Crystal and Molecular Structures of Two Crystalline Forms of Isothiocyanato-[1,7-bis-(2-pyridyl)-2,6-diazaheptane]copper(II) Thiocyanate

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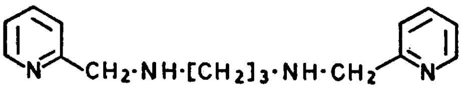
The single-crystal, X-ray analyses of two of the crystalline forms (α and γ) of the title compound have shown the crystals to be: α, triclinic, space group $P\bar{1}$, a = 16·66(4), b = 7·88(2), c = 9·11(3) Å, α = 124·4(1), β = 83·0(1), γ = 91·6(1)°; γ, monoclinic, space group $B2_1/c$, a = 26·75(7), b = 7·62(2), c = 19·08(5) Å, β = 90·36(5)°. The structures, which have refined to R 0·103 (α, 2648 independent reflections) and 0·116 (γ, 2358 independent reflections), are conformational isomers each involving a complex cation containing five-co-ordinate copper(II) in a distorted trigonal bipyramidal geometry and a thiocyanate ion in the lattice. The isomerism arises from the different configurations at the aliphatic nitrogen atoms of the tetramine ligands in the two compounds. All copper–nitrogen(tetramine) distances are close to the mean value of 2·016 Å with a slight tendency for equatorial bonds to be longer than axial bonds. In the co-ordinated isothiocyanate groups the mean Cu–N–C angle is 155·7°; Cu–NCS is 2·141 Å.

THE preparation and identification have been reported [1] recently of nine different crystalline forms of the molecule Cu(bispictn)(NCS)$_2$ [where bispictn is the quadridentate ligand 1,7-bis-(2-pyridyl)-2,6-diazaheptane (I)].



(I)

Of these nine, two were particularly suitable for full, three-dimensional, X-ray studies. They were clearly distinguishable as blue 'bricks' and blue–green needles in the first preparations of the compound (henceforth referred to as the α- and γ-forms respectively). Both were anhydrous and appeared to contain five-co-ordinate copper(II) but only a full crystallographic investigation could determine unequivocally the nature of the isomerism.

The analysis establishes that both molecules have similar five-co-ordinate structures, differing mainly in the configurations of the quadridentate ligands: a preliminary report of the structures has already appeared.[2] Thus they add to the large and ever-growing list of copper(II) compounds for which this stereochemistry has been proven.

EXPERIMENTAL

Crystals were obtained as a mixture from aqueous solution.

α-Form: Crystal Data.—$C_{17}H_{20}CuN_6S_2$, M = 436·0, Triclinic; a = 16·66(4), b = 7·88(2), c = 9·11(3) Å, α = 124·4(1), β = 83·0(1), γ = 91·6(1)°, U = 978·7 Å^3 (from precession and Weissenberg photographs), D_m = 1·478, Z = 2, D_c = 1·479, F(000) = 450. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 36·1 cm^{-1}. Space group $P\bar{1}$ (C_i^1, No. 2), confirmed by the successful completion of the analysis.

Three-dimensional, X-ray data of the type h, k, 1-k through h, k, 7-k, hk0 and h0l (about a face-diagonal axis) were collected photographically using equi-inclination Weissenberg geometry with Ni-filtered Cu-K_α radiation; data of the type hkk were collected by precession methods using Zr-filtered Mo-K_α radiation (λ = 0·7107 Å). The data were estimated visually and corrected for Lorentz, polarisation, and spot-shape variation effects; no corrections were made for absorption. The complete data

TABLE 1

Atomic positional parameters for the α-form, with estimated standard deviations in parentheses

