and two O atoms of the water molecules. Distances from the central metal ion to the donor atoms lie in the broad range of 2·027 (3) to 2·453 (1) Å (see Table 2). The coordination geometry of Ni deviates from an ideal octahedron; the angles vary from 82·39 (7) for S4—Ni—N13 to 97·0 (1)° for O61—Ni—N23 (see Table 2).

The bhdhx molecule is not only coordinated to the Ni^{II} ion but is also hydrogen-bonded, through the H atoms on the non-coordinating azole N atoms, to two of the O atoms of the nitrates, with N···O contacts of 2·800 (5) and 2·914 (4) Å. The presence of relatively strong hydrogen bridges was also inferred from the infrared spectrum of this compound, where strong bands in the 2500 to 3200 cm^{-1} region occurred.

The precise coordination mode of the nitrates could not be inferred from the infrared spectrum as strong ligand bands occur in the same region as the nitrate absorptions (Kleywegt, Wiesmeijer, van Driel, Driessen, Reedijk & Noordik, 1985).

Bond angles around the thioether S atoms are close to 100°, which indicates that one of the lone electron pairs on each of these S atoms is directed towards the Ni ion. The relatively long Ni—S contact of 2·45 Å suggests a weak bond, and is quite normal for Ni—S(thioether) distances (Setzer, Ogle, Wilson & Glass, 1983; Hill & Hope, 1974).

The imidazole rings are planar (distances to the least-squares planes not exceeding 0·008 Å). The imidazole rings are not mutually coplanar; the dihedral angle is 87·7 (2)°. There is no intermolecular stacking of the aromatic rings. The packing of the molecules is due to normal van der Waals contacts and to the hydrogen bonds described above.

References

BOUWMAN, E. & DRIESSEN, W. L. (1988). *Synth. Commun.* In the press.

BOUWMAN, E., TEN HOVE, J. C., DRIESSEN, W. L. & REEDIJK, J. (1988). Submitted.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Enraf–Nonius (1979). *Structure Determination Package.* Enraf–Nonius, Delft, The Netherlands.

HILL, N. L. & HOPE, H. (1974). *Inorg. Chem.* **13**, 2079–2082.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

KLEYWEGT, G. J., WIESMEIJER, W. G. R., VAN DRIEL, G. J., DRIESSEN, W. L., REEDIJK, J. & NOORDIK, J. H. (1985). *J. Chem. Soc. Dalton Trans.* pp. 2177–2184.

SETZER, W. N., OGLE, C. A., WILSON, G. S. & GLASS, R. S. (1983). *Inorg. Chem.* **22**, 266–271.

Structure of a Binuclear Copper(II) Complex:
Tetrakis(μ-2-chloropropanoato)-bis(triphenylphosphine oxide)dicopper(II)

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Abstract. [Cu$_2$(C$_3$H$_4$ClO$_2$)$_4${OP(C$_6$H$_5$)$_3$}$_2$], M_r = 1113·738, monoclinic, $P2_1/n$, a = 11·191 (8), b = 17·161 (8), c = 13·102 (4) Å, β = 91·69 (3)°, V = 2515 (2) Å^3, Z = 2, D_x = 1·47, D_m = 1·45 g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, μ = 12·1 cm^{-1}, $F(000)$ = 1140, T = 300 K, final R = 0·061 for 2698 observed reflections. The Cu^{II} atoms are bridged by 2-chloropropanoate groups forming binuclear [Cu$_2$(2-chloropropanoato)$_4$(triphenylphosphine oxide)$_2$] molecules. The Cu^{II} atoms are coordinated by four O atoms from

the carboxylate groups and by one O atom from the triphenylphosphine oxide ligand at the apex of a slightly distorted square pyramid. The displacement of the Cu atom from the basal plane is 0.230 (1) Å. The Cu$\cdots$Cu distance is 2.696 (2) Å.

Introduction. In recent years increased attention has been paid to the bactericidal and fungicidal properties of Cu^{II} carboxylates. A series of experiments (Melník, Anderová & Holko, 1982) showed that antibacterial and antifungal ability significantly increase in the presence of halogen substituents in chains of aliphatic carboxylates. Sharrock, Melník, Bélanger-Gariépy & Beauchamp (1985) investigated [Cu$_2$(3-chloropropanoato)$_4$(Ph$_3$PO)$_2$], which is similar to the subject of the present paper [Cu$_2$(2-chloropropanoato)$_4$-(Ph$_3$PO)$_2$].

