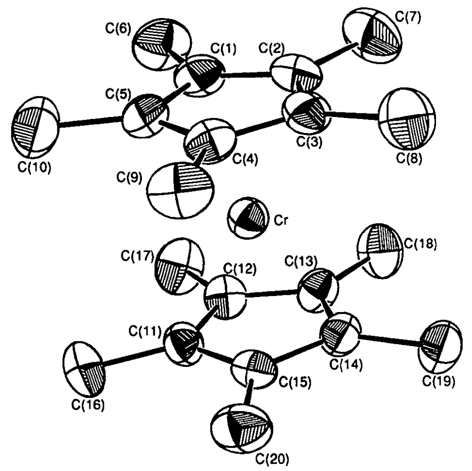

Fig. 1. *ORTEP* plot (Johnson, 1965) of $[Cr(C_5Me_5)_2]^+.I^-$. Thermal ellipsoids are drawn at the 50% probability level.

1·863 (5) Å]. The average metal—ring-centroid distance for this formally Cr^{3+} complex is slightly shorter than the distance found for $(C_5Me_5)_2Cr_2O_4$ [1·931 (6) Å] (Heberhold, Kremnitz, Razavi, Schollhorn & Thewalt, 1985) but slightly longer than that found for $(C_5Ph_4H)_2Cr$ [1·832 (5) Å] (Castellani, Geib, Rheingold & Trogler, 1987) which have formal oxidation states of +5 and +2 respectively. Metal—ring-C-atom averages are more consistent with values of 2·200 (4), 2·200 (6) and 2·197 (5) Å for complexes with oxidation states of +5, +3 and +2 respectively.

Financial support of this work was provided by the Natural Sciences and Engineering Research Council of Canada in the form of a grant to TSS. Access to the diffractometer was provided by K. A. Kerr.

References

Castellani, M. P., Geib, S. J., Rheingold, A. L. & Trogler, W. C. (1987). *Organometallics*, **6**, 1703–1712.

Cromer, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Fischer, E. O., Ulm, K. & Kuzel, P. (1963). *Z. Anorg. Allg. Chem.* **319**, 253–265.

Frenz, B. A. (1978). *The Enraf-Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.

Heberhold, M., Kremnitz, W., Razavi, A., Schollhorn, H. & Thewalt, U. (1985). *Angew. Chem. Int. Ed. Engl.* **24**, 601–602.

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

Köhler, F. H., de Cao, R., Ackermann, K. & Seldlmair, J. (1983). *Z. Naturforsch. Teil B*, **38**, 1406–1411.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1990). C**46**, 747–750

Structural Chirality of [Bis(desferrithiocin)]copper(II)

By Cäcilie Maichle, Wolfgang Hiller and Joachim Strähle

Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18, *D*-7400 *Tübingen, Federal Republic of Germany*

and Thomas Schechinger and Ulrich Weser

Anorganische Biochemie, Physiologisch-chemisches Institut der Universität Tübingen, Hoppe-Seyler-Strasse 4, *D*-7400 *Tübingen, Federal Republic of Germany*

(*Received* 20 *July* 1989; *accepted* 21 *August* 1989)

Abstract. [2-(3-Hydroxy-2-pyridyl)-4-methyl-4,5-dihydro-4-thiazolecarboxylato(2−)][2-(3-hydroxy-2-pyridyl)-4-methyl-4,5-dihydro-4-thiazolecarboxylic acid]-copper(II), $[Cu(C_{10}H_8N_2O_3S)(C_{10}H_{10}N_2O_3S)]$, M_r = 538·06, monoclinic, $P2_1$, a = 10·412 (1), b = 6·656 (4), c = 16·788 (1) Å, β = 98·59 (3)°, V = 1150·5 Å^3, Z = 2, D_x = 1·553 Mg m^{-3}, Cu $K\alpha$, λ = 1·54184 Å, μ = 3·3739 mm^{-1}, $F(000)$ = 550, T = 293 K. The final R value is 0·039 for 3465 significant [$I > 3\cdot\sigma(I)$] reflections. The Cu atom has a square-pyramidal coordination sphere and is bound to two O and two N atoms, each in a *trans* position, and to one N atom in an axial position. The last bond exhibits a pronounced elongation [2·340 (4) Å] due to Jahn–Teller distortion.

