

uniform chain compounds has values in the 2.75–3.21 Å range (Hatfield, 1985). For di- $\mu$ -chloro-copper(II) dimers this same distance is 2.45–3.02 Å. The values reported for di- $\mu$ -bromo-copper(II) dimers are between 2.80 and 3.87 Å (Hatfield, 1985; Garland *et al.*, 1987).

The Cu–Cu distance in the two Cu<sub>2</sub>Cl<sub>2</sub> planar units of (I) are 3.802 (1) and 3.876 (1) Å, and 3.974 (1) Å for the Cu<sub>2</sub>Br<sub>2</sub> planar units of (II). The Cu atoms form an angle of 143.31 (2)° in the chain along the *x* axis of (I) and an angle of 140.38 (7)° in the chain along the *z* axis of (II). The dihedral angles between the two alternating planar units of (I) and (II) are 89.1 and 89.8° respectively.

The unweighted mean plane through the four donor atoms N(1), N(1'), Br(1) and Br(1') shows a lack of planarity with displacements of –0.062, 0.062, 0.047 and –0.047 Å respectively. The Cu atom is placed on this plane, while the two apical Br atoms, Br(1'') and Br(1''') are symmetrically located from this plane at a distance of 3.157 Å.

In the case of the homologous plane for the chloro complex, the displacements of N(1), N(2), Cl(1) and Cl(2) donor atoms are 0.095, –0.095, –0.076 and 0.076 Å respectively. The Cu atom is displaced by 0.017 from this plane in the direction of the apical Cl(1'). The two apical Cl(1<sup>i</sup>) and Cl(2<sup>ii</sup>) are at a distance of 3.027 and 3.052 Å from this plane.

The dihedral angle between the planes through Cu, N(1) and N(1') and Cu, Br(1), Br(1') is 4.3° for compound (II), and the homologous planes for compound (I) form a dihedral angle of 6.9°. This indicates no tendency to tetrahedrality.

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## (Dioxane)dineopentylmagnesium: a Polymeric Structure

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**Abstract.** *catena*-Poly[(dineopentylmagnesium)- $\mu$ -(dioxane-*O:O'*)], [Mg(C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>)], *M<sub>r</sub>* = 254.71, monoclinic, *C*2/*c*, *a* = 17.040 (4), *b* = 9.362 (1), *c* = 10.833 (5) Å,  $\beta$  = 98.64 (2)°, *V* = 1708.6 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 0.990 Mg m<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.71073 Å,  $\mu$  = 0.091 mm<sup>-1</sup>, *F*(000) = 568, *T* = 293 (1) K, *R* = 0.042 for 1213 observed reflections with *I* > 3 $\sigma$ (*I*). The structure has dineopentylmagnesium units linked through dioxanes (having chair conformations) to form polymeric chains that run parallel to the *z* axis. An Mg

atom is bonded in an approximately tetrahedral fashion to two O atoms [Mg–O 2.132 (1) Å], one from each of two dioxane molecules, and to two neopentyl C atoms [Mg–C 2.133 (2) Å] with an unusually large C–Mg–C angle [139.95 (9)°].

**Introduction.** The title compound has been isolated on several occasions in our laboratory from reaction mixtures in which dioxane was an accidental and only minor component. The usual preparation of

dineopentylmagnesium ( $\text{np}_2\text{Mg}$ ) is by addition of dioxane to a diethyl ether solution of a Grignard reagent prepared from neopentyl chloride and magnesium.  $\text{MgCl}_2$  is precipitated by the addition of dioxane and then  $\text{np}_2\text{Mg}$  recovered by removing the solvent from the filtrate. Even after the  $\text{np}_2\text{Mg}$  is sublimed, a small amount of dioxane seems always to remain (and the amount is larger if more dioxane was added than that just necessary to precipitate  $\text{MgCl}_2$ ).  $\text{np}_2\text{Mg}(\text{dioxane})$  is relatively insoluble in benzene and diethyl ether, and it is from reactions in those solvents that it has been obtained. This paper describes the novel polymeric structures of  $\text{np}_2\text{Mg}(\text{dioxane})$  which, as outlined in the *Experimental* section, can also be prepared more deliberately.