	X/a	Y/b	Z/c
Cu(1)	0·2466(1)	0·3254(2)	0·0485(2)
S(1)	0·0608(2)	0·2382(5)	−0·3416(5)
S(2)	0·3028(2)	0·3959(7)	0·5105(6)
N(1)	0·1760(6)	0·1056(13)	0·0240(12)
N(2)	0·1831(6)	0·4984(13)	0·2973(13)
N(3)	0·3201(5)	0·5488(13)	0·0943(12)
N(4)	0·3515(6)	0·1562(14)	−0·0973(13)
N(5)	0·1840(6)	0·3454(16)	−0·1305(15)
N(6)	0·4142(8)	0·5044(21)	0·3265(18)
C(1)	0·1799(7)	−0·0880(18)	−0·1197(18)
C(2)	0·1276(8)	−0·2330(17)	−0·1286(17)
C(3)	0·0710(8)	−0·1701(19)	0·0186(19)
C(4)	0·0665(7)	0·0293(18)	0·1638(17)
C(5)	0·1178(7)	0·1684(16)	0·1679(15)
C(6)	0·1116(7)	0·3920(18)	0·3082(18)
C(7)	0·1605(8)	0·7148(17)	0·3610(18)
C(8)	0·2356(8)	0·8320(18)	0·3583(20)
C(9)	0·2782(8)	0·7557(18)	0·1785(20)
C(10)	0·3705(8)	0·4717(18)	−0·0774(17)
C(11)	0·4015(7)	0·2579(18)	−0·1448(16)
C(12)	0·4756(8)	0·1760(22)	−0·2455(19)
C(13)	0·5017(9)	−0·0177(24)	−0·2914(21)
C(14)	0·4517(9)	−0·1206(21)	−0·2397(22)
C(15)	0·3762(8)	−0·0322(19)	−0·1475(19)
C(16)	0·1324(7)	0·2999(16)	−0·2182(16)
C(17)	0·3692(8)	0·4608(21)	0·4067(19)
H(1)[C(1)]	0·225	−0·135	−0·233
H(2)[C(2)]	0·131	−0·390	−0·245
H(3)[C(3)]	0·030	−0·279	0·017
H(4)[C(4)]	0·021	0·076	0·277
H(5)[C(6)]	0·104	0·415	0·438
H(6)[C(6)]	0·059	0·458	0·295
H(7)[N(2)]	0·222	0·515	0·385
H(8)[C(7)]	0·120	0·710	0·275
H(9)[C(7)]	0·130	0·795	0·497
H(10)[C(8)]	0·216	0·991	0·422
H(11)[C(8)]	0·278	0·822	0·434
H(12)[C(9)]	0·323	0·864	0·190
H(13)[C(9)]	0·235	0·743	0·094
H(14)[N(3)]	0·356	0·580	0·192
H(15)[C(10)]	0·335	0·466	−0·171
H(16)[C(10)]	0·420	0·570	−0·058
H(17)[C(12)]	0·515	0·259	−0·284
H(18)[C(13)]	0·560	−0·086	−0·367
H(19)[C(14)]	0·472	−0·271	−0·277
H(20)[C(15)]	0·337	−0·115	−0·108

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[1] J. G. Gibson and E. D. McKenzie, *J. Chem. Soc.* (*A*), 1971, 1666.

[2] N. A. Bailey, E. D. McKenzie, and J. R. Mullins, *Chem. Comm.*, 1970, 1103.

set, after inter-layer scaling using cross-correlating reflections, comprised 2648 independent reflections.

The structure was solved by the conventional heavy-atom and Fourier methods and was refined by block-diagonal, least-squares methods to a final value for R of 0·103: individual anisotropic thermal parameters were allowed for all non-hydrogen atoms; contributions from hydrogen atoms, in positions consistent with normal chemical requirements, were included in the structure-factor calculations but neither positions nor the assigned isotropic thermal vibration parameter (B = 5·0 Å^2) were refined. Little evidence for the hydrogen atoms was observed on a difference Fourier synthesis. Atomic scattering factors were taken from ref. 3.

Tables 1 and 2 list, respectively, atomic positional and vibrational parameters together with their estimated standard deviations; Table 1 also includes the predicted positions for hydrogen atoms.

TABLE 2

Atomic anisotropic thermal vibrational parameters * for the α-form with estimated standard deviations in parentheses

