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catena-Poly[potassium [copper(II)-μ-isothiocyanato-μ-*N*-salicylidene-β-alaninato(2−)]]

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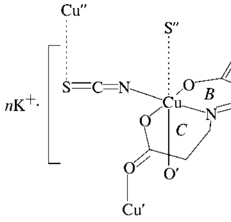
The title polymeric compound, *catena*-poly[dipotassium [bis[μ-*N*-salicylidene-β-alaninato(2−)]-$\kappa^4O,N,O':O'';\kappa^4O''$:-$O,N,O'$-dicopper(II)]-di-$\mu$-isothiocyanato-$\kappa^2N{:}S;\kappa^2S{:}N$], $\{K[Cu(NCS)(C_{10}H_9NO_3)]\}_n$, consists of [isothiocyanato(*N*-salicylidene-β-alaninato)copper(II)]$^-$ anions connected through the two three-atom thiocyanate (μ-NCS) and the two *anti*,*anti*-μ-carboxylate bridges into infinite one-dimensional polymeric anions, with coulombically interacting K^+ counter-ions with coordination number 7 constrained between the chains. The Cu^{II} atoms adopt a distorted tetragonal–bipyramidal coordination, with three donor atoms of the tridentate Schiff base and one N atom of the bridging μ-NCS ligand in the basal plane. The first axial position is occupied by a thiocyanate S atom of a symmetry-related μ-NCS ligand at an apical distance of 2.9770 (8) Å, and the second position is occupied by an O atom of a bridging carboxylate group from an adjacent coordination unit at a distance of 2.639 (2) Å.

Comment

Both thiocyanate and carboxylate groups can act as monodentate, bidentate or one- or three-atom bridging ligands (Goher *et al.*, 2000; Zou *et al.*, 1998), forming various types of monomeric, oligomeric or polymeric structures. The coordination mode of these groups has a significant impact on the magnetic and spectroscopic characteristics of their complexes. In addition to the various coordination modes of the carboxylate group, the various bonding arrangements in polynuclear complexes, in particular *syn*,*syn*, *syn*,*anti* or *anti*,*anti* arrangements, significantly alter the whole form of the polymeric structure.

The group of copper(II) Schiff base complexes derived from salicylaldehyde and amino acids contains a number of examples of various coordination modes and arrangements of the carboxylate group. The first coordination mode of the carboxylate group is found in the structure of aqua(*N*-salicylideneglycinato)copper(II) hemihydrate (Bkouche-Waksman *et al.*, 1988), where Cu—OCO—Cu′ bridges are formed in the polymeric chain. Another coordination mode of the carboxylate group is present in the structure of (μ-*N*-salicylidene-L-valinato)-*N*-salicylidene-L-valinato-diaquadicopper(II) (Korhonen & Hämelainen, 1979), where one-atom Cu—O—Cu′ bridges are formed, probably due to the large volume of the isopropyl group of L-valine.

Considering the arrangement of the bidentate carboxylate group, structures with *syn*,*syn* (acetate type) and, mostly, *syn*,*anti* arrangements are formed (Warda, 1997*a*,*b*; Wanga *et al.*, 2002). Only a minority of structures from the group of (*N*-salicylideneamino-acidato)copper(II) complexes display the *anti*,*anti* arrangement of the multidentate carboxylate group (Warda *et al.*, 1997; Warda, 1997*c*,*d*; Butcher *et al.*, 2003). As reported previously, pseudohalogeno (NC*X*, where *X* is O or S) Schiff base cuprates(II) derived from α-alanine (Friebel *et al.*, 1997), DL-phenylalanine (Sivý *et al.*, 1990) and DL-valine (Vančo *et al.*, 2003) display dimeric structures formed by opposite enantiomeric coordination units connected through two linear three-atom pseudohalogeno bridges. The formation of enantiomeric coordination units, however, cannot occur in the case of pseudohalogeno (*N*-salicylidene-β-alaninato)-cuprates(II), and under the influence of this absence the crystal or molecular structures may alter significantly. The first example supporting this assumption was the structure of tetrasodium bis{(μ-isothiocyanato-*N*,*S*)(*N*-salicylidene-β-alaninato)}dicuprate(II) dithiocyanate tetrahydrate (Kettmann *et al.*, 1992), with two uncoordinated thiocyanate groups per dimer. As a further direct proof in support of this assumption, we report here the crystal structure of the title compound, (I).