Experimental. The compound under study was prepared by mixing together methanolic solutions of Cu(CH$_3$CHClCOO)$_2$ and (C$_6$H$_5$)$_3$PO in equimolar ratio. After heating and then slowly cooling this solution, a microcrystalline product precipitated. This was crystallized from methanol.

The dark-green crystal used was of prismatic shape with dimensions $0.3 \times 0.2 \times 0.1$ mm. D_m was determined by flotation (CCl$_4$/CH$_3$COCH$_3$). Weissenberg photographs (Cu $K\alpha$; $\lambda = 1.5418$ Å) showed that the compound under study crystallizes in the monoclinic space group $P2_1/c$ but with $\beta = 129°$; it was therefore transformed into space group $P2_1/n$ with β near 90°. The unit-cell parameters were refined using a Syntex $P2_1$ diffractometer (with graphite monochromator) applying the least-squares method to the setting of 15 selected reflections with $3.91 < 2\theta < 10.21°$. Three standard reflections were checked after measuring every 98 reflections; variations were 2·4, 1·8 and 3·6%. 4709 reflections were measured ($2\theta_{max} = 50°$), 2698 reflections [$I > 1.96\sigma(I)$] were observed. $R_{int} = 0.03$, hkl ranges $0/13$, $-20/0$ and $-15/15$. Intensities were corrected for Lorentz–polarization factors and an empirical correction was also made for absorption, though maximum and minimum values of the transmission factor were the same (0·85).

The structure was solved with $MULTAN80$ (Main et al., 1980) using molecular scattering factors for the calculation of E values. The structure was refined on F by the full-matrix least-squares method of $SHELX76$ (Sheldrick, 1976). The positions of two H atoms from the methyl group of the chloropropanoate molecule were calculated; the remaining H atoms were found from a difference Fourier synthesis: the positions of the H atoms and their temperature factors ($B = 4.97$ Å^2) were fixed. Final $R = 0.061$ and $wR = 0.064$. In the final refining cycles the weighting scheme $w = 1.0/[\sigma^2(F_o) + 0.000715 F_o^2]$ was applied; in the last cycle $(\Delta/\sigma)_{max} = 0.060$; the maximum and minimum values

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cu	0·4475 (1)	−0·0014 (1)	0·0913 (1)	2·17 (3)
O	0·3627 (3)	0·0053 (4)	0·2315 (4)	3·6 (2)
P	0·2755 (2)	0·0488 (1)	0·2960 (2)	3·14 (6)
O(1)D	0·3344 (4)	−0·0724 (1)	0·0236 (3)	4·7 (2)
O(2)D	0·4204 (4)	−0·0712 (4)	−0·1272 (3)	4·2 (2)
C(1)D	0·3442 (3)	−0·0928 (4)	−0·0662 (5)	4·0 (3)
C(2)D	0·2611 (5)	−0·1610 (4)	−0·1001 (5)	4·8 (2)
ClD	0·3162 (4)	−0·2285 (6)	−0·1659 (5)	5·6 (3)
C(3)D	0·1412 (6)	−0·1683 (5)	−0·0452 (6)	5·1 (3)
O(1)E	0·3567 (4)	0·0888 (4)	0·0319 (4)	4·8 (2)
O(2)E	0·4457 (4)	0·0914 (4)	−0·1198 (5)	4·4 (2)
C(1)E	0·3753 (6)	0·1170 (4)	−0·0543 (5)	3·3 (3)
C(2)E	0·3121 (6)	0·1903 (5)	−0·0830 (6)	4·3 (2)
ClE	0·1758 (4)	0·2014 (3)	−0·0286 (4)	7·2 (3)
C(3)E	0·3982 (5)	0·2662 (4)	−0·0511 (6)	3·7 (3)
C(1)A	0·3116 (6)	0·0337 (4)	0·4288 (5)	3·2 (3)
C(2)A	0·3269 (6)	−0·0411 (5)	0·4651 (6)	4·9 (3)
C(3)A	0·3631 (5)	−0·0546 (6)	0·5660 (5)	6·2 (3)
C(4)A	0·3787 (6)	0·0069 (6)	0·6311 (5)	4·6 (3)
C(5)A	0·3652 (5)	0·0805 (6)	0·5971 (6)	5·5 (3)
C(6)A	0·3307 (6)	0·0957 (5)	0·4964 (5)	5·1 (3)
C(1)B	0·2719 (6)	0·1521 (4)	0·2760 (5)	4·1 (3)
C(2)B	0·1638 (6)	0·1947 (4)	0·2847 (5)	5·4 (3)
C(3)B	0·1620 (5)	0·2737 (6)	0·2773 (6)	6·2 (3)
C(4)B	0·2688 (5)	0·3117 (5)	0·2629 (5)	4·6 (3)
C(5)B	0·3760 (5)	0·2715 (5)	0·2531 (6)	5·0 (3)
C(6)B	0·3769 (5)	0·1918 (4)	0·2600 (5)	5·3 (3)
C(1)C	0·1242 (6)	0·0135 (4)	0·2731 (5)	4·0 (3)
C(2)C	0·0873 (6)	−0·0031 (5)	0·1738 (4)	5·1 (3)
C(3)C	−0·0279 (6)	−0·0257 (4)	0·1520 (5)	5·5 (3)
C(4)C	−0·1061 (5)	−0·0362 (6)	0·2301 (5)	6·7 (3)
C(5)C	−0·0711 (5)	−0·0201 (5)	0·3281 (6)	4·8 (3)
C(6)C	0·0459 (6)	0·3501 (6)	0·3501 (6)	5·6 (3)

