

with a short H(9a)⋯H(17b) distance of ~2.7 Å. As a result, the dihedral angles between the xylenyl groups and Pd coordination plane are 20.9 (1) and 46.6 (1)°. The dihedral angle between the two xylenyl ligands is 43.8 (2)°. There are other examples in which relatively close intramolecular contacts between methyl groups of two adjacent xylenyl ligands are observed. For instance, methyl–methyl separations of 3.89 and 3.532 Å, and dihedral angles of 35.85, and 9.52 and 16.04° have been reported for *trans*-FeCl₂·[2,6-(CH₃)₂-C₆H₃NC]₄ (Drew, Dodd, Williamson & Willy, 1986) and Re₂(CO)₆[2,6-(CH₃)₂-C₆H₃NC]₄ (Harris, Boeyens & Coville, 1985), respectively.

Other minor effects are also noticed; the Pd—C(1)—N(1) and Pd—C(10)—N(2) angles are bent outward from each other by 4.3 (7) and 4.2 (7)°, respectively, and the C(10) and C(1) atoms lie at -0.119 (8) and +0.174 (8) Å from the Pd coordination plane.

The crystal packing attracts significant interest (Fig. 2). Obvious quasi-one-dimensional (1D) packing is observed; (1) crystallizes in a 1D fashion *via* an alternating pattern *ABABAB*... (Fig. 2) where the *AB* unit possesses the *C_i* local point group. The two Pd⋯Pd intermolecular separations are 4.186 (2) and 4.061 (2) Å and the Pd⋯Pd⋯Pd angle is 170.17 (2)°. The Pd⋯Pd distances are larger than the van der Waals radii (3.20 Å; Cotton, Wilkinson & Gauss, 1987) and *M*⋯*M* distances found for other related 1D Pd and Pt complexes, which typically range from 2.8–3.5 Å (Miller, 1982). Occasionally, greater values for Pt⋯Pt distances are found: 3.60 Å for Sr[Pt(CN)₄]₂·5H₂O (Krogmann & Stephan, 1968); ~3.71 Å for Na₂[Pt(CN)₄]₂·3H₂O (Johnson, Koch & Williams, 1977); 3.554 and 3.855 Å for [Cu(en)₂][Pt(C₂O₄)₂] (en = H₂NCH₂CH₂NH₂) (Krogmann, 1968). (1) appears to be the first example of

an organometallic Pd compound which exhibits a 1D structure in the solid state. However, the long Pd⋯Pd excludes the possibility of any strong Pd⋯Pd interactions. Indeed, the solid state and solution UV–visible spectra of (1) are almost identical in the aromatic region (220–300 nm), and exhibit only a small shift of the low-energy band going from 310 (shoulder) to ~320 nm in the solid state. We come to the conclusion that only crystal packing forces are responsible for the 1D structure of (1).

This research was supported by grants from the NSERC (Canada), the FCAR (Québec), and the Bureau de la recherche (Université de Sherbrooke).

References

- COTTON, F. A., WILKINSON, G. & GAUSS, P. L. (1987). Editors. *Basic Inorganic Chemistry*, second edition, p. 60. Toronto: John Wiley.
- DREW, M. G. B., DODD, G. H., WILLIAMSON, G. R. & WILLY, G. R. (1986). *J. Organomet. Chem.* **314**, 163–172.
- GABE, E. J., LEE, F. L. & LE PAGE, Y. (1985). *The NRCVAX Crystal Structure System*. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and Databases*, edited by G. M. SHELDRIK, C. KRÜGER & R. GODDARD, pp. 167–174. Oxford: Clarendon Press.
- HARRIS, G. W., BOEYENS, J. C. A. & COVILLE, N. J. (1985). *Organometallics*, **4**, 914–918.
- JOHNSON, P. L., KOCH, T. R. & WILLIAMS, J. M. (1977). *Acta Cryst.* **B33**, 1976–1979.
- KITANO, Y. & HORI, T. (1981). *Acta Cryst.* **B37**, 1919–1921.
- KROGMANN, K. (1968). *Z. Naturforsch. Teil B*, **23**, 1012–1012.
- KROGMANN, K. & STEPHAN, D. (1968). *Z. Anorg. Chem.* **362**, 290–300.
- MILLER, J. S. (1982). Editor. *Extended Linear Chain Compounds*, Vol. 1, p. 491. New York: Plenum.
- MONDAL, T. K., BANERJEE, T. K. & SEN, D. (1980). *Indian J. Chem.* **19A**, 846–848.
- YAMAMOTO, Y. & YAMAZAKI, H. (1985). *Bull. Chem. Soc. Jpn*, **58**, 1843–1844.