(I)

Compound (I) consists of [Cu(sal-β-ala)(NCS)] coordination units (Fig. 1). The Cu^{II} ion adopts a distorted tetragonal–bipyramidal geometry, defined by an O,N,O'-tridentate *N*-salicylidene-β-alanine dianion and the N atom of the NCS^- ligand in the basal plane (selected geometric parameters are given in Table 1). The first axial position is occupied by the thiocyanate atom S^i from a neighbouring molecule, with a Cu—S^i distance of 2.9770 (8) Å [symmetry code: (i) $1 - x$, $1 - y$, $1 - z$]. This is comparable with the average length (3.014 Å) of this bond in related complexes in the Cambridge Structural Database (Version 5.24.3; Allen, 2002). The second axial position is occupied by atom $O2^{ii}$ of a bridging carboxylate group from an adjacent coordination unit [symmetry code: (ii) $1 - x$, $-y$, $1 - z$]. Thus, [Cu(sal-β-ala)(NCS)]$^-$ ions form infinite one-dimensional polymeric polyanions in the [010] direction (Fig. 2). The Cu—O1—C1—O2 and O1—C1—O2—Cu^{ii} metal–carboxyl torsion angles are

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−145.2 (2) and 114.9 (2)°, respectively, indicating an *anti*,*anti* arrangement of the bridging carboxylate group.

The mean planes through the Cu atom and the four basal atoms, and through the six-membered phenyl ring *A* and the chelate ring *B* (see scheme) are almost parallel, with the angles between the basal plane and ring *A*, the basal plane and ring *B*, and rings *A* and *B* being 6.75 (9), 3.98 (6) and 3.06 (8)°, respectively. For the six-membered chelate ring *C*, the Cremer–Pople puckering parameters (Cremer & Pople, 1975) are $Q = 0.705$ (3) Å, $\theta = 96.6$ (2)° and $\varphi_2 = 41.8$ (2)°, indicating a conformation close to the twisted-boat form.

The crystal packing in (I) is dominated by interactions between the K^+ ions and the heteroatoms of neighbouring chains of polyanions, which leads to the formation of two-dimensional nets of molecules parallel to (110). The coordination number of the K^+ ion is 7 and its coordination geometry can be described as a distorted pentagonal bipyramid, with atoms S^i and $O2^{iii}$ in the apical positions [symmetry code: (iii) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$].

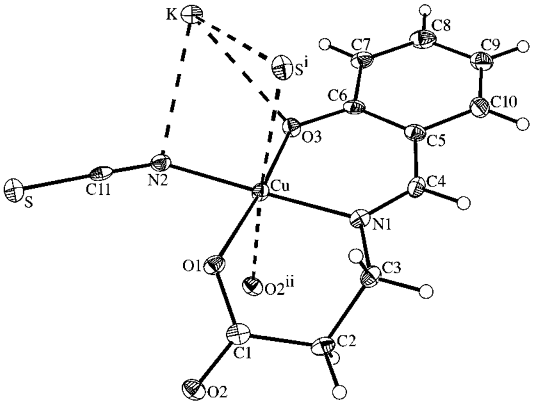

Figure 1
A molecular view of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, -y, 1-z$].