	10^5b_{11}	10^4b_{22}	10^4b_{33}	10^4b_{23}	10^5b_{13}	10^5b_{12}
Cu(1)	380(1)	238(1)	236(1)	318(1)	−194(4)	−136(4)
S(1)	365(2)	265(1)	251(1)	303(2)	−643(8)	−435(8)
S(2)	502(3)	473(2)	309(2)	578(3)	−162(11)	91(12)
N(1)	466(7)	171(4)	178(3)	207(6)	−482(26)	−317(24)
N(2)	354(6)	207(4)	243(4)	306(7)	−303(26)	−100(23)
N(3)	376(6)	197(4)	165(3)	215(6)	−455(23)	−204(23)
N(4)	326(6)	254(4)	201(4)	282(7)	20(24)	85(24)
N(5)	500(8)	303(5)	262(4)	374(8)	−988(31)	−625(31)
N(6)	576(10)	511(8)	347(6)	622(12)	−474(38)	−13(42)
C(1)	408(9)	234(5)	258(5)	320(9)	−255(34)	−213(31)
C(2)	545(10)	178(5)	204(5)	211(8)	−558(35)	−523(32)
C(3)	477(9)	287(6)	304(6)	467(10)	−409(38)	−594(36)
C(4)	417(9)	265(5)	241(5)	351(9)	−122(34)	−334(33)
C(5)	365(8)	214(5)	174(4)	244(8)	−222(28)	13(28)
C(6)	374(8)	239(5)	243(5)	266(9)	−232(33)	−214(31)
C(7)	475(9)	181(5)	271(5)	245(9)	−479(36)	86(31)
C(8)	500(10)	174(5)	328(6)	249(9)	−316(40)	98(33)
C(9)	454(9)	214(5)	343(6)	399(10)	−628(38)	−330(32)
C(10)	489(10)	269(5)	199(4)	323(9)	−150(34)	−332(34)
C(11)	381(8)	284(6)	190(4)	296(9)	−213(31)	−374(32)
C(12)	395(9)	373(7)	236(5)	314(11)	222(36)	−436(39)
C(13)	417(10)	395(8)	281(6)	281(12)	2(40)	−53(42)
C(14)	494(11)	288(7)	327(7)	254(11)	−50(43)	526(40)
C(15)	423(9)	238(5)	262(5)	252(9)	20(36)	240(33)
C(16)	387(8)	186(4)	209(4)	286(8)	−115(30)	−107(27)
C(17)	440(9)	363(7)	257(5)	413(10)	−176(36)	646(38)

The expression used for the temperature factor was:

$$\exp\left[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + klb_{23} + hlb_{13} + hkb_{12})\right].$$

γ-Form: Crystal Data.—$C_{17}H_{20}CuN_6S_2$, M = 436·0, Monoclinic, a = 26·75(7), b = 7·62(2), c = 19·08(5) Å, β = 90·36(5)°, U = 3886 Å^3 (from precession and Weissenberg photographs), D_m = 1·47, Z = 8, D_c = 1·49; F(000) = 1800. Cu-K_α Radiation, λ = 1·5418 Å; μ(Cu-K_α) = 36·4 cm^{-1}. Space group $B2_1/c$ [a non-standard form of $P2_1/c$, (C^5_{2h}, No. 14) chosen because of the associated value of β].

Three-dimensional, X-ray data of the type $h0$—$5l$ were collected photographically using equi-inclination Weissenberg geometry with Ni-filtered Cu-K_α radiation; data of the type $hk0$ and $0kl$ were collected by precession methods using Zr-filtered Mo-K_α radiation (λ = 0·7107 Å). The data were estimated and corrected, and the structure solved and refined in a similar way to that used for the α-form; the total number of independent reflections was 2358 and the final value of R was 0·116. In the case of the γ-form, allowance was made for anomalous scattering by the copper and sulphur atoms, the precession data having been removed from the data set. The final atomic positional and vibrational parameters, together with their estimated standard deviations, are listed in Tables 3 and 4.

TABLE 3

Atomic positional parameters for the γ-form, with estimated standard deviations in parentheses

