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Concomitant polymorphism: Crystallising dichloro-bis(2,4-lutidine)-zinc as both chiral and racemic phases

Anders Lennartson *, Susanne Olsson, Jonas Sundberg, Mikael Håkansson

Department of Chemistry, University of Gothenburg, SE 412 96 Gothenburg, Sweden

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ABSTRACT

The crystallisation of dichloro-bis(2,4-lutidine)-zinc from various solvents (*e.g.* ethanol, THF and 2,4-lutidine) has been investigated and two phases were isolated. The structures of both phases were determined by single crystal X-ray diffraction and both types of crystals were found to be composed of conformationally chiral molecules. One phase (**α-1**) is racemic and crystallises in space group $P2_1/c$, while the other phase (**β-1**) crystallises in the enantiomorphous space group $P4_12_12$ with a low Flack parameter. In a few cases the chiral and racemic phases crystallised concomitantly; this phenomenon is rare and can be useful in the development of tools for the prediction of crystal structures.

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1. Introduction

Concomitant polymorphism refers to the appearance of two or more polymorphs within the same crystal batch [1]. The concomitant crystallisation of polymorphs is controlled by kinetic and/or by thermodynamic factors. Thermodynamically, two phases can only coexist in equilibrium at the transition point, where the two phases have the same free energy. A special case is the concomitant crystallisation of a racemic phase and a conglomerate (chiral phase). If there is fast interconversion between the two enantiomers in solution, or if the molecules are achiral, this can be regarded as a form of polymorphism. The phenomenon appears to be rather rare; a list of examples extracted from the CSD was published in 2004 [2]. Information from these cases may be used for structure predictions [1], and one may perhaps also find such information useful in the design of conglomerates. We recently reported concomitant crystallisation of chiral and racemic phases of 10-nitro-phenantren-9-yl phenyl sulphide [3]. Compared to several other cases [4–6], there is a relatively large difference between these two crystal structures. Both phases give rise to similar homochiral chains, but in the racemic phase these chains are associated by π–π stacking to form racemic double chains, while in the chiral phase hydrogen bonding gives rise to helices. We have also reported concomitant polymorphism of the chiral organometallic reagent bis(3-methylpyridine)-di(1-indenyl)-zinc, which may be obtained as a chiral or a racemic phase from THF [7]. The racemic phase is obtained from dilute solutions, while the chiral phase is obtained from more concentrated solutions. Solutions of intermediate concentration deposit a mixture of the two phases. The racemic phase is less soluble than the chiral phase, and the chiral crystals will dissolve and disappear in the presence of racemic crystals. Several other thorough investigations of polymorphism have appeared recently [8–16]. In this work we set out to investigate the potential concomitant crystallisation of a coordination compound, *viz.* $[ZnCl_2(lut)_2]$ (**1**) where lut = 2,4-lutidine.

2. Experimental

2.1. General

$ZnCl_2$ (Riedel-deHaën), 2,4-lutidine (E. Merck), ethanol (Solveco), methanol (Fluka), THF (Aldrich), toluene (Aldrich), benzene (Aldrich), acetonitrile (Riedel-deHaën), dichloromethane (Fluka), acetone (Riedel-deHaën) and ethyl acetate (Fluka) were used as received. All product samples were carefully investigated using microscope and from each sample several crystals were picked for single-crystal X-ray diffraction. In addition, some samples were investigated by powder X-ray diffraction.

2.2. Crystallisation of **1** from ethanol

$ZnCl_2$ (0.15 g, 1.1 mmol), ethanol (1.0 ml) and 2,4-lutidine (0.25 ml, 2.1 mmol) were heated to dissolution. On cooling to ambient temperature, crystals formed within 2 h. Yield: 0.11 g (74%). IR (**α-1**, KBr): 3037 (w), 2923 (w), 1626 (s), 1560 (s), 1498

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* Corresponding author. Tel.: +46 (0)31 772 3843; fax: +46 (0)31 772 3840.
E-mail address: anle@chem.gu.se (A. Lennartson).

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(m), 1456 (m), 1381 (w), 1309 (s), 1262 (w), 1241 (w), 1183 (m), 1098 (w), 1028 (s), 930 (s), 836 (s), 796 (s), 548 (m), 540 (m) cm^{-1}. IR (**β-1**, KBr): 3028 (w), 2925 (w), 1626 (s), 1559 (m), 1498 (m), 1455 (m), 1309 (s), 1274 (w), 1243 (w), 1182 (m), 1129 (w), 1028 (s), 931 (s), 836 (s), 539 (m) cm^{-1}. Mp(**α-1**) = 127.8–128.9 °C, mp(**β-1**) = 118.9–119.7 °C.

2.3. Crystallisation of **1** from methanol

$ZnCl_2$ (0.15 g, 1.1 mmol), methanol (1.0 ml) and 2,4-lutidine (0.25 ml, 2.1 mmol) were heated to dissolution. On cooling to ambient temperature, crystals formed within 15 min. Yield: 0.15 g (97%).

2.4. Crystallisation of **1** from THF

$ZnCl_2$ (0.50 g, 3.7 mmol) was dissolved in hot THF (6.0 ml). 2,4-lutidine (0.80 ml, 6.9 mmol) was added. The solution was cooled to ambient temperature and layered with hexane (8.0 ml). Crystals formed over night. Yield: 0.30 g (60%).

2.5. Crystallisation of **1** from 2,4-lutidine

$ZnCl_2$ (0.37 g, 2.7 mmol) was dissolved in hot 2,4-lutidine (3.0 ml). On cooling to ambient temperature, crystals formed within 2 h. Yield: 0.27 g (73%).