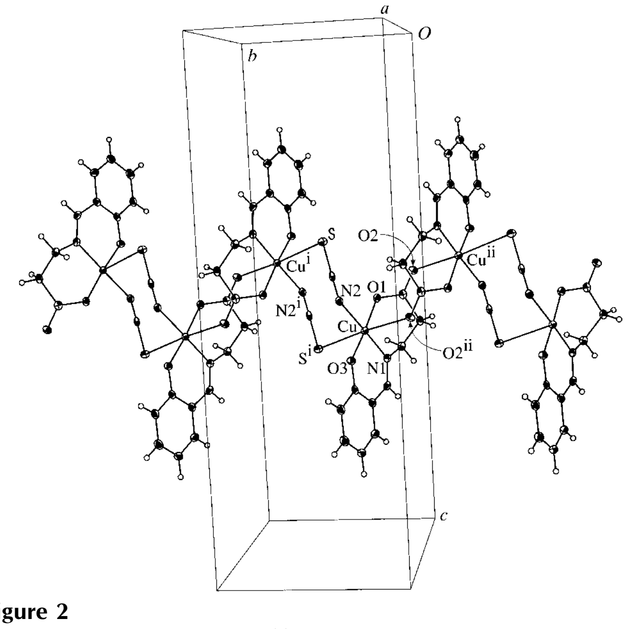

Figure 2
Part of the crystal structure of (I), showing the formation of a polymeric chain of Cu^{II} coordination units [symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, -y, 1-z$].

Experimental

The title compound was prepared using the patented procedure of Krätsmár-Šmogrovič *et al.* (1991), by reaction of the corresponding aqua complex Cu(sal-*β*-ala)(H_2O) (Werner *et al.*, 1983) with potassium thiocyanate in an ethanol–water solution. The reaction mixture was made up of Cu(sal-*β*-ala)(H_2O) (20 mmol, 5.45 g) and KSCN (80 mmol, 7.77 g) dissolved in ethanol–water (240 ml, 2:1 *v*/*v*), and was heated to 333 K and mixed vigorously for 60 min until the solid phase disappeared. The solution was filtered and left to cool to room temperature. Dark-green well developed crystals of (I) were isolated and analyzed. Analysis (Carlo–Erba 1180 instrument) calculated for $C_{11}H_9CuKN_2O_3S$: C 37.5, H 2.6, N 8.0%; found: C 37.7, H 2.6, N 7.9%. Single crystals of (I) suitable for diffraction analysis were prepared by the diffusion method from a propan-2-ol solution using $CHCl_3$ as the precipitant.

Crystal data

$K[Cu(NCS)(C_{10}H_9NO_3)]$
$M_r = 351.90$
Orthorhombic, *Pbca*
$a = 12.5103$ (7) Å
$b = 8.4276$ (6) Å
$c = 24.401$ (2) Å
$V = 2572.6$ (3) $Å^3$
$Z = 8$
$D_x = 1.817$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 3558 reflections
$\theta = 2.3$–31.0°
$\mu = 2.19$ mm^{-1}
$T = 120$ (2) K
Prism, dark green
0.40 × 0.30 × 0.15 mm

Data collection

Kuma KM-4 diffractometer with a CCD area detector
Rotation method, *ω* scan
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2002)
$T_{min} = 0.444$, $T_{max} = 0.750$
10 607 measured reflections

2248 independent reflections
2040 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 25.0°$
$h = -14 \rightarrow 14$
$k = -10 \rightarrow 8$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.080$
$S = 1.03$
2248 reflections
172 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 5P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.45$ e $Å^{-3}$
$\Delta\rho_{min} = -0.42$ e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

Cu—O3	1.921 (2)	K—O1^{ii}	2.742 (2)
Cu—N1	1.950 (3)	K—N2	2.895 (3)
Cu—O1	1.965 (2)	K—O3	2.938 (2)
Cu—N2	1.999 (3)	K—O2^{ii}	3.134 (2)
Cu—O2^{i}	2.639 (2)	K—S^{ii}	3.3857 (10)
Cu—S^{ii}	2.9771 (8)	S—C11	1.635 (3)
K—O2^{iii}	2.687 (2)	N2—C11	1.159 (4)
K—O3^{iv}	2.724 (2)		
O3—Cu—N1	93.55 (10)	N1—Cu—N2	175.43 (10)
O3—Cu—O1	173.66 (9)	O1—Cu—N2	85.52 (10)
N1—Cu—O1	92.48 (9)	N2—C11—S	179.1 (3)
O3—Cu—N2	88.61 (10)		
Cu—O1—C1—O2	−145.2 (2)	O1—C1—O2—Cu^{i}	114.9 (2)

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (iv) $\frac{3}{2}-x, \frac{1}{2}+y, z$.

All H atoms were located from difference maps and were then treated as riding atoms, with C—H distances of 0.95 and 0.99 Å.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Johnson & Burnett, 1996); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1279). Services for accessing these data are described at the back of the journal.

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