	X/a	Y/b	Z/c
Cu(1)	0·1284(1)	0·1998(3)	−0·1342(1)
S(1)	0·1465(1)	0·5916(6)	−0·3306(2)
S(2)	0·0573(3)	0·6525(8)	−0·0385(3)
N(1)	0·0762(4)	0·1048(17)	−0·1982(6)
N(2)	0·0703(4)	0·2207(16)	−0·0655(6)
N(3)	0·1777(4)	0·3035(15)	−0·0675(5)
N(4)	0·1874(3)	0·0347(14)	−0·1552(5)
N(5)	0·1410(5)	0·4123(17)	−0·2071(6)
N(6)	0·1560(3)	0·7135(8)	−0·0230(3)
C(1)	0·0816(5)	0·0790(25)	−0·2683(8)
C(2)	0·0422(6)	0·0447(27)	−0·3125(9)
C(3)	−0·0058(6)	0·0512(27)	−0·2839(10)
C(4)	−0·0118(5)	0·0734(27)	−0·2113(10)
C(5)	0·0302(5)	0·0969(21)	−0·1718(8)
C(6)	0·0278(5)	0·1152(24)	−0·0926(8)
C(7)	0·0819(6)	0·1617(24)	0·0089(7)
C(8)	0·1264(6)	0·2599(22)	0·0397(7)
C(9)	0·1763(6)	0·2114(24)	0·0037(7)
C(10)	0·2277(5)	0·2761(22)	−0·0987(8)
C(11)	0·2308(4)	0·0979(18)	−0·1313(6)
C(12)	0·2754(5)	0·0069(19)	−0·1385(7)
C(13)	0·2744(5)	−0·1469(21)	−0·1706(7)
C(14)	0·2302(5)	−0·2225(20)	−0·1945(7)
C(15)	0·1868(5)	−0·1209(20)	−0·1842(7)
C(16)	0·1428(4)	0·4853(17)	−0·2574(7)
C(17)	0·1161(3)	0·6888(8)	−0·0293(3)
C(17′)	0·0972(3)	0·6772(8)	−0·0322(3)
H(1)[C(1)]	0·119	0·081	−0·291
H(2)[C(2)]	0·047	0·024	−0·368
H(3)[C(3)]	−0·038	0·030	−0·317
H(4)[C(4)]	−0·049	0·071	−0·189
H(5)[C(6)]	0·029	−0·014	−0·069
H(6)[C(6)]	−0·007	0·179	−0·079
H(7)[N(2)]	0·062	0·354	−0·062
H(8)[C(7)]	0·050	0·186	0·041
H(9)[C(7)]	0·090	0·023	0·008
H(10)[C(8)]	0·129	0·229	0·095
H(11)[C(8)]	0·120	0·399	0·034
H(12)[C(9)]	0·178	−0·003	0·071
H(13)[C(9)]	0·207	0·255	0·036
H(14)[N(3)]	0·170	0·436	−0·059
H(15)[C(10)]	0·234	0·375	−0·138
H(16)[C(10)]	0·256	0·287	−0·058
H(17)[C(12)]	0·311	0·058	−0·120
H(18)[C(13)]	0·309	−0·219	−0·177
H(19)[C(14)]	0·230	−0·350	−0·220
H(20)[C(15)]	0·151	−0·172	−0·202

Atom C(17′) represents the carbon atom of the ionic thiocyanate group in the component of lower population.

Tables of observed structure amplitudes and calculated structure factors for both the α- and γ-forms, together with analyses of the atomic thermal vibration ellipsoids, are listed in Supplementary Publication No. SUP 20374 (47 pages, 1 microfiche).*

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[3] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, 202.

RESULTS AND DISCUSSION

The molecular structures (with atom labelling) are shown in the Figure; Table 5 lists the molecular geometries (with estimated standard deviations) of both isomers. In both α- and γ-forms, the compound consists of a five-co-ordinate copper(II) cation with an anionic thiocyanate in the lattice. The co-ordination polyhedra are of intermediate type[4] but may be most conveniently described in terms of a trigonal bipyramidal geometry. In both cases, the covalently bonded isothiocyanato-group occupies an equatorial site in the distorted trigonal bipyramidal co-ordination polyhedron of the copper. The important difference between the two isomers lies in the different configurations

TABLE 4

Atomic anisotropic thermal vibrational parameters for the γ-form, with estimated standard deviations in parentheses

