

Dipotassium di- μ -isothiocyanato- $\kappa^4N:S$ -bis[(*N*-salicylidene-DL-valinato- κ^3O,N,O')cuprate(II)]

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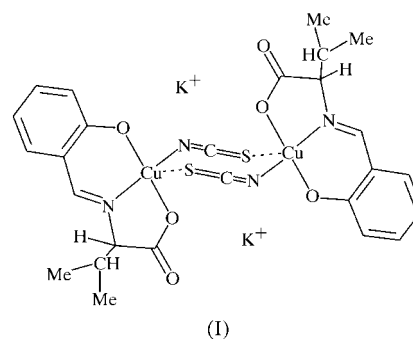
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The title compound, $K_2[Cu_2(NCS)_2(C_{12}H_{13}NO_3)_2]$, consists of two K^+ cations and (*N*-salicylidene-D-valinato)copper(II) and (*N*-salicylidene-L-valinato)copper(II) coordination units connected through three-atom thiocyanate (μ -NCS) bridges into a centrosymmetric dianion. The Cu^{II} atom adopts a square-pyramidal coordination, with three donor atoms of the tridentate Schiff base and one N atom of the bridging ligand (μ -NCS) in the basal plane. The axial position is occupied by the thiocyanate S atom of a symmetry-related ligand at an apical distance of 2.9332 (10) Å. Coulombic interactions between six-coordinated K^+ ions and the heteroatoms of neighbouring dimeric anions leads to the formation of one-dimensional chains of molecules parallel to [010]. The superposition of the normals of the pyramidal base planes in a direction close to [001] indicates possible π - π interactions between neighbouring units.

Comment

Copper(II) complexes of tridentate Schiff bases (TSBs) derived from salicylaldehyde and amino acids are of interest both as simple structural models of more complicated bio-inorganic systems, such as SOD-mimic (SOD is superoxide dismutase; Bergendi *et al.*, 1991; Valentová *et al.*, 1995) or vitamin B6-mimic activities (Metzler *et al.*, 1954; Koh *et al.*, 1996), and for their antimicrobial (Sokolík *et al.*, 1997), antifungal (Švajlenová *et al.*, 2002), antipyretic and immunoprotective activities. Another interesting feature of Cu-TSB complexes is the coordination geometry around the metal ion. If an additional ligand is present, square-pyramidal 4+1 complexes, with an elongated bond distance (up to 3 Å) between the central atom and the donor atom situated at the apex of the pyramid (Friebel *et al.*, 1997), are usually formed, and the resulting units can be further involved in the forma-

tion of dimeric (Pavelčík *et al.*, 1981; Werner *et al.*, 1983; Warda, 1997, 1998a) or even polymeric (Warda, 1998b) structures. The reasons for studying the title derivative, (I), of the (*N*-salicylidene-DL-valinato)copper(II) complex were not only the different magnetic and spectral [UV-vis and electron spin resonance (ESR)] properties of $Cu(sal-DL-val)$ (*sal-DL-val* is *N*-salicylidene-DL-valinate; Švajlenová & Krätzmár-Šmögrovíč, 1978) and dimeric $Cu(sal-L-val)(H_2O)$ (Korhonen & Hämeläinen, 1979), but also the proposed significant biological activities discovered in other Cu-TSB complexes. The spectral and ESR properties of compounds similar to (I) indicate a square-pyramidal environment around the Cu^{II} atom (Kettmann *et al.*, 1989, 1992; Sívý *et al.*, 1990). As a direct proof of this assumption, we report here the crystal structure of (I).



The dimer (I) consists of $[Cu(sal-D-val)(NCS)]$ and $[Cu(sal-L-val)(NCS)]$ coordination units (Fig. 1). The copper ions adopt a 4+1 square-pyramidal geometry, defined by an *O,N,O'*-tridentate *N*-salicylidene-D-valinate (or -L-valinate) dianion and the N atom of the NCS^- ligand in the basal plane (selected geometric parameters are given in Table 1). The apical position is occupied by the S^i atom from a neighbouring molecule, with a $Cu-S^i$ distance of 2.9332 (10) Å [symmetry code: (i) $-x, 1-y, 1-z$]. This length is comparable to the average length (2.88 Å) of this bond in related complexes in

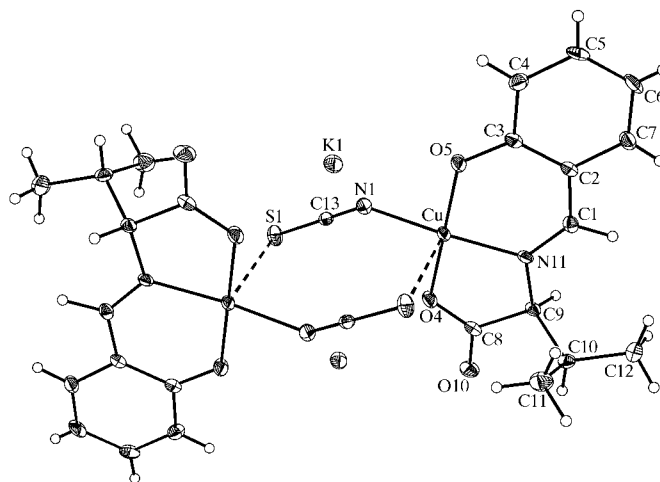


Figure 1
ORTEP (Johnson & Burnett, 1996) plot of the title dimer. Non-H atoms are shown as displacement ellipsoids at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dependent part of the dimer is at the symmetry position ($-x, 1-y, 1-z$).

