C15	0.7702 (7)	0.3955 (8)	0.2803 (5)	0.080 (5)
C16	0.6220 (7)	0.3776 (7)	0.2601 (5)	0.072 (5)
C21	0.3424 (7)	0.3479 (6)	0.1367 (4)	0.066 (4)
C22	0.2909 (12)	0.3202 (8)	0.0493 (5)	0.115 (8)
C23	0.2763 (10)	0.4240 (7)	0.0032 (5)	0.101 (6)
C24	0.2284 (11)	0.5054 (9)	0.0555 (6)	0.136 (8)
C25	0.2913 (13)	0.5398 (8)	0.1420 (6)	0.127 (8)
C26	0.3046 (11)	0.4368 (8)	0.1882 (5)	0.113 (7)
C31	0.1508 (8)	−0.1598 (6)	0.3512 (4)	0.073 (5)
C32	0.1474 (9)	−0.1357 (7)	0.4449 (4)	0.084 (5)
C33	0.2052 (11)	−0.2138 (10)	0.4961 (5)	0.117 (8)
C34	0.1618 (13)	−0.3401 (9)	0.4656 (6)	0.137 (10)
C35	0.1645 (10)	−0.3666 (7)	0.3705 (5)	0.104 (7)
C36	0.1114 (11)	−0.2894 (7)	0.3181 (5)	0.111 (7)
C41	−0.0838 (6)	−0.0989 (6)	0.2826 (4)	0.059 (4)
C42	−0.1615 (6)	−0.2146 (6)	0.2239 (5)	0.070 (5)
C43	−0.3150 (8)	−0.2352 (8)	0.2150 (6)	0.090 (6)
C44	−0.3786 (8)	−0.2269 (9)	0.2971 (6)	0.098 (7)
C45	−0.3021 (7)	−0.1117 (9)	0.3540 (5)	0.088 (6)
C46	−0.1497 (7)	−0.0911 (9)	0.3669 (5)	0.093 (6)
C100	0.3066 (15)	0.4157 (10)	0.5198 (7)	0.052 (7)
O100	0.4146 (13)	0.4760 (13)	0.4828 (8)	0.130 (11)

Table 2. *Geometric parameters* (Å, °)

Re—Co	2.786 (1)	Co—P1	2.111 (1)
Re—P1	2.544 (1)	Co—P2	2.116 (1)
Re—P2	2.541 (1)		
Co—Re—P1	46.4 (1)	Re—Co—P2	60.6 (1)
Co—Re—P2	46.5 (1)	P1—Co—P2	121.3 (1)
P1—Re—P2	92.9 (1)	Re—P1—Co	72.9 (1)
Re—Co—P1	60.8 (1)	Re—P2—Co	72.8 (1)

Synthesis was carried out by reaction of $Re_2(CO)_{10}$, $Co_2(CO)_8$ and $HP(C_6H_{11})_2$ (molar ratio 1:1:2) in xylene solution for 10 h at 423 K in a glass tube. Recrystallization from methanol gave red crystals.

The enclosed CH_3OH solvent molecule had a site occupation factor of 0.5. Cyclohexyl H atoms were fixed at ideal positions with common isotropic displacement parameters (U_{iso} = 0.08 Å^2). Structure solution and refinement used *SHELXTL-Plus* (Sheldrick, 1990). Other programs include *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71340 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SE1031]

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Structure of Isothiocyanato(1,4,7,11-tetraazacyclotetradecane)copper(II) Thiocyanate

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Abstract

There are two independent similar copper(II) complexes in the asymmetric unit. The coordination about copper(II) in each complex forms a distorted square pyramid with the tetraamine N atoms equatorial and the N atom of the isothiocyanato group axial. The two five-membered rings are in skew forms and the two six-membered rings in chair forms. The isothiocyanato groups are almost linear. Hydrogen bonds help stabilize the crystal structure.

