Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1138). Services for accessing these data are described at the back of the journal.

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Bis[(1,4,7,10-tetraazacyclododecane-κ^4N)(thiocyanato-*S*)copper(II)] Diaquatetrakis(isothiocyanato-*N*)calcate(2–) Dihydrate

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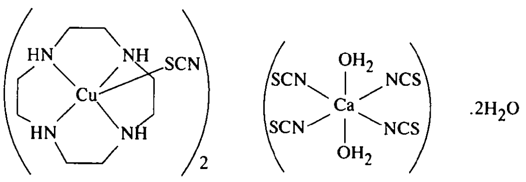
Abstract

The Ca^{II} ion of the title complex, $[Cu(SCN)(C_8H_{20}N_4)]_2[Ca(NCS)_4(H_2O)_2].2H_2O$, is situated at an inversion center. The coordination geometry around the Cu^{II} ion is a symmetrical square pyramid with the tetraamine N atoms equatorial and thiocyanato S atom axial. The four donor N atoms of the macrocyclic ligand form a buckled plane, with the Cu^{II} ion lying 0.553 (1) Å out of this plane towards the thiocyanato group. Hydrogen bonds between the water molecules and thiocyanato groups help stabilize the crystal structure. A water molecule binds the Cu^{II} complex and the Ca^{II} complex together through hydrogen bonds.

Comment

Metal complexes of the thiocyanate ion have been extensively investigated (Burmeister, 1990). One aspect of these compounds which is of interest is the bonding mode of the thiocyanate ligand; either the N or the S atom may be bound to the metal ion. According to Pearson (1963) and Ahrland, Chatt & Davies (1958), S in SCN^- is soft and prefers to coordinate with soft acids (class *b* metals), whereas N in SCN^- is hard and coordinates with hard acids (class *a* metals). The Cu^{II} ion is borderline between hard and soft (Yingst & McDaniel, 1967). Thus, the nature of the other ligands attached to it has a great effect on the coordination behavior of the thiocyanato group (Bennett, Clark & Goodwin, 1967; Wu & Chung, 1986). In order to investigate the influence of the ligand on the Cu^{II} ion, we determined the crystal structure of the title complex, (I).



(I)

The Cu^{II} ion is five coordinate with tetraamine N atoms equatorial and the thiocyanato S atom axial. The distribution of Cu^{II}—N distances, ranging from 2.018 (2) to 2.040 (2) Å, is comparable with the average Cu—N length of 2.03 (3) Å for Cu^{II} macrocyclic complexes (Lu, Chung & Ashida, 1991). All four H atoms of the N—H groups are on the same side of the metal–nitrogen plane. The four donor N atoms of the macrocyclic ligand form a buckled plane, with the Cu^{II} ion lying 0.553 (1) Å above the plane towards the thiocyanato group. The four five-membered rings are in the skew form and the inter-chelate N—Cu—N bond angles are 85.68 (10), 85.39 (9), 85.62 (10) and 86.12 (9)°. The Ca^{II} ion at a special position is six-coordinate with four isothiocyanato N atoms equatorial and two water O atoms axial. Its coordination geometry is octahedral. The Ca—N distances range from 2.386 (3) to 2.436 (3) Å. Hydrogen bonds (Table 2) between coordinated water and the thiocyanato group help stabilize the crystal structure.

