

The diselanylbis(1,3-dimethyl-1*H*-imidazol-3-ium) dication stabilized by the polymeric *catena*-pentachlorido-tricuprate(I) anion

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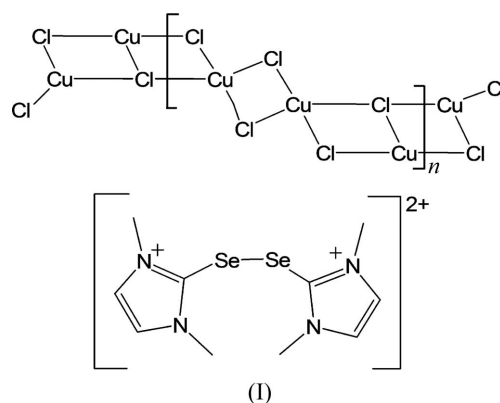
In the title compound, *catena*-poly[diselanylbis(1,3-dimethyl-1*H*-imidazol-3-ium) [μ_3 -chlorido-tetra- μ_2 -chlorido-tricuprate(I)]], $\{(\text{C}_{10}\text{H}_{16}\text{N}_4\text{Se}_2)[\text{Cu}_3\text{Cl}_5]\}_n$, the diselenide dication is stabilized by *catena*- $[\text{Cu}_3\text{Cl}_5]^{2-}$ anions which associate through strong Cu—Cl bonds [average length = 2.3525 (13) Å] to form polymeric chains. The polymeric $[\text{Cu}_3\text{Cl}_5]^{2-}$ anion contains crystallographically imposed twofold rotation symmetry, with distorted trigonal-planar and tetrahedral geometries around the two symmetry-independent Cu atoms. Likewise, the Se—Se bond of the cation is centered on a twofold rotation axis.

Comment

The interactions of selenium- and sulfur-containing compounds with copper have attracted recent interest, since these compounds are potent antioxidants in the prevention of metal-mediated DNA damage (Battin *et al.*, 2006, 2011; Battin & Brumaghim, 2008, 2009; Ramoutar & Brumaghim, 2007; Kimani *et al.*, 2010). Of particular interest is the coordination chemistry of 1,3-dimethylimidazole selone (dmise) and thione (dmit), which are structurally similar to the naturally occurring radical scavengers selenoneine (Yamashita & Yamashita, 2010) and ergothioneine (Ey *et al.*, 2007). Dmise and dmit have been shown to prevent effectively both metal-mediated DNA damage (Akanmu *et al.*, 1991) and peroxynitrite-mediated tyrosine nitration (Bhabak & Mugesh, 2010).

Previous reports indicate that Cu^+ complexes can be prepared *via* reduction of Cu^{2+} salts using different seleno- and thioamide ligands (Battaglia *et al.*, 1979; Hussein *et al.*, 1985; Devillanova *et al.*, 1986; Piro *et al.*, 2000). Additionally, selenium-containing ligands can also be oxidized to form dication salts upon Cu^{2+} reduction (Batchelor *et al.*, 1990). It is also well known that halogens such as diiodine, iodobromide, iodochloride and dibromine (Bigoli, Demartin *et al.*, 1996), and acids such as HCl and HF (Choi *et al.*, 2009), can oxidize dmise to diselenide dications. Because of the importance of

$\text{Cu}^{2+}/\text{Cu}^+$ redox cycling for selenium and sulfur antioxidant activity, we have investigated the ability of dmise and dmit to reduce Cu^{2+} to Cu^+ . Thus, we carried out the reaction of anhydrous CuCl_2 with one molar equivalent of dmise in a mixed-solvent system of ethanol and dichloromethane. In this reaction, reduction of Cu^{2+} to Cu^+ occurs simultaneously with formation of the diselenide dication by dmise oxidation without forming a Cu^+ -dmise complex. Instead, the dmise ligand reacts with CuCl_2 to yield a red-colored solid (66% yield) with a polymeric $[\text{Cu}_3\text{Cl}_5]^{2-}$ dianion and a diselanylbis(1,3-dimethyl-1*H*-imidazol-3-ium) dication, as revealed by X-ray structural analysis of the title compound, (I) (Fig. 1). The structure of (I) is of interest because there are only a limited number of documented metal-organic diselenide salts (Fujihara *et al.*, 1993).



