CHEMISTRY LETTERS, pp. 355-358, 1990.

Crystal Structure and Properties of $[NMe_4]_2[Cu(C_3Se_5)_2]\cdot 2MeCN$

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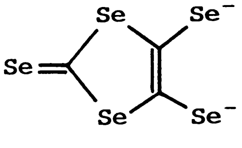
An X-ray crystal structure analysis of the title complex has revealed that the $CuSe_4$ geometry around the copper(II) ion is greatly distorted from a square-planar one, with a dihedral angle of 53.7° between the two diselenolato ligand planes and that the anion moieties are arranged with some Se-Se contacts to form a two-dimensional molecular sheet. The complex behaves as a semiconductor.



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Several dmit-metal complexes (dmit = 4,5-dimercapto-1,3-dithiole-2-thionate) exhibit metallic[1)] and superconductive behaviors.[2-4)] The selenium analog of the dmit ligand, 4,5-diselenolato-1,3-diselenole-2-selonate (**A**), attracts much attention from the standpoint that its metal complexes may be good electrical conductors with effective conduction pathways through selenium-selenium contacts in the crystal phase. However, there have been very few reports on $C_3Se_5{}^{2-}$-metal complexes[5,6)] and only $[PPh_4]_2[Zn(C_3Se_5)_2]$ was clarified crystallographically.[6)] In the course of studies of $C_3Se_5{}^{2-}$-metal complexes,[6,7)] we have found an unusual nonplanar geometry of the $[Cu(C_3Se_5)_2]^{2-}$ anion with a large dihedral angle between the ligand planes. This paper reports the crystal structure and electrical properties of the title complex.

4,5-Bis(benzoylseleno)-1,3-diselenole-2-selone[8)] prepared from $[PPh_4]_2$-$[Zn(C_3Se_5)_2]$[6)] was dissolved into an methanol solution containing 2.5 molar amounts of sodium metal. To the solution was added an excess amount of N-ethylpyridinium(epy) perchlorate or tetramethylammonium bromide, followed by addition of a methanol solution of one molar dichlorocopper(II). Black solids which precipitated immediately were recrystallized from acetonitrile to afford black

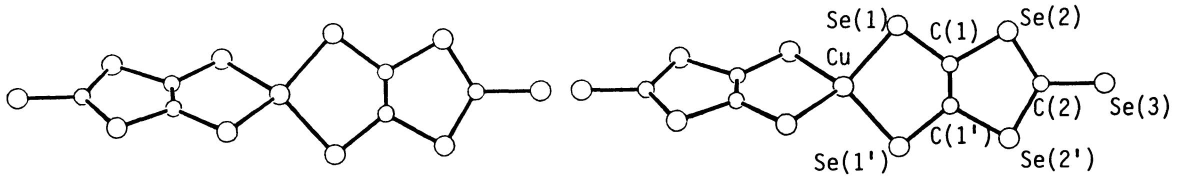

Fig. 1. Stereoview of molecular geometry of the $[Cu(C_3Se_5)_2]^{2-}$ anion Relevant bond distances and angles: Cu-Se(1), 2.366(3); Se(1)-C(1), 1.90(3); Se(2)-C(1), 1.95(3); Se(2)-C(2), 1.81(2); Se(3)-C(2),1.89(4); C(1)-C(1'), 1.21(4) Å, Se(1)-Cu-Se(1'), 95.6(1); Cu-Se(1)-C(1), 94.9(9); Se(1)-C(1)-C(1'), 127(2); Se(1)-C(1)-Se(2),114(2); C(1)-Se(2)-C(2), 93(1); Se(2)-C(2)-Se(2'), 117(2)°.

crystals of $[epy]_2[Cu(C_3Se_5)_2]\cdot MeCN$ and $[NMe_4]_2[Cu(C_3Se_5)_2]\cdot 2MeCN$ (yield, 65 and 70%, respectively). The crystal structure of the latter complex was determined by a single crystal X-ray analysis. Crystal data: $C_{18}H_{30}N_4CuSe_{10}$, M = 1155.60, orthorhombic, space group Ibam, a = 10.289(3), b = 23.367(6), c = 15.519(7) Å, U = 3731(2) $Å^3$, Z = 4, D_c = 2.057(1) g cm^{-3}. Intensity data ($2\theta < 50°$) were collected on a Rigaku four-circle diffractometer using graphite-monochromated Mo-Kα radiation and a ω-2θ scan technique and absorption correction was made. Block-diagonal least-squares refinement based on 704 independent reflections with $|F_o| > 3\sigma(F)$ yielded an R factor of 0.065.