of the difference electron density were 0·44 and -0.49 e Å^{-3}, respectively; the atomic scattering factors f' and f'' were taken from *International Tables for X-ray Crystallography* (1962). The positions of the non-H atoms with their equivalent isotropic temperature factors are listed in Table 1.*

Discussion. The structure consists of centrosymmetric [Cu$_2$(CH$_3$CHClCOO)$_4$\{(C$_6$H$_5$)$_3$PO\}$_2$] units (Fig. 1), bonded by van der Waals forces. Fig. 2 shows the arrangement of structure units in the unit cell.

The Cu atom is coordinated in the equatorial plane by four O atoms of the chloropropanoate groups and axially by one O from the triphenylphosphine oxide ligand, to give a slightly distorted tetragonal pyramid. The bond distances and angles are listed in Table 2.

Such Cu coordination dimers can be characterized by the distances Cu$\cdots$Cu, Cu–L (L = neutral ligand coordinated to Cu by an O atom), Cu$\cdots$basal plane (basal plane formed by four O from the carboxylate groups) and basal plane–basal plane (Yablokov, Mosina, Simonov, Milkova & Ablov, 1978). The presence of four carboxylate ligands is a

stabilizing factor (the geometrical expression of which is the basal plane–basal plane distance) in this type of complex (Koreñ, Valach, Sivý & Melník, 1985). From the data of Melník (1982), the mean parameter values for CuO$_5$ units in dimers are: Cu···Cu 2·62 ± 0·03; Cu–O 2·17 ± 0·06; Cu–basal plane 0·20 ± 0·01; basal plane–basal plane 2·22 ± 0·03 Å. There are only two examples, [Cu{CH$_3$(CH$_2$)$_2$COO}$_2$] (Bird & Lomer, 1972) and [Cu(C$_2$H$_5$COO)$_2$] (Simonov & Malinovsky, 1970), in which the value of the interplanar distance basal plane–basal plane (2·185 and 2·138 Å) is significantly smaller than the mean (2·22 ± 0·03 Å). However, it must be noted that these two dimers are incorporated in a polynuclear chain. It seems that 2·22 Å is a constant for binuclear Cu^{II} carboxylates. Comparing the dimer parameters of the present compound with those of [Cu(ClCH$_2$CH$_2$COO)$_2${(C$_6$-H$_5$)$_3$PO}] (Sharrock et al., 1985), a significant deviation is only found for the Cu···Cu and Cu–O distances.

The dimensions of the triphenylphosphine oxide molecule do not show any significant differences from the Ph$_3$PO molecule in [Cu(ClCH$_2$CH$_2$COO)$_2$-(Ph$_3$PO)] (Sharrock et al., 1985) or from the mean values of 62 Ph$_3$PO fragments (Bay, Schweizer & Dunitz, 1982). These authors introduced the parameter d, expressing the deviation of the Ph$_3$PO fragment from
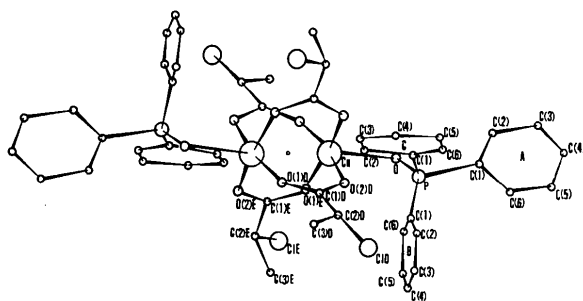

Fig. 1. Structure of the title compound showing the atomic numbering.
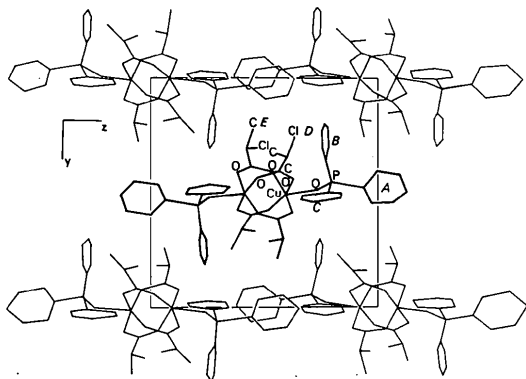

Fig. 2. Projection of the crystal structure on (100).

