

ker, 1973) and $\text{Co}(\text{acac})_3$ and $\text{Al}(\text{acac})_3$ (Hon & Pfluger, 1973).

This gallium structure provides an example of a spherical d^{10} ion coordinated to three acetylacetonates. These data are important in explaining the variation of ligand bite with the metal–oxygen distance. Hon & Pfluger (1973) discussed the variation of bite with M–O distance and found, with the exception of Al, a linear correlation for the Co, Mn, Cr, V and Fe cases. However, the addition of the Ga(III), Sc(III) (Anderson, Neuman & Melson, 1973) and Rh(III) (Morrow & Parker, 1973) data makes the linear relationship much poorer. In fact, the Rh(III) case deviates approximately as much as the Al complex. Although this observation suggests that only the trivalent ions of a given row such as Sc–Ga will have a linear correlation between bite and M–O distance, the fit is poor even in the Sc–Ga series. Hon & Pfluger (1973) have suggested that Al(III) is anomalous because of the greater ionic character in the Al–O bond but this explanation does not appear completely valid. If one assumes that the acidity of the hexaquo ions reflects ionic character in the M–O bond, then the Ga(III) case should also be anomalous since the K_a 's for the $\text{M}(\text{H}_2\text{O})_6^{3+}$ species are 3.5×10^{-3} for Ga and 1.12×10^{-5} for Al (Cotton & Wilkinson, 1964). Furthermore, simple geometrical arguments would predict that in order to maintain approximately octahedral geometry about the metal (*i.e.* O–M–O about 90°), the bite must

vary with M–O distance in approximately the observed manner. One can conclude that since the ligand bite will depend on several different factors, such as the M–O distance, the O···O nonbonded contacts, the electron distribution in the metal ion, and the relative ease of deformation of the acetylacetonate ion, a simple correlation between bite and M–O distance probably does not exist. Nevertheless, the fundamental questions regarding chemical bonding which are raised by this series of compounds deserve further study.

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1,3-Dichloroacetone

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Abstract. 1,3-Dichloroacetone, $(\text{CH}_2\text{Cl})_2\text{CO}$, monoclinic, $P2_1/c$, $a = 14.635(6)$, $b = 5.261(4)$, $c = 16.426(9)$ Å, $\beta = 124.08(4)^\circ$, $Z = 8$, $D_m = 1.62$ (floatation in KI solution), $D_x = 1.62$ g cm $^{-3}$. The two crystallographically independent molecules are, within the accuracy of the determination, identical. In each molecule the atoms Cl–C–C(O)–C–Cl are coplanar, the conformation of the atoms Cl–C–C=O being synperiplanar. No short intermolecular contacts exist.

Introduction. X-ray intensities were collected on a Nonius three-circle automatic diffractometer. Details of the data collection were as follows. Radiation: crystal-monochromated Mo $K\alpha$, $\lambda = 0.71069$ Å; measuring technique: moving-crystal-stationary-detector with scan speed 1.2° min $^{-1}$ in the θ range 2.5 – 21° ; the crys-

tal ($0.46 \times 0.40 \times 0.38$ mm) was mounted in a glass capillary and oriented with **b** parallel to the ϕ axis of the goniostat; 1235 independent reflexions were measured having $|F_{\text{re}}|$ values in the range 0 to 150; 894 reflexions with $|F_{\text{re}}| > 3$ were used in the least-squares refinement. μ (Mo $K\alpha$) is 10.9 cm $^{-1}$, and no absorption correction was applied.

The structure was solved by a symbolic addition procedure (Dewar, 1968). Full-matrix least-squares refinement of the non-hydrogen atoms resulted in $R = 0.13$ and a subsequent difference map revealed the eight hydrogen atoms. Further least-squares refinement of positional parameters for all atoms and anisotropic temperature parameters for the non-hydrogen atoms led to a final R of 0.04. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with a weighting scheme $w = (6.0 + |F_o|$