The diselenide dication of (I) sits across a twofold axis and has an Se1—Se1ⁱ [symmetry code: (i) $-x, y, -z + \frac{1}{2}$] bond length of 2.3946 (13) Å. The torsion angle about this bond (C1—Se1—Se1ⁱ—C1ⁱ) is 70.9 (2)°, larger than in similar previously reported diselenide cations, such as $[(\text{C}_5\text{H}_8\text{N}_2-$

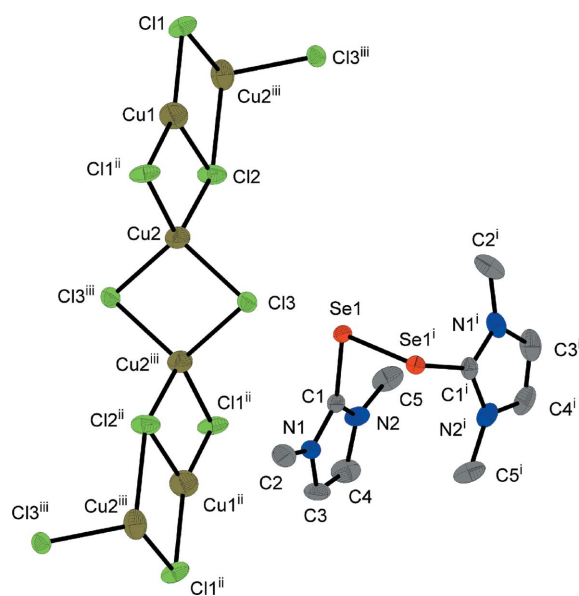


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry codes: (i) $-x, y, -z + \frac{1}{2}$; (ii) $-x + 2, y, -z + \frac{3}{2}$; (iii) $-x + 2, -y, -z + 1$.]

Se)₂]²⁺ (28.6–32.0°; Bigoli, Demartin *et al.*, 1996). The Se–Se bond length is comparable with those found in [[SeC(NH₂)₂]₂]Cl₂ [2.380 (6) Å; Villa *et al.*, 1970], but shorter than in [(C₅H₈N₂Se)₂]Br₂ [2.409 (2) Å], [(C₅H₈N₂Se)₂]I₂ [2.434 (2) Å], [(C₅H₈N₂Se)₂]ClI₃ [2.440 (2) Å], [(C₅H₁₀N₂Se)₂Br](IBr₂) [2.424 (1) Å], [(C₅H₇N₂Se)₂]I₃(I₄)_{0.5} [2.416 (2) Å] (Bigoli, Demartin *et al.*, 1996) and [2(ebis)₂][2(TCNQ)₃] [2.451 (2) Å; TCNQ is tetracyanoquinodimethane and ebis is bis(selenoimidazolyl)ethane; Bigoli, Deplano *et al.*, 1996]. Formation of the diselenide cation results in relatively unchanged Se–C bond lengths [1.884 (5) Å] compared with the unoxidized dmise ligand (1.89 Å; Williams *et al.*, 1993).

