molecule [O(4)] giving the shortest *M*—O distance involved in the shortest, and presumably strongest, intermolecular H-bonding. The orientation of the two $C_7H_4NO_3S$ ligands, which are basically coplanar, is such that the ligand planes are close to the plane containing the two nitrogens, the metal and the O(4) oxygens. The dihedral angle between the two planes defined by the ligand ring atoms and the *M*, N and O(4) atoms is ~16°, and that between the ligand plane and the *M*,N,O(5) plane is ~72°. Such an arrangement will place the lone pairs on the sp^2 N atoms approximately parallel to the *M*—O(5) bonds, and it is possible that these will exert some repulsive effect on the O(5) water molecules leading to a weakening of these bonds. It is the *M*—O(5) bond that suffers Jahn–Teller elongation in the Cu complex, and in such distortions it is invariably the weakest bonds that are lengthened. The results of thermal studies of the seven hexahydrates (Haider, Malik & Wadsten, 1983) indicate that the energy of dehydration is minimum for the Cu complex and maximum for the Ni complex. All six H_2O molecules are removed within 350–490 K. The energy of dehydration, which is related to the binding energy of the H_2O molecules in the crystal, increases in the order $Cu < Cd < Mn \sim Zn < Fe \sim Co < Ni$, and has values of 355·8, 385·1, 418·6, 427·0, 594·4, 602·8 and 670·0 Jg^{-1}, respectively.

The saccharinato ligands are planar and have comparable dimensions in all the complexes.

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Dimeric *N-tert*-Butyl(chloroarsine)imine, $C_8H_{18}As_2Cl_2N_2$*

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Abstract. $M_r = 362\cdot99$, *Pbca*, $a = 11\cdot490\,(2)$, $b = 16\cdot093\,(3)$, $c = 15\cdot954\,(2)$ Å, $U = 2950\cdot0$ Å^3, $Z = 8$, $D_x = 1\cdot634$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 4\cdot86$ mm^{-1}, $F(000) = 1440$, $T = 291$ K, $R = 0\cdot036$ for 1410 observed reflections. The As—Cl bonds lie on the same side of the four-membered $[AsN]_2$ ring, and the coordination about N is approximately planar. The two *tert*-butyl groups adopt different conformations, so that the approximate overall molecular symmetry is only *m*. NMR indicates that only one isomer is present in solution.

Introduction. Olah & Oswald (1960) prepared alkyl (chloroarsine)imines $[R\text{NAsCl}]_n$ from primary amines and arsenic trichloride; molecular weight measurements indicated $n = 2$ for $R =$ *tert*-butyl, and $n \geq 3$ for other alkyl substituents. Vetter, Strametz & Nöth (1963) also prepared the *tert*-butyl derivative and proposed a dimeric structure. The crystal structure of the methyl analogue (Weiss & Eisenhuth, 1967) showed it to be trimeric with a six-membered $[AsN]_3$ ring. We report here the structure of $[t\text{-BuNAsCl}]_2$, prepared by a new route.

Experimental. 4·6 g $LiN(SiMe_3)(t\text{-Bu})$ in 40 ml *n*-hexane was added slowly to 5·6 g $AsCl_3$ in 50 ml

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* 1,3-Di-*tert*-butyl-2,4-dichlorocyclodiarsazane.

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n-hexane cooled in ice. Stirring was continued for two further hours, allowing the mixture to warm up to room temperature. LiCl was filtered off and the product purified by vacuum distillation; yield *ca* 5 g (90%). Found: C 26·9; H 5·1%; calc: C 26·4; H 5·0%. IR (Nujol): 2980–2900 *vs*(br), 1460 *vs*, 1396 *w*, 1378 *m*, 1368 *s*, 1240 *w*, 1220 *m*, 1200 *s*, 1034 *w*, 984 *s*, 806 *vs*, 784 *m* cm^{-1}. ^{1}H NMR (CH_2Cl_2): 1·38 p.p.m., single line throughout temperature range 173 to 333 K, m.p. 334–337 K.

Crystal 0·2 × 0·2 × 0·04 mm grown from *n*-hexane, mounted in capillary. Stoe–Siemens AED, unit cell from 2θ values of 31 reflections ($20 < 2\theta < 24°$). 4260 reflections with $2\theta < 45°$ collected by profile fitting (Clegg, 1981) for $+h$, $\pm k$, $+l$. No significant variation of 3 standard reflections, semi-empirical absorption corrections (transmission 0·21 to 0·34) based on measurements of equivalent reflections at different azimuthal angles. 1930 unique non-extinguished data ($R_{\text{int}} = 0{\cdot}028$), 1410 with $F > 4\sigma(F)$. Multisolution direct methods, least squares on F, $w^{-1} = \sigma^2(F) + 0{\cdot}0001F^2$, complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), rigid methyl groups with C—H 0·96 Å, H—C—H 109·5°, $U(\text{H}) = 1{\cdot}5U_{\text{eq}}(\text{C})$, non-hydrogen atoms anisotropic, no extinction correction necessary, 145 parameters, $R = 0{\cdot}036$, $wR = 0{\cdot}033$, slope of normal probability plot = 1·17, max. final $\Delta/\sigma = 0{\cdot}03$, mean = 0·01, largest peak in final difference map 0·28 Å^{-3}, largest trough −0·34 Å^{-3}, *SHELXTL* program system (Sheldrick, 1983).*

