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Structure of Tetrakis(tetraethylammonium) Hexakis(1,1-dicyanoethylene-2,2-diselenolato-*Se*,*Se′*)octacuprate

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Abstract. $[(C_2H_5)_4N]_4[Cu_8\{Se_2C{=}C(CN)_2\}_6]$, $4C_8H_{20}N^+.C_{24}N_{12}Cu_8Se_{12}^{4-}$, $M_r = 2433{\cdot}3$, monoclinic, $P2_1/c$, $a = 14{\cdot}830\,(2)$, $b = 17{\cdot}690\,(3)$, $c = 16{\cdot}040\,(3)$ Å, $\beta = 100{\cdot}61\,(4)^\circ$, $V = 4136{\cdot}0\,(7)$ Å^3, $Z = 2$, $D_x = 1{\cdot}954$ Mg m^{-3}, $\lambda(\text{Ag } K\alpha) = 0{\cdot}5597$ Å, $\mu = 4{\cdot}68$ mm^{-1}, $F(000) = 2336$, $T = 298$ K, $R = 0{\cdot}056$ for 3844 observed reflections. The title compound is isostructural with the corresponding sulfur ligand compound $[(C_2H_5)_4N]_4[Cu_8\{S_2C{=}C(CN)_2\}_6]$ and consists of a distorted cube of Cu atoms with an average Cu—Cu distance of 2·842 Å. The diselenolate ligands are directed perpendicular to the Cu_8 cube faces and are bridged *via* the Se_2C-bite to each of two parallel Cu—Cu edges with an average Cu—Se distance of 2·371 Å.

Introduction. In recent years, extensive studies have been carried out on compounds containing Cu_8S_{12} cores with 1,1- or 1,2-disulfur ligands (Hollander & Coucouvanis, 1977; Dietrich, Storck & Manecke, 1981). The first compound with 1,1-dicyanoethylene-2,2-dithiolate (*iso*-maleonitriledithiolate, *i*-mnt), was published as $(Pr_4N)_2[Cu_4(i\text{-mnt})_3]$ (Fackler & Coucouvanis, 1966) but the X-ray crystal structure analysis revealed the existence of a $[Cu_8(i\text{-mnt})_6]^{4-}$ anion (McCandlish, Bissell, Coucouvanis, Fackler & Knox, 1968). Up to now, there is no information about structural changes introduced by selenium substitution for sulfur in the ligands. In the present paper we describe the results of the X-ray crystal structure analysis of the compound $(Et_4N)_4[Cu_8(i\text{-mns})_6]$ with the 1,1-dicyanoethylene-2,2-diselenolate ligand (*i*-mns).

Experimental. The compound $(Et_4N)_4[Cu_8(i\text{-mns})_6]$ was prepared by adding an aqueous solution of Et_4NBr and $K_2(i\text{-mns})$ (Jensen & Henriksen, 1970) to a solution of $[Cu(CH_3CN)_4]ClO_4$ in acetonitrile at room temperature. Recrystallization from acetone–water gave grey lustrous single crystals suitable for X-ray structure determination.

Crystal 0·06 × 0·07 × 0·09 mm. Precession photographs showed monoclinic crystal system with Laue class $2/m$, systematic extinctions $h0l$, $l = 2n + 1$, $0k0$, $k = 2n + 1$, space group $P2_1/c$. Intensities were measured on a Philips PW1100 diffractometer equipped with graphite-monochromated Ag $K\alpha$ radiation. Cell dimensions based on 82 reflections with $7 \le \theta \le 15^\circ$. 12 100 reflections were recorded over the range $3 \le \theta \le 18^\circ$ with h: $-16\rightarrow16$, k: $-19\rightarrow19$, l: $0\rightarrow17$, ω-scan mode was used with scan width $(1{\cdot}00 + 0{\cdot}2\tan\theta)^\circ$. Three orientation and intensity control reflections were checked every 100 reflections and showed no significant variation.

Correction for Lorentz and polarization effects. Structure solved by direct methods (*SHELXS*86; Sheldrick, 1986). 5795 symmetry independent (unique) reflections ($R_{\text{int}} = 0{\cdot}046$), 3844 observed reflections $[F_{\text{obs}} > 5\sigma(F)]$ in blocked full-matrix least-squares refinement (*SHELX*76; Sheldrick, 1976). 466 parameters. H atoms geometrically fixed with common isotropic temperature factor. $\sum||F_o| - |F_c||^2$ minimized; unit weights, $(\Delta/\sigma)_{\max} = 0{\cdot}109$, $(\Delta/\sigma)_{\min} = 0{\cdot}000$, $(\Delta/\sigma)_{\text{av}} = 0{\cdot}007$, $\Delta\rho = 0{\cdot}63$ e Å^{-3}. Final refinement converged to $R = 0{\cdot}056$, $wR = 0{\cdot}053$. Scattering factors, f' and f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final atomic parameters are given in Table 1,† and selected distances and angles of the Cu_8Se_{12} cluster in Table 2. Table 3 lists details of the