Introduction. Desferrithiocin ($dftH_2$) is known to be a naturally occurring chelator and was isolated as the

0108-2701/90/050747-04$03.00

Table 1. *Data-collection and structure-refinement parameters*

Crystal shape	Needles
Diffractometer used	CAD-4, Enraf–Nonius
Method of intensity measurement	ω/θ scan
No.; θ range (°) of reflections for lattice parameters	25; 18–28
Method used for absorption correction	*DIFABS* (Walker & Stuart, 1983)
Minimum absorption correction	0·5842
Maximum absorption correction	1·5790
Average absorption correction	1·0177
Maximum value of $(\sin\theta)/\lambda$ (Å^{-1}) reached in intensity measurement	0·588
Range of h, k and l	$0\rightarrow12$, $0\rightarrow7$, $-19\rightarrow19$
Standard reflections	206, 125, 026
Interval, standard reflections measured (h)	2, no intensity variation
Total No. of reflections measured; θ range (°)	4443; 65 (219 unobserved reflections)
No. of observed reflections	3465 with $I > 3\sigma(I)$ (Friedel opposites)
Methods used to solve structure	Patterson
Use of F or F^2 in LS refinement	F
Method of locating H atoms	From difference electron density map, positions included in structure-factor calculation
Weighting scheme	$1/\sigma_F^2$
Parameters refined	298
Value of R	0·039 (inverse model: 0·047)
Value of wR	0·045 (inverse model: 0·051)
Ratio of max. LS shift to e.s.d. (Δ/σ)	0·0007
Max. height in final ΔF map (e Å^{-3})	0·572
Error in an observation of unit weight	0·985
Secondary-extinction coefficient	3·62 (1) × 10^{-6} (Zachariasen, 1963)
Sources of atomic scattering factors	*International Tables for X-ray Crystallography* (1974)
Computer used	DEC MicroVAX 3500
Programs used	VAX*SDP* (B. A. Frenz & Associates Inc., 1986)

Table 2. *Atomic positional and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu	0·2895 (1)	0·8500	0·7547 (1)	0·034 (1)
dft^{2-}				
S1	0·4650 (2)	0·7902 (3)	0·5349 (1)	0·078 (1)
O7	0·1445 (3)	0·9761 (5)	0·6859 (2)	0·041 (2)
O51	0·6510 (4)	0·6224 (7)	0·7957 (2)	0·068 (3)
O52	0·4493 (3)	0·7080 (5)	0·8098 (2)	0·040 (2)
N1	0·3966 (4)	0·8816 (7)	0·6715 (2)	0·040 (3)
N2	0·2077 (5)	0·9348 (7)	0·4778 (3)	0·061 (4)
C1	0·3558 (5)	0·8777 (9)	0·5954 (3)	0·046 (3)
C2	0·5725 (7)	0·705 (1)	0·6239 (4)	0·080 (5)
C3	0·5339 (4)	0·8264 (9)	0·6937 (3)	0·047 (3)
C4	0·6143 (6)	1·021 (1)	0·7089 (5)	0·082 (5)
C5	0·5457 (5)	0·7069 (8)	0·7728 (3)	0·042 (3)
C6	0·2249 (5)	0·9329 (8)	0·5607 (3)	0·045 (3)
C7	0·1268 (5)	0·9723 (7)	0·6055 (3)	0·041 (3)
C8	0·0024 (6)	1·0090 (9)	0·5630 (3)	0·054 (3)
C9	−0·0157 (7)	1·0072 (9)	0·4802 (4)	0·063 (4)
C10	0·0871 (7)	0·9765 (9)	0·4407 (3)	0·065 (5)
dftH$_2$				
S21	0·1161 (1)	0·6862 (2)	0·9750 (1)	0·048 (1)
O27	0·2597 (3)	0·9903 (6)	1·0648 (2)	0·051 (2)
O251	0·0577 (3)	0·2684 (5)	0·7615 (2)	0·046 (2)
O252	0·1949 (3)	0·4766 (6)	0·7132 (2)	0·048 (2)
N21	0·1806 (3)	0·7466 (5)	0·8336 (2)	0·028 (2)
N22	0·3188 (4)	1·0799 (6)	0·8614 (2)	0·037 (2)
C21	0·1971 (4)	0·8121 (6)	0·9068 (2)	0·031 (3)
C22	0·0659 (5)	0·4950 (8)	0·8995 (3)	0·041 (3)
C23	0·0800 (4)	0·5903 (7)	0·8186 (3)	0·032 (2)
C24	−0·0465 (5)	0·6934 (9)	0·7806 (3)	0·048 (3)
C25	0·1194 (4)	0·4402 (7)	0·7583 (3)	0·034 (2)
C26	0·2759 (4)	0·9958 (7)	0·9258 (3)	0·033 (2)
C27	0·3000 (4)	1·0843 (8)	1·0028 (3)	0·039 (3)
C28	0·3645 (5)	1·2680 (8)	1·0098 (3)	0·044 (3)
C29	0·4046 (4)	1·352 (1)	0·9433 (3)	0·047 (3)
C210	0·3825 (5)	1·2546 (8)	0·8695 (3)	0·045 (3)