The diselenide dication is stabilized by a polymeric chloridocuprate [Cu₃Cl₅]²⁻ dianion (Fig. 1). The [Cu₃Cl₅]²⁻ dianion contains two geometrically different Cu⁺ centers connected by bridging chloride ligands, with rhomboid Cu₂Cl₂ segments linked by CuCl₃ units. Atoms Cu1 and Cl2 lie on a twofold rotational symmetry axis, with the Cu1–Cl2 bond along this axis. Atom Cu1 adopts a distorted trigonal-planar geometry, with an average Cu–Cl bond length of 2.3167 (11) Å, and Cl1–Cu1–Cl1ⁱⁱ, Cl1–Cu1–Cl2 and Cl1ⁱⁱ–Cu1–Cl2 bond angles of 146.13 (10), 106.94 (5), and 106.94 (5)°, respectively [symmetry code: (ii) $-x + 2, y, -z + \frac{3}{2}$]. The second copper center, Cu2, adopts a distorted tetrahedral geometry, with an average Cu–Cl bond length of 2.3883 (15) Å, and Cl1ⁱⁱⁱ–Cu2–Cl2, Cl3–Cu2–Cl1ⁱⁱ, Cl2–Cu2–Cl3ⁱⁱⁱ and Cl3ⁱⁱⁱ–Cu2–Cl3 bond angles of 102.47 (6), 117.47 (6), 109.15 (6) and 101.00 (5)°, respectively [symmetry code: (iii) $-x + 2, -y, -z + 1$]. The Cu–Cl–Cu angles in the chloridocuprate network of complex (I) range from 71.94 (5) to 143.88 (10)°. These angles are similar to those reported for (H₂Pip)[Cu₂Cl₄] (77.53–149.03°; Pip is piperazinium; Kuperstock *et al.*, 2009), but dramatically different from those found in [(C₅H₄NH)NC₄H₈NH(C₃H₅)] [Cu₃Cl₅] (86.6–138.4°; Goreshnik & Myskiv, 2006) and (H₂MePip)[Cu₃Cl₅] (85.94–137.84°; Kuperstock *et al.*, 2009). The distance between the two geometrically different Cu⁺ centers is 2.9201 (12) Å, longer than sum of the van der Waals radii for two Cu atoms (2.80 Å; Bondi, 1964) and indicating no interaction between these ions. The average Cu–Cl bond length of 2.3525 (13) Å in the [Cu₃Cl₅]²⁻ dianion is shorter than those reported in piperazinium chloridocuprates such as (H₂Pip)[Cu₂Cl₄] [2.3805 (10) Å; Kuperstock *et al.*, 2009], but longer than those in (H₂MePip)[Cu₃Cl₅] [2.3194 (10) Å], (H₂Me₂Pip)[Cu₄Cl₆] [2.2936 (5) Å; Kuperstock *et al.*, 2009], [(C₅H₄NH)NC₄H₈NH(C₃H₅)] [Cu₃Cl₅] [2.306 (12) Å; Goreshnik & Myskiv, 2006] and (C₄H₁₂N₂)[Cu₂Cl₄] [2.3194 (10) Å; Redel *et al.*, 2009].

The diselenide dication in the crystal packing of (I) are arranged parallel to each other along the *b* axis ([001] direction), with the [Cu₃Cl₅]²⁻ dianions positioned between the cations (Fig. 2). Such an arrangement leads to the involvement of the Cl atoms in short-contact interactions with Se and H atoms, thereby forming a two-dimensional network. The packing diagram of (I) reveals weak interactions of 3.3826 (16) Å for Se1–Cl1 and 3.0811 (16) Å for Se1–Cl3, shorter than the sum of their van der Waals radii (3.80 Å; Bondi, 1964).

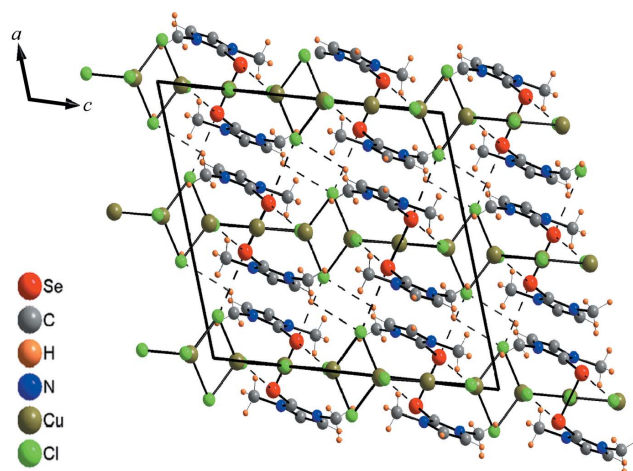


Figure 2
The crystal packing of (I), viewed along the *b* axis, showing the short-contact Se···Cl and H···Cl interactions (dashed lines).

