle. <sup>b</sup> Dihedral angle refers to the angle between planes I and II presented in Table 5 and corresponding angles in the other structures.

Table 5. Deviations (Å) of atoms from least-squares planes.

Plane I: N1, N2, O1, O9				Plane II: N3, N4, O4, O9			
N1	0.049	Ni1	0.028	N3	-0.015	Ni2	-0.055
N2	-0.044	C1	0.306	N4	0.014	C7	-0.221
O1	-0.048	C2	-0.437	O4	0.015	C8	0.521
O9	0.043			O0	-0.014		
Plane III: O1, O2, C13, C14				Plane IV: O3, O4, C15, C16			
O1	0.003	Ni1	-0.071	O3	0.000	Ni1	0.207
O2	0.003	Ni2	0.374	O4	0.000	Ni2	-0.290
C13	-0.007	C11	1.699	C15	0.001	C13	1.343
C14	0.002	C12	-0.853	C16	0.000	C14	-1.533
Plane V: O5, O6, C17, C18				Plane VI: O7, O8, C19, C20			
O5	-0.006	Ni1	0.472	O7	0.005	Ni2	0.332
O6	-0.006	O9	0.227	O8	0.005	O9	0.155
C17	0.016	C15	1.439	C19	-0.014	C17	1.674
C18	-0.004	C16	-0.190	C20	0.004	C18	-1.027

The acetate groups in the dichloroacetate ligands are approximately planar but the chlorine atoms do not lie in these planes (Table 5). The C–O bond distances are equal but the O–C–C angles are nonequivalent, with the greater one located at the side of the oxygen atom nearest the  $\alpha$ -chloro-substituents.

The dimensions of the  $N,N,N',N'$ -tetramethylethylenediamine ligands are as expected.<sup>8</sup> The diamine chelate rings are in normal unsymmetric *gauche* configuration as in the other similar nickel(II) dimers.

6. Bondi, A. *J. Phys. Chem.* 68 (1964) 441.
7. Doedens, R. J. *Prog. Inorg. Chem.* 21 (1976) 227.
8. Turpeinen, U. *Ann. Acad. Sci. Fenn. Ser. A 2* 182 (1977) 15.

Received October 12, 1977.

## REFERENCES

1. a. Turpeinen, U., Ahlgrén, M. and Hämäläinen, R. *Finn. Chem. Lett.* (1977) 246; b. Turpeinen, U. *Finn. Chem. Lett.* (1976) 173; c. Ahlgrén, M., Hämäläinen, R. and Turpeinen, U. *Cryst. Struct. Commun.* 6 (1977) 829; d. Turpeinen, U. *Finn. Chem. Lett.* (1977) 36; e. Turpeinen, U. *Finn. Chem. Lett.* (1977) 123.
2. *The X-RAY System, Version of June 1972*, Technical Report TR-192, Computer Science Center, University of Maryland, College Park 1972.
3. Cromer, D. and Mann, J. B. *Acta Crystallogr. A* 24 (1968) 321.
4. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys.* 42 (1965) 3175.
5. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV, p. 149.