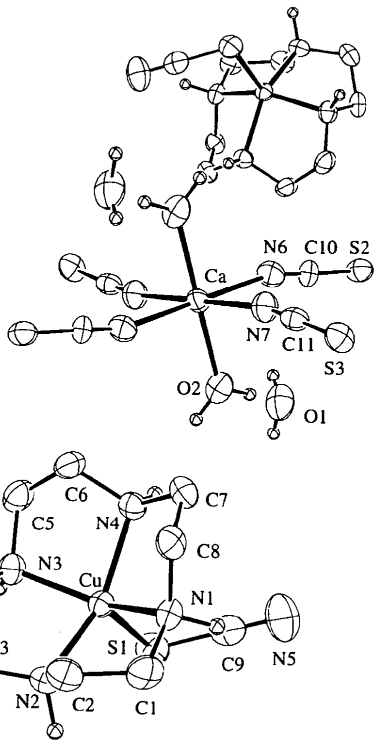


Fig. 1. A perspective view of the molecular structure with the atom-numbering scheme of the Cu^{II} and Ca^{II} complexes excluding the H atoms attached to the C atoms. The displacement ellipsoids are plotted at the 50% probability level. There is an inversion center at the position of calcium.

Experimental

(1,4,7,10-Tetraazacyclododecane)copper(II) sulfate was prepared according to a previously described procedure (Barbucci, Cialdi, Ponticelli & Paoletti, 1969; Hay & Pujari, 1985). The complex (1 g) in water (25 ml) was treated with $Ca(SCN)_2.4H_2O$ (0.5 g) in water (25 ml). The resulting blue solution was evaporated to dryness. It was then dissolved in CH_3NO_2 (30 ml), filtered and evaporated to yield a blue solid which was dissolved in CH_3OH and passed through a silica-gel column. Evaporation yielded another blue solid. Single crystals were obtained from a methanol solution by slow evaporation.

Crystal data

$[Cu(SCN)(C_8H_{20}N_4)]_2$-$[Ca(NCS)_4(H_2O)_2].2H_2O$
$M_r = 932.24$
Monoclinic
$P2_1/c$
$a = 8.0500(10)$ Å
$b = 12.490(2)$ Å
$c = 20.193(4)$ Å
$\beta = 95.970(10)°$
$V = 2019.3(6)$ Å^3
$Z = 2$
$D_x = 1.533$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.8$–$17.0°$
$\mu = 1.52$ mm^{-1}
$T = 293$ K
Block
0.42 × 0.41 × 0.31 mm
Blue

Data collection

Nonius CAD-4 diffractometer
$\theta/2\theta$ scan
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.574$, $T_{max} = 0.624$
3811 measured reflections
3542 independent reflections

2976 reflections with $I_{net} > 2.5\sigma(I_{net})$
$R_{int} = 0.015$
$\theta_{max} = 25°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 23$
3 standard reflections
frequency: 60 min
intensity decay: 1.5%

Refinement

Refinement on F
$R = 0.026$
$wR = 0.028$
$S = 1.12$
2976 reflections
224 parameters
H atoms not refined
Unit weights applied
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 2.1 (2) × 10^3
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Cu—S1	2.4808 (8)	Ca—O2	2.331 (2)
Cu—N1	2.018 (2)	Ca—N6	2.386 (3)
Cu—N2	2.040 (2)	Ca—N7	2.436 (3)
Cu—N3	2.020 (2)	Ca—N6^i	2.386 (3)
Cu—N4	2.035 (2)	Ca—N7^i	2.436 (3)
S1—Cu—N1	108.26 (7)	N2—Cu—N4	148.10 (9)
S1—Cu—N2	110.54 (7)	N3—Cu—N4	86.12 (9)
S1—Cu—N3	103.31 (7)	O2—Ca—N6	83.98 (9)
S1—Cu—N4	101.34 (7)	O2—Ca—N6^i	96.02 (9)
N1—Cu—N2	85.68 (10)	O2—Ca—N7	92.74 (9)
N1—Cu—N3	148.33 (9)	O2—Ca—N7^i	87.26 (9)
N1—Cu—N4	85.39 (9)	N6—Ca—N7	88.56 (10)
N2—Cu—N3	85.62 (10)	N6—Ca—N7^i	91.44 (10)

