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Poly[(μ_3-*O*-ethyl dithiocarbonato-$\kappa^5O,S:S,S':S'$)-[(1,10-phenanthroline-κ^2N,N')potassium(I)]]

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The title compound, $[\mathrm{K}(\mathrm{C}_3\mathrm{H}_5\mathrm{OS}_2)(\mathrm{C}_{12}\mathrm{H}_8\mathrm{N}_2)]_n$, was prepared from potassium ethylxanthate and 1,10-phenanthroline. A one-dimensional structure is formed *via* coordination to a K^I atom from symmetry-unique and symmetry-related atoms through four S, one O and two N atoms. The coordination geometry is best described as distorted pentagonal–bipyramidal. In the crystal structure, significant π–π stacking interactions connect one-dimensional chains into sheets perpendicular to the *b* axis.

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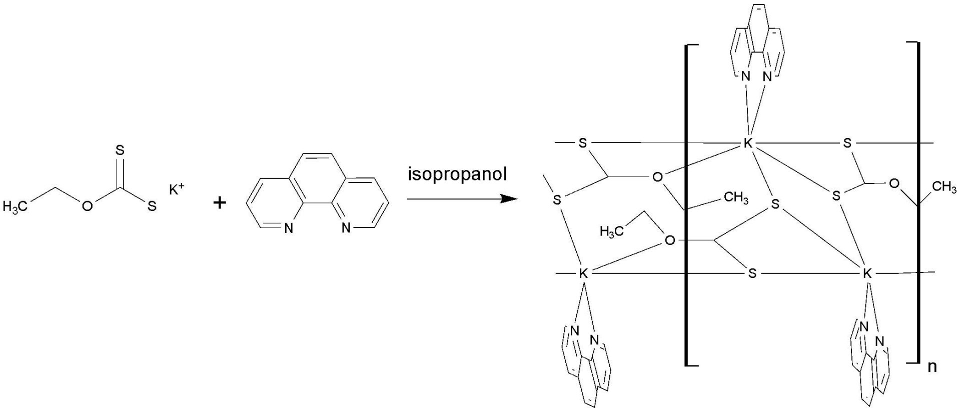
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.005 Å
R factor = 0.054
wR factor = 0.158
Data-to-parameter ratio = 18.1

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

Comment

Among sulfur-containing organic compounds 1,1-dithiolates, which include dithiocarbamates and xanthates, have been used as excellent metal-complexing agents. They have applications as fungicides, pesticides, chelating agents for the removal of heavy metal ions from toxic waste, precursors for metal-organic chemical vapour deposition (MOCVD) and synthesis of semiconductor nanoparticles (Cox & Tiekink, 1999; Nair *et al.* 2002). However, among these dithiolates, xanthate is unique in terms of its ability to form metal complexes of varied structural diversity (Cox & Tiekink, 1999).



(I)

The metal xanthates show remarkable variations in structural motif when compared with the related metal dithiocarbamates (Tiekink, 1987). This arises from the difference in the coordination mode of the two S atoms in these two compounds, xanthate showing diverse coordination modes (Winter, 1980). However, it is also observed that the alkyl group in xanthates and dithiocarbamates plays a crucial role in deciding the structure of the complex molecule. For example, $\mathrm{Hg}(\mathrm{S}_2\mathrm{CO}R)_2$ shows a linear polymeric structure when R = Me, an interconnected two-dimensional 16-membered tetrameric structure when R = Et and a three-dimensional network

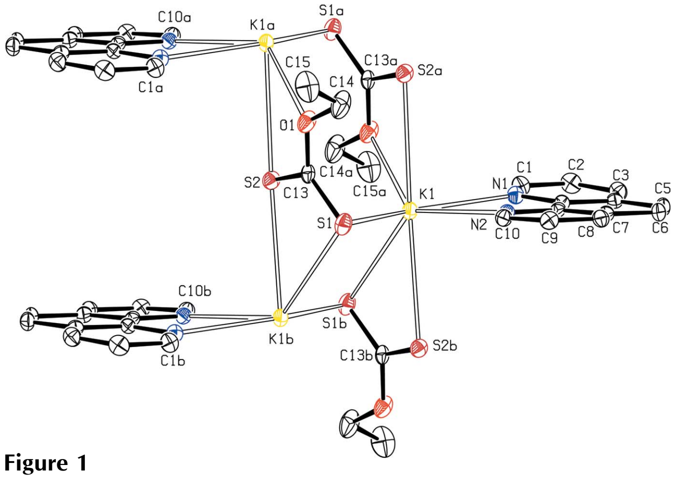


Figure 1
Part of the one-dimensional structure of (I), showing 30% probability displacement ellipsoids (H atoms omitted). Atoms labelled with suffixes 'a' and 'b' are related by the symmetry operators ($-x$, $-y$, $2 - z$) and ($1 - x$, $-y$, $2 - z$), respectively.

structure when $R = i$Pr (Tiekink, 1987; Watanabe, 1977; Chieh & Moynihan, 1980). Potassium ethylxanthate is a starting material for the synthesis of many transition and non-transition metal xanthates, and can be prepared by the reaction of ethanol and CS_2 in the presence of KOH. The title structure, (I), appears to be the first reported of an adduct derived from potassium xanthate and a chelating nitrogen donor.