iron complex from *Streptomyces antibioticus* (Peter, 1985). Likewise its copper complexes are of remarkable thermodynamical stability and are able to compete successfully with biological chelators including serum albumin. An interesting phenomenon of the Cu complexes is their Cu_2Zn_2 superoxide dismutase mimetic activity (Schechinger, 1988).

Experimental. A green single crystal of approximate dimensions 0·10 × 0·15 × 0·15 mm was mounted on a glass fiber. The systematic absences indicated space group $P2_1/m$ or $P2_1$, of which the non-centrosymmetric space group was confirmed by further calculations. In the final full-matrix least-squares refinement, all non-H atoms were assigned anisotropic atomic displacement parameters. The structure was successfully distinguished from its inverse by least-squares refinement of both alternative models. The R value of the incorrect model converged to 0·047, whereas the correct model led to R = 0·039 in the final refinement. Furthermore, all starting values of the parameter η refine to +1 also indicating the correct choice (Rogers, 1981; Jones, 1984). A summary of data-collection and structure-refinement parameters is given in Table 1. Final atomic coordinates are listed in Table 2, distances and angles in Table 3 and intermolecular hydrogen bonds in Table 4.* A graphic representation (Keller, 1988) of the molecule is shown in Fig. 1, a stereoview of the unit cell in Fig. 2.

Discussion. The Cu atom in the title compound Cu(dft^{2-})(dftH$_2$) has a similar coordination sphere to that of the previously reported compound Cu(dft^{2-})(H_2O)$_2$ (Schechinger, Hiller, Maichle, Strähle & Weser, 1988). In both compounds one dft^{2-} group is bound to the Cu atom *via* the nitrogen (N1) of the dihydrothiazole, and, in *trans* positions, one oxygen (O52) of the carboxyl group and the oxygen (O7) of the phenolic hydroxyl group. Instead of the two water molecules in Cu(dft^{2-})(H_2O)$_2$ these positions are now occupied by a dftH$_2$ molecule coordinating *via* the two N atoms N21 and N22. The Cu atom is situated 0·154 (1) Å above the plane O7,O52,N1,N21. Owing to Jahn–Teller distortion the bond distance to the axially bound N atom

---

* Lists of structure factors, H-atom positions, least-squares-planes details, and anisotropic atomic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52515 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Distances* (Å) *and angles* (°) *with e.s.d.'s*

