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(1,3-Dimethylimidazolidine-2-selone- κ Se)bis(1,10-phenanthroline- κ^2 N,N')copper(II) bis(perchlorate) and bis(2,2'-bipyridyl- κ^2 N,N')(imidazolidine-2-thione- κ S)copper(II) bis(perchlorate)

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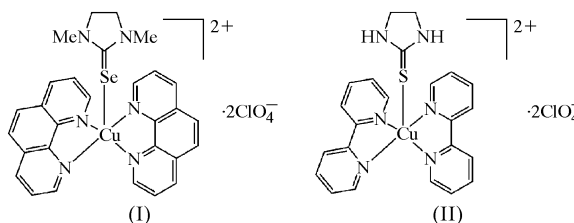
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In the first title salt, [Cu(C₁₂H₈N₂)₂(C₅H₁₀N₂Se)](ClO₄)₂, the Cu^{II} centre occupies a distorted trigonal-bipyramidal environment defined by four N donors from two 1,10-phenanthroline (phen) ligands and by the Se donor of a 1,3-dimethylimidazolidine-2-selone ligand, with the equatorial plane defined by the Se and by two N donors from different phen ligands and the axial sites occupied by the two remaining N donors, one from each phen ligand. The Cu–N distances span the range 1.980 (10)–2.114 (11) Å and the Cu–Se distance is 2.491 (3) Å. Intermolecular π – π contacts between imidazolidine rings and the central rings of phen ligands generate chains of cations. In the second salt, [Cu(C₁₀H₈N₂)₂(C₃H₆N₂S)](ClO₄)₂, the Cu^{II} centre occupies a similar distorted trigonal-bipyramidal environment comprising four N donors from two 2,2'-bipyridyl (bipy) ligands and an S donor from an imidazolidine-2-thione ligand. The equatorial plane is defined by the S donor and two N donors from different bipy ligands. The Cu–N distances span the range 1.984 (6)–2.069 (7) Å and the Cu–S distance is 2.366 (3) Å. Intermolecular π – π contacts between imidazolidine and pyridyl rings form chains of cations. A major difference between the two structures is due to the presence in the second complex of two N–H...O hydrogen bonds linking the imidazolidine N–H hydrogen-bond donors to perchlorate O-atom acceptors.

Comment

Copper plays an important role in redox-active metalloproteins where evidence for metal-sulfur coordination is consistent with a chemical environment favouring the

copper(I) state (Karlin *et al.*, 1982; Lippard & Berg, 1994). Thio- and seleno-amido ligands, –NR–CS(Se)–, react with copper(II) salts yielding S- and Se-bonded copper(I) complexes. In particular, several copper(I) complexes have been prepared and structurally characterized by reacting ligands such as imidazolidine-, thiazolidine-, benzothiazole- and oxazolidine-2-thione, and, when possible, also their 2-selone parent compounds, with Cu^{II} salts (Hussein *et al.*, 1985; Devillanova *et al.*, 1986; Battaglia *et al.*, 1979). One approach to studying the redox and coordination chemistry of Cu^{II} in the presence of soft reducing S- or Se-ketonic donors is to consider complexes of polydentate ligands containing N atoms in which copper is stabilized in the +2 oxidation state (McKee, 1993).



To preserve the Cu^{II} oxidation state in the reaction with thiourea and other reducing ligands, Montenero & Pelizzi (1972) have used as starting materials copper(II)-chelated complexes with π -acceptor ligands, such as 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy). We report here the synthesis and structural characterization of (1,3-dimethylimidazolidine-2-selone- κ Se)bis(1,10-phenanthroline- κ^2 N,N')-copper(II) bis(perchlorate), (I), and bis(2,2'-bipyridyl- κ^2 N,N')(imidazolidine-2-thione- κ S)copper(II) bis(perchlorate), (II).