	10^5b_{11}	10^4b_{22}	10^5b_{33}	10^4b_{23}	10^5b_{13}	10^4b_{12}
Cu(1)	94(2)	156(4)	244(5)	−10(3)	5(5)	−8(2)
S(1)	192(6)	187(10)	292(11)	11(5)	21(13)	−22(4)
S(2)	291(16)	278(21)	914(41)	−108(13)	−219(36)	88(8)
N(1)	112(15)	191(29)	302(36)	−13(17)	−3(37)	−19(11)
N(2)	116(15)	146(27)	311(35)	−3(16)	80(36)	7(10)
N(3)	139(16)	105(24)	258(31)	−29(15)	32(35)	10(11)
N(4)	109(14)	82(22)	271(32)	−34(14)	10(34)	−25(9)
N(5)	221(23)	138(29)	297(38)	46(17)	36(46)	−26(13)
N(6)	378(31)	242(29)	501(42)	−7(17)	94(50)	−43(14)
C(1)	166(24)	298(48)	302(47)	−9(24)	1(53)	−70(18)
C(2)	197(28)	347(55)	388(57)	−5(29)	−67(64)	−87(21)
C(3)	153(25)	318(53)	531(71)	3(31)	−256(68)	−18(19)
C(4)	113(21)	328(54)	567(73)	−44(32)	−21(63)	−20(17)
C(5)	109(18)	193(38)	394(52)	−24(23)	39(49)	−11(14)
C(6)	128(21)	282(46)	379(53)	−30(25)	79(53)	−48(16)
C(7)	187(25)	285(48)	251(42)	48(23)	110(52)	−6(17)
C(8)	217(27)	215(42)	214(38)	−12(19)	55(51)	18(16)
C(9)	216(27)	254(43)	239(41)	−18(23)	19(53)	30(18)
C(10)	123(19)	222(40)	365(49)	−28(23)	28(49)	−13(14)
C(11)	120(18)	122(31)	222(36)	2(17)	−31(40)	0(12)
C(12)	113(18)	145(35)	325(45)	7(20)	−4(45)	−7(12)
C(13)	129(20)	197(40)	318(45)	−3(20)	55(47)	19(32)
C(14)	169(22)	130(34)	309(43)	−18(20)	−73(49)	27(14)
C(15)	137(20)	155(34)	322(45)	−1(20)	−25(47)	1(14)
C(16)	123(18)	53(27)	306(42)	−22(17)	19(43)	−9(11)

C(17) and C(17′) were assigned isotropic temperature factors of 7·95 Å^2. The expression used for the anisotropic temperature factor is given in the footnote to Table 2.

TABLE 5

Geometries of α- and γ-forms with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

	α-form	γ-form
Cu(1)–N(1)	1·987(11)	1·984(11)
Cu(1)–N(2)	2·029(11)	2·045(11)
Cu(1)–N(3)	1·989(10)	1·991(11)
Cu(1)–N(4)	2·038(11)	2·061(10)
Cu(1)–N(5)	2·119(12)	2·162(14)
S(1)–C(16)	1·613(13)	1·616(13)
N(5)–C(16)	1·156(18)	1·111(17)
S(2)–C(17)	1·624(16)	1·605 *
N(6)–C(17)	1·162(22)	1·090 *
N(1)–C(1)	1·332(18)	1·361(20)
N(1)–C(5)	1·373(16)	1·334(18)
C(1)–C(2)	1·389(20)	1·372(24)
C(2)–C(3)	1·378(21)	1·397(26)
C(3)–C(4)	1·363(21)	1·404(26)
C(4)–C(5)	1·358(19)	1·360(23)
C(5)–C(6)	1·477(19)	1·519(22)
N(2)–C(6)	1·463(18)	1·483(19)
N(2)–C(7)	1·499(18)	1·517(19)
C(7)–C(8)	1·540(21)	1·523(22)
C(8)–C(9)	1·475(22)	1·548(22)
N(3)–C(9)	1·500(18)	1·530(19)
N(3)–C(10)	1·467(18)	1·481(18)
C(10)–C(11)	1·511(20)	1·496(19)
C(11)–C(12)	1·371(21)	1·387(18)
C(12)–C(13)	1·401(24)	1·322(20)
C(13)–C(14)	1·369(25)	1·391(20)
C(14)–C(15)	1·378(23)	1·410(20)
N(4)–C(11)	1·338(18)	1·333(16)
N(4)–C(15)	1·343(18)	1·308(17)

TABLE 5 (*Continued*)

(*b*) Bond angles (°)