Cu	O7	1·948 (3)		Cu	N21	1·990 (4)	
Cu	O52	2·015 (4)		Cu	N22	2·340 (4)	
Cu	N1	1·925 (4)		Cu	O252	2·727 (4)	
S1	C1	1·735 (5)		S21	C21	1·736 (5)	
S1	C2	1·819 (7)		S21	C22	1·817 (6)	
O7	C7	1·334 (6)		O27	C27	1·335 (6)	
O51	C5	1·240 (6)		O251	C25	1·317 (6)	
O52	C5	1·256 (7)		O252	C25	1·195 (7)	
N1	C1	1·284 (5)		N21	C21	1·291 (5)	
N1	C3	1·470 (6)		N21	C23	1·471 (6)	
N2	C6	1·376 (6)		N22	C26	1·350 (6)	
N2	C10	1·344 (8)		N22	C210	1·336 (7)	
C1	C6	1·447 (7)		C21	C26	1·480 (6)	
C2	C3	1·526 (8)		C22	C23	1·526 (7)	
C3	C4	1·545 (9)		C23	C24	1·537 (7)	
C3	C5	1·537 (7)		C23	C25	1·521 (7)	
C6	C7	1·382 (8)		C26	C27	1·409 (7)	
C7	C8	1·405 (8)		C27	C28	1·391 (7)	
C8	C9	1·376 (8)		C28	C29	1·368 (8)	
C9	C10	1·36 (2)		C29	C210	1·388 (8)	
O7	Cu	O52	171·1 (1)	O52	Cu	N21	92·6 (1)
O7	Cu	N1	90·2 (1)	O52	Cu	N22	87·3 (1)
O7	Cu	N21	94·3 (1)	N1	Cu	N21	165·9 (2)
O7	Cu	N22	100·0 (1)	N1	Cu	N22	117·5 (2)
O52	Cu	N1	81·8 (1)	N21	Cu	N22	75·0 (1)
C1	S1	C2	90·0 (3)	C21	S21	C22	89·8 (2)
Cu	O7	C7	124·7 (3)	Cu	O252	C25	105·6 (3)
Cu	O52	C5	116·3 (3)				
Cu	N1	C1	125·3 (3)	Cu	N21	C21	120·5 (3)
Cu	N1	C3	115·9 (3)	Cu	N21	C23	126·4 (3)
C1	N1	C3	114·4 (5)	C21	N21	C23	113·1 (4)
C6	N2	C10	116·2 (5)	C26	N22	C210	119·9 (4)
				Cu	N22	C26	108·7 (3)
				Cu	N22	C210	130·8 (3)
S1	C1	N1	116·1 (4)	S21	C21	N21	117·1 (3)
S1	C1	C6	120·6 (3)	S21	C21	C26	124·4 (3)
N1	C1	C6	123·3 (5)	N21	C21	C26	118·3 (4)
S1	C2	C3	105·5 (4)	S21	C22	C23	105·9 (3)
N1	C3	C2	107·2 (4)	N21	C23	C22	107·6 (3)
N1	C3	C4	108·4 (5)	N21	C23	C24	107·4 (4)
N1	C3	C5	107·4 (4)	N21	C23	C25	108·8 (4)
C2	C3	C4	111·9 (6)	C22	C23	C24	111·4 (5)
C2	C3	C5	113·2 (5)	C22	C23	C25	112·9 (4)
C4	C3	C5	108·7 (4)	C24	C23	C25	108·5 (4)
O51	C5	O52	125·7 (5)	O251	C25	O252	124·9 (4)
O51	C5	C3	117·1 (4)	O251	C25	C23	111·2 (4)
O52	C5	C3	117·2 (5)	O252	C25	C23	123·9 (4)
N2	C6	C1	112·5 (5)	N22	C26	C21	114·1 (4)
N2	C6	C7	123·7 (5)	N22	C26	C27	121·7 (4)
C1	C6	C7	123·8 (4)	C21	C26	C27	124·1 (4)
O7	C7	C6	123·6 (4)	O27	C27	C26	119·1 (4)
O7	C7	C8	119·3 (5)	O27	C27	C28	123·4 (4)
C6	C7	C8	117·1 (5)	C26	C27	C28	117·6 (5)
C7	C8	C9	119·3 (6)	C27	C28	C29	119·6 (5)
C8	C9	C10	119·8 (6)	C28	C29	C210	120·4 (5)
N2	C10	C9	123·8 (5)	N22	C210	C29	120·9 (6)

Table 4. *Intermolecular hydrogen bonds* O—H···O

Symmetry operators: (i) $1 - x$, $0·5 + y$, $2 - z$; (ii) x, $y - 1$, z.

H27—O27	1·11 (1) Å	O27—H27···O51^{i}	171 (1)°
H27···O51^{i}	1·44 (1)		
H251—O251	0·92 (1) Å	O251—H251···O7^{ii}	172 (1)°
H251···O7^{ii}	1·64 (1)		

[2·340 (4) Å] is significantly longer than the sum of the covalent radii. A weak electrostatic interaction is observed between Cu and O252. The distance Cu···O252 [2·727 (4) Å] is 0·65 Å shorter compared with the sum of the van der Waals radii but significantly longer than the sum of the covalent radii (Pauling, 1968).