Table 1. Atomic parameters for 1,3-dichloroacetone

Estimated standard deviations are given in parentheses. Fractional coordinates for the heavy atoms are $\times 10^4$, anisotropic thermal parameters $\times 10^2$, and hydrogen atom coordinates $\times 10^3$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Cl(11)	-588 (1)	-1525 (3)	3332 (1)	635 (6)	575 (8)	678 (7)	-134 (6)	323 (5)	-71 (6)
Cl(12)	3434 (1)	1597 (3)	4260 (1)	563 (6)	850 (10)	649 (7)	-21 (6)	346 (5)	-193 (7)
O(11)	1475 (3)	-1625 (7)	3438 (3)	719 (18)	451 (19)	645 (18)	20 (16)	371 (15)	-132 (16)
C(11)	399 (4)	941 (10)	3798 (4)	565 (22)	435 (25)	525 (22)	-50 (22)	282 (19)	-35 (23)
C(12)	1407 (4)	245 (10)	3817 (3)	541 (21)	365 (25)	350 (17)	97 (21)	215 (16)	61 (20)
C(13)	2304 (4)	2178 (11)	4352 (4)	533 (22)	451 (28)	477 (21)	16 (22)	264 (18)	-64 (23)
Cl(21)	1603 (1)	8453 (3)	714 (1)	637 (20)	569 (27)	463 (21)	-38 (22)	248 (18)	0 (21)
Cl(22)	5286 (1)	3666 (3)	3690 (1)	609 (19)	504 (23)	799 (20)	97 (21)	388 (17)	30 (22)
O(21)	3277 (3)	4423 (7)	1726 (3)	764 (19)	374 (17)	634 (17)	-53 (15)	392 (15)	-148 (16)
C(21)	2684 (4)	8403 (10)	1971 (4)	547 (6)	427 (7)	472 (5)	-25 (6)	242 (5)	-77 (5)
C(22)	3431 (3)	6154 (10)	2262 (3)	527 (6)	342 (7)	504 (7)	-101 (6)	327 (6)	-62 (7)
C(23)	4410 (5)	6313 (11)	3316 (4)	644 (26)	397 (26)	585 (25)	89 (23)	268 (21)	24 (24)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(111)	59 (3)	121 (8)	447 (3)	5	H(112)	0 (4)	243 (12)	331 (4)	5
H(131)	203 (4)	388 (9)	411 (3)	5	H(132)	252 (4)	214 (12)	502 (4)	5
H(211)	235 (4)	843 (10)	233 (4)	5	H(212)	304 (5)	986 (12)	213 (4)	5
H(231)	483 (4)	782 (13)	337 (4)	5	H(232)	411 (5)	650 (13)	373 (5)	5

Distances (Å)				Angles (°)			
Molecule (1)		Molecule (2)		Molecule (1)		Molecule (2)	
Cl(11)—C(11)	1.766 (5)	Cl(21)—C(21)	1.762 (4)	Cl(11)—C(11)—C(12)	112.7 (4)	Cl(21)—C(21)—C(22)	113.7 (4)
Cl(12)—C(13)	1.768 (7)	Cl(22)—C(23)	1.754 (6)	Cl(12)—C(13)—C(12)	112.8 (4)	Cl(22)—C(23)—C(22)	113.3 (4)
C(11)—C(12)	1.198 (7)	O(21)—C(22)	1.197 (7)	C(11)—C(12)—C(13)	112.0 (5)	C(21)—C(22)—C(23)	112.1 (4)
C(11)—C(12)	1.504 (9)	C(21)—C(22)	1.496 (7)	C(11)—C(12)—O(11)	123.7 (4)	C(21)—C(22)—O(21)	124.3 (4)
C(13)—C(12)	1.496 (7)	C(23)—C(22)	1.509 (6)	C(13)—C(12)—O(11)	124.3 (5)	C(23)—C(22)—O(21)	123.6 (4)
C(11)—H(111)	0.99 (6)	C(21)—H(211)	0.96 (7)	Cl(11)—C(11)—H	104 104	Cl(21)—C(21)—H	107 109
C(11)—H(112)	1.04 (6)	C(21)—H(212)	0.88 (6)	Cl(12)—C(13)—H	108 112	Cl(22)—C(23)—H	108 111
C(13)—H(131)	0.97 (5)	C(23)—H(231)	0.97 (7)	C(12)—C(11)—H	111 110	C(22)—C(21)—H	111 113
C(13)—H(132)	0.97 (5)	C(23)—H(232)	0.99 (10)	C(12)—C(13)—H	111 106	C(22)—C(23)—H	107 107
Cl(11)····O(11)	2.927 (5)	Cl(21)····O(21)	2.949 (4)				
Cl(12)····O(11)	2.928 (4)	Cl(22)····O(21)	2.930 (3)				

Least-squares planes and distances from the planes in Å

Molecule (1):		Molecule (2):		Molecule (2):		Molecule (2):	
-1.12X - 2.54Y + 12.58Z = 4.59		12.31X + 2.47Y - 11.38Z = 3.19					
Cl(11)	0.06	C(12)	-0.01	Cl(21)	0.06	C(22)	-0.02
Cl(12)	-0.02	C(13)	0.08	Cl(22)	0.02	C(23)	0.02
C(11)	-0.09	O(11)	-0.02	C(21)	-0.05	O(21)	-0.03

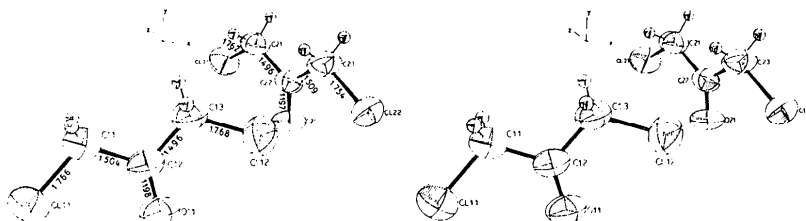


Fig. 1. Stereo diagram illustrating the conformation of the two independent molecules.