Table 2. *Bond distances (Å) and angles (°) with e.s.d.'s in parentheses*

Environment of the Cu^{II} atom

Cu–O(1)D	1·951 (6)
Cu–O(1)E	1·997 (6)
Cu–O	2·095 (5)

μ-Chloropropanoate molecule

	D	E
C(1)–O(1)	1·236 (8)	1·252 (9)
C(1)–O(2)	1·242 (7)	1·261 (9)
C(1)–C(2)	1·55 (1)	1·49 (1)
C(2)–C(3)	1·546 (9)	1·66 (1)
C(2)–Cl	1·58 (1)	1·713 (8)

Triphenylphosphine oxide molecule

O–P	1·507 (6)

	A	B	C
P–C(1)	1·793 (7)	1·792 (7)	1·815 (7)
C(1)–C(2)	1·38 (1)	1·421 (9)	1·383 (9)
C(2)–C(3)	1·39 (1)	1·36 (1)	1·368 (9)
C(3)–C(4)	1·36 (1)	1·379 (9)	1·378 (9)
C(4)–C(5)	1·35 (1)	1·393 (9)	1·36 (1)
C(5)–C(6)	1·39 (1)	1·37 (1)	1·392 (9)
C(6)–C(1)	1·39 (1)	1·380 (9)	1·367 (9)

Environment of the Cu^{II} atom

O(1)D–Cu–O(1)E	89·5 (2)
O(1)D–Cu–O	97·4 (2)
O(1)E–Cu–O	93·5 (2)
Cu–O–P	146·7 (4)

μ-Chloropropanoate molecule

	D	E
Cu–O(1)–C(1)	122·4 (4)	123·7 (5)
O(1)–C(1)–C(2)	114·7 (5)	117·7 (6)
O(2)–C(1)–C(2)	117·3 (6)	115·5 (6)
O(1)–C(1)–O(2)	127·6 (6)	127·1 (7)
C(1)–C(2)–C(3)	116·7 (6)	109·3 (5)
C(1)–C(2)–Cl	118·0 (4)	114·3 (6)
C(3)–C(2)–Cl	123·5 (7)	108·9 (5)

Triphenylphosphine oxide molecule

C(1)A–P–C(1)B	106·8 (3)
C(1)A–P–C(1)C	107·1 (3)
C(1)B–P–C(1)C	106·8 (3)

	A	B	C
O–P–C(1)	110·0 (3)	114·8 (4)	111·0 (3)
P–C(1)–C(2)	119·5 (5)	120·8 (5)	118·4 (5)
P–C(1)–C(6)	122·1 (5)	119·7 (5)	122·4 (5)
C(2)–C(1)–C(6)	118·4 (6)	119·3 (6)	119·2 (6)
C(1)–C(2)–C(3)	120·8 (8)	121·2 (6)	120·5 (6)
C(2)–C(3)–C(4)	119·6 (9)	118·0 (7)	119·8 (6)
C(3)–C(4)–C(5)	120·5 (7)	122·0 (8)	120·2 (6)
C(4)–C(5)–C(6)	121·0 (8)	119·5 (6)	119·8 (6)
C(5)–C(6)–C(1)	119·5 (8)	119·9 (6)	120·3 (6)

C_3 symmetry and showed that the greater the value of d, the higher the energy of the Ph$_3$PO fragment. For Ph$_3$PO in the compound studied d = 45° and is thus in an energetically less advantageous state than the Ph$_3$PO in [Cu(ClCH$_2$CH$_2$COO)$_2$(Ph$_3$PO)] (Sharrock et al., 1985) for which d = 36°.

References

BAY, E., SCHWEIZER, W. B. & DUNITZ, J. D. (1982). *J. Am. Chem. Soc.* **104**, 5893–5898.
BIRD, M. J. & LOMER, T. R. (1972). *Acta Cryst.* B**28**, 242–247.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 202, 215. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
KOREÑ, B., VALACH, F., SIVÝ, P. & MELNÍK, M. (1985). *Acta Cryst.* C**41**, 1160–1162.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MELNÍK, M. (1982). *Coord. Chem. Rev.* 42, 259–293.