Figure 1 shows the geometry of the $[Cu(C_3Se_5)_2]^{2-}$ anion, together with relevant atomic bond distances and angles. The copper atom as well as C(2) and Se(3) is located on the C_2 axis and is coordinated by four equivalent selenium atoms. The anion exhibits a pronounced nonplanar geometry with a dihedral angle of 53.7° between the least-squares planes of the two ligands. This is very uncommon since bis(dithiolato)- and bis(diselenolato)metal complexes usually assume planar structures,$^{9)}$ although very few bis(diselenolato)metal complexes have been analyzed crystallographically.$^{10-12)}$ The present finding is very close to the unusual nonplanar geometry around the copper(II) ion with a dihedral angle of 57.3° between the dithiolato ligand planes observed for $[epy]_2[Cu(dmit)_2]$.$^{13)}$ Another example of nonplanar CuS_4 geometry is $[mb]_2[Cu(C_4N_2S_2)_2](acetone)$ [mb = the methylene blue cation, 3,7-bis(dimethylamino)phenothiazin-5-ium; $C_4N_2S_2{}^{2-}$ = 1,2-dicyanoethylene-1,2-dithiolato(2-)]: the dihedral angle between the two ligand planes is 47.3°.$^{14)}$ Thus, divalent dithiolato and diselenolato ligands are possibly able to form a nonplanar geometry around the copper(II) ion greatly distorted from the planarity, avoiding some repulsion among the negatively charged

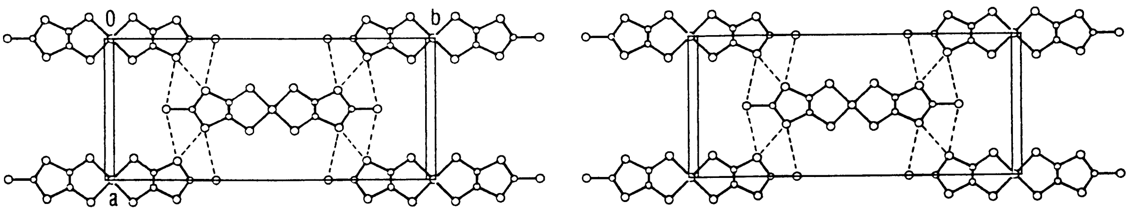

Fig. 2. Stereoscopic packing diagram of the $[Cu(C_3Se_5)_2]^{2-}$ anion moieties projected along the c axis: dashed lines indicate Se-Se contacts within the sum of van der Waals radii of selenium (3.47-3.92 Å).

sulfur or selenium atoms of the ligands.

The Cu-Se distance of the present complex is longer than the Cu-S distance [av. 2.272(3) Å] for the $[Cu(dmit)_2]^{2-}$ anion.$^{13)}$ This difference comes mainly from a larger atomic covalent radius of selenium (1.17 Å) than sulfur (1.04 Å).$^{15)}$ However, the difference (0.09 Å) between the Cu-Se and Cu-S distances is somewhat smaller than that (0.17 Å) between the Se(1)-C(1) distance [1.90(3) Å] and the corresponding S-C one [av. 1.729(9) Å] of the $[Cu(dmit)_2]^{2-}$ anion,$^{13)}$ which may suggest that the Cu-Se bond is of higher order than the Cu-S.

Figure 2 shows the molecular packing of the anion moieties projected along the c axis. The anions, in which the copper atoms are located on the (0,0,1/4) and on (1/2,1/2,1/4), interact with each other through selenium-selenium contacts (3.47-3.92 Å) within the sum of van der Waals radius of selenium, forming a two-dimensional sheet of interacting anions parallel to the ab plane. The tetramethylammonium cations and acetonitrile molecules are alternatively arranged along the b axis strictly midway between the sheets.

$[epy]_2[Cu(C_3Se_5)_2]\cdot MeCN$ and $[NMe_4]_2[Cu(C_3Se_5)_2]\cdot 2MeCN$ behave as semiconductors with electrical conductivities of 1.2×10^{-7} and 7.1×10^{-7} S cm^{-1}, respectively (measured at 25°C for compacted pellets), which seem to arise from conduction pathways constructed with the above-mentioned sheet. This finding is compared with the fact that in $[epy]_2[Cu(dmit)_2]$ the anion moieties have a one-dimensional chain arrangement with weak sulfur-sulfur contacts, exhibiting a conductivity of 7.1×10^{-10} S cm^{-1}.$^{13)}$

Further studies of structures and properties of several $C_3Se_5{}^{2-}$-metal complexes are in progress.

This work has been partially supported by an Izumi Research Grant, for which we thank Izumi Science and Technology Foundation.

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(Received November 20, 1989)