2.6. Crystallisation of **1** from toluene

$ZnCl_2$ (0.15 g, 1.1 mmol), toluene (5.0 ml) and 2,4-lutidine (0.25 ml, 2.1 mmol) were heated to dissolution. On cooling to ambient temperature, crystals formed over night. Yield: 0.090 g (60%).

2.7. Crystallisation of **1** from benzene

$ZnCl_2$ (0.15 g, 1.1 mmol), benzene (4.0 ml) and 2,4-lutidine (0.25 ml, 2.1 mmol) were heated until no more material dissolved. The clear solution was transferred to a new test tube, and allowed to cool to ambient temperature. Crystals formed over night. Yield: 0.075 g (50%).

2.8. Crystallisation of **1** from acetonitrile

$ZnCl_2$ (0.15 g, 1.1 mmol), acetonitrile (1.0 ml) and 2,4-lutidine (0.25 ml, 2.1 mmol) were heated to dissolution. On cooling to ambient temperature, crystals formed over night. Yield: 0.081 g (54%).

2.9. Crystallisation of **1** from dichloromethane

$ZnCl_2$ (0.15 g, 1.1 mmol), dichloromethane (1.0 ml) and 2,4-lutidine (0.25 ml, 2.1 mmol) were heated to dissolution. No crystals formed over night. The volume was reduced to *c.* 0.8 ml, whereupon crystals formed. Yield: 0.12 g (83%).

2.10. Crystallisation of **1** from acetone

$ZnCl_2$ (0.15 g, 1.1 mmol), acetone (1.0 ml) and 2,4-lutidine (0.25 ml, 2.1 mmol) were heated to dissolution. On cooling to ambient temperature, crystals formed within 1 h. Yield: 0.085 g (57%).

2.11. Crystallisation of **1** from ethyl acetate

$ZnCl_2$ (0.15 g, 1.1 mmol), ethyl acetate (1.0 ml) and 2,4-lutidine (0.25 ml, 2.1 mmol) were heated, until no more material dissolved. The clear solution was transferred to a new test tube, and allowed to cool to ambient temperature. Crystals formed over night. Yield: 0.079 g (53%).

2.12. Crystallography

Crystals of **α-1** and **β-1** were carefully selected using microscope and mounted in glass capillaries using low-temperature techniques [17]. Refracted intensities were measured using a Rigaku R-AXIS IIc area detector with graphite monochromated Mo Kα radiation from a Rigaku RU-H3R rotating anode, and 90 oscillation photos with a rotation angle of 2° were collected. Data were processed using the CRYSTALCLEAR software package [18], and an empirical absorption correction was applied using the REQAB program included in CRYSTALCLEAR. The structures were solved using the program SIR-92 [19], and the structures were refined using full-matrix least squares calculations on F^2 using the SHELXL-97 program [20]. Plots were drawn using ORTEP3 [21] for WINDOWS and PLUTON [22]. SIR-92, SHELXL-97, ORTEP3 and PLUTON were enclosed in the WINGX-software package [23]. Crystal and refinement data are collected

Table 1
Crystal and refinement data for **α-1** and **β-1**.

Parameter	**α-1**	**β-1**
Empirical formula	$ZnC_{14}H_{18}Cl_2N_2$	$ZnC_{14}H_{18}Cl_2N_2$
M	350.59	350.59
Crystal system	monoclinic	tetragonal
Space group	$P2_1/c$	$P4_12_12$
a (Å)	13.512(2)	7.4401(10)
b (Å)	15.7361(18)	7.4401(10)
c (Å)	16.347(2)	27.578(4)
α (°)	90	90
β (°)	113.780(3)	90
γ (°)	90	90
V (Å^3)	3180.7(7)	1526.6(4)
Z	8	4
D_{calc} g cm^{-3}	1.464	1.525
μ(Mo Kα) mm^{-1}	1.868	1.946
T (K)	100(2)	100(2)
Crystal size/mm	0.25 × 0.25 × 0.1	0.25 × 0.2 × 0.1
θ Range (°)	1.25–25.49	3.11–25.50
Reflections collected	20629	9967
Unique reflections, R_{int}	5838 (0.0428)	1398 (0.340)
No. of parameters	350	89
Goodness-of-fit (GOF) on F^2	1.095	1.127
Final $R_1(F)$[a]$(I > 2\sigma(I))/wR_2(F^2)$[b]	0.0356/0.0868	0.0176/0.0442
R_1[a]$/wR_2(F^2)$[b] (all data)	0.0450/0.0904	0.0180/0.0444
Flack x parameter	–	0.007(12)

[a] $R_1(F) = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$.

[b] $wR_2(F^2) = \{\Sigma[w(F_o{}^2-F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

Table 2
Selected bond distance (Å) and angles (°) for **α-1** and **β-1**.

Selected bond distance (Å) and angles (°)	**α-1**	**β-1**
Zn–Cl	2.2430(7), 2.2468(7), 2.2358(7), 2.2559(7)	2.2518(5)
Zn–N	2.059(2), 2.076(2), 2.053(2), 2.069(2)	2.0538(15)
Cl–Zn–Cl	113.82(3), 114.24(3)	115.04(3)
N–Zn–Cl	107.68(6), 110.20(6), 110.49(6), 105.22(6), 109.15(6), 104.85(6), 105.93(6), 109.53(6),	107.43(4), 106.31(4)
N–Zn–N	109.37(8), 113.33(8)	114.57(9)

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