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† Lists of structure factors, anisotropic thermal parameters, full bond lengths and angles including those for H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54171 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic coordinates and equivalent isotropic temperature factors* (× 10^4) *of the non*-H *atoms with e.s.d.'s in parentheses*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$(Å^2)
Cu(1)	9230 (1)	8843 (1)	4354 (1)	521 (2)
Cu(2)	8784 (1)	332 (1)	3777 (1)	512 (2)
Cu(3)	1195 (1)	9206 (1)	4535 (1)	488 (2)
Cu(4)	726 (1)	664 (1)	3988 (1)	498 (2)
Se(11)	505 (1)	8007 (1)	4651 (1)	444 (2)
Se(12)	509 (1)	8554 (1)	6642 (1)	472 (2)
C(11)	671 (10)	7801 (8)	5835 (9)	398 (10)
C(12)	942 (11)	7093 (8)	6123 (9)	500 (10)
C(13)	1050 (12)	6486 (9)	5545 (10)	595 (10)
C(14)	1099 (15)	6882 (10)	7008 (13)	864 (11)
N(11)	1110 (12)	5991 (8)	5115 (10)	835 (11)
N(12)	1193 (15)	6709 (1)	7698 (12)	1266 (11)
Se(21)	8023 (1)	8729 (1)	5138 (1)	493 (2)
Se(22)	7489 (1)	492 (1)	4440 (1)	498 (2)
C(21)	2865 (10)	530 (8)	5306 (9)	464 (10)
C(22)	3752 (11)	708 (10)	5470 (10)	614 (10)
C(23)	9056 (14)	3553 (12)	292 (13)	907 (11)
C(24)	9448 (13)	4787 (12)	863 (12)	783 (11)
N(21)	9338 (13)	2973 (11)	128 (12)	1223 (11)
N(22)	9958 (13)	4817 (11)	8838 (11)	934 (11)
Se(31)	8811 (1)	9238 (1)	2919 (1)	439 (2)
Se(32)	1057 (1)	9649 (1)	3121 (1)	484 (2)
C(31)	9922 (1)	9305 (8)	2503 (9)	545 (10)
C(32)	90 (11)	922 (10)	8343 (10)	610 (10)
C(33)	886 (15)	1214 (13)	8856 (13)	862 (11)
C(34)	692 (15)	9121 (13)	1272 (13)	881 (11)
N(31)	6532 (15)	3508 (13)	4277 (14)	1410 (12)
N(32)	1369 (14)	9137 (13)	1000 (12)	1254 (11)
N(4)	7421 (10)	3041 (9)	7011 (9)	769 (10)
C(41)	7271 (17)	2335 (13)	6427 (14)	1077 (11)
C(42)	6757 (18)	1705 (15)	6889 (18)	1318 (12)
C(43)	6539 (15)	3327 (14)	7174 (15)	1183 (11)
C(44)	5809 (16)	3531 (14)	6386 (15)	1148 (12)
C(45)	7835 (17)	3596 (14)	6439 (15)	1153 (11)
C(46)	8063 (16)	4371 (13)	6902 (15)	1111 (11)
C(47)	8035 (16)	2891 (14)	7820 (14)	1074 (11)
C(48)	9039 (15)	2710 (14)	7784 (15)	1150 (11)
N(5)	1862 (10)	3842 (7)	6173 (9)	540 (9)
C(51)	2838 (19)	3719 (16)	6216 (18)	1214 (12)
C(52)	3375 (18)	4239 (16)	5997 (16)	1217 (12)
C(53)	1359 (19)	3972 (17)	5301 (17)	1301 (12)
C(54)	1494 (16)	3504 (14)	4601 (15)	992 (11)
C(55)	1744 (19)	4540 (15)	6700 (17)	1295 (11)
C(56)	755 (17)	4712 (15)	6779 (16)	1298 (12)
C(57)	1486 (19)	3151 (15)	6535 (17)	1219 (12)
C(58)	1702 (17)	3018 (14)	7486 (15)	1150 (12)

