Crystal structure of bis(thiocyanato)(γ-*C*-*meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecanecopper(II), $C_{18}H_{36}CuN_6S_2$

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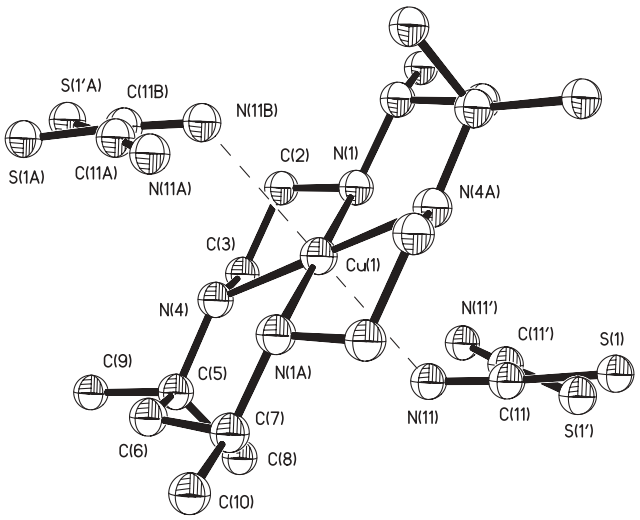

Abstract

$C_{18}H_{36}CuN_6S_2$, monoclinic, $P12_1/c1$ (No. 14), a = 7.691(1) Å, b = 9.449(3) Å, c = 16.380(2) Å, β = 101.08(2)°, V = 1168.1 Å^3, Z = 2, $R_{gt}(F)$ = 0.037, $wR_{ref}(F^2)$ = 0.098, T = 293 K.

Source of material

The ligand (called " tet a") was prepared according to the method of Curtis [1]. For the preparation of [Cu(tet a)(NCS)$_2$], stoichiometric amounts of copper(II) perchlorate, sodium thiocyanate (two equivalent) and tet a were mixed in water and stirred for 1h during which time tet a dissolved in water and the solution was slowly evaporated to give red prismatic crystals. Analysis, calculated for $C_{18}H_{36}N_6S_2Cu$: C, 50.94%; H, 7.82%; N, 18.11%; Cu, 13.69%; found: C, 51.20%; H, 8.02%; N, 17.89%; Cu, 13.65%.

Discussion

The metal complexes of synthetic macrocyclic ligands have attracted considerable attention due to their distinctive coordination and biological significance. The extreme kinetic inertness and very high thermodynamic stability of tetra-amine macrocyclic ligand complexes are of particular stereochemical interest. Copper(II) derivatives [2-4] of tetraazamacrocycles obviously serve as model compounds for such important biologically active molecules as Cu_2Zn_2SOD. Earlier studies [5] reported the crystal structure of [Cu(tet a)(ClO$_4$)$_2$], in which the Cu(II) atom has an elongated octahedral coordination geometry ("tet a" is *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane). However, the preparation and crystal structure of [(tet a)Cu] complexes with SCN anions was not reported before.

The molecular structure of the title complex is shown in the figure. The thiocyanates were refined disordered with the S.O.F. = 0.6 for S11, N11 and C11, S.O.F. = 0.4 for S11′, N11, and C11′. There are two kinds of coordination geometry about copper. The minor conformer is a centrosymmetric square plane with four nitrogen atoms from (tet a) forming the coordination plane. The separations of Cu···S11′ (4.199(6) Å) and Cu1···N11′ (3.252(6) Å) are too long to be considered as coordinate bonds. The major conformer is a centrosymmetric elongated octahedron with four nitrogen atoms from (tet a) forming the equatorial plane and two nitrogen atom from thiocyanates situated at the axial positions forming a trans conformation. The structure greatly minimizes the steric effects brought about the substrate thiocyanate anions. S11 or S11A (of the thiocyanates) is 4.596(4) Å under or above the plane and the distance between Cu and N11 is 2.590(4) Å, which is shorter than the Cu—N(CS) bond length (2.674(6) Å) in the structure of [(1,2-ethylenediamine)$_2$Cu(NCS)]Br [6]. Only one red component was obtained for the title complex whether in water or in anhydrous solvents, which is different from the relative perchlorate, [Cu(tet a)(ClO$_4$)$_2$], from which two components, the red and the blue compounds, were isolated [5].

Table 1. Data collection and handling.

