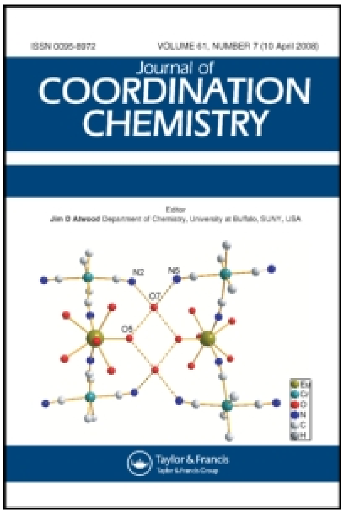

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The isothiocyanate complex [Cu(DOHPN)(NCS)] (DOHPN = 3,3′-trimethylenedinitrilobis-(2-butanone oxime)) has been prepared and characterized by infrared spectroscopy and X-ray crystallography as the isomer of the thiocyanate complex whose crystal structure is found in the literature. The formula unit of the title compound, is $[Cu(DOHPN)(NCS)]_2[Cu(DOHPN)(H_2O)](ClO_4)$ corresponding to $C_{35}H_{59}ClCu_3N_{14}O_{11}S_2$. The crystal is triclinic, space group P-1, $Z = 2$, and has the following lattice constants: $a = 7.460(1)$ Å, $b = 11.541(2)$ Å, $c = 29.149(6)$ Å, $\alpha = 97.44(3)°$, $\beta = 91.32(3)°$, $\gamma = 96.68(3)°$. In each of the three complexes which compose the formula unit, the copper(II) lies in a square pyramidal environment made of an axial ligand and four nitrogen atoms of the tetraaza ligand.

The stronger the interaction between copper(II) and the axial ligand, the more the DOHPN bends resulting in a "butterfly-like" geometry. Formation of the thiocyanate isomer is kinetically favored over the thermodynamically more stable isothiocyanate isomer. This system is one of the very few examples of structurally characterized copper(II) thiocyanate–isothiocyanate linkage isomers. Its study should contribute to understanding of the isomerization phenomena.

Keywords: Thiocyanate–isothiocyanate isomerization; copper(II) complex; iminooxime tetraaza macrocycle; crystal structure; IR spectra

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INTRODUCTION

Isomerizable systems are widely studied due to their possible applications in molecular information storage devices.[1] In the field of coordination chemistry, linkage isomers have been reported in the literature, including a great variety of chemical systems such as ruthenium(II)-bis(bipyridine),[2] ruthenium(II)/(III)-pentaamine,[3] chromium(III)-dicyanoamine,[4] cobalt(III)-pentaamine,[5] the classic nitro–nitrito[6] and our own contribution to the field with the pentacyanoferrate[7] and osmium(II)-pentaamine complexes.[8] Amongst the isomerizable ligands the amphiphilic thiocyanate, first recognized by Alfred Werner in 1899,[9] still is the subject of intense investigation (see a recent review by Kabesová *et al.*).[10]

Copper ion is related to the active site of natural proteins with many synthetic models studied.[11]

The stability of metal-tetraaza macrocycle bonds has proven to be useful for systematic study of structural variations in five-coordinate complexes.[12] Also single axially by bridged copper(II)-macrocycles have contributed to a better understanding of electron exchange processes between paramagnetic ions.[13]

Planar tetraaza macrocyclic compounds such as DOHPN usually bind to metals as a quadridentate ligand as demonstrated in complexes of nickel,[14] cobalt,[15] iron[16] and copper.[17] In [Cu(DOHPN)(axial ligand)]$^{n+}$ the copper(II) ion lies in an approximately square pyramidal environment bound to an axial ligand and to four nitrogen atoms of the tetraaza macrocycle that form the square base. Complexes with imidazole,[17a] methanol,[17b] ethanol,[17c] thiophenol and p-chlorothiophenol,[17d] bromide,[17e] thiocyanate[17f] and water[17g] as axial ligands have been prepared and structurally characterized.

On going from weak to strong metal–axial ligand interaction in [Cu(DOHPN)(axial ligand)]$^{n+}$ the metal–axial ligand bond shortens, the metal-tetraaza plane distance increases and the equatorial ligand is forced to bend resulting in a "butterfly-like" geometry (see crystal structure discussion below). These three structural parameters will be used throughout the text when comparing the various [Cu(tetraaza)(axial ligand)]$^{n+}$ complexes.

In an attempt to prepare the dimeric compound [Cu(DOHPN)]$_2$(μ-SCN)](ClO$_4$) we have obtained the monomer complex [Cu(DOHPN)-(NCS)]. Since the structure of the thiocyanate isomer [Cu(DOHPN)(SCN)] had been published recently[17f] and knowing that only a few pairs of structurally characterized thiocyanate-isothiocyanate isomers of copper(II)-tetraaza have been reported[18] we investigated the new complex.

From a comparison between the synthetic conditions used to produce each linkage isomer we suggest that the isothiocyanate isomer is thermodynamically favored but not kinetically favored over the thiocyanate isomer.