Experimental

1,3-Dimethylimidazole selone (dmise) was synthesized according to the procedure of Roy *et al.* (2007) and CuCl₂ (Alfa Aesar) was used as received. For the synthesis of (I), CuCl₂ (135 mg, 1 mmol) was dissolved in ethanol (15 ml) and to this was added a solution of dmise (175 mg, 1 mmol) in dichloromethane (10 ml) *via* a cannula. Upon addition, the color of the solution changed from light brown to dark brown. The dark-brown reaction mixture was stirred for 6 h, resulting in the formation of a red-brown precipitate. This solid was filtered, dried *in vacuo* and analyzed. Crystals suitable for X-ray diffraction were grown by slow vapor diffusion of ether into an acetonitrile solution [yield 34%, based on dmise (244 mg, 0.341 mmol); m.p. 445 K]. ¹H NMR (*d*₆-DMSO): 3.89 (*s*, 12H, 4 × CH₃), 7.61 (*s*, 4H, 4 × CH); ¹³C NMR (*d*₆-DMSO): 37.02 (CH₃), 125.27 (CH), C–Se (not observed); IR (Nujol, *v*, cm⁻¹): 467 (*w*), 504 (*w*), 660 (*v*), 739 (*v*), 761 (*s*), 1079 (*w*), 1155 (*s*), 1223 (*v*), 1243 (*s*), 1377 (*v*), 1463 (*v*), 1494 (*s*), 1562 (*s*), 2855 (*s*), 2928 (*b*). ESI-MS (CNCH₃, positive ionization): *m/z* 175.9 [(C₅N₂H₈Se₂)₂]²⁺. Analysis calculated for C₁₀H₁₆Cl₅Cu₃N₄Se₂: C 16.73, N 7.80, H 2.25%; found: C 16.71, N 7.97, H 2.35%.

Crystal data

(C ₁₀ H ₁₆ N ₄ Se ₂)[Cu ₃ Cl ₅]	<i>V</i> = 2001.2 (7) Å ³
<i>M_r</i> = 718.06	<i>Z</i> = 4
Monoclinic, <i>C</i> 2/ <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 12.238 (2) Å	<i>μ</i> = 7.47 mm ⁻¹
<i>b</i> = 12.217 (2) Å	<i>T</i> = 168 K
<i>c</i> = 14.123 (3) Å	0.32 × 0.25 × 0.23 mm
<i>β</i> = 108.61 (3)°	

Data collection

Rigaku AFC-8S diffractometer	8327 measured reflections
Absorption correction: multi-scan [REQAB (Jacobson, 1998) and CrystalClear (Rigaku/MS, 2006)]	2022 independent reflections
<i>T</i> _{min} = 0.199, <i>T</i> _{max} = 0.279	1698 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.047

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.044	112 parameters
<i>wR</i> (<i>F</i> ²) = 0.114	H-atom parameters constrained
<i>S</i> = 1.11	Δρ _{max} = 1.22 e Å ⁻³
2022 reflections	Δρ _{min} = -1.12 e Å ⁻³

In the final cycle of least-squares refinement, the H atoms were fixed in idealized positions, with C–H = 0.93 (aromatic) and 0.96 Å (methyl), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic C})$ or $1.5U_{\text{eq}}(\text{methyl C})$. The largest peak in the final difference Fourier map was located 0.11 Å from atom Cl1 and the lowest peak was located 0.73 Å from atom Cu2.

Data collection: *CrystalClear* (Rigaku/MS, 2006); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Version 6.10; Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3080). Services for accessing these data are described at the back of the journal.

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