**Experimental.** Dineopentylmagnesium ( $\text{np}_2\text{Mg}$ ) was prepared as already described (Squiller, Whittle & Richey, 1985). Sublimed  $\text{np}_2\text{Mg}$  (40 mg) was dissolved in benzene (1.0 ml). Addition of dioxane (less than one mole per mole of  $\text{np}_2\text{Mg}$  generally was used) resulted in immediate formation of a microcrystalline precipitate: m.p. 468 K. This solid dissolved readily in benzene upon addition of *N,N,N',N'*-tetramethylethylenediamine (tmeda; several moles per mole of  $\text{np}_2\text{Mg}$  were used). Such solutions (benzene- $d_6$ ) showed  $^1\text{H}$  NMR absorptions (chemical shifts relative to internal benzene- $d_6$  as  $\delta$  7.15) characteristic of  $\text{np}_2\text{Mg}$  coordinated by tmeda (Squiller, 1984; Farkas, 1985) and of dioxane, the areas indicating the presence of one dioxane per  $\text{np}_2\text{Mg}(\text{tmeda})$ :  $\delta$  -0.07 (s, 2,  $\text{CH}_2\text{Mg}$ ), 1.50 [s, 9,  $(\text{CH}_3)_3\text{C}$ ], 3.35 (s, 4,  $\text{CH}_2\text{O}$ ). Crystals suitable for X-ray diffraction were obtained by recrystallizing the precipitate from benzene or by carefully layering dioxane over a benzene solution of  $\text{np}_2\text{Mg}$  and permitting this mixture to stand. The crystals lost their transparency at 407 K, fragmented at 445 K, and melted at 468 K.

A colorless prismatic crystal with approximate dimensions  $0.27 \times 0.36 \times 0.45$  mm, handled under a nitrogen atmosphere, was sealed in a glass capillary. Accurate cell dimensions were obtained from 22 reflections with  $10 < \theta < 15^\circ$  on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator. Intensity data were collected by the  $\omega/2\theta$  scan technique using variable scans (scan speed in the range  $1.5$ – $5.5^\circ \text{ min}^{-1}$ ) in the range  $2 < \theta < 27^\circ$  with  $h$  0→21,  $k$  0→11, and  $l$  -13→13. The intensities of 1908 unique reflections were measured, of which 1213 had  $I > 3\sigma(I)$ . The intensities of three reflections, chosen as standards and measured at regular intervals, decreased by 2.7%; the data were corrected for decay by appropriate scaling. Data were also corrected for Lorentz and polarization effects and for empirical absorption (North, Phillips & Mathews, 1968); maximum and minimum correction factors were 0.9957 and 0.9793, respectively.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations on  $F^2$ 's. Anisotropic thermal parameters were allowed for non-H atoms. H atoms were located from a difference map and included in the refinement with an overall isotropic temperature factor ( $B = 5.0 \text{ \AA}^2$ ) in subsequent refinement. The refinement converged with  $R = 0.042$  and  $wR = 0.061$ , where  $w = [\sigma^2(F_o) + (0.080 F_o)^2]^{-1}$ . At the conclusion of the refinement, the maximum shift/e.s.d. was  $< 0.01$ , the difference map had no peak larger than  $0.20 e \text{ \AA}^{-3}$ , and  $S = 1.26$ . Atomic scattering factors for non-H atoms were taken from Cromer & Mann (1968) and for H atoms from Stewart, Davidson & Simpson (1965); allowance was made for anomalous dispersion (Cromer & Liberman, 1970). The computer programs used in this study were from the Enraf-Nonius *Structure Determination Package* (B. A. Frenz & Associates, Inc., 1985).

**Discussion.** Fig. 1 shows a segment of the polymer and indicates the atom-numbering scheme. Final fractional coordinates and equivalent isotropic thermal parameters are given in Table 1 and molecular dimensions in Table 2.\* Fig. 2 is a stereoview of the crystal packing.

\* Tables of H-atom coordinates, bond lengths and angles involving H atoms, anisotropic temperature factors, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44859 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

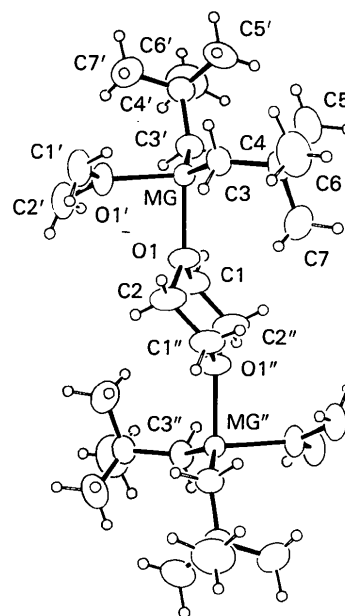


Fig. 1. ORTEP (Johnson, 1976) drawing of a segment of the polymer indicating the atom labeling. Thermal ellipsoids are drawn with 50% probability surfaces.

