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Dichlorobis(2-methylquinoline *N*-oxide-κ*O*)zinc(**II**) from powder data

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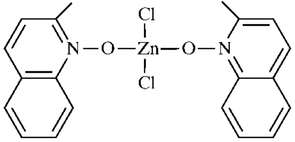
The crystal structure of the title compound, $[ZnCl_2(C_{10}H_9NO)_2]$, has been determined from laboratory powder diffraction data. Although the powder pattern was initially indexed with tetragonal unit-cell dimensions, the correct solution was found in an orthorhombic space group using a combination of grid-search and simulated-annealing techniques. The subsequent bond-restrained Rietveld refinement gave bond lengths and angles within expected ranges. The molecule has crystallographically imposed twofold symmetry.

Comment

Heteroatomic *N*-oxides and their complexes and salts demonstrate a broad spectrum of biological activity. Some are used as medical remedies (Albini & Pietra, 1991) or plant-growth activators (Ponomarenko, 1999). *N*-Oxidation is one of the detoxification pathways of heterocycles in living things (Murray *et al.*, 1997; Hecht, 1996). The necessity of establishing structure–property relationships for this class of compounds led to the crystal structure determination of the title compound, (I).



(I)

In the crystal structure of (I), the Zn atom is situated on a twofold axis (Fig. 1). Selected geometric parameters are given in Table 1. The coordination polyhedron of the Zn atom is a slightly distorted tetrahedron, with edge lengths of Cl1···Cl1^i 3.885 (6), O1···O1^i 3.20 (2), Cl1···O1 3.41 (1) and Cl1···O1^i 3.38 (1) Å [symmetry code: (i) $-x, y, \frac{1}{2}-z$]. The distortions of the Zn tetrahedron in (I) are less than those in dichlorobis(2,6-lutidine *N*-oxide)zinc(II) (Sager & Watson, 1968) and dichlorobis(pyridine *N*-oxide-*O*)zinc(II) (McConnell *et al.*, 1986). The molecules of (I) form bent chains stretching along the *a* axis. The distance between Zn atoms in the chain is 9.95 Å.

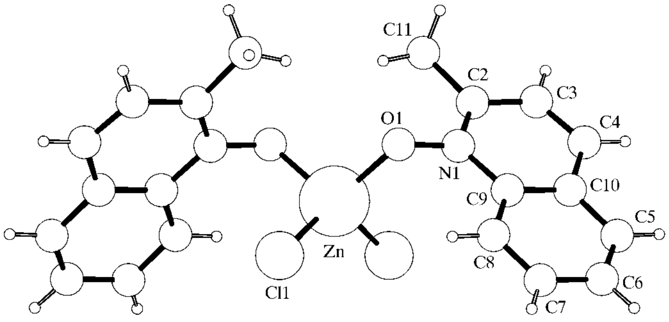


Figure 1
The molecular structure of (I) with the atomic numbering.

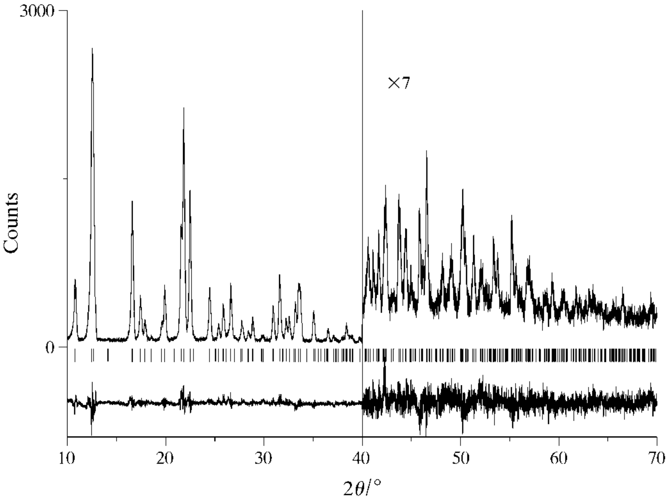


Figure 2
The Rietveld plot showing the observed and difference profiles for (I). The reflection positions are shown above the difference profiles.

Although the unit-cell dimensions seemed to be tetragonal, the crystal structure solution of (I) from powder data turned out not to be an easy task. The measured powder patterns admitted a long list of possible space groups. Therefore, various space groups [first, tetragonal, such as $P4_22_12$ (94), $P4_2/m$ (84), $P4_2$ (77) and some others, and then orthorhombic] were tested while also using grid-search (Chernyshev & Schenk, 1998) and simulated annealing (Zhukov *et al.*, 2001) techniques to solve the crystal structure. The solution was found in the orthorhombic space group $Pna2_1$ (33) and was transformed into $Pbcn$ (60).

Experimental

2-Methylquinoline *N*-oxide was synthesized according to the procedure of Ochiai (1953). Compound (I) was prepared in polycrystalline form by mixing warm saturated 2-methylquinoline *N*-oxide and zinc chloride solutions in ethanol in a molar ratio, and subsequent washing with ethanol and diethyl ether of the precipitate obtained (yield:

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Table 1
Selected geometric parameters (Å, °).