Acta Cryst. (1991). **C47**, 754–757

Structure of 1% Copper(II)-Doped Dichlorobis(1,2-dimethylimidazole)zinc(II)

BY PARIMAL K. BHARADWAJ, HARVEY J. SCHUGAR AND JOSEPH A. POTENZA

Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903, USA

(Received 16 April 1990; accepted 22 October 1990)

Abstract. [Zn_{0.99}Cu_{0.01}Cl₂(C₅H₈N₂)₂], *M_r* = 328.43, monoclinic, *P*2₁/*c*, *a* = 13.587 (1), *b* = 7.1324 (7), *c* = 16.356 (2) Å, β = 112.87 (1)°, *V* = 1460.4 (5) Å³, *Z* = 4, *D_m* = 1.50 (1), *D_x* = 1.492 g cm⁻³, μ(Mo Kα, λ = 0.71073 Å) = 20.8 cm⁻¹, *F*(000) = 672.0, *T* =

297 (1) K, *R* = 0.028 for 1782 unique observed reflections. The structure contains discrete dichlorobis(1,2-dimethylimidazole)zinc(II) molecules. Pseudotetrahedral N₂Cl₂ coordination about zinc is effected by coordination to two imidazole and two

chloride ligands. The Zn—N [2.006 (3), 2.008 (3) Å] and Zn—Cl [2.2509 (8), 2.2468 (8) Å] distances lie within ± 0.01 Å of those in the structurally similar compound [ZnCl₂(imidazole)₂]. Angles within the coordination sphere L —Zn— L' range from 105.39 (7) to 115.37 (8)°. The N—Zn—N angle [115.37 (8)°] is 5–10° larger than those for several [ZnL₂Cl₂] complexes where L is imidazole, 4-substituted pyridine or 3,5-dimethylpyrazole.

Introduction. For some time we have been interested in low-molecular-weight copper-containing complexes with biologically relevant ligation such as imidazole (Knapp, Keenan, Zhang, Fikar, Potenza & Schugar, 1990) and thiolate (John, Bharadwaj, Potenza & Schugar, 1986). Complexes of this type serve as structural and spectroscopic models for the active sites of native and metal-substituted copper metalloproteins, many of which show copper in unusual coordination geometries. In the blue copper proteins plastocyanin (Guss & Freeman, 1983) and azurin (Norris, Anderson & Baker, 1986), for example, the Cu^{II} sites exhibit elongated C_{3v} geometry while, for Cu^{II} doped into the native Zn^{II} site of superoxide dismutase, a distorted tetrahedral geometry had been inferred for Cu^{II} (Pantoliano, Valentine & Nafie, 1982). The doped title compound was studied because it mimics the unusual rhombically distorted EPR spectrum of stellacyanin (Gewirth, Cohen, Schugar & Solomon, 1987) and because it provides a magnetically dilute approximately tetrahedral host environment for Cu^{II} with which to probe the magnetic parameters of the remotely coupled (*i.e.* non-ligating) N atoms of imidazoles. The results of a single-crystal electron spin echo envelope modulation (ESEEM) study of this system have been presented elsewhere (Colaneri, Potenza, Schugar & Peisach, 1990). We report here the crystal structure of the title compound.

Experimental. Preparation of Cu^{II}-doped dichlorobis(1,2-dimethylimidazole)zinc(II) followed the procedure of Goodgame, Goodgame & Rayner Canham (1971). A green solution of 1.33 g (9.76 mmol) ZnCl₂, 0.03 g (0.18 mmol) CuCl₂·2H₂O and 1.92 g (20.0 mmol) of ligand in 200 ml of warm (323 K) acetone was filtered warm and partially evaporated in air. Well formed rectangular plates deposited and exhibited colorless/yellow–orange dichroism when viewed in polarized light. Atomic absorption spectroscopy revealed a Zn/Cu mole ratio of 0.991/0.009, indicating doping at about half the nominal level.