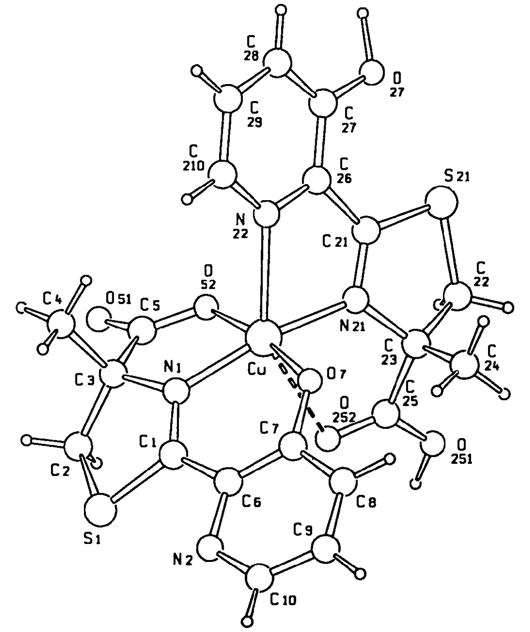

Fig. 1. Plot of the molecule and numbering scheme.

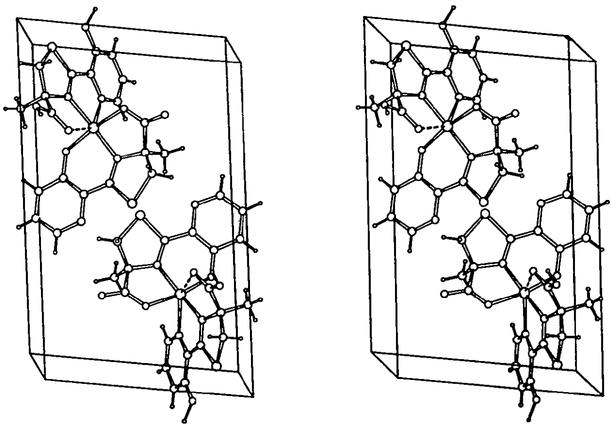

Fig. 2. Stereoview of the unit cell; projection parallel to **b**.

We thank the DFG for financial support (We 401/21-1). Desferrithiocin was kindly donated by Ciba-Geigy, Basel, Switzerland.

References

B. A. Frenz & Associates Inc. (1986). VAX*SDP. Structure Determination Package*, version 3.0. College Station, Texas, USA, and Enraf-Nonius, Delft, The Netherlands.

International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.2A. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Jones, P. G. (1984). *Acta Cryst.* **A40**, 660–662.

Keller, E. (1988). *SCHAKAL*. Univ. of Freiburg, Federal Republic of Germany.

PAULING, L. (1968). In *Die Natur der chemischen Bindung*. Weinheim: Verlag Chemie.

PETER, H. (1985). *Industrial Aspects of Iron Chelators: Pharmaceutical Applications*, edited by G. SPIK, J. MONTREUIL, R. R. CRICHTON & J. MAZURIER, pp. 293–303. Amsterdam: Elsevier.

ROGERS, D. (1981). *Acta Cryst.* A37, 734–741.

SCHECHINGER, T. (1988). Thesis, Univ. of Tübingen, Federal Republic of Germany.

SCHECHINGER, T., HILLER, W., MAICHLE, C., STRÄHLE, J. & WESER, U. (1988). *Biol. Met.* **1**, 112–116.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* A39, 158–166.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1990). C46, 750–753

Structures of Polymeric Zinc 3,3-Dimethylacrylate and Zinc 2-Chlorobenzoate

BY WILLIAM CLEGG, DALE R. HARBRON, PAUL A. HUNT, IAN R. LITTLE AND BRIAN P. STRAUGHAN

*Department of Chemistry, The University, Newcastle upon Tyne NE*1 *7RU, England*

(*Received* 28 *June* 1989; *accepted* 1 *September* 1989)