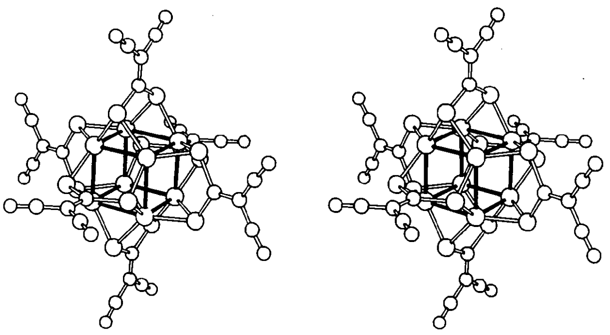
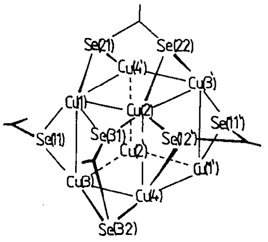


Fig. 1. *SCHAKAL* (Keller, 1990) drawing of the $[Cu_8(i\text{-mns})_6]^{4-}$ complex anion.

$[Se_2C{=}C(CN)_2]^{2-}$ ligand geometry. The molecular structure of the $[Cu_8(i\text{-mns})_6]^{4-}$ anion has point symmetry C_1 while the idealized point symmetry is T_h (Fig. 1).

Table 2. *Selected distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses for the* Cu_8Se_{12} *polyhedron*

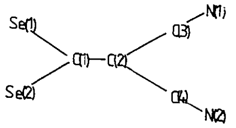


Cu(1)—Cu(2)	2·830 (3)	Cu(2)—Se(12)	2·386 (3)
Cu(1)—Cu(3)	2·945 (2)	Cu(2)—Se(22)	2·378 (2)
Cu(1)—Cu(4′)	2·788 (3)	Cu(2)—Se(31)	2·379 (3)
Cu(2)—Cu(3′)	2·823 (3)	Cu(3)—Se(11)	2·377 (3)
Cu(2)—Cu(4)	2·898 (2)	Cu(3)—Se(32)	2·373 (2)
Cu(3)—Cu(4)	2·771 (3)	Cu(3)—Se(22$^{\rm i}$)	2·371 (2)
Cu(1)—Se(11)	2·379 (2)	Cu(4$^{\rm i}$)—Se(12)	2·368 (2)
Cu(1)—Se(21)	2·378 (2)	Cu(4$^{\rm i}$)—Se(21$^{\rm i}$)	2·367 (2)
Cu(1)—Se(31)	2·376 (2)	Cu(4$^{\rm i}$)—Se(32)	2·377 (3)

Cu(4$^{\rm i}$)—Cu(1)—Cu(2)	89·07 (7)	Cu(2$^{\rm i}$)—Cu(3)—Cu(1)	89·67 (7)
Cu(4$^{\rm i}$)—Cu(1)—Cu(3)	89·36 (6)	Cu(3)—Cu(4)—Cu(1$^{\rm i}$)	91·64 (7)
Cu(2)—Cu(1)—Cu(3)	89·81 (7)	Cu(3)—Cu(4)—Cu(2)	91·95 (7)
Cu(3$^{\rm i}$)—Cu(2)—Cu(1)	89·72 (7)	Cu(1$^{\rm i}$)—Cu(4)—Cu(2)	91·32 (7)
Cu(3$^{\rm i}$)—Cu(2)—Cu(4)	89·63 (6)	Cu(1)—Se(11)—Cu(3)	76·52 (8)
Cu(1)—Cu(2)—Cu(4)	89·02 (6)	Cu(2)—Se(12)—Cu(4)	75·10 (7)
Cu(4)—Cu(3)—Cu(2$^{\rm i}$)	89·55 (7)	Cu(1)—Se(21)—Cu(4$^{\rm i}$)	71·96 (7)
Cu(4)—Cu(3)—Cu(2$^{\rm i}$)	89·55 (7)	Cu(2)—Se(22)—Cu(3$^{\rm i}$)	72·94 (7)
Cu(4)—Cu(3)—Cu(1)	89·21 (6)	Cu(3)—Se(32)—Cu(4)	71·39 (8)

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

Table 3. *Selected distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses as well as maximum deviations from mean planes for the selenolate ligands i-mns* (i) (i = 1,2,3)