Structure solution: D_m by flotation; yellow plate 0.20 × 0.30 × 0.33 mm; Enraf–Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$ radiation; θ – 2θ scan. Systematic absences: $h0l$, l odd; $0k0$, k odd. Cell constants from setting angles of 25

reflections with $9.52 < \theta < 24.72^\circ$; data corrected for Lorentz, polarization and absorption (empirical correction, ψ scan; transmission coefficient range 0.86 to 1.00) effects. Variation in intensity of three standard reflections $\pm 0.1\%$; 2569 unique reflections measured with $2 < 2\theta < 50^\circ$; 1782 with $I > 3\sigma(I)$ used in refinement. Data collected: h , 0–16; k , 0–8; l , –19–19. Structure solved by direct methods (MULTAN11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and difference Fourier techniques; H atoms from difference maps and calculated positions; B_H set to $1.3 B_N$ before final refinement cycles; H-atom coordinates refined. Full-matrix refinement of F ; all non-H atoms anisotropic; $w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$. Final $R = 0.028$, $wR = 0.038$, $S = 1.34$, $(\Delta/\sigma) < 0.34$; $\Delta\rho_{\max} = 0.26$, $\Delta\rho_{\min} = -0.36$ e Å⁻³. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV); because of the low level of doping only the Zn scattering factor was used for the metal site and this was assumed to be completely occupied. Programs from Enraf–Nonius (1985) SDP.

Discussion. Final positional parameters and their e.s.d.'s are given in Table 1.* A view of the title compound, showing the atom-numbering scheme, is given in Fig. 1. Selected bond distances and angles are listed in Table 2.

The structure consists of discrete Zn_{0.99}Cu_{0.01}·[N₂C₃H₂(CH₃)₂]Cl₂ molecules; the shortest intermolecular contacts [N(2)···C(3'), 3.456 (3); C(2)···C(2'), 3.488 (6); C(5)···C(6''), 3.484 (4) Å] are between centrosymmetrically related imidazole groups. Hydrogen bonding from the amine nitrogen to the chloride of an adjacent molecule, as reported for [Zn(imidazole)₂Cl₂] (Lundberg, 1966), is precluded in the present structure by methylation at N(2) and N(4).

Each Zn ion is coordinated in a tetrahedral fashion by two chlorides and by the amine N atoms of two 1,2-dimethylimidazole groups. Pseudo twofold axes parallel to c^* bisect the N—Zn—N and Cl—Zn—Cl angles of each molecule. Both the Zn—N and Zn—Cl distances are equivalent within ± 0.01 Å to those reported for [Zn(imidazole)₂Cl₂] [Zn—Cl, 2.258 (3), 2.239 (3) Å; Zn—N, 1.995 (11), 2.020 (11) Å (Lundberg, 1966)]. However, the N—Zn—N angle [115.37 (8)°] is about 10° larger than that reported [105.2 (5)°] for the imidazole complex and 5–10° larger than those in a variety of

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53667 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters

$$B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

	x	y	z	B _{eq} (Å ²)
Zn	0.24597 (2)	0.25201 (5)	0.49800 (2)	3.149 (7)
Cl(1)	0.20825 (6)	0.0421 (1)	0.58445 (5)	5.08 (2)
Cl(2)	0.36178 (6)	0.4768 (1)	0.57284 (5)	4.60 (2)
N(1)	0.3133 (2)	0.1034 (3)	0.4293 (1)	2.93 (5)
N(2)	0.4228 (2)	0.0386 (3)	0.3642 (1)	3.37 (5)
N(3)	0.1108 (2)	0.3869 (3)	0.4245 (1)	3.20 (5)
N(4)	-0.0600 (2)	0.4368 (4)	0.3540 (1)	3.71 (6)
C(1)	0.3614 (2)	0.1720 (4)	0.3787 (2)	3.01 (6)
C(2)	0.4135 (2)	-0.1209 (4)	0.4072 (2)	3.87 (7)
C(3)	0.3465 (2)	-0.0816 (4)	0.4467 (2)	3.53 (7)
C(4)	0.0186 (2)	0.3103 (4)	0.3728 (2)	3.22 (6)
C(5)	-0.0171 (2)	0.6007 (5)	0.3942 (2)	4.45 (8)
C(6)	0.0885 (2)	0.5720 (4)	0.4372 (2)	4.00 (7)
C(7)	0.3491 (2)	0.3637 (5)	0.3419 (2)	4.79 (8)
C(8)	0.4906 (2)	0.0626 (6)	0.3132 (2)	5.59 (9)
C(9)	0.0029 (2)	0.1155 (5)	0.3404 (2)	5.04 (9)
C(10)	-0.1741 (2)	0.4025 (6)	0.3015 (2)	5.9 (1)