	α-form	γ-form
N(1)–Cu(1)–N(2)	83·4(4)	83·6(5)
N(1)–Cu(1)–N(3)	174·5(4)	176·7(5)
N(1)–Cu(1)–N(4)	100·4(4)	101·3(4)
N(1)–Cu(1)–N(5)	90·5(5)	89·4(5)
N(2)–Cu(1)–N(3)	93·3(4)	93·6(4)
N(2)–Cu(1)–N(4)	145·1(4)	139·3(4)
N(2)–Cu(1)–N(5)	108·5(5)	118·5(5)
N(3)–Cu(1)–N(4)	79·7(4)	81·9(4)
N(3)–Cu(1)–N(5)	94·8(5)	90·5(4)
N(4)–Cu(1)–N(5)	106·1(5)	102·1(4)
Cu(1)–N(1)–C(1)	125·2(9)	125·3(10)
Cu(1)–N(1)–C(5)	114·7(8)	115·6(9)
Cu(1)–N(2)–C(6)	110·0(8)	108·5(9)
Cu(1)–N(2)–C(7)	115·1(8)	115·2(8)
Cu(1)–N(3)–C(9)	114·7(8)	111·5(8)
Cu(1)–N(3)–C(10)	105·8(8)	106·5(8)
Cu(1)–N(4)–C(11)	111·6(9)	112·3(8)
Cu(1)–N(4)–C(15)	130·2(9)	128·8(9)
Cu(1)–N(5)–C(16)	151·6(11)	159·8(11)
S(1)–C(16)–N(5)	179·2(13)	179·0(13)
S(2)–C(17)–N(6)	176·8(15)	180·0 *
C(1)–N(1)–C(5)	120·0(11)	118·0(12)
N(1)–C(1)–C(2)	122·1(13)	123·0(15)
C(1)–C(2)–C(3)	117·5(13)	117·2(16)
C(2)–C(3)–C(4)	120·0(14)	120·0(17)
C(3)–C(4)–C(5)	121·2(13)	117·6(16)
N(1)–C(5)–C(4)	119·2(12)	123·8(14)
C(4)–C(5)–C(6)	125·3(12)	121·7(14)
N(1)–C(5)–C(6)	115·3(11)	114·5(13)
N(2)–C(6)–C(5)	113·3(11)	111·1(12)
C(6)–N(2)–C(7)	111·0(10)	108·4(11)
N(2)–C(7)–C(8)	111·7(12)	111·7(12)
C(7)–C(8)–C(9)	115·3(13)	112·7(13)
N(3)–C(9)–C(8)	111·2(12)	108·1(12)
C(9)–N(3)–C(10)	114·4(10)	108·6(11)
N(3)–C(10)–C(11)	105·8(11)	110·4(11)
N(4)–C(11)–C(10)	114·9(12)	114·8(11)
C(10)–C(11)–C(12)	122·3(13)	123·0(12)
N(4)–C(11)–C(12)	122·8(13)	122·1(12)
C(11)–C(12)–C(13)	118·3(15)	118·3(13)
C(12)–C(13)–C(14)	119·2(16)	122·2(13)
C(13)–C(14)–C(15)	118·8(16)	115·3(13)
N(4)–C(15)–C(14)	122·6(14)	123·2(13)
C(11)–N(4)–C(15)	118·2(12)	118·8(11)

(c) Other significant contacts (Å)

	α-form	γ-form
H(1) · · · H(20)	2·20	2·76
S(2) · · · N(2)	3·35	3·34
N(3) · · · N(6)	2·96	3·29
S(2) · · · H(7)	2·40	2·32
N(6) · · · H(14)	1·99	2·23

* The geometry of the thiocyanate involving S(2), C(17), and N(6) was constrained during refinement.

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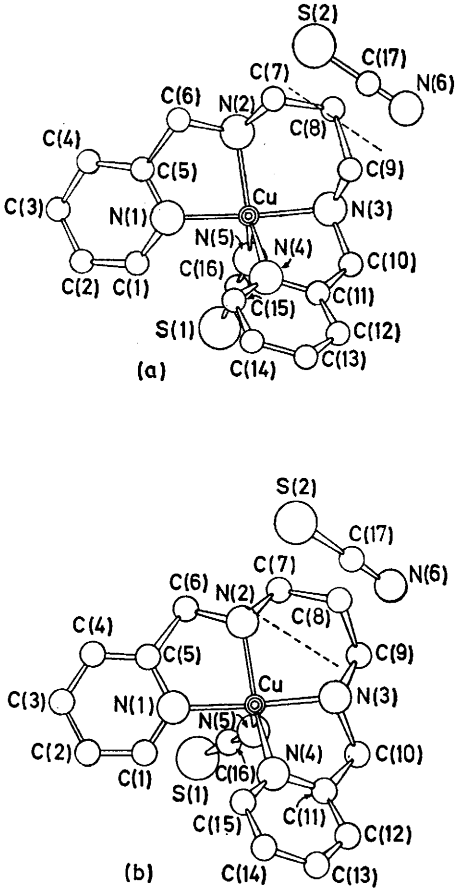
[4] E. L. Muetterties and R. A. Schunn, *Quart. Rev.*, 1966, 245.