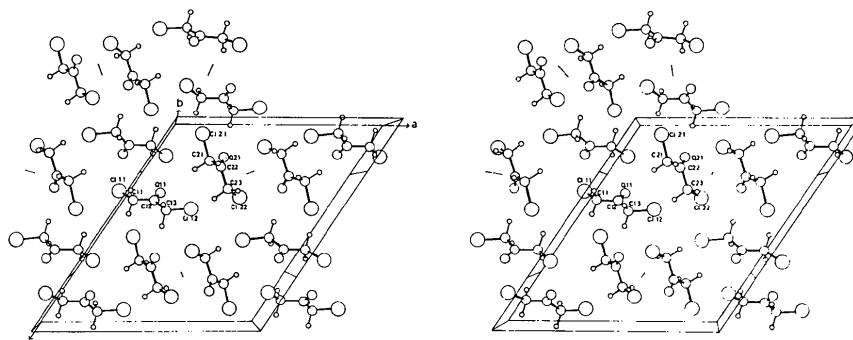


Fig. 2. Stereo diagram illustrating the molecular packing. The view is down *b*, with *a* horizontal. Unit-cell outline and screw axes are indicated.

+0.013| F_o |²)⁻¹. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).*

Final values of atomic positions and temperature parameters are listed in Table 1. The conformations of the two independent molecules are illustrated in Fig. 1. The programs used in the refinement were the X-RAY System (Stewart, Kundell & Baldwin, 1970) and the figures were drawn with the program *ORTEP* (Johnson, 1965).

Discussion. 1,3-Dichloroacetone has an unusually high melting point of 45°C compared with other chlorinated acetones, ranging from monochloroacetone (m.p. -44.4°C) to hexachloroacetone (m.p. -2°C). This could be due to a favourable packing of the molecules and/or the presence of O...Cl charge-transfer bonds.

Bond lengths and angles for the two independent molecules are listed in Table 1. Due to the synperi-

planar conformation of the Cl-C-C=O groups short intramolecular O...Cl distances of 2.93-2.95 Å are found.

Least-squares planes through the non-hydrogen atoms are listed in Table 1 with distances of the atoms from the planes.

The packing of the molecules is shown in Fig. 2. No intermolecular contacts significantly shorter than the expected van der Waals contacts are found in the structure. A packing coefficient was calculated (Kitaigorodskii, 1961) and found to be 0.664, indicating a favourable packing of the molecules.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30339 (26 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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The Nitroxide Radical *exo*-2-Iodomethyl-2,4,4-*exo*-6-tetramethyl-3-azabicyclo[3,3,1]nonan-7-on-3-oxyl

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Abstract. C₁₂H₂₁INO₂, $M = 350.32$. Orthorhombic, $P2_12_12_1$, $a = 16.16$ (2), $b = 14.46$ (2), $c = 6.20$ (1) Å, from precession photographs, refined by diffractometer. $Z = 4$, D_m (floatation) = 1.60 g cm⁻³, $D_c = 1.605$ g cm⁻³. The compound, whose structure could not be established spectroscopically, was crystallized from chloroform as thin red needles. The structure, refined to $R = 0.049$, shows the compound to be the 2-*exo* isomer in the chair-chair conformation. The nitroxide group shows a distortion from planarity of 17°.

Introduction. Systematic absences $h00$, h odd, $0k0$, k odd and $00l$, l odd gave the space group as $P2_12_12_1$. Data were collected for layers $h0l$ to $h5l$ and $hk0$ to $hk5$ with a Hilger-Watts linear diffractometer (Mo $K\alpha$ radiation). 1978 reflexions were collected of which 1474 had intensities greater than 3σ . The agreement between the two sets of data is shown in a merging R of 0.048 [$R = \sum|(F_1 - F_2)| / \frac{1}{2} \sum(F_1 + F_2)$]. Lorentz and polarization corrections were applied (but none for absorption) and

layer scales were obtained through common reflexions. The iodine atom was located from a sharpened Patterson function and the remaining non-hydrogen atoms from a Fourier synthesis. Refinement was by full-matrix least-squares calculations with our adaptation of the *PORFLS* program in the *CRYSTAL 69* system of Powell & Griffiths (1968). Scattering factors were taken from *International Tables for X-ray Crystallography* (1968). Five cycles of refinement of positional and isotropic thermal parameters gave $R = 0.100$ ($R = \sum|F_o| - |F_c| / \sum|F_o|$), and a further six cycles including anisotropic thermal parameters with the weighting scheme $w = 1$ if $F_o < 40$, $w = 1/[1 + (F_o - 40)^2/2500]$ otherwise, converged with $R = 0.049$.* No attempt was made

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30213 (10 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.