Table 2. Selected bond lengths (Å) and angles (°)

Zn—Cl(1)	2.2509 (8)	N(3)—C(4)	1.326 (3)
Zn—Cl(2)	2.2468 (8)	N(3)—C(6)	1.389 (4)
Zn—N(1)	2.006 (3)	N(4)—C(4)	1.339 (3)
Zn—N(3)	2.008 (3)	N(4)—C(5)	1.357 (4)
N(1)—C(1)	1.331 (3)	N(4)—C(10)	1.472 (5)
N(1)—C(3)	1.389 (3)	C(1)—C(7)	1.477 (4)
N(2)—C(1)	1.345 (3)	C(2)—C(3)	1.335 (5)
N(2)—C(2)	1.369 (4)	C(4)—C(9)	1.473 (5)
N(2)—C(8)	1.474 (4)	C(5)—C(6)	1.345 (5)
Cl(1)—Zn—Cl(2)	114.50 (3)	C(4)—N(3)—C(6)	106.3 (2)
Cl(1)—Zn—N(1)	105.39 (7)	C(4)—N(4)—C(5)	108.4 (2)
Cl(1)—Zn—N(3)	108.44 (7)	C(4)—N(4)—C(10)	125.9 (4)
Cl(2)—Zn—N(1)	107.87 (6)	C(5)—N(4)—C(10)	125.6 (3)
Cl(2)—Zn—N(3)	105.58 (7)	N(1)—C(1)—N(2)	109.7 (2)
N(1)—Zn—N(3)	115.37 (8)	N(1)—C(1)—C(7)	126.0 (3)
Zn—N(1)—C(1)	126.6 (2)	N(2)—C(1)—C(7)	124.2 (3)
Zn—N(1)—C(3)	124.7 (2)	N(2)—C(2)—C(3)	106.9 (3)
C(1)—N(1)—C(3)	106.2 (2)	N(1)—C(3)—C(2)	109.1 (3)
C(1)—N(2)—C(2)	108.0 (2)	N(3)—C(4)—N(4)	109.9 (3)
C(1)—N(2)—C(8)	125.8 (3)	N(3)—C(4)—C(9)	125.9 (3)
C(2)—N(2)—C(8)	126.2 (3)	N(4)—C(4)—C(9)	124.2 (3)
Zn—N(3)—C(4)	127.0 (2)	N(4)—C(5)—C(6)	107.0 (3)
Zn—N(3)—C(6)	124.6 (2)	N(3)—C(6)—C(5)	108.5 (3)

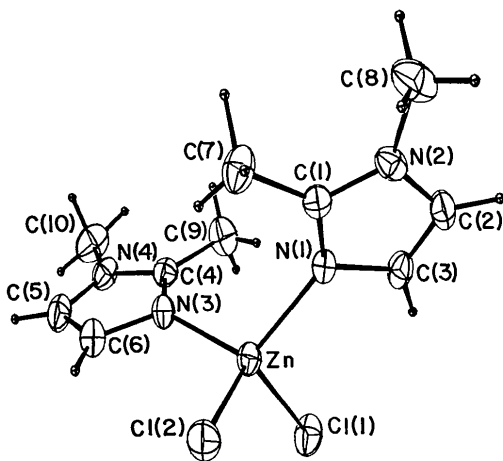


Fig. 1. View of the dichlorobis(1,2-dimethylimidazole)zinc(II) molecule showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% level; thermal parameters for H atoms are shown arbitrarily small for clarity.