Symmetry code: (i) $-x, 1-y, -z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D···A	D—H···A
O1—HW11···N5^i	2.927 (5)	158.8
O1—HW12···N7^{ii}	3.247 (4)	168.0
O2—HW21···N5	2.920 (4)	157.0
O2—HW22···O1^{iii}	2.749 (3)	169.0
N1—HN1···S2^{iv}	3.478 (2)	130.5
N2—HN2···S2^{v}	3.424 (3)	151.0
N3—HN3···S3^{vi}	3.538 (3)	148.9
N4—Hn4···S3^{vii}	3.443 (2)	142.7

Symmetry codes: (i) $1-x, -y, -z$; (ii) $1+x, y-1, z$; (iii) $x, 1+y, z$; (iv) $1-x, 1-y, -z$; (v) $x, y-1, z$; (vi) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (vii) $1+x, y, z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX DATRD*2 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *SHELXTL* (Sheldrick, 1985) in *NRCVAX*. Software used to prepare material for publication: *NRCVAX TABLES* (version of January 1994).

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Tris(acetato-*O*,*O*′)(2,4-dimethoxyphenyl)-lead(IV)

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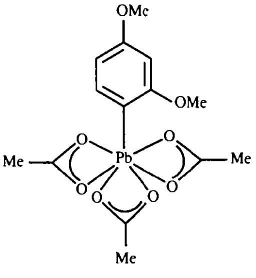
Abstract

The coordination around the Pb atom in the title compound, $[Pb(C_8H_9O_2)(C_2H_3O_2)_3]$, can be described as distorted dodecahedral with O atoms of the bidentate acetate groups occupying six of the coordination sites and the remaining sites occupied by the bonded C atom of the 2,4-dimethoxyphenyl group and a methoxy O atom.

Comment

Little data has been published on the coordination of lead in organolead compounds. The Pb atom has approximate trigonal bipyramidal coordination with bridging acetate groups in $[(CH_3)_3PbOAc]$ (Sheldrick & Taylor, 1975). In $[(CH_3)_4N][Ph_2Pb(OAc)_3]$, the metal atom is eight-coordinate with its ligands forming an approximate hexagonal bipyramid (Alcock, 1972). The O atoms around the Pb atom in $[Pb(OAc)_4]$ form a flattened trigonal dodecahedron with no bridging acetate groups (Kamenar, 1963). In the isostructural $[Sn(OAc)_4]$, the Sn atom has a pseudo-dodecahedral coordination with four bidentate acetate groups (Alcock & Tracy, 1979); the Sn—O distances are, however, variable. In order to determine the coordination of the Pb atom in the title compound, (I), the structure was investigated by single-crystal X-ray diffraction.



(I)

The molecular structure of (I) shows approximate mirror symmetry. All non-H atoms of the 2,4-dimethoxyphenyl group, Pb1 and one of the acetate groups lie in a plane [maximum deviation 0.114 (8) Å, unit weights] which bisects the plane occupied by the two other acetate groups and Pb1 [maximum deviation 0.166 (6) Å] with an interplanar angle of 89.8 (1)°. The coordination about Pb1 can be described as distorted rhombic dodecahedral with the O atoms of the acetate groups occupying six of the coordination sites and the remaining sites occupied by the bonded carbon (C5) of the phenyl group and a methoxy O atom (O2). The long Pb1—O2 bond [2.874 (5) Å] is facilitated by the significant distortion of the bond between Pb1 and the phenyl group such that the angles Pb1—C5—C4 and Pb1—C5—C6 are 125.9 (5) and 112.7 (4)°, respectively.

Each of the bidentate coordinated acetate ligands have unequal C—O bond distances with one longer (*ca* 2.5 Å) and one shorter (*ca* 2.2 Å). A similar but less pronounced effect observed for the Sn—O distances of $[Sn(OAc)_4]$ is attributed to overcrowding of the coordination about the Sn atom. The longer Pb1—O bond distances of (I) are similar to those found in the anion of $[(CH_3)_4N][Ph_2Pb(OAc)_3]$ which are in the range 2.48 (2)–2.63 (2) Å. The four shortest edges of the polyhedron are those of the bidentate atom pairs, the O···O distances of the acetate groups

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