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Key indicators

Single-crystal X-ray study
 T = 120 K
 Mean $\sigma(C-C)$ = 0.007 Å
 Disorder in main residue
 R factor = 0.051
 wR factor = 0.118
 Data-to-parameter ratio = 17.1

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

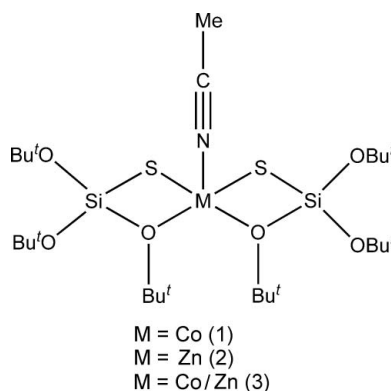
Solid solution of $[M\{SSi(OBu^t)_3\}_2(NCMe)]$, where $M = Zn$ and Co

For the first time, cocrystallization of two isomorphous silanethiolate complexes has been carried out. (Acetonitrile)-bis(tri-*tert*-butoxysilanethiolato- $\kappa^2 O,S$)cobalt(II) and (acetonitrile)bis(tri-*tert*-butoxysilanethiolato- $\kappa^2 O,S$)zinc(II) gave orthorhombic monocrystals of their solid solution with a Co:Zn ratio refined to 0.81 (5):0.19 (5), *viz.* $[Co(C_{12}H_{27}O_3SSi)_2(C_2H_3N)]_{0.81}[Zn(C_{12}H_{27}O_3SSi)_2(C_2H_3N)]_{0.19}$. The product retained the structural characteristics of the substrates, *viz.* distorted trigonal-bipyramidal arrangement of ligands around the M^{II} atom and crystallographically imposed C_2 symmetry with the $M-NCMe$ fragment lying on a twofold rotation axis.

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Comment

Isomorphism, similarity of crystal structure between two or more distinct substances, is common, especially in the case of simple inorganic compounds. Metal complexes may also show this property, as exemplified by Zn, Co, Ni and Cd thiolates (Holah & Coucouvanis, 1975; Silver *et al.*, 1993), which are the closest ones to the object of our investigations. Among silanethiolate complexes two cases are well documented: $[M\{SSi(OBu^t)_3\}_2(1-MeImid)_2]$ where $M = Co$ (Becker *et al.*, 2001) and Zn (Dołęga *et al.*, 2004), and $[M\{SSi(OBu^t)_3\}_2(NCMe)]$ where $M = Co$ (Becker *et al.*, 1995), Zn (Becker *et al.*, 1996) and Mn (Kropidłowska *et al.*, 2006).



We wondered if it is possible, using isomorphous pairs, to obtain monocrystals of silanethiolate complexes containing simultaneously two metals. To check this possibility, (acetonitrile)bis(tri-*tert*-butoxysilanethiolato- O,S)cobalt(II), (1), and (acetonitrile)bis(tri-*tert*-butoxysilanethiolato- O,S)zinc(II), (2), have been chosen for examination.

A simple crystallization procedure has shown that a saturated solution of (2) in acetonitrile may be seeded with crystals of (1). We obtained crystals with sizes up to 10 mm where



Figure 1
Image of the crystal obtained by seeding the saturated solution of (2) with crystals of (1). The inner part contains the blue–violet Co^{II} complex; the outer part is composed of the colourless Zn^{II} complex.

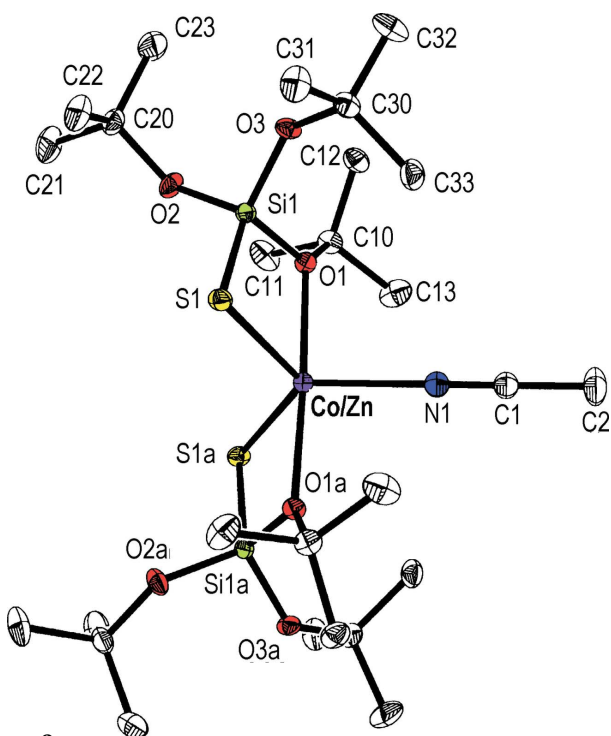


Figure 2
Ellipsoid plot of $[\text{M}\{\text{SSi}(\text{OBU}^t)_3\}_2(\text{NCMe})]$, (3), where $M = \text{Co}/\text{Zn}$, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (a) $-x, -y + 1, z$.]

domains of the two complexes may be easily distinguished (Fig. 1).