Part of the polymeric structure of (I) is shown in Fig. 1. A one-dimensional chain is formed, through coordination by symmetry-related atoms (Table 1), where the K^I atom is in a seven-coordinate environment, best described as distorted pentagonal–bipyramidal. Atoms N1 and S1 are in axial positions; atom N2, $O1^i$, $S2^i$, $S1^{ii}$ and $S2^{ii}$ form the equatorial plane (symmetry codes as in Table 1). In the crystal structure, there are significant π–π stacking interactions between the phenanthroline ligands from neighbouring chains (Fig. 2) [where $Cg1\cdots Cg1(-x, -y, 1 - z)$ is 3.5516 (18) Å ($Cg1$ is the centroid defined by atoms N2/C7–C11) with a perpendicular distance of 3.32 Å], connecting chains into sheets perpendicular to the b axis.

Experimental

Potassium ethylxanthate (1.6 g, 10 mmol) was dissolved in 2-propanol (20 ml) by gentle warming and 1,10-phenanthroline monohydrate (3.96 g, 20 mmol) dissolved in 2-propanol (30 ml) was added. The mixture was warmed for about 30 min and allowed to cool slowly. Colourless crystals were obtained from the cold solution and collected by suction filtration.

Crystal data

$[K(C_3H_5OS_2)(C_{12}H_8N_2)]$
$M_r = 340.49$
Triclinic, $P\bar{1}$
$a = 6.7148$ (5) Å
$b = 10.5307$ (7) Å
$c = 12.2614$ (9) Å
$\alpha = 64.580$ (3)°
$\beta = 89.405$ (4)°
$\gamma = 80.336$ (5)°
$V = 770.12$ (10) Å^3
$Z = 2$
$D_x = 1.468$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.62$ mm^{-1}
$T = 150$ (1) K
Needle, colourless
$0.20 \times 0.10 \times 0.08$ mm

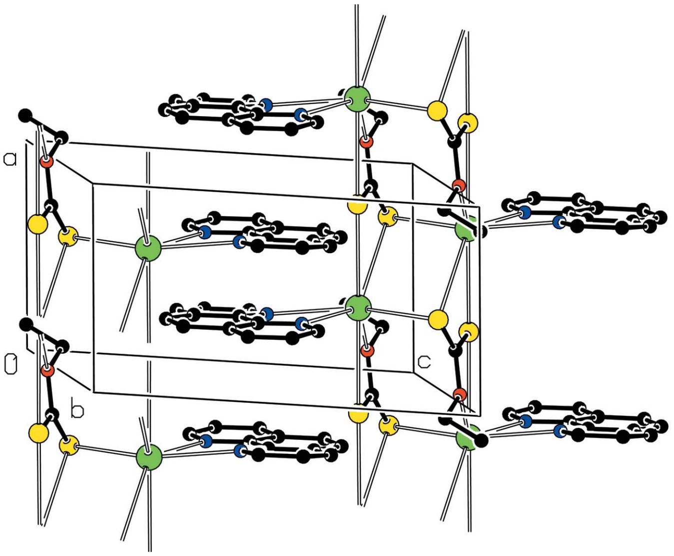


Figure 2
A partial packing plot (Spek, 2003) of (I). H atoms have been omitted.

Data collection

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.542$, $T_{max} = 0.955$
8041 measured reflections
3442 independent reflections
2371 reflections with $I > 2\sigma(I)$
$R_{int} = 0.079$
$\theta_{max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.158$
$S = 1.04$
3442 reflections
190 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0804P)^2 + 0.0809P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

K1—N1	2.837 (2)	K1—$S2^i$	3.3543 (10)
K1—N2	2.849 (2)	K1—$S2^{ii}$	3.3645 (10)
K1—$O1^i$	2.860 (2)	K1—$S1^{ii}$	3.4011 (12)
K1—S1	3.3116 (10)		
N1—K1—N2	57.77 (7)	N2—K1—$S2^{ii}$	84.39 (5)
N1—K1—$O1^i$	88.23 (7)	$O1^i$—K1—$S2^{ii}$	136.51 (5)
N2—K1—$O1^i$	131.57 (7)	S1—K1—$S2^{ii}$	83.74 (2)
N1—K1—S1	143.08 (6)	$S2^i$—K1—$S2^{ii}$	176.02 (3)
N2—K1—S1	85.51 (5)	N1—K1—$S1^{ii}$	105.62 (6)
$O1^i$—K1—S1	117.50 (5)	N2—K1—$S1^{ii}$	133.82 (5)
N1—K1—$S2^i$	84.61 (5)	$O1^i$—K1—$S1^{ii}$	84.81 (5)
N2—K1—$S2^i$	92.25 (5)	S1—K1—$S1^{ii}$	102.86 (2)
$O1^i$—K1—$S2^i$	47.47 (5)	$S2^i$—K1—$S1^{ii}$	131.39 (3)
S1—K1—$S2^i$	93.88 (3)	$S2^{ii}$—K1—$S1^{ii}$	52.44 (2)
N1—K1—$S2^{ii}$	95.36 (6)		

Symmetry codes: (i) $-x, -y, -z + 2$; (ii) $-x + 1, -y, -z + 2$.

H atoms were placed in calculated positions with C—H distances of 0.95 Å (aromatic), 0.99 Å (methylene) or 0.98 Å (for methyl groups). They were included in the refinement in the riding-model approximation with $U_{iso}(H) = 1.2U_{eq}(C)$, or $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms.

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction:

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DENZO-SMN; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 2001); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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