Table 1. Final fractional coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{1}{3} \{ a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3) \}$$

	x	y	z	$B_{\text{eq}}$
Mg*	0.50000	0.23672 (9)	0.25000	2.66 (1)
O(1)	0.4920 (1)	0.0749 (2)	0.1101 (1)	3.62 (3)
C(1)	0.4248 (1)	0.0488 (2)	0.0157 (2)	4.20 (4)
C(2)	0.5499 (1)	-0.0365 (3)	0.1083 (2)	4.69 (5)
C(3)	0.6190 (1)	0.3148 (2)	0.2822 (2)	3.61 (4)
C(4)	0.6507 (1)	0.4149 (2)	0.1899 (2)	4.01 (4)
C(5)	0.6035 (2)	0.5521 (3)	0.1770 (3)	6.35 (7)
C(6)	0.7384 (2)	0.4510 (4)	0.2363 (4)	7.44 (8)
C(7)	0.6453 (2)	0.3443 (4)	0.0633 (3)	6.54 (7)

\* The x and z coordinates of Mg were not allowed to refine.

Table 2. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

Mg—O(1)	2.132 (1)	C(3)—C(4)	1.528 (3)
Mg—C(3)	2.133 (2)	C(4)—C(5)	1.510 (3)
O(1)—C(1)	1.437 (2)	C(4)—C(6)	1.541 (3)
O(1)—C(2)	1.438 (3)	C(4)—C(7)	1.512 (4)
C(1)—C(2'')	1.475 (3)		
O(1)—Mg—O(1')	89.47 (6)	O(1)—C(2)—C(1'')	111.4 (2)
O(1)—Mg—C(3)	108.51 (7)	Mg—C(3)—C(4)	121.6 (1)
O(1)—Mg—C(3')	99.74 (7)	C(3)—C(4)—C(5)	110.3 (2)
C(3)—Mg—C(3')	139.95 (9)	C(3)—C(4)—C(6)	110.0 (2)
Mg—O(1)—C(1)	125.9 (1)	C(3)—C(4)—C(7)	110.2 (2)
Mg—O(1)—C(2)	123.6 (1)	C(5)—C(4)—C(6)	108.7 (2)
C(1)—O(1)—C(2)	110.0 (2)	C(5)—C(4)—C(7)	109.2 (2)
O(1)—C(1)—C(2'')	110.5 (2)	C(6)—C(4)—C(7)	108.4 (2)

Symmetry code: (')  $-x + 1, y, \frac{1}{2} - z$ ; (')'  $-x + 1, -y, -z$ .

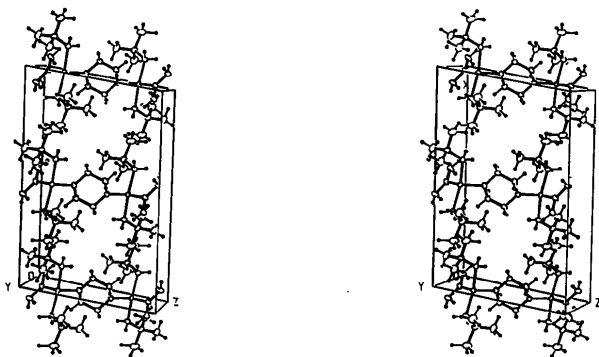


Fig. 2. Stereoscopic view of the crystal packing, which has the polymer chains running parallel to the z axis.

The structure consists of parallel linear chains, constructed from (neopentyl)<sub>2</sub>Mg units linked through chair dioxane units. There are no unusual interactions between the chains. The packing is relatively inefficient, the density being only  $0.990 \text{ Mg m}^{-3}$ . Apparently, the only other polymeric organomagnesium structures reported are of dimethylmagnesium (Weiss, 1964) and diethylmagnesium (Weiss, 1965); in those linear

structures, adjoining Mg atoms are linked by two bridging alkyl groups.