Discussion. Atomic coordinates are given in Table 1, bond lengths and angles in Table 2. The molecular structure shown in Fig. 1 confirms the presence of a four-membered $[AsN]_2$ ring. The $[AsN(C)]_2$ unit is almost planar [r.m.s. deviation 0·09 (5) Å from least-squares plane]. The two chlorine atoms lie 2·073 (3) Å to the same side of this plane, with Cl···Cl 4·367 (5) Å (twice the van der Waals radius is about 3·6 Å). In $[CH_3NAsCl]_3$ (Weiss & Eisenhuth, 1967) one Cl lies on the opposite side of the slightly puckered $[AsN]_3$ ring from the other two. The two *tert*-butyl conformations are different, reducing the approximate molecular symmetry from *mm* to *m*. The single-line ^{1}H NMR spectrum throughout the 173 to 333 K temperature range indicates that only one isomer is present, and that the *tert*-butyl groups rotate on a NMR time scale.

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Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{eq}*
As(1)	−663 (1)	4406 (1)	4050 (1)	59 (1)
As(2)	−662 (1)	3073 (1)	2951 (1)	63 (1)
Cl(1)	−2443 (2)	4606 (2)	4604 (1)	109 (1)
Cl(2)	−2449 (2)	2508 (2)	2868 (1)	128 (1)
N(1)	−971 (3)	4169 (3)	2957 (2)	50 (2)
N(2)	−540 (4)	3275 (3)	4075 (2)	61 (2)
C(1)	−1356 (5)	4733 (4)	2276 (3)	58 (2)
C(2)	86 (5)	2769 (4)	4704 (3)	64 (2)
C(3)	−2678 (5)	4739 (6)	2225 (5)	106 (4)
C(4)	−915 (6)	5603 (4)	2465 (4)	91 (3)
C(5)	−809 (6)	4441 (5)	1456 (4)	99 (3)
C(6)	1392 (6)	2891 (7)	4614 (6)	148 (5)
C(7)	−263 (7)	1862 (4)	4562 (4)	96 (3)
C(8)	−329 (6)	3034 (5)	5574 (4)	85 (3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and angles* (°)

As(1)—As(2)	2·769 (2)	As(1)—Cl(1)	2·252 (2)
As(1)—N(1)	1·819 (4)	As(1)—N(2)	1·826 (5)
As(2)—Cl(2)	2·249 (3)	As(2)—N(1)	1·799 (5)
As(2)—N(2)	1·827 (4)	N(1)—C(1)	1·482 (7)
N(2)—C(2)	1·479 (7)	C(1)—C(3)	1·522 (8)
C(1)—C(4)	1·520 (9)	C(1)—C(5)	1·525 (8)
C(2)—C(6)	1·520 (9)	C(2)—C(7)	1·530 (9)
C(2)—C(8)	1·527 (8)		
As(2)—As(1)—Cl(1)	111·1 (1)	As(2)—As(1)—N(1)	39·8 (1)
Cl(1)—As(1)—N(1)	103·3 (1)	As(2)—As(1)—N(2)	40·7 (1)
Cl(1)—As(1)—N(2)	101·8 (1)	N(1)—As(1)—N(2)	80·1 (2)
As(1)—As(2)—Cl(2)	110·5 (1)	As(1)—As(2)—N(1)	40·3 (1)
Cl(2)—As(2)—N(1)	102·5 (1)	As(1)—As(2)—N(2)	40·7 (2)
Cl(2)—As(2)—N(2)	101·5 (2)	N(1)—As(2)—N(2)	80·6 (2)
As(1)—N(1)—As(2)	99·9 (2)	As(1)—N(1)—C(1)	129·2 (4)
As(2)—N(1)—C(1)	130·9 (3)	As(1)—N(2)—As(2)	98·6 (2)
As(1)—N(2)—C(2)	126·9 (3)	As(2)—N(2)—C(2)	127·3 (4)
N(1)—C(1)—C(3)	110·0 (5)	N(1)—C(1)—C(4)	108·6 (4)
N(1)—C(1)—C(5)	108·5 (5)	N(2)—C(2)—C(6)	110·1 (5)
N(2)—C(2)—C(7)	107·3 (5)	N(2)—C(2)—C(8)	108·1 (5)