Comment

In the case of 3*d*-metal complexes with saturated unsubstituted macrocyclic ligands, the whole series of 12- to 16-membered tetraaza macrocycles have been investigated extensively (Hinz & Margerum, 1974; Fabbrizzi, 1979). The 14-membered tetraaza system is unique among these ligands since it exists as two isomeric forms: cyclam (1,4,8,11-tetraazacyclotetradecane) and isocyclam (1,4,7,11-tetraazacyclotetradecane). The crystal structure of $[Cu(cyclam)(ClO_4)_2]$ has been reported (Tasker & Sklar, 1975). In this paper, we determine the crystal structure of $[Cu(isocyclam)(SCN)_2]$.

(1,4,7,11-Tetraazacyclotetradecane)copper(II) perchlorate was prepared by the procedure reported by Sabatini & Fabbrizzi (1979). 1 g of the complex in 25 ml of water was treated with 0.5 g of KSCN in 10 ml of water. The resulting blue solution was evaporated to dryness. It was then dissolved in 30 ml of CH_3NO_2, filtered and evaporated to yield blue solids. Single crystals were obtained from methanol solution by slow evaporation.

A perspective view of the molecules with the numbering scheme showing displacements above and below the best planes formed by atoms N(1), N(2), N(3), N(4) and N(6), N(7), N(8), N(9) is shown in Fig. 1.

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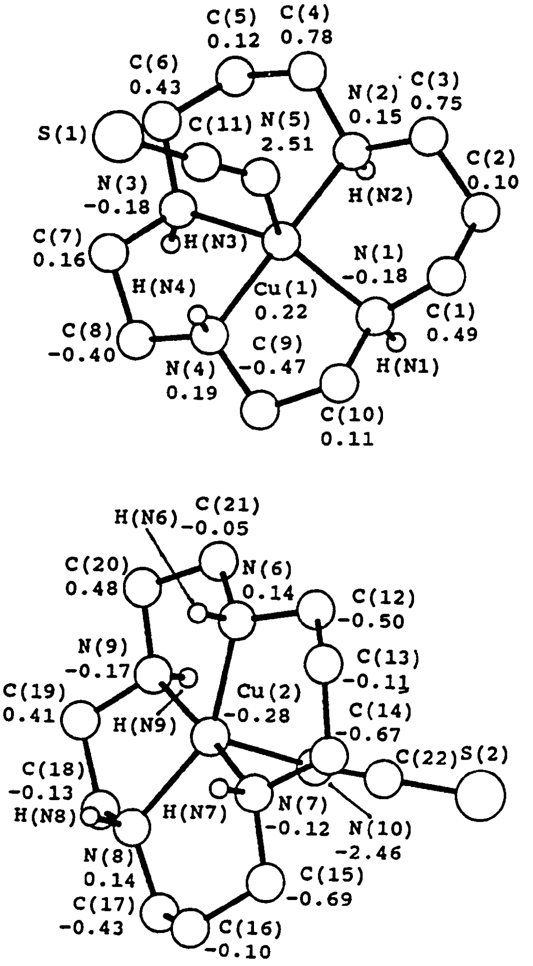

Fig. 1. A perspective view of the atom-numbering scheme of the molecules, excluding thiocyanate groups and the H atoms attached to the C atoms. The displacements from the best planes formed by the four nearest atoms coordinated to Cu(1) [N(1), N(2), N(3) and N(4)] and Cu(2) [N(6), N(7), N(8) and N(9)], respectively, are indicated.

The crystal structure of the title compound consists of two crystallographically independent [Cu(isocyclam)(NCS)]$^+$ complexes and two thiocyanate anions. In each complex cation, the coordination about copper(II) forms a distorted square pyramid with the tetraamine N atoms equatorial and the isothiocyanato N atom axial; the equatorial N atoms undergo a slight tetrahedral distortion. The largest deviation from the least-squares plane is 0.19 Å. The deviations of Cu(1) and Cu(2) atoms from the relevant planes are 0.22 and 0.28 Å, respectively, towards the isothiocyanato N atoms. In each cation, three amine H atoms are on one side of the macrocyclic plane, one amine H atom is alongside SCN$^-$ and the isothiocyanato group is on the other side of the plane. In both cations, each of the two five-membered rings is in a skew form and each of the two six-membered rings is in a chair form. The two complex cations are bound together by hydrogen bonds and these help stabilize the crystal structure.