The Mg atom in the title compound is four-coordinate with a greatly distorted tetrahedral bond arrangement. The C—Mg—C angle is  $139.95 (9)^\circ$  and the O—Mg—O angle  $89.47 (6)^\circ$ . Similar bond angles were observed (Spek, Schat, Holtkamp, Blomberg & Bickelhaupt, 1977) in di- $\mu$ -pentamethylene-bis[bis(tetrahydrofuran)magnesium],  $[(\text{C}_5\text{H}_{10})\text{Mg}(\text{THF})_2]_2$ , [C—Mg—C  $141.5 (3)^\circ$ , O—Mg—O  $90.8 (3)^\circ$ ] and (Lappert, Martin, Raston, Skelton & White, 1982) in cyclo-tri- $\mu$ -(*o*-phenylenedimethyl)-tris[bis(tetrahydrofuran)magnesium],  $[(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{o})\text{Mg}(\text{THF})_2]_3$ , [C—Mg—C  $126.8 (3)$  and  $130.5 (3)^\circ$ , O—Mg—O  $94.1 (2)$  and  $94.0 (2)^\circ$ ], species that also have Mg linked to two alkyl C atoms and two ether O atoms. It is possible that the ring structures have a significant influence on the C—Mg—C bond angle, particularly in the second of these structures. Large C—Mg—C bond angles, however, are also found (Toney & Stucky, 1970) in  $\text{Me}_2\text{Mg}(\text{quinuclidine})_2$  [ $129.0 (3)^\circ$ ] and (Greiser, Kopf, Thoennes & Weiss, 1980) in  $\text{Me}_2\text{Mg}(\text{tmeda})$  [ $130.0 (4)^\circ$ ], species that have Mg linked to two unconstrained alkyl C atoms and two amine N atoms. All bond distances in  $\text{np}_2\text{Mg}(\text{dioxane})$  fall within normal ranges.

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## Study of Imidazo[1,2-*a*]pyridin-8-ol. 2. Crystal Structure

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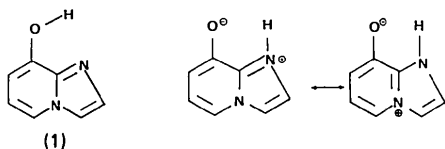
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**Abstract.** C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>O, *M<sub>r</sub>* = 134.048, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 13.432 (9), *b* = 13.071 (8), *c* = 13.678 (9) Å, β = 148.05 (8)°, *V* = 1270.8 Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.401 g cm<sup>-3</sup>, Mo *K*α, λ = 0.7107 Å, μ = 0.917 cm<sup>-1</sup>, *F*(000) = 560, *T* = 293 K, *R* = 0.046 for 1021 observed reflections. The molecule is nearly planar and the structure is stabilized by the formation of intermolecular N–H...O hydrogen bonds 2.646 and 2.631 Å, ∠N–H...O 171 and 164°, between two molecules forming infinite helices. The two molecules analysed by high-resolution solid-state CP/MAS <sup>13</sup>C NMR show two different signals for five of the seven carbons in accordance with different packing in the solid state.

**Introduction.** The title compound (1) contains a phenolic group and two basic sites, thus allowing the possibility of several tautomeric forms (Rydzkowski, Blondeau, Sliwa & Cazé, 1986).



Infrared spectral data give no information on which structure is adopted. UV spectra recorded at different pH's clearly show a zwitterionic structure in neutral

aqueous solution, in equilibrium with the neutral structure. A <sup>13</sup>C NMR study performed in neutral, basic and acidic aqueous solutions afforded the conclusion that the zwitterionic tautomer predominates in the neutral medium. A potentiometric study gives all the dissociation constants. These values are in favour of the zwitterionic structure in neutral aqueous conditions.

A careful <sup>1</sup>H NMR study shows that intermolecular hydrogen bonding occurs in a neutral aprotic medium (CDCl<sub>3</sub>) in place of an intramolecular bond.

Despite this fact, we enhanced the solid-state study by determining first the X-ray structure and secondly <sup>13</sup>C NMR spectral data because, in the solid state, as for pyridoxal and pyridoxamine dihydrate (MacLaurin & Richardson, 1985), it was possible for our compound to crystallize in the dipolar (zwitterionic species) structure or in a non-polar form.

**Experimental.** The title compound was obtained by a previously described procedure (Rydzkowski, Blondeau, Sliwa & Cazé, 1986). After several recrystallizations from water and ethanol, a crystal of about 0.3 × 0.3 × 0.4 mm was obtained. Lattice parameters from 25 reflections with θ < 10°. Intensities measured by an ω–2θ scan in the range 2 < θ < 30° on a Philips PW1100 automated four-circle diffractometer with graphite-monochromatized Mo *K*α radiation, ω-scan width 1.40°, scan speed 0.03° s<sup>-1</sup> and background counts of each extremity for half the scan time. 1021

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