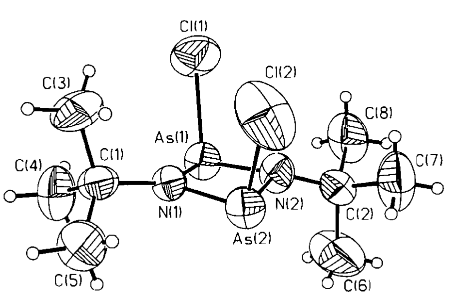

Fig. 1. The molecule of $[t\text{-BuNAsCl}]_2$, showing 50% probability thermal ellipsoids and numbering of the non-hydrogen atoms. Hydrogen atoms have been drawn as spheres of arbitrary radius 0·12 Å.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39326 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraaquabis(hydrogen maleato)nickel(II), $[Ni(C_4H_3O_4)_2(H_2O)_4]$

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Abstract. $M_r = 360{\cdot}9$, triclinic, $P\bar{1}$, $Z = 1$, $a = 7{\cdot}309\ (3)$, $b = 9{\cdot}731\ (2)$, $c = 5{\cdot}170\ (2)$ Å, $\alpha = 105{\cdot}97\ (3)$, $\beta = 87{\cdot}12\ (3)$, $\gamma = 117{\cdot}05\ (2)°$, $V = 313{\cdot}6\ (4)$ Å^3, $D_m = 1{\cdot}890$, $D_x = 1{\cdot}911$ Mg m^{-3} (flotation in $CHBr_3$/toluene), Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 1{\cdot}61$ mm^{-1}, $F(000) = 186$, room temperature, $R_w = 0{\cdot}036$ for 1336 reflections with $I \geq 2\sigma(I)$. The nickel ion is sixfold coordinated by oxygen atoms in a slightly distorted octahedron. The hydrogen maleate ion (HM) behaves as a unidentate ligand to the metal. A very short asymmetric intramolecular H bond [2·438 (3) Å] connects the hydroxyl-group O atom of the non-ionized carboxyl group with an O atom of the ionized one, effectively closing a non-planar seven-membered ring. A three-center bifurcated donor H bond is observed.

Introduction. Crystals of tetraaquabis(hydrogen maleato)metal, $M(C_4H_3O_4)_2.4H_2O$ with M=Mn, Co, Zn, Ni, Fe have been investigated in the past by one of us (MPG) and co-workers but, except for $Mn^{II}(C_4H_3O_4)_2.4H_2O$ (Gupta & Mahanta, 1978), results of these studies have not been published. These crystals are isostructural and the purpose of the studies was to determine the effect of different metal ions on the geometry of the HM ion, as well as the scheme of hydrogen bonds in the crystals. However, as hydrogen atoms in the studies could not be properly located, the conclusions remained indecisive. Similar investigations by Antsishkina, Porai-Koshits & Guseinov (1974) equally remained inconclusive. The present work, therefore, reports on a new investigation of the nickel compound $Ni(C_4H_3O_4)_2.4H_2O$. Crystals were grown from a solution of the compound in water by slow evaporation. The solution was prepared by addition of maleic acid to nickel carbonate.

Experimental. 1375 reflections up to $\theta = 27°$ measured, Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite-crystal monochromator, ω/θ scan, scan angle $(1{\cdot}0 + 1{\cdot}5\ \tan\theta)°$, aperture of detection unit 2·0 mm. Lattice parameters from angle settings of 25 high-order reflections. 3 intensity and orientation control reflections measured every 2 h, no significant drift. Because of small size of crystal (0·1 × 0·1 × 0·15 mm) and low μ no absorption correction. $-9 \leq h \leq 9$, $-12 \leq k \leq 11$, $0 \leq l \leq 6$. Earlier workers had used the space group $P\bar{1}$, but as intensity statistics showed an acentric distribution, we started the determination in $P1$. Structure solved by *MULTAN* (Germain, Main & Woolfson, 1971). Most likely E map with 200 terms revealed all non-hydrogen atoms. Data refined by least squares on F using Gauss–Seidel block method (Sparks, 1974), and Enraf–Nonius *SDP* package (Frenz, 1978), giving a weight to each reflection based on counting statistics. Even though R decreased satisfactorily, no hydrogen atoms could be found and the two HM ions had differences in geometries larger than was considered physically acceptable. Since there is no *a priori* reason to believe that the two HM ions, acting as unidentate ligands to the metal, would be significantly different, we changed the space group to $P\bar{1}$. Refinement proceeded smoothly and a difference Fourier map revealed all hydrogen atoms; their inclusion in further least-squares refinements, with fixed thermal temperature factors (2·5 Å^2) for H atoms, brought R_w to 0·036 and conventional R to 0·030, $w = 1/\sigma^2(F)$. Max. $\Delta/\sigma = 0{\cdot}3$, max. peak, representing max. noise level, in final difference map, 0·3 e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Refined

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