	1	2	3
C(i1)—Se(i1)	1·90 (1)	1·90 (1)	1·89 (2)
—Se(i2)	1·90 (2)	1·95 (2)	1·89 (2)
—C(i2)	1·37 (2)	1·33 (2)	1·42 (2)
C(i2)—C(i3)	1·44 (2)	1·42 (3)	1·41 (3)
—C(i4)	1·44 (3)	1·41 (3)	1·41 (3)
C(i3)—N(i1)	1·13 (2)	1·16 (3)	1·18 (3)
C(i4)—N(i2)	1·14 (3)	1·16 (3)	1·17 (3)
Se(i1)—C(i1)—Se(i2)	122·4 (7)	122·6 (8)	125·8 (9)
Se(i1)—C(i1)—C(i2)	119 (1)	120 (1)	118 (1)
Se(i2)—C(i1)—C(i2)	119 (1)	118 (1)	116 (1)
C(i1)—C(i2)—C(i3)	122 (1)	121 (2)	122 (2)
C(i1)—C(i2)—C(i4)	124 (1)	124 (2)	123 (2)
C(i3)—C(i2)—C(i4)	115 (1)	115 (2)	116 (2)
C(i2)—C(i3)—N(i1)	177 (2)	177 (2)	177 (2)
C(i2)—C(i4)—N(i2)	177 (2)	177 (2)	176 (2)
$\Delta_{\rm max}$	0·08 (2)	0·12 (2)	0·12 (2)

The Cu—Cu distances (Hall & Stewart, 1988) within the Cu_8 cube vary between 2·771 and 2·945 Å and are similar to values in the corresponding dithiolato complex $[Cu_8(i\text{-mnt})_6]^{4-}$ (Hanhui & Xiufen, 1989). Each Cu atom is linked to the Se atoms of three different *i*-mns ligands. No significant variations from the average Cu—Se distance of 2·376 Å is

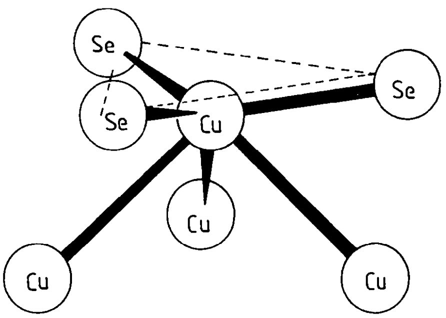


Fig. 2. Coordination of one Cu atom in the $[Cu_8(i\text{-mns})_6]^{4-}$ complex anion.

observed and the Se atoms form an equilateral triangle with the Cu atom nearly in the plane (av. = 0·73 Å; Fig. 2). The average Cu—Se bond is longer by 0·13 Å than the mean Cu—S value in $(Et_4N)_4[Cu_8(i\text{-mnt})_6]$ (Hanhui & Xiufen, 1989). However, this lengthening is expected on the basis of the different covalent radii of Se and S (1·17 and 1·04 Å, respectively) (Pauling, 1960). The selenolate ligands are directed perpendicular to the rectangular faces of the Cu_8 cube and are bridged to each of two parallel Cu—Cu edges. The values for the Se—C bonds lie in the narrow range 1·89–1·95 Å, which agrees well with the values published before, and seems to be normal for a Se—C(sp^2) distance (Bonamico & Dessy, 1971). Although bond lengths for C(2)—C(3) and C(2)—C(4), are close to 1·42 Å which is the value for a C_{sp^2}—C_{sp} bond with a bond order of 4/3 (Bent, 1961), the values for the central C—C bond vary considerably. In *i*-mns (1) and *i*-mns (2) the values are 1·37 and 1·33 Å, respectively, which are close to localized C—C double bonds without any resonance contribution, while in *i*-mns (3) a typical mesomeric value of 1·42 Å is observed (Bent, 1961). Similar differences in bond lengths for diselenolate ligands *i*-mns have been mentioned recently for the structure of $(Et_4N)[TcO\{Se_2C{=}C(CN)_2\}_2]$ (Bandoli, Mazzi, Abram, Spies & Münze, 1987), while in $[As(C_6H_5)_4]_2[Ni^{IV}\{Se_2C{=}C(CN)_2\}_3]$ the value for three crystallographically different ligands is 1·36 (3) Å (Kaiser, Dietzsch, Richter, Golič & Šiftar, 1980).

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Bis(cyclopentadienyl)bis(*m*-methoxybenzoato)titanium(IV)

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Abstract. $[Ti(C_8H_7O_3)_2(C_5H_5)_2]$, $M_r = 480{\cdot}4$, monoclinic, $P2_1/n$, $a = 15{\cdot}739\ (5)$, $b = 7{\cdot}466\ (1)$, $c = 20{\cdot}286\ (5)$ Å, $\beta = 97{\cdot}21\ (2)°$, $V = 2364{\cdot}9\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}349$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}39$ mm^{-1}, $F(000) = 1000$, room temperature, $wR = 0{\cdot}047$, $R = 0{\cdot}043$ for 1308 observed $[I \geq 3\sigma(I)]$ reflections from 3731 measured, and 298 variables. The geometries of the two cyclopentadienyl moieties do not differ significantly. The same holds for the benzoato ligands. Moreover, they follow closely the

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