MELNÍK, M., ANDEROVÁ, M. & HOĽKO, M. (1982). *Inorg. Chim. Acta*, 67, 117–122.

SHARROCK, P., MELNÍK, M., BÉLANGER-GARIÉPY, F. & BEAUCHAMP, A. L. (1985). *Can. J. Chem.* 63, 2564–2570.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SIMONOV, YU. A. & MALINOVSKY, T. I. (1970). *Sov. Phys. Crystallogr.* 15, 310–319.

YABLOKOV, J. V., MOSINA, M. N., SIMONOV, YU. A., MILKOVA, L. N. & ABLOV, A. V. (1978). *Zh. Strukt. Khim.* 19, 42–51.

Structures of Three α-Chloro-γ-lactones

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Abstract. 4-Chloro-2-oxatricyclo[4.2.1.0^{4,8}]nonan-3-one, (2), $C_8H_9ClO_2$, $M_r = 172.61$, monoclinic, $P2_1/c$, $a = 6.442$ (4), $b = 10.063$ (1), $c = 11.758$ (2) Å, $\beta = 95.82$ (3)°, $V = 758.3$ (7) Å^3, $Z = 4$, $D_x = 1.51$ Mg m^{-3}, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 0.442$ mm^{-1}, $F(000) = 360$, $T = 293$ K, $R = 0.035$ for 1815 reflections with $I > 3\sigma(I)$. 4-Chloro-2-oxatricyclo[5.2.1.0^{4,9}]decan-3-one, (4), $C_9H_{11}ClO_2$, $M_r = 186.64$, monoclinic, $P2_1/n$, $a = 6.148$ (1), $b = 11.150$ (4), $c = 12.577$ (2) Å, $\beta = 100.95$ (1)°, $V = 846.5$ (6) Å^3, $Z = 4$, $D_x = 1.46$ Mg m^{-3}, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 0.401$ mm^{-1}, $F(000) = 392$, $T = 293$ K, $R = 0.045$ for 1321 reflections with $I > 3\sigma(I)$. ($\pm$)-2aα-Chloro-3,4,4aα,5,6,7,7aα,7bα-octahydro-2aH-indeno[7,1-*b,c*]furan-2-one, (6), $C_{10}H_{13}ClO_2$, $M_r = 200.67$, monoclinic, $P2_1/n$, $a = 8.120$ (2), $b = 9.454$ (3), $c = 12.624$ (4) Å, $\beta = 97.26$ (2)°, $V = 961.3$ (9) Å^3, $Z = 4$, $D_x = 1.39$ Mg m^{-3}, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 0.358$ cm^{-1}, $T = 293$ K, $F(000) = 424$, $R = 0.036$ for 1018 reflections with $I > 3\sigma(I)$. In all three compounds, the bond lengths are unexceptional, the angles in the five-membered rings are significantly smaller than tetrahedral values and the angles in the six-membered rings [(4) and (6)] are somewhat enlarged. In (2), the three five-membered rings all have envelope conformations. In (4), the five-membered rings have envelope conformations and the six-membered ring is in a twist boat conformation. In (6), the five-membered rings also have envelope conformations while the six-membered ring is a chair which is slightly distorted owing to its fusion to two five-membered rings.

Introduction. Recently we reported methodology for the selective formation of carbocyclic α,γ-dichloroesters and/or annulated α-chloro-γ-lactones *via* transition-metal-promoted intramolecular radical cyclizations of olefinic α,α-dichloroesters and acids (Hayes, Freyer, Parvez & Weinreb, 1986). Several γ-lactones have been produced using this methodology, including simple cyclopentane and cyclohexane derivatives, along with bridged and fused tricyclic systems. X-ray studies have been carried out on some of these α-chloro-γ-lactones to confirm structural assignments made by NMR, and to establish unambiguously stereochemical relationships. Cyclization of 3-(3-cyclopentenyl)-2,2-dichloropropionic acid (1) with 1·2 mol% of RuCl₂-(PPh₃)₃ gave bridged lactone (2) in 88% yield. Likewise, lactone (4) was synthesized (88% yield) from 3-(3-cyclohexenyl)-2,2-dichloropropionic acid (3) and 2·2 mol% of catalyst. The fused bicyclic lactone (6) was prepared from 4-(2-cyclohexenyl)-2,2-dichlorobutyric acid (5) using 1·5 mol% of RuCl₂(PPh₃)₃ in 46% yield.