Crystal:	red block, size 0.30 × 0.35 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.28 cm^{-1}
Diffractometer, scan mode:	Siemens P4, $\omega/2\theta$
$2\theta_{max}$:	50.1°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2868, 2048
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1676
$N(param)_{refined}$:	224
Programs:	SHELXTL [7], SHELXTL-plus [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(6B)	4*e*	0.834(4)	0.186(3)	0.132(2)	0.055(8)
H(6A)	4*e*	0.790(4)	0.192(3)	0.222(2)	0.061(9)
H(7A)	4*e*	0.647(4)	–0.036(3)	0.194(2)	0.042(7)
H(2B)	4*e*	0.375(4)	0.251(3)	–0.113(2)	0.042(7)
H(2A)	4*e*	0.166(4)	0.258(3)	–0.109(2)	0.057(8)
H(8C)	4*e*	0.339(5)	0.258(4)	0.177(2)	0.08(1)
H(3B)	4*e*	0.339(4)	0.367(4)	0.012(2)	0.07(1)
H(3A)	4*e*	0.246(4)	0.237(3)	0.036(2)	0.055(9)

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Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(9C)	4*e*	0.507(5)	0.449(4)	0.130(2)	0.08(1)
H(1A)	4*e*	0.202(4)	0.038(3)	–0.062(2)	0.044(8)
H(10C)	4*e*	1.021(5)	–0.024(4)	0.199(2)	0.07(1)
H(4A)	4*e*	0.588(3)	0.242(3)	0.021(2)	0.030(7)
H(8B)	4*e*	0.386(5)	0.100(4)	0.173(2)	0.08(1)

Table 2. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(10B)	4*e*	0.928(5)	–0.019(4)	0.277(2)	0.07(1)
H(9B)	4*e*	0.701(6)	0.421(5)	0.117(3)	0.11(2)
H(9A)	4*e*	0.649(5)	0.409(4)	0.208(3)	0.08(1)
H(8A)	4*e*	0.483(6)	0.193(5)	0.246(3)	0.11(1)
H(10A)	4*e*	0.922(5)	–0.161(4)	0.226(2)	0.09(1)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	2*b*		1/2	0	0	0.0617(3)	0.0323(3)	0.0503(3)	0.0159(2)	–0.0162(2)	–0.0099(2)
N(1)	4*e*		0.2845(3)	0.0654(2)	–0.0843(1)	0.042(1)	0.037(1)	0.036(1)	0.005(1)	0.008(1)	0.0018(9)
N(4)	4*e*		0.5078(3)	0.2032(2)	0.0454(1)	0.043(1)	0.033(1)	0.037(1)	0.003(1)	0.012(1)	–0.0019(9)
C(2)	4*e*		0.2875(5)	0.2227(3)	–0.0826(2)	0.059(2)	0.038(2)	0.048(2)	0.013(1)	0.002(1)	0.004(1)
C(3)	4*e*		0.3357(4)	0.2692(3)	0.0068(2)	0.060(2)	0.037(2)	0.057(2)	0.018(1)	0.003(2)	–0.004(1)
C(5)	4*e*		0.5711(4)	0.2351(3)	0.1364(2)	0.054(2)	0.040(1)	0.040(1)	0.004(1)	0.009(1)	–0.009(1)
C(6)	4*e*		0.7471(4)	0.1562(3)	0.1663(2)	0.047(2)	0.048(2)	0.041(2)	–0.004(1)	0.006(1)	–0.009(1)
C(7)	4*e*		0.7444(4)	–0.0050(3)	0.1701(2)	0.043(1)	0.048(2)	0.036(1)	0.006(1)	0.005(1)	0.000(1)
C(8)	4*e*		0.4320(5)	0.1923(5)	0.1860(2)	0.068(2)	0.099(3)	0.054(2)	0.030(2)	0.029(2)	0.012(2)
C(9)	4*e*		0.6111(7)	0.3954(4)	0.1477(3)	0.102(3)	0.044(2)	0.077(3)	0.012(2)	–0.016(3)	–0.022(2)
C(10)	4*e*		0.9164(5)	–0.0589(5)	0.2246(2)	0.064(2)	0.081(3)	0.046(2)	0.025(2)	–0.008(2)	–0.004(2)
S(1′)	4*e*	0.437(9)	0.2274(9)	–0.3351(9)	0.0875(4)	0.087(3)	0.109(4)	0.093(3)	0.039(3)	0.044(2)	0.039(3)
N(11′)	4*e*	0.437	0.112(1)	–0.063(1)	0.0432(6)	0.085(6)	0.069(5)	0.112(6)	0.005(5)	0.059(5)	0.021(5)
C(11′)	4*e*	0.437	0.160(2)	–0.172(2)	0.063(1)	0.037(7)	0.08(1)	0.061(7)	–0.002(6)	0.029(6)	0.012(6)
S(1)	4*e*	0.563	0.1488(7)	–0.3631(3)	0.0614(3)	0.076(2)	0.054(1)	0.123(2)	–0.002(1)	0.034(2)	–0.007(1)
N(11)	4*e*	0.563	0.2831(9)	–0.0927(6)	0.0907(4)	0.095(6)	0.073(4)	0.072(4)	–0.017(3)	0.046(4)	–0.005(3)
C(11)	4*e*	0.563	0.222(2)	–0.206(1)	0.0803(7)	0.052(6)	0.050(5)	0.056(5)	0.002(5)	0.029(5)	0.003(4)

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