[ZnL₂Cl₂] systems [100.6 (2) to 109.0 (4)°] where L is pyridine (Steffen & Palenik, 1976), 4-substituted pyridine (Steffen & Palenik, 1977; Lynton & Sears, 1971) or 3,5-dimethylpyrazole (Bouwman, Driessen, de Graaff & Reedijk, 1984). For the pyridine complexes the Zn—N distances are significantly longer [2.040 (5)–2.069 (6) Å] than those in the imidazole complexes while the Zn—Cl distances are significantly shorter [2.204 (2)–2.228 (2) Å]. This effect is analogous to the *trans* effect for square-planar complexes and has been noted previously (Steffen & Palenik, 1977).

The neat [Cu(*N*-methylimidazole)₂Cl₂] compound has a tetrahedrally distorted *trans* planar N₂Cl₂ coordination sphere with *cis* bond angles ranging from 94.0 (1) to 95.4 (1)° and *trans* angles of

143.57 (6) and 149.7 (1)° (van Ooijen, Reedijk & Spek, 1979). It exhibits a *g*_{||} EPR absorption at 2.28 and is green owing to its highest energy *d*–*d* absorption [12 200 cm⁻¹ (Goodgame, Goodgame & Rayner Canham, 1969)]. The lower energy *d*–*d* absorptions (11 100 and 8700 cm⁻¹) and larger *g*_{||} absorption (2.34) of the neat [Cu(1,2-dimethylimidazole)₂Cl₂] complex suggest increased tetrahedral distortion relative to the complex with *N*-methylimidazole (Goodgame, Goodgame & Rayner Canham, 1971). Polarized single-crystal spectra at 77 K reveal further red shifts of the *d*–*d* absorptions to 10 250, 6920 and 6640 cm⁻¹, and unusual rhombically distorted EPR spectra qualitatively similar to those reported for the blue copper protein stellacyanin (Gewirth *et al.*, 1987). These observations are consistent with additional tetrahedral distortion in the Cu^{II}-doped title complex. Since the doped crystals survive temperature cycling over the 77–298 K range, a first-order phase transition of the Zn^{II} host lattice appears unlikely. The yellow–orange color of the title compound originates from tailing of intense Cl⁻→Cu^{II} charge-transfer bands into the visible region and not from *d*–*d* transitions.

We thank the National Science Foundation for support of research (Grant CHE 8919120) and the National Institutes of Health for an instrumentation grant (Grant 1510 RRO 1486 O1A1).

References

- BOUWMAN, E., DRIESSEN, W. L., DE GRAAFF, R. A. G. & REEDIJK, J. (1984). *Acta Cryst.* C40, 1562–1563.
COLANERI, M. J., POTENZA, J. A., SCHUGAR, H. J. & PEISACH, J. (1990). *J. Am. Chem. Soc.* 112, 9451–9458.

- Enraf-Nonius (1985). *Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
- GEWIRTH, A. A., COHEN, S. L., SCHUGAR, H. J. & SOLOMON, E. I. (1987). *Inorg. Chem.* **26**, 1133–1146.
- GOODGAME, D. M. L., GOODGAME, M. & RAYNER CANHAM, G. W. (1969). *Inorg. Chim. Acta*, **3**, 406–410.
- GOODGAME, D. M. L., GOODGAME, M. & RAYNER CANHAM G. W. (1971). *J. Chem. Soc. (A)*, pp. 1923–1927.
- GUSS, J. M. & FREEMAN, H. C. (1983). *J. Mol. Biol.* **169**, 521–563.
- JOHN, E., BHARADWAJ, P. K., POTENZA, J. A. & SCHUGAR, H. J. (1986). *Inorg. Chem.* **25**, 3065–3069.
- KNAPP, S., KEENAN, T. P., ZHANG, X., FIKAR, R., POTENZA, J. A. & SCHUGAR, H. J. (1990). *J. Am. Chem. Soc.* **112**, 3452–3464.
- LUNDBERG, B. K. S. (1966). *Acta Cryst.* **21**, 901–909.
- LYNTON, H. & SEARS, M. C. (1971). *Can. J. Chem.* **49**, 3418–3424.
- MAIN, P., FISKE, S., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- NORRIS, G. E., ANDERSON, B. F. & BAKER, E. N. (1986). *J. Am. Chem. Soc.* **108**, 2784–2785.
- OOJEN, J. A. C. VAN, REEDIJK, J. & SPEK, A. L. (1979). *J. Chem. Soc. Dalton Trans.* pp. 1183–1186.
- PANTOLIANO, M. W., VALENTINE, J. S. & NAFIE, L. A. (1982). *J. Am. Chem. Soc.* **104**, 6310–6317.
- STEFFEN, W. L. & PALENIK, G. J. (1976). *Acta Cryst.* **B32**, 298–300.
- STEFFEN, W. L. & PALENIK, G. J. (1977). *Inorg. Chem.* **16**, 1119–1127.