Experimental

Crystal data

$[Cu(NCS)(C_{10}H_{24}N_4)](NCS)$
M_r = 380.032
Monoclinic
$P2_1/n$
a = 9.688 (2) Å
b = 14.157 (2) Å
c = 25.520 (3) Å
β = 94.72 (1)°
V = 3488 (1) Å^3
Z = 8

D_x = 1.447 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.7093 Å
Cell parameters from 25 reflections
θ = 9.66 - 17.13°
μ = 1.49 mm^{-1}
T = 298 K
Parallelepiped
0.53 × 0.38 × 0.34 mm
Blue

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{\min}$ = 0.55402, $T_{\max}$ = 0.55905
6283 measured reflections
6139 independent reflections

3927 observed reflections [$I > 2.5\sigma(I)$]
$R_{\rm int}$ = 0.047
$\theta_{\max}$ = 24.9°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 30$
3 standard reflections
frequency: 60 min
intensity variation: 2%

Refinement

Refinement on F
Final R = 0.044
wR = 0.050
S = 1.38
3927 reflections
428 parameters
Only H-atom U's refined
Unit weights applied
$(\Delta/\sigma)_{\max}$ = 0.121

$\Delta\rho_{\max}$ = 0.85 e Å^{-3}
$\Delta\rho_{\min}$ = −0.56 e Å^{-3}
Secondary-extinction correction: Zachariasen (1968)
Extinction coefficient: 2.39 (9)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

The structure was solved by direct methods and refined by full-matrix least squares; H atoms were found by difference Fourier syntheses. Program used: *NRCVAX* (Gabe, Le Page, White & Lee, 1987).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{\rm eq} = (32\pi^2/3)\textstyle\sum_i\sum_j U_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Cu(1)	0.30325 (7)	0.83710 (5)	0.15201 (3)	2.88 (3)
Cu(2)	0.72899 (7)	0.33783 (6)	0.10186 (3)	3.03 (3)
S(1)	0.34764 (24)	1.00650 (16)	0.30924 (7)	5.73 (10)
S(2)	0.75752 (20)	0.35496 (13)	−0.08275 (6)	4.34 (8)
S(3)	0.6840 (3)	0.52221 (20)	0.23806 (10)	8.36 (14)
S(4)	0.3537 (3)	0.22519 (20)	0.00474 (10)	7.27 (13)
N(1)	0.4458 (5)	0.8575 (4)	0.09849 (20)	3.40 (22)
N(2)	0.1425 (5)	0.8891 (4)	0.10599 (19)	3.23 (21)
N(3)	0.1859 (5)	0.7570 (4)	0.19842 (18)	3.17 (22)
N(4)	0.4635 (5)	0.7781 (4)	0.19634 (19)	3.33 (21)