of the ligand (I); in both cases, the six-membered chelate ring adopts a chair conformation: equations of planes are given in Table 6. These differences in configuration are clearly shown in the Figure and in Table 6(c) where the deviations of each atom from the mean plane through Cu, N(1), N(2), and N(3) are listed. The differences between close H · · · H intramolecular contacts between aromatic hydrogen atoms [as listed in Table 4(*c*)] also illustrates this difference in configuration of the two isomers. It is also clear from Table 4(*c*) that in both isomers the ionic thiocyanate is weakly hydrogen bonded at both sulphur and nitrogen atoms to the two N(H) groups within the same molecule. In the case of the γ-form, this thiocyanate was found to be disordered with respect to the reversed linear anion. The disorder was taken into account during least-square refinement by refining two mutually reversed linear ions of constrained geometry with coincident terminal atoms; the populations of the two components were found to be 0·74 and 0·26. In all discussion, Tables, and in the Figure, the atom symbols used refer to the component of higher population.



The molecular structures and atomic labelling of (a) the γ- and (b) the α-form. To avoid confusion, the ionic thiocyanate is displaced from its true position which is indicated by the broken line: the ions lie respectively above (α-form) and below (γ-form) the plane of the projection

TABLE 6

Equations of molecular planes in the α- and γ-forms (referred to axes *a*, *b**, *c*′) with deviations (Å) of atoms from the planes given in square brackets

(a) α-form

Plane (1): Cu(1), N(2), N(3)

Equation: $0{\cdot}6949X - 0{\cdot}3337Y + 0{\cdot}6370Z - 1{\cdot}4947 = 0$
Deviation: C(7) [−0·96], C(8) [−0·71], C(9) [−1·00]

Plane (2): N(2) [0·0135], N(3) [−0·0135], C(7) [−0·0155], C(9) [0·0155]

Equation: $0{\cdot}6371X + 0{\cdot}3668Y + 0{\cdot}6779Z - 3{\cdot}6051 = 0$
Deviation: Cu(1) [−0·91], C(8) [0·70]

Plane (3): C(7), C(8), C(9)

Equation: $0{\cdot}6084X - 0{\cdot}6245Y + 0{\cdot}4898Z + 1{\cdot}0796 = 0$
Deviation: Cu(1) [1·75], N(2) [1·28], N(3) [1·31]

Plane (4): N(1) [0·0119], C(1) [−0·0022], C(2) [−0·0087], C(3) [0·0099], C(4) [−0·0002], C(5) [−0·0107]

Equation: $0{\cdot}7159X - 0{\cdot}2468Y + 0{\cdot}6531Z - 1{\cdot}7556 = 0$
Deviations: Cu(1) [−0·01], C(6) [−0·19]

Plane (5): N(4) [−0·0026], C(11) [−0·0186], C(12) [0·0202], C(13) [−0·0022], C(14) [−0·0181], C(15) [0·0212]

Equation: $-0{\cdot}5189X - 0{\cdot}4221Y - 0{\cdot}7434Z + 2{\cdot}2189 = 0$
Deviations: Cu(1) [−0·05], C(10) [−0·10]

Angles (°) between planes: (1)–(2) −41·2, (1)–(3) +19·4, (2)–(3) +60·6°.

(*b*) γ-form

Plane (1): Cu(1), N(2), N(3)

Equation: $-0{\cdot}2050X + 0{\cdot}9121Y - 0{\cdot}3550Z - 1{\cdot}5893 = 0$
Deviations: C(7) [−0·98], C(8) [−0·75], C(9) [−1·11]

Plane (2): N(2) [−0·0454], N(3) [0·0451], C(7) [0·0522], C(9) [−0·0519]

Equation: $-0{\cdot}1620X + 0{\cdot}9062Y + 0{\cdot}3907Z - 0{\cdot}7749 = 0$
Deviations: Cu(1) [−0·96], C(8) [0·77]

Plane (3): C(7), C(8), C(9)

Equation: $-0{\cdot}1361X + 0{\cdot}7367Y - 0{\cdot}6624Z - 0{\cdot}4971 = 0$
Deviations: Cu(1) [1·85], N(2) [1·31], N(3) [1·41]

Plane (4): N(1) [−0·0166], C(1) [−0·0136], C(2) [0·0356], C(3) [−0·0293], C(4) [0·0002], C(5) [0·0237]