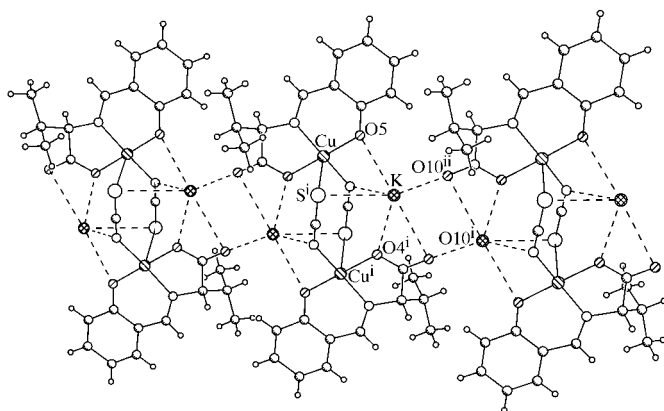


Figure 2
Part of the crystal structure of (I), showing the formation of a molecular chain between K^+ cations and dimeric dianions. [Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $x, y - 1, z$.]

the Cambridge Structural Database (Version 5.24.1; Allen, 2002).

The mean plane through Cu and the four basal atoms shows that the N atom of the NCS⁻ ligand is significantly shifted [deviation of 0.532 (3) Å]. The five-membered chelate ring and the phenyl ring of the sal-val moiety are nearly planar (the average deviations of contributing atoms from the least-squares planes are 0.013 and 0.002 Å, respectively). The six-membered chelate ring is more deformed; atom N11 is displaced by 0.120 (3) Å from the mean plane through the five remaining atoms [their average deviation from the plane is 0.006 Å; the Cremer & Pople (1975) puckering parameters for the ring are $Q = 0.083$ (3) Å, $\theta = 51$ (2)° and $\varphi_2 = 46$ (3)°]. The angle between the planes of the phenyl and six-membered chelate rings and the angle between the planes of the six-membered and five-membered chelate rings are 1.46 (7) and 4.40 (7)°, respectively.

The crystal packing is dominated by Coulomb interactions between the K^+ ions and the heteroatoms of neighbouring dimeric anions, which leads to the formation of one-dimensional chains of molecules in the [010] direction (Fig. 2). The coordination number of the K^+ ion is 6.

The chelate ring system resulting from the TSB coordination could show metalloaromaticity (Masui, 2001) and related interactions. In the crystals of (I), we observed superposition of the normals of the pyramidal base planes, with possible π - π interactions in a direction close to [001].

Experimental

The title compound was prepared according to published patented procedures (Krätšmár-Šmogrovič *et al.*, 1989, 1991). The reaction mixture, composed of Cu(sal-DL-val) (10 mmol, 2.8 g) and KSCN (30 mmol, 2.9 g) dissolved in ethanol/water (2:1 v/v, 50 ml), was heated and mixed vigorously for 20 min until the solid phase disappeared. The solution was filtered and left to cool to room temperature. Dark-green well developed crystals were isolated and analyzed. Analysis (Carlo-Erba 1180 instrument) calculated for $C_{13}H_{13}CuKN_2O_3S$: C 41.09, H 3.45, N 7.37%; found: C 40.71, H 3.40, N 7.38%.

Crystal data

$K_2[Cu_2(NCS)_2(C_{12}H_{13}NO_3)_2]$
 $M_r = 759.0$
Triclinic, $P\bar{1}$
 $a = 8.4753$ (8) Å
 $b = 9.5364$ (8) Å
 $c = 10.1210$ (11) Å
 $\alpha = 76.128$ (8)°
 $\beta = 72.381$ (9)°
 $\gamma = 69.917$ (8)°
 $V = 723.76$ (12) Å³

$Z = 1$
 $D_x = 1.753$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 1760 reflections
 $\theta = 2.9$ – 27.4 °
 $\mu = 1.95$ mm⁻¹
 $T = 120$ (2) K
Prism, dark green
0.50 × 0.20 × 0.20 mm

Data collection

Kuma KM-4-Plus CCD diffractometer
 ω scans
4202 measured reflections
2479 independent reflections
2335 reflections with $I > 2\sigma(I)$

$R_{int} = 0.050$
 $\theta_{max} = 25.0$ °
 $h = -7 \rightarrow 10$
 $k = -10 \rightarrow 11$
 $l = -12 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.112$
 $S = 0.98$
2479 reflections
197 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.075P)^2 + 1.75P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.65$ e Å⁻³
 $\Delta\rho_{min} = -0.82$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu—O5	1.897 (2)	K—N1	2.920 (3)
Cu—N11	1.929 (3)	K—O5	2.970 (2)
Cu—O4	1.938 (2)	S—C13	1.625 (3)
Cu—N1	1.982 (3)	N1—C13	1.164 (4)
Cu—S1 ⁱ	2.9332 (10)	N11—C1	1.286 (4)
O5—Cu—N11	96.19 (11)	C13—N1—Cu	140.3 (3)
O5—Cu—O4	177.31 (10)	C1—N11—Cu	123.6 (2)
N11—Cu—O4	84.05 (10)	N11—C1—C2	125.8 (3)
O5—Cu—N1	90.14 (11)	N11—C9—C10	115.1 (3)
N11—Cu—N1	162.93 (12)	N1—C13—S	179.6 (3)
O4—Cu—N1	88.90 (11)		

Symmetry code: (i) $-x, 1 - y, 1 - z$.

All H atoms were fixed geometrically and refined isotropically. Three free variables were used to describe the U_{iso} values of H atoms during refinement, *viz.* two for H atoms attached to the methyl atoms C11 and C12, and one for H atoms on the aromatic C4, C5, C6 and C7 atoms.

Data collection: *CrysAlis* (Oxford Diffraction, 2002); cell refinement: *CrysRed* (Oxford Diffraction, 2002); data reduction: *CrysRed*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson & Burnett, 1996); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1132). Services for accessing these data are described at the back of the journal.

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