N(5)	0.3331 (7)	0.9725 (4)	0.20088 (25)	5.1 (3)
N(6)	0.6161 (6)	0.4568 (4)	0.10608 (21)	4.2 (3)
N(7)	0.9095 (5)	0.4062 (4)	0.09751 (20)	3.79 (24)
N(8)	0.8139 (6)	0.2169 (4)	0.13201 (21)	4.2 (3)
N(9)	0.5486 (6)	0.2725 (4)	0.11643 (21)	4.3 (3)
N(10)	0.7063 (6)	0.3018 (5)	0.01845 (21)	5.0 (3)
N(11)	0.8189 (7)	0.3542 (5)	0.22486 (23)	5.4 (3)
N(12)	0.0933 (7)	0.1720 (6)	−0.0194 (3)	5.3 (4)
C(1)	0.4343 (8)	0.9465 (5)	0.0690 (3)	4.8 (3)
C(2)	0.2919 (8)	0.9536 (5)	0.0389 (3)	4.7 (3)
C(3)	0.1762 (7)	0.9727 (5)	0.0745 (3)	4.2 (3)
C(4)	0.0219 (7)	0.9128 (6)	0.1365 (3)	4.4 (3)
C(5)	−0.0340 (7)	0.8290 (6)	0.1640 (3)	4.9 (4)
C(6)	0.0539 (7)	0.7977 (6)	0.2123 (3)	4.9 (4)
C(7)	0.2763 (7)	0.7289 (5)	0.2454 (3)	4.1 (3)
C(8)	0.4122 (7)	0.6985 (5)	0.2260 (3)	4.2 (3)
C(9)	0.5748 (7)	0.7574 (6)	0.1616 (3)	4.5 (3)
C(10)	0.5842 (6)	0.8433 (6)	0.1272 (3)	4.8 (4)
C(11)	0.3416 (7)	0.9865 (5)	0.2458 (3)	4.1 (3)
C(12)	0.6489 (10)	0.5334 (6)	0.0706 (3)	5.5 (4)
C(13)	0.7932 (11)	0.5650 (6)	0.0806 (3)	6.1 (5)
C(14)	0.8992 (9)	0.4934 (6)	0.0652 (3)	5.4 (4)
C(15)	1.0223 (7)	0.3456 (7)	0.0802 (3)	5.5 (4)
C(16)	1.0516 (8)	0.2606 (7)	0.1138 (3)	5.9 (4)
C(17)	0.9435 (9)	0.1841 (6)	0.1109 (3)	5.8 (4)
C(18)	0.7066 (10)	0.1447 (5)	0.1311 (3)	5.4 (4)
C(19)	0.5790 (9)	0.1900 (6)	0.1493 (3)	5.5 (4)
C(20)	0.4547 (8)	0.3416 (7)	0.1357 (3)	5.7 (4)
C(21)	0.4684 (8)	0.4286 (7)	0.1037 (3)	5.7 (4)
C(22)	0.7281 (6)	0.3238 (4)	−0.02313 (23)	3.1 (3)
C(23)	0.7651 (7)	0.4240 (6)	0.23091 (24)	4.1 (3)
C(24)	0.1829 (13)	0.1918 (6)	−0.0093 (3)	6.3 (6)

Table 2. *Selected geometric parameters* (Å, °)