Equation: $0{\cdot}0770X - 0{\cdot}9855Y + 0{\cdot}1512Z + 1{\cdot}1829 = 0$
Deviations: Cu(1) [−0·44], C(6) [0·11]

Plane (5): N(4) [−0·0171], C(11) [0·0059], C(12) [0·0107], C(13) [−0·0159], C(14) [0·0045], C(15) [0·0119]

Equation: $-0{\cdot}1474X - 0{\cdot}4374Y + 0{\cdot}8871Z + 3{\cdot}4663 = 0$
Deviations: Cu(1) [0·02], C(10) [−0·02]

Angles (°) between planes: (1)–(2) −43·9, (1)–(3) +20·8, (2)–(3) +64·5°.

(*c*) Atoms referred to plane through Cu, N(1)—(3)

Equations: $0{\cdot}7087X - 0{\cdot}2877Y + 0{\cdot}6442Z - 1{\cdot}6935 = 0$ (α-form)
$-0{\cdot}2026X + 0{\cdot}9189Y - 0{\cdot}3384Z - 1{\cdot}5850 = 0$ (γ-form)

Cu(1) [−0·05, 0·02],* N(1) [0·03, −0·01], N(2) [0·00, 0·00], N(3) [0·03, −0·01], S(1) [−4·40, −3·89], S(2) [3·32, −2·92], N(4) [1·05, 1·36], N(5) [−2·07, −1·87], N(6) [2·89, −2·71], C(1) [0·07, −0·25], C(2) [0·10, −0·51], C(3) [0·10, −0·63], C(4) [0·03, −0·35], C(5) [−0·02, −0·04], C(6) [−0·25, 0·33], C(7) [−0·90, 0·95], C(8) [−0·61, 0·71], C(9) [−0·92, 1·09], C(10) [−0·14, 0·25], C(11) [0·83, 1·30], C(12) [1·44, 2·14], C(13) [2·39, 3·00], C(14) [2·64, 3·14], C(15) [1·93, 2·26], C(16) [−3·04, −2·69], C(17) [3·10, −2·79]

* The deviation of the α-forms listed first.

As a result of this disorder, the lengths of the N(H) · · · N and N(H) · · · S interactions determined in the γ-form are intermediate between the very different values [N(H) · · · N 2·96, and N(H) · · · S 3·35 Å] observed for the α-form where no disorder occurs.

All bond lengths in both molecules are close to expected values although there is a significant tendency for axial Cu–N bonds to be slightly shorter (mean 1·99 Å) than equatorial Cu–N(tetramine) bonds (mean value of 2·04 Å). Similar differences between axial and equatorial bond lengths have been noticed in at least two other trigonal bipyramidal copper(II) co-ordination polyhedra.[5,6]

Significant angular distortions are confined to the following. (*a*) The expected deviations from 120° at the aromatic nitrogen atoms consequent on the steric strain involved in co-ordination to the copper atom. (*b*) Non-colinearity at the nitrogen atom of the co-ordinated isothiocyanate; such deviations from colinearity (Cu–N–C 152 and 160°) are large but not more than has been observed in a variety of other isothiocyanato compounds of first-row transition metals. (*c*) Distortions of the trigonal bipyramidal co-ordination polyhedra of the copper ion are substantially restricted to the equatorial plane; the principal distortion involves the N(2)–Cu–N(4) angle which is increased to 145 (α-form) or 139° (γ-form). The variation in the angles in the equatorial plane involving N(5) probably arise mainly from packing considerations.

Table 6 details the mean planes of the pyridyl fragments in the two molecules: all are closely coplanar. The large deviation of the copper atom from the mean plane of the 'axial' pyridyl fragment in the γ-form is worthy of note. There are no intermolecular contacts less than the sum of van der Waals radii in either structure. The only significant intramolecular close contact in either molecule is that between H(1) and H(20) [attached to C(1) and C(15) respectively] in the α-form. This contact of 2·20 Å (which is slightly shorter than the accepted van der Waals diameter for hydrogen) reflects the closer approach of the two pyridyl fragments in the α-form, consequent on the different configurations of the tetrahedral nitrogen atoms of the tetramine ligands in the two forms: the corresponding distance in the γ-form is 2·76 Å.

Programs used in this structure determination form part of the Sheffield *X*-ray System; calculations were performed on the Chilton Atlas and Sheffield University ICL 1907 computers.

[2/133 *Received, 21st January,* 1972]

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