The Cu^{II} centre in (I) is coordinated in a distorted trigonal-bipyramidal (TBP) environment by four N donors from the two phen ligands and by an Se atom from the dimethylimidazolidine-2-selone ligand (Fig. 1). The equatorial plane is defined by the Se atom and by two N donors (N8A and N8B) from different phen ligands, with angles subtended at Cu1 ranging from 112.5 (3) to 128.8 (3)°. The axial sites are occupied by the two remaining N donors (N1A and N1B) from

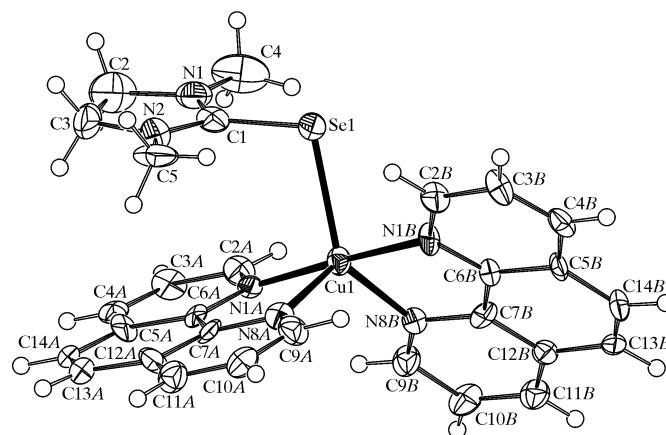


Figure 1
A view of the structure of (I), showing the atom-numbering scheme adopted. The perchlorate anions are not shown. Displacement ellipsoids are drawn at the 50% probability level.

each phen ligand and the N1A—Cu1—N1B angle is 177.6 (5)°. Owing to the narrow bite angle of the phen ligands (*ca* 80°) which bridge pairs of axial and equatorial sites, the N1A—Cu1—N1B vector deviates significantly from orthogonality with the equatorial plane. A TBP coordination geometry is not common in the case of Cu^{II} complexes, particularly when they contain ligands with reducing properties (Barclay *et al.*, 1963; Ferrari *et al.*, 1973, 1975). Thus, (I) represents, to our knowledge, the only case of a structurally characterized Cu^{II} mixed-ligand complex featuring a TBP coordination geometry in which the coordination environment contains an Se donor and chelating ligands such as 1,10-phenanthroline (phen) and 2,2'-bipyridine (bipy) with strong π -conjugation properties.

The Cu—N distances range from 1.980 (10) to 2.114 (11) Å, while the Cu—Se distance is 2.491 (3) Å (Table 1). Each phen ligand participates in one long and one short Cu—N bond to the metal atom, an asymmetry that we attribute to the steric congestion between the two bidentate ligands. This congestion is also expressed in the high degree of twist between the phen units; the dihedral angle between the least-squares mean planes through the five-membered rings Cu1/N1A/C6A/C7A/N8A and Cu1/N1B/C6B/C7B/N8B is 59.6 (3)°. The N—C—C—N torsion angles are essentially zero, indicating that there is no twisting of this unit in either phen ligand. The dihedral angle between the plane through the dimethylimidazolidine-2-selone ring and that through the phen ligand containing atoms N1A and N8A [16.3 (6)°] is much smaller than the corresponding dihedral angle involving the other phen ligand [57.4 (4)°], and therefore only the former is involved in possible π - π stacking with the N1A—C6A ring [the centroid-

centroid distance is 3.506 (10) Å and the perpendicular distance 3.466 (10) Å].

Intermolecular π - π contacts with a centroid-centroid distance of 3.829 (10) Å between the imidazolidine ring in one cation and the central ring (C5B—C7B/C12B—C14B) of the phen ligand in a neighbouring cation at ($\frac{1}{2} + x, \frac{3}{2} - y, -z$)

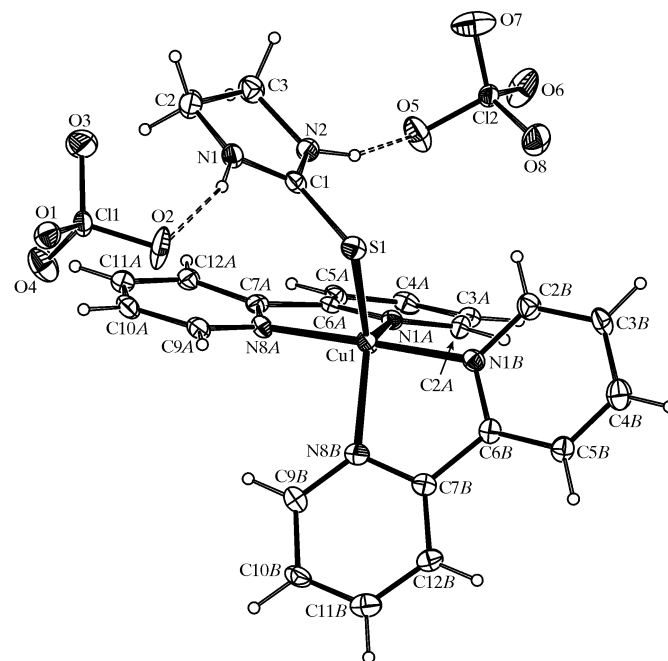


Figure 3
A view of the structure of (II), showing the atom-numbering scheme adopted and the N—H...O hydrogen bonds (dashed lines) between the imidazolidine ring and the perchlorate anions. Displacement ellipsoids are drawn at the 50% probability level.