Cu(1)—N(1)	2.041 (5)	N(2)—C(4)	1.494 (8)
Cu(1)—N(2)	2.011 (5)	N(3)—C(6)	1.473 (9)
Cu(1)—N(3)	2.050 (5)	N(3)—C(7)	1.480 (8)
Cu(1)—N(4)	2.025 (5)	N(4)—C(8)	1.467 (9)
Cu(1)—N(5)	2.292 (6)	N(4)—C(9)	1.481 (8)
Cu(2)—N(6)	2.016 (6)	N(5)—C(11)	1.16 (1)
Cu(2)—N(7)	2.010 (5)	N(6)—C(12)	1.47 (1)
Cu(2)—N(8)	2.023 (6)	N(6)—C(21)	1.48 (1)
Cu(2)—N(9)	2.038 (6)	N(7)—C(14)	1.48 (1)
Cu(2)—N(10)	2.182 (5)	N(7)—C(15)	1.49 (1)
S(1)—C(11)	1.641 (8)	N(8)—C(17)	1.48 (1)
S(2)—C(22)	1.631 (6)	N(8)—C(18)	1.46 (1)
S(3)—C(23)	1.615 (8)	N(9)—C(19)	1.45 (1)
S(4)—C(24)	1.73 (1)	N(9)—C(20)	1.45 (1)
N(1)—C(1)	1.467 (9)	N(10)—C(22)	1.142 (8)
N(1)—C(10)	1.488 (8)	N(11)—C(23)	1.13 (1)
N(2)—C(3)	1.483 (8)	N(12)—C(24)	0.93 (2)
N(1)—Cu(1)—N(2)	95.3 (2)	C(3)—N(2)—C(4)	108.6 (5)
N(1)—Cu(1)—N(3)	154.5 (2)	Cu(1)—N(3)—C(6)	117.1 (4)
N(1)—Cu(1)—N(4)	84.4 (2)	Cu(1)—N(3)—C(7)	107.3 (4)
N(1)—Cu(1)—N(5)	100.6 (2)	C(6)—N(3)—C(7)	112.2 (5)
N(2)—Cu(1)—N(3)	95.8 (2)	Cu(1)—N(4)—C(8)	109.2 (4)
N(2)—Cu(1)—N(4)	176.9 (2)	Cu(1)—N(4)—C(9)	108.0 (4)
N(2)—Cu(1)—N(5)	94.0 (2)	C(8)—N(4)—C(9)	116.8 (5)
N(3)—Cu(1)—N(4)	83.4 (2)	Cu(1)—N(5)—C(11)	132.6 (6)
N(3)—Cu(1)—N(5)	101.5 (2)	Cu(2)—N(6)—C(12)	116.1 (5)
N(4)—Cu(1)—N(5)	89.1 (2)	Cu(2)—N(6)—C(21)	107.4 (5)
N(6)—Cu(2)—N(7)	94.5 (2)	C(12)—N(6)—C(21)	115.6 (6)
N(6)—Cu(2)—N(8)	153.1 (2)	Cu(2)—N(7)—C(14)	114.4 (4)
N(6)—Cu(2)—N(9)	83.8 (3)	Cu(2)—N(7)—C(15)	113.8 (5)
N(6)—Cu(2)—N(10)	103.7 (2)	C(14)—N(7)—C(15)	109.4 (6)
N(7)—Cu(2)—N(8)	95.8 (2)	Cu(2)—N(8)—C(17)	117.2 (5)
N(7)—Cu(2)—N(9)	172.6 (2)	Cu(2)—N(8)—C(18)	108.7 (5)
N(7)—Cu(2)—N(10)	94.4 (2)	C(17)—N(8)—C(18)	113.5 (6)
N(8)—Cu(2)—N(9)	82.8 (3)	Cu(2)—N(9)—C(19)	109.5 (5)
N(8)—Cu(2)—N(10)	100.3 (2)	Cu(2)—N(9)—C(20)	109.1 (5)
N(9)—Cu(2)—N(10)	93.0 (2)	C(19)—N(9)—C(20)	116.7 (6)
Cu(1)—N(1)—C(1)	116.0 (4)	Cu(2)—N(10)—C(22)	146.2 (6)
Cu(1)—N(1)—C(10)	106.4 (4)	N(6)—C(12)—C(13)	111.7 (6)
C(1)—N(1)—C(10)	113.4 (5)	S(2)—C(22)—N(10)	179.4 (6)
Cu(1)—N(2)—C(3)	114.5 (4)	S(3)—C(23)—N(11)	178.0 (7)
Cu(1)—N(2)—C(4)	112.3 (4)	S(4)—C(24)—N(12)	175.4 (9)

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71313 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1033]

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Structure of *meso*-Chloro(1,4,7,11,14-pentaazacycloheptadecane)cobalt(III) Chloride Perchlorate

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Abstract

The coordination geometry about the Co^{III} ion in the title compound, chloro[(1*RS*,7*SR*,11*SR*,14*RS*)-1,4,7,-11,14-pentaazacycloheptadecane]cobalt(III) chloride perchlorate, is distorted square bipyramidal with four tetraamine N atoms equatorial and a Cl and an N atom axial. The equatorial N atoms are nearly coplanar with the largest deviation from the least-squares plane of 0.018 Å; the deviation of the Co^{III} ion from the plane is 0.039 Å. Both six-membered