Abstract. (1): *catena*-Poly[zinc-tris-μ-(3,3-dimethylacrylato-O,O')-zinc-μ-(3,3-dimethylacrylato-O,O')] [$Zn_2\{\mu\text{-}O_2CCH{:}C(CH_3)_2\}_3\{O_2CCH{:}C(CH_3)_2\}$], M_r = 527·2, orthorhombic, *Pbcn*, a = 19·881 (2), b = 14·488 (2), c = 17·049 (2) Å, V = 4910·7 Å^3, Z = 8, D_x = 1·426 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 2·04 mm^{-1}, F(000) = 2176, T = 295 K, R = 0·0554 for 2272 unique observed reflections. (2): *catena*-Poly[zinc-tris-μ-(2-chlorobenzoato-O,O')-zinc-μ-(2-chlorobenzoato-O,O')] [$Zn_2(\mu\text{-}O_2CC_6H_4Cl)_3(O_2CC_6H_4Cl)$], M_r = 753·0, monoclinic, $P2_1/n$, a = 11·219 (1), b = 13·536 (1), c = 19·790 (2) Å, β = 103·827 (9)°, V = 2918·2 Å^3, Z = 4, D_x = 1·714 Mg m^{-3}, λ(Cu $K\alpha$) = 1·54184 Å, μ = 5·94 mm^{-1}, F(000) = 1504, T = 295 K, R = 0·0447 for 3996 unique observed reflections. Both structures contain polymeric chains in which binuclear Zn_2(carboxylate)$_3^+$ units with three *syn–syn* bridging ligands are connected by single *syn–anti* carboxylate links.

Introduction. Anhydrous zinc carboxylates adopt a variety of structures. Features common to all so far reported are a tetrahedral coordination of Zn atoms and a bridging function for the carboxylate ligands. The acetate and propionate are both known in two different forms, with exclusively *syn–anti* carboxylate bridges which link the Zn atoms into either two-dimensional sheets or a three-dimensional cross-linked network (Capilla & Aranda, 1979; Clegg, Little & Straughan, 1986*b*; Goldschmied, Rae & Stephenson, 1977; Clegg, Little & Straughan, 1987). The benzoate (Guseinov, Musaev, Usubaliev, Amiraslanov & Mamedov, 1984) and crotonate (Clegg, Little & Straughan, 1986*a*) form polymeric chains in which Zn_2(carboxylate)$_3^+$ binuclear units with three *syn–syn* bridges are connected by single *syn–anti* carboxylates. Only *syn–syn* bridges occur in the structure of the 2-chlorobenzoate reported by Nakacho, Misawa, Fujiwara, Wakahara & Tomita (1976), pairs of carboxylates linking the Zn atoms into chains.

As part of a continuing study of zinc carboxylate structures, in an attempt to understand the factors influencing the choice of structure adopted for a particular carboxylate, and to investigate polymorphism in these compounds, we have determined the structure of zinc 3,3-dimethylacrylate and a second form of zinc 2-chlorobenzoate, which are reported here.

Experimental. The compounds were synthesized by refluxing freshly prepared zinc hydroxide with the corresponding carboxylic acids in water and recrystallized from ethanol (1) or acetone (2). Information for (2) is given in square brackets where it differs from that for (1). Crystal size 0·37 × 0·37 × 0·42 mm [0·08 × 0·20 × 0·40 mm], Stoe–Siemens diffractometer, unit-cell parameters from 2θ values of 32 reflections (20–25°) [(20–40°)] measured at $\pm\,\omega$. Data collection in ω–θ scan mode, scan width 0·765° [0·68°] below α_1 to 0·765° [0·68°] above α_2, scan time 14–56 s, $2\theta_{\max}$ 50° [130°], index ranges h 0→23, k 0→17, l 0→20 [h −13→13, k 0→15, l −23→23], correction for small decay in intensities of three standard reflections, semi-empirical absorption corrections, transmission 0·303–0·352 [0·168–0·327], 4320 [9807] reflections measured, 4320 [4943] unique, 2272 [3996] with $F > 4\sigma(F)$, [$R_{\rm int}$ = 0·0428].

Structure solution by Patterson and difference syntheses, blocked-cascade least-squares refinement on F, weighting $w^{-1} = \sigma^2(F)$, anisotropic thermal parameters for all non-H atoms, H atoms constrained (C—H 0·96 Å, H—C—H 109·5°), aromatic and olefinic H atoms on angle external bisectors, U(H) = 1·2$U_{\rm eq}$(C), extinction parameter x = 1·0 (2) × 10^{-7} [1·7 (1) × 10^{-6}], whereby $F_c' = F_c/(1 + xF_c^2/\sin2\theta)^{1/4}$. [Twofold disorder of orientation for one 2-chlorobenzoate ligand; occupancy factors refined

0108-2701/90/050750-04$03.00