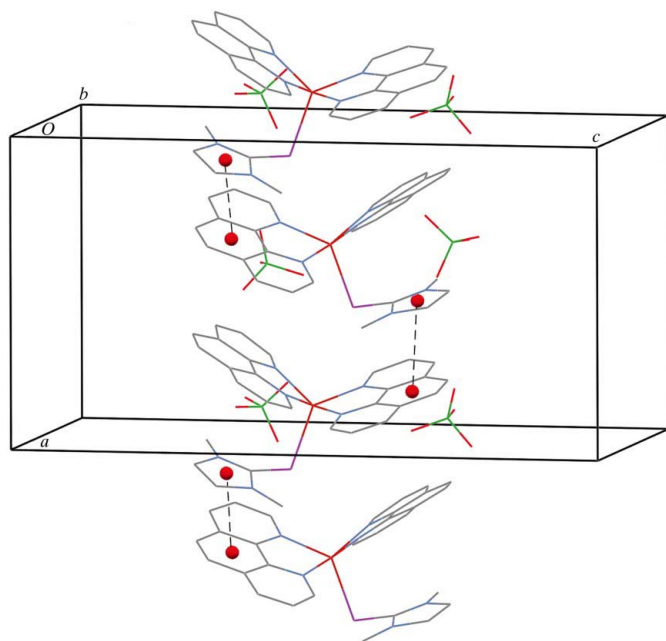


Figure 2
Chains running along the *a* axis in (I) formed *via* intermolecular π - π contacts of 3.829 (10) Å between the imidazolidine ring in one cation and the central ring of the phen ligand.

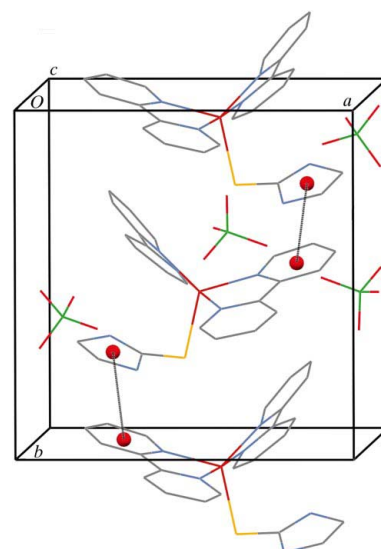


Figure 4
Chains of cations formed along the *b* axis in (II) *via* intermolecular π - π contacts of 3.820 (10) Å between the imidazolidine ring in one cation and a pyridyl ring in a neighbouring cation.

(Fig. 2) give rise to chains running along the *a* axis in (I). The mutual inclination of these rings is only 1.6 (6)° and the perpendicular distance is 3.515 (10) Å.

In (II), the Cu^{II} centre also occupies a distorted TBP environment, similarly consisting of four N donors from two bipy ligands but with the fifth site occupied by an S donor from an imidazolidine-2-thione ligand (Fig. 3). The equatorial plane is defined by coordination from the S atom and atoms N1A and N8B from different bipy ligands; the angles subtended at atom Cu1 occupy a somewhat narrower range between 115.44 (18) and 124.72 (19)°, and the axial donors N1B and N8A subtend an angle of 176.7 (2)° at Cu1. The principal deviation from ideal TBP geometry is the result of the narrow bite angle of the bipy ligand; there is a significant deviation from orthogonality between the equatorial plane and the N1B–Cu1–N8A vector.