Acta Cryst. (1991). **C47**, 757–759

Structure and Absolute Configuration of (23*R*)-6 α -Chloro-5 β ,17 β -dihydroxy-12 β -methoxy-1-oxo-12,22-epoxyergosta-2,24-dien-23,26-olide, a New Withanolide from *Jaborosa magellanica*

BY MASOOD PARVEZ, VICTOR FAJARDO* AND MAURICE SHAMMA

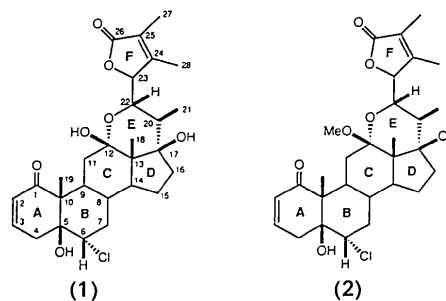
Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA

(Received 17 October 1989; accepted 14 May 1990)

Abstract. C₂₉H₃₉ClO₇, *M_r* = 535.08, orthorhombic, *P*2₁2₁2₁, *a* = 8.944 (4), *b* = 11.906 (4), *c* = 25.443 (6) Å, *V* = 2709 (3) Å³, *Z* = 4, *D_x* = 1.312 Mg m⁻³, λ(Mo *K*α) = 0.71073 Å, μ = 0.182 mm⁻¹, *F*(000) = 1144, *T* = 293 (1) K, *R* = 0.0374 for 2337 observed reflections with *I* > 3σ(*I*). The crystal structure consists of discrete molecules of the title compound separated by normal van der Waals distances. Ring *A* is in a half-chair conformation, rings *B*, *C* and *E* are regular chairs, and ring *D* is a C(13) envelope; the lactone ring *F* has a nearly planar conformation. Atoms C(18) and C(19), both the hydroxyl groups, and the methoxyl group are all β, and Cl and the lactone moiety are α oriented. The bond lengths and angles are in accord with accepted values.

Introduction. The withanolides are a group of oxygenated steroidal lactones found among members of the Solanaceae (Tursunova, Maslennikova & Abubakirov, 1977; Kamernitskii, Reshetova & Krivoruchko, 1977; Vasina, Maslennikova & Abubakirov, 1986). Our continued investigations of *Jaborosa magellanica* (Griseb.) Dusen (Solanaceae) whole plants, collected along the Strait of Magellan, Chile, has yielded a new chlorowithanolide, (+)-

jaborochlorotriol, (1), containing a hemiacetal ring (Fajardo, Podesta & Shamma, 1990). During the isolation of (1), a new withanolide (2), was also isolated as a minor product and its crystal structure and absolute configuration were determined by the X-ray method.



* Permanent address: Universidad de Magallanes, Punta Arenas, Chile.

Experimental. Colorless prismatic crystals of (2) for X-ray study were grown by slow evaporation of a methanol solution at room temperature. A crystal of approximate dimensions 0.35 × 0.25 × 0.43 mm was used for data collection. Cell parameters and crystal orientation matrix were determined on an Enraf-Nonius CAD-4 diffractometer by a least-squares refinement of the setting angles of 25 reflections with 10 < θ < 15°. Intensity data were collected by the ω/2θ scan method using variable scan speed (1.10–