In further experiments we grew crystals from solutions containing mixtures of (1) and (2). We isolated homogeneous, uniformly coloured monocrystals of (3), whose composition is best described as a solid mixture of (1) and (2). The crystal and molecular structure determinations for these crystals indicated

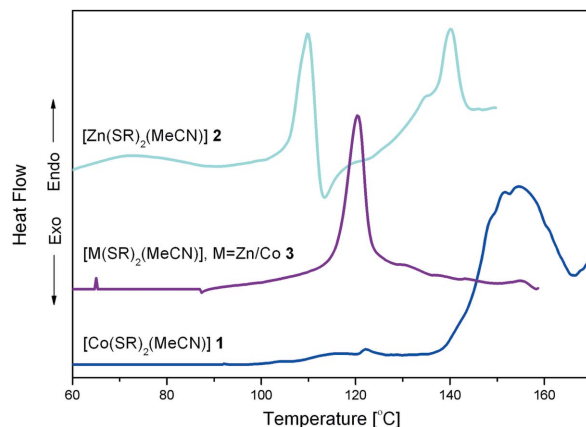


Figure 3
DSC curves (the first heating scan) for (1), (2) and (3) recorded in a dynamic nitrogen atmosphere.

that (3) is isomorphous with its substrates (scheme, Fig. 2 and Table 1). It features the same trigonal–bipyramidal arrangement of ligands around the M^{II} atom ($M\text{NO}_2\text{S}_2$ core) and crystallographically imposed C_2 symmetry with the M –NCMe fragment lying on a twofold rotation axis. The Co:Zn ratio in crystals of (3) was refined as 0.81 (5):0.19 (5), although in the starting solution the Co:Zn ratio was 1:2.

Comparison of bond lengths and angles within the central parts of (1), (2) and (3) shows that related parameters are very close. Since the structure determinations of (1) and (2) were carried out at 293 K, while the current study was performed at 120 K, no detailed comparison can be made, however.

Investigations using differential scanning calorimetry (Fig. 3) have shown that (3) exhibits thermal properties such as a sharp melting point, which are characteristic for well defined homogeneous substances but not for inhomogeneous mixtures. The thermal features of (3) are somewhat intermediate between those of (1) and (2), suggesting that cocrystallization may be considered as a tool for tailoring at least some properties of these species.

Experimental

All commercially available reagents were of analytical or reagent grade purity and were used as received. (Acetonitrile)bis(tri-*tert*-butoxysilanethiolato)cobalt(II) (13.5 mg) (Becker *et al.*, 1995) and (acetonitrile)bis(tri-*tert*-butoxysilanethiolato)zinc(II) (30 mg) (Becker *et al.*, 1996) (molar ratio Co/Zn = 1/2), which were both prepared according to the known procedures, were dissolved in 15 ml of acetonitrile and refluxed under argon for 1 h. The resulting solution was left for crystallization at 277 K. After several days, violet crystals of (3) were collected.

Crystal data

$[\text{Co}(\text{C}_{12}\text{H}_{27}\text{O}_3\text{SSi})_2(\text{C}_2\text{H}_3\text{N})]_{0.81} \cdot$	$V = 7266.9 (15) \text{ \AA}^3$
$[\text{Zn}(\text{C}_{12}\text{H}_{27}\text{O}_3\text{SSi})_2(\text{C}_2\text{H}_3\text{N})]_{0.19}$	$Z = 8$
$M_r = 659.76$	$D_x = 1.206 \text{ Mg m}^{-3}$
Orthorhombic, $Fdd2$	Mo $K\alpha$ radiation
$a = 17.832 (3) \text{ \AA}$	$\mu = 0.71 \text{ mm}^{-1}$
$b = 45.098 (4) \text{ \AA}$	$T = 120 (2) \text{ K}$
$c = 9.0363 (7) \text{ \AA}$	Prism, violet
	$0.2 \times 0.19 \times 0.14 \text{ mm}$

Data collection

Oxford Diffraction KM-4 CCD diffractometer	3183 independent reflections
ω scans	2972 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{\text{int}} = 0.08$
9144 measured reflections	$\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 37.5182P]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.118$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.63 \text{ e } \text{\AA}^{-3}$
3183 reflections	$\Delta\rho_{\text{min}} = -0.54 \text{ e } \text{\AA}^{-3}$
186 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	1470 Friedel pairs
	Flack parameter: 0.10 (2)

Table 1

Comparison of selected bond lengths (\AA) and angles ($^\circ$) for $[M\{\text{SSi}(\text{O}-\text{Bu}^t)_3\}_2(\text{NCMe})]$ where $M = \text{Co}$ for (1), $M = \text{Zn}$ for (2) and $M = \text{Co/Zn}$ for (3).

	(1) ^a	(2) ^b	(3) ^c
$M-S$	2.2680 (7)	2.2491 (1)	2.2873 (12)
$M-N$	2.065 (4)	2.087 (4)	2.083 (5)
$M-O$	2.283 (2)	2.378 (2)	2.289 (3)
$Si-S$	2.0666 (8)	2.0680 (11)	2.0821 (14)
$S-M-S$	119.14 (4)	125.81 (5)	121.77 (6)

Notes: (a) Becker *et al.* (1995); (b) Becker *et al.* (1996); (c) this work.

All H atoms were placed in calculated positions with C–H = 0.98 \AA and refined as riding with $U_{\text{iso}}(\text{H})$ values of $1.5U_{\text{eq}}(\text{C})$ for CMe_3 H atoms and $1.2U_{\text{eq}}(\text{C})$ for MeCN H atoms.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005).; cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005).; data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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