The Cu–N distances range from 1.984 (6) to 2.069 (7) Å, while the Cu–S distance is 2.366 (3) Å (Table 2). This latter is of the same order of magnitude as that found in Cu^I-thiourea complexes (Okaya & Knobler, 1964), a feature also observed in Cu^{II}-thiourea complexes containing coordinated bipy or phen-chelating ligands (Ferrari *et al.*, 1973, 1975). This observation suggests charge transfer to the metal centre by the chelating ligands through a π-donor effect. The same pattern of asymmetry seen in (I) appears in the Cu–N distances, and in the twist between the Cu1/N1A/C6A/C7A/N8A and Cu1/N1B/C6B/C7B/N8B rings [61.2 (2)°]. While the N–C–C–N torsion angle in one ligand is essentially zero, as in (I), the value of –7.7 (10)° for N1A–C6A–C7A–N8A indicates a slight twist for the other. There are again marked differences in the dihedral angles between the imidazolidine ring and the five-membered rings formed by the coordination of the two bipy ligands. For the Cu1/N1A/C6A/C7A/N8A ring, this angle is 59.2 (2)°, but the lower value of 30.9 (3)° suggests the possibility of π–π interaction between the imidazolidine and C7A–C12A rings; the relevant centroid–centroid distance is 3.559 (7) Å, the perpendicular distance is 3.455 (7) Å and the rings are mutually inclined at an angle of 24.1 (3)°.

A major difference between the two structures arises from the presence of imidazolidine NH hydrogen-bond donors in (II) instead of the NMe groups in (I). This leads to the formation of two N–H...O hydrogen bonds to perchlorate O atoms (Fig. 3 and Table 3).

The imidazolidine ring and a pyridyl ring in two neighbouring cations related by the symmetry operation (2 – *x*, –½ + *y*, ½ – *z*) are involved in intermolecular π–π contacts, with a centroid–centroid distance of 3.820 (10) Å, forming chains of cations (Fig. 4) running along the *b* axis in (II). The rings are inclined to each other at an angle of only 6.7 (6)° and the perpendicular distance is 3.392 (10) Å.

Experimental

[Cu(phen)₂](ClO₄)₂ and [Cu(bipy)₂](ClO₄)₂ were prepared by reacting Cu(ClO₄)₂ with phen or bipy in a 1:2 molar ratio in ethanol. The products separated out of the reaction mixtures and were washed with ethanol and dried under reduced pressure. For the preparation

of (I), a solution of *N,N'*-dimethylimidazolidine-2-selone (30.0 mg, 0.17 mmol) in MeCN (2 ml) was added dropwise at room temperature to a solution of [Cu(phen)₂](ClO₄)₂ (53.0 mg, 0.085 mmol) in MeCN (3 ml). The colour of the reaction mixture turned green immediately. Crystals of the title compound were obtained by slow evaporation of the solvent (yield 52.0 mg, 76.5%). Analysis found (calculated for C₂₉H₂₆Cl₂CuN₆O₈Se): C 43.20 (43.54), H 3.30 (3.27), N 10.35% (10.50%). For the preparation of (II), a solution of imidazolidine-2-thione (30.0 mg, 0.29 mmol) in MeCN (3 ml) was added dropwise at room temperature to a solution of [Cu(bipy)₂](ClO₄)₂ (83.4 mg, 0.145 mmol) in MeCN (3 ml). The colour of the reaction mixture turned green immediately. Crystals of the title compound were obtained by slow evaporation of the solvent (yield 88.0 mg, 89.6%). Analysis found (calculated for C₂₃H₂₂Cl₂CuN₆O₈S): C 40.60 (40.81), H 3.25 (3.28), N 12.35 (12.41), S 4.52% (4.74%).

Salt (I)

Crystal data

[Cu(C ₁₂ H ₈ N ₂) ₂ (C ₅ H ₁₀ N ₂ Se)]-(ClO ₄) ₂	<i>V</i> = 3120.5 (18) Å ³
<i>M_r</i> = 799.96	<i>Z</i> = 4
Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	Mo <i>K</i> α radiation
<i>a</i> = 11.606 (6) Å	<i>μ</i> = 2.10 mm ^{–1}
<i>b</i> = 12.155 (2) Å	<i>T</i> = 150 (2) K
<i>c</i> = 22.120 (4) Å	0.51 × 0.14 × 0.10 mm

Data collection

Stoe Stadi-4 four-circle diffractometer	2621 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: numerical (<i>X-RED</i> ; Stoe & Cie, 1996)	<i>R</i> _{int} = 0.052
<i>T</i> _{min} = 0.700, <i>T</i> _{max} = 0.830	3 standard reflections
3878 measured reflections	frequency: 60 min
3511 independent reflections	intensity decay: random variation, ±5%

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.074	H-atom parameters constrained
<i>wR</i> (<i>F</i> ²) = 0.144	Δρ _{max} = 0.80 e Å ^{–3}
<i>S</i> = 1.23	Δρ _{min} = –0.67 e Å ^{–3}
3511 reflections	Absolute structure: Flack (1983),
427 parameters	780 Friedel pairs
147 restraints	Flack parameter: 0.41 (3)

Table 1

Selected geometric parameters (Å, °) for (I).