Zn—Cl1	2.238 (5)	O1—N1	1.341 (16)
Zn—O1	1.979 (9)		
O1—Zn—O1^i	107.9 (6)	Cl1^i—Zn—Cl1	120.4 (2)
O1—Zn—Cl1	107.8 (3)	N1—O1—Zn	114.0 (7)
O1^i—Zn—Cl1	106.2 (3)		
Cl1—Zn—O1—N1	135.0 (8)	Zn—O1—N1—C2	90 (1)

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

60%). The intensities of the N—O bands in the IR spectra (1340 and 1272 cm^{-1}) decreased in comparison with the spectrum of the parent *N*-oxide. Bands are also present at 1188 cm^{-1} (induced by connection of zinc chloride to the N—O group) and 328–305 cm^{-1} (Zn—Cl bonds) (Whyman *et al.*, 1967; Garvey *et al.*, 1968).

Crystal data

$[ZnCl_2(C_{10}H_9NO)_2]$
$M_r = 454.63$
Orthorhombic, *Pbcn*
$a = 14.052$ (6) Å
$b = 10.192$ (5) Å
$c = 14.047$ (6) Å
$V = 2011.8$ (16) Å^3
$Z = 4$
$D_x = 1.501$ Mg m^{-3}
Cu $K\alpha_1$ radiation
Cell parameters from 30 reflections
$\theta = 5.4$–18.6°
$\mu = 4.28$ mm^{-1}
$T = 293$ (2) K
Specimen shape: flat sheet
20 × 20 × 0.1 mm
Particle morphology: no specific habit, light grey

Data collection

XPert PRO X-ray diffraction system
University of Amsterdam
Specimen mounting: sprinkled on sample holder using a small sieve; layer thickness ≤0.1 mm
Specimen mounted in reflection mode
$\theta_{max} = 35°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 10$
$2\theta_{min} = 10.00$, $2\theta_{max} = 70.00°$
Increment in $2\theta = 0.01°$

Refinement

$R_p = 0.083$
$R_{wp} = 0.114$
$R_{exp} = 0.086$
$S = 1.32$
$2\theta_{min} = 10$, $2\theta_{max} = 70°$
Increment in $2\theta = 0.01°$
Wavelength of incident radiation: 1.54056 Å
Profile function: split-type pseudo-Voigt (Toraya, 1986)
440 reflections
64 parameters
H-atom parameters constrained
Weighting scheme based on measured s.u.s
$(\Delta/\sigma)_{max} = 0.01$
$\Delta\rho_{max} = 0.5$ e Å^{-3}
$\Delta\rho_{min} = -0.7$ e Å^{-3}

Two X-ray powder diffraction patterns were measured in reflection mode on an XPert PRO X-ray powder diffraction system equipped with a PW 3050/60 standard resolution goniometer and PW 3011/20 proportional point detector. The first pattern, measured in the range 2–40° with the narrowest beam attenuator, was used for indexing, while the second was used for structure solution and refinement. The powder was sprinkled onto the sample holder using a small sieve, to avoid a preferred orientation. The thickness of the sample was no more than 0.1 mm. During the exposures, the specimen was spun in its plane to improve particle statistics. The unit-cell dimensions were determined with the indexing program *TREOR* (Werner *et al.*, 1985), and were refined in tetragonal space groups with the program *LSPAID* (Visser, 1986) to $M_{20} = 47$ and $F_{30} = 85$ (0.006, 61) using the first 30 peak positions. However, several of the tetragonal space groups tested could not provide an appropriate solution. A correct solution was found in the orthorhombic space group $Pna2_1$ (No. 33) in a two-step procedure. First, the rigid $ZnCl_2O_2$ fragment was located in the asymmetric part of the unit cell using the grid-search procedure (Chernyshev & Schenk, 1998), using a set of 150 high-angle X_{obs} values extracted from the pattern by the full pattern decomposition procedure. Second, the orientations of the two 2-methylquinoline *N*-oxide fragments were found with the simulated-annealing technique (Zhukov *et al.*, 2001), using a set of 70 low-angle X_{obs} values. Preliminary bond-restrained Rietveld refinement showed the presence of local symmetry, axis 2. The crystal structure obtained at this stage was tested with the *ADDSYM* option of *PLATON* (Spek, 2000) and transformed into space group *Pbcn* (No. 60). The final bond-restrained Rietveld refinement was performed in the correct space group, *Pbcn*. The strength of the restraints was a function of interatomic separation and, for intramolecular bond lengths, corresponds to an r.m.s. deviation of 0.03 Å. An additional restraint was applied to the planarity of the 2-methylquinoline *N*-oxide fragment. Three isotropic atomic displacement parameters were refined: two for Zn and Cl1, and an overall U_{iso} parameter for the rest of non-H atoms. H atoms were placed in geometrically calculated positions and allowed to refine using bond restraints, with a common isotropic displacement parameter fixed at 0.05 Å^2.

Data collection: local program; cell refinement: *LSPAID* (Visser, 1986); data reduction: local program; program(s) used to solve structure: *MRIA* (Zlokazov & Chernyshev, 1992); program(s) used to refine structure: *MRIA*; molecular graphics: *PLATON* (Spek, 2000); software used to prepare material for publication: *MRIA*, *SHELXL*97 (Sheldrick, 1997) and *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1538). Services for accessing these data are described at the back of the journal.

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