Cu1–N1A	1.980 (10)	Cu1–N8A	2.114 (11)
Cu1–N1B	1.999 (10)	Cu1–Se1	2.491 (3)
Cu1–N8B	2.080 (10)		
N1A–Cu1–N1B	177.6 (5)	N8B–Cu1–N8A	118.5 (4)
N1A–Cu1–N8B	97.4 (4)	N1A–Cu1–Se1	93.4 (3)
N1B–Cu1–N8B	81.6 (4)	N1B–Cu1–Se1	88.9 (3)
N1A–Cu1–N8A	81.4 (4)	N8B–Cu1–Se1	128.8 (3)
N1B–Cu1–N8A	97.1 (4)	N8A–Cu1–Se1	112.5 (3)

Salt (II)

Crystal data

[Cu(C ₁₀ H ₈ N ₂) ₂ (C ₃ H ₆ N ₂ S)](ClO ₄) ₂	<i>V</i> = 2749 (3) Å ³
<i>M_r</i> = 676.97	<i>Z</i> = 4
Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	Mo <i>K</i> α radiation
<i>a</i> = 11.493 (7) Å	<i>μ</i> = 1.12 mm ^{–1}
<i>b</i> = 11.861 (9) Å	<i>T</i> = 150 (2) K
<i>c</i> = 20.166 (10) Å	0.54 × 0.27 × 0.18 mm

Data collection

Stoe Stadi-4 four-circle diffractometer	3420 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (<i>X-RED</i> ; Stoe & Cie, 1996)	$R_{\text{int}} = 0.024$
$T_{\text{min}} = 0.747$, $T_{\text{max}} = 0.840$	3 standard reflections
4959 measured reflections	frequency: 60 min
3932 independent reflections	intensity decay: random variation, $\pm 6\%$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.061$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.164$	$\Delta\rho_{\text{max}} = 1.18 \text{ e } \text{\AA}^{-3}$
$S = 1.01$	$\Delta\rho_{\text{min}} = -0.56 \text{ e } \text{\AA}^{-3}$
3932 reflections	Absolute structure: Flack (1983), 1186 Friedel pairs
377 parameters	Flack parameter: 0.00 (3)
2 restraints	

Table 2

Selected geometric parameters (\AA , $^\circ$) for (II).

Cu1—S1	2.366 (3)	Cu1—N8A	1.995 (6)
Cu1—N1A	2.057 (7)	Cu1—N8B	2.069 (7)
Cu1—N1B	1.984 (6)		
S1—Cu1—N1A	124.72 (19)	N1A—Cu1—N8A	79.9 (3)
S1—Cu1—N1B	89.35 (18)	N1A—Cu1—N8B	119.8 (2)
S1—Cu1—N8A	93.73 (18)	N1B—Cu1—N8A	176.7 (2)
S1—Cu1—N8B	115.44 (18)	N1B—Cu1—N8B	80.6 (3)
N1A—Cu1—N1B	97.3 (3)	N8A—Cu1—N8B	99.2 (3)

Table 3

Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O2	0.90 (5)	2.05 (7)	2.913 (11)	160 (7)
N2—H2 \cdots O5	0.90 (4)	2.11 (7)	2.878 (10)	143 (7)

NH and NMe hydrogens were located in difference Fourier syntheses. The NH hydrogens were then refined subject to an N—H distance restraint of 0.90 (2) \AA and with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{N})$; NMe hydrogens were refined as part of a rigid rotating group, with $U_{\text{iso}}(\text{H})$ values of $1.5U_{\text{eq}}(\text{C})$. All other H atoms were included in calculated positions and refined using a riding model, with $U_{\text{iso}}(\text{H})$

values of $1.2U_{\text{eq}}(\text{C})$. Similarity restraints were applied to the Cl—O distances in (I). The intermediate value of 0.41 (3) for the Flack parameter of (I) suggests that the crystal selected was a racemic twin with approximately equal amounts of each twin component.

For both compounds, data collection: *STADI4* (Stoe & Cie, 1996); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004), *PLATON* (Spek, 2003) and *pubCIF* (Westrip, 2007).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3135). Services for accessing these data are described at the back of the journal.

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