EXPERIMENTAL

Materials

The ligand DOHPN was synthesized by the procedure of Gagné.[19] Basic copper(II) carbonate (Qeel), perchloric acid (60%, $d = 1.53$ g/mL, Merck), sodium thiocyanate (Merck), methanol (Merck), carbon tetrachloride (Merck) and methyl iodide (Merck) were used as supplied. $Cu(ClO_4)\cdot xH_2O$ was prepared from neutralization of $CuCO_3\cdot Cu(OH)_2$ with $HClO_4$ as described by Rorobacher.[20] $[Cu(DOHPN)(H_2O)](ClO_4)$ was obtained as indicated by Gagné.[19]

Synthesis

Bis [(isothiocyanate)3,3′-(trimethylenedinitrilo)bis(2-butanone oximato) copper(II)] [(aquo)3,3′-(trimethylenedinitrilo)bis(2-butanone oximato) Copper(II)] (perchlorate), $[Cu(DOHPN)(NCS)]_2$ $[Cu(DOHPN)(H_2O)](ClO_4)$. The salt NaSCN 27.8 mg (0.3 mmol) was dissolved in a minimum of water and mixed with 30 mL of a warm methanolic solution of [Cu(DOHPN)-$(H_2O)](ClO_4)$ 278 mg (0.6 mmol). The resulting solution was then stirred on a hot plate for ca 20 min. Upon standing in an open beaker, dark wine crystals separated from the solution and were collected by filtration, washed several times with small volumes of a diethyl ether/methanol mixture 2 : 1 (v/v) and dried over silica gel under vacuum. The yield was 10%. Anal. Calcd. for $C_{35}H_{59}ClCu_3N_{14}O_{11}S_2$(%): C, 36.8; H, 5.21; N, 17.17. Found: C, 36.94; H, 4.90; N, 17.19. The crystal density was determined by the flotation method in mixtures of carbon tetrachloride and methyl iodide and was found to be between 1.47 and 1.60 g/mL. Selected IR and far-IR data: 448(w) and 457(w) (δNCS), 798(w) (νCS), 2024(sh) and 2082(s) (νCN–NCS), 1227(w) (νNO–DOHPN), 1627(w) (νCN–DOHPN), 2927(w) (ν_{as}CH–DOHPN), 1118(vs) and 1087 (s) (νClO–ClO_4^-).

Physical Measurements

IR Spectroscopy

Infrared spectra were obtained with a Bomen Hartmann & Braun MB series spectrophotometer in the region 4000–400 cm^{-1} as KBr pellets, and with a

Bomem DA8 instrument in the region 700–200 cm^{-1} as a nujol mull with high density polyethylene windows.

Crystallographic Measurements

A long and thin, prismatic, dark wine single-crystal of $[Cu(DOHPN)(NCS)]_2[Cu(DOHPN)(H_2O)](ClO_4)$ was mounted in the goniometer head of an Enraf-Nonius CAD4 diffractometer. A summary of data collection and refinement is in Table I. An empirical absorption correction was applied.[21] The structure was solved by direct methods using the program SHELXS-86[22] which revealed the positions of most heavy atoms. The remaining heavy atoms were located in successive refinement cycles using the program SHELXL-93.[23] Drawings were made with the program ORTEPII.[24] The carbon atoms C(6A) and C(6C) (the atom numbering scheme is in the Results section) were disordered in a chair, boat configuration and were modeled as C(6A1) and C(6A2) (with 50% site occupation) and as C(6C1) and C(6C2) (with 60 and 40% site occupation), respectively. These site occupation factors were fixed after being refined isotropically in earlier stages. Hydrogen atoms were added in idealized positions and refined with U (eq) 0.08 $Å^2$ using a riding model. In each complex (A, B and C) one hydrogen atom was added to the oxime oxygen O12 and three hydrogen atoms were added to each carbon atom C14, C15, C16 and C17. In complex B two hydrogen atoms were added to the each carbon atom C5, C6,

TABLE I Crystallographic data for $[Cu(DOHPN)(NCS)]_2[Cu(DOHPN)(H_2O)](ClO_4)$

Chemical formula	$Cu_3C_{35}H_{59}N_{14}O_{11}S_2Cl$	Max. shift/esd	0.018
Z	2	h	$0 < h < 8$
a	7.460(1) Å	k	$-13 < k < 13$
b	11.541(2) Å	l	$-34 < l < 34$
c	29.149(6) Å	Reflections measured	6431
α	97.44(3)°	Independent reflections	6193
β	91.32(3)°	R (obs)[a], %	5.56
γ	96.68(3)°	R (all)[a], %	14.07
Wavelength	0.71073 Å	wR (obs)[a], %	13.41
T	25°C	wR (all)[a], %	34.72
Radiation	MoKα	max. peak	0.640
Monochromator	yes	max. hole	−0.550
Space group	P-1	V, $Å^3$	2469.7(7)
μ, mm^{-1}	1.486	ρ(calcd.), g mL^{-1}	1.536
Diffractometer	CAD4 Enraf Nonius	ρ(meas.), g mL^{-1}	$1.47 < \rho < 1.60$
Diffraction geometry	θ–2θ	F(000)	1182
2θ range	$1.4 < 2\theta < 45.0$	Data/parameter	10.1

[a] Same meaning as the CIF entries: _refine_ls_R(or wR)_factor_obs(or all).

C7.† All heavy atoms were refined anisotropically in the last full-matrix refinement, no geometrical constraints were used.

RESULTS

Crystal Structure

The formula unit of crystal $[Cu(DOHPN)(NCS)]_2[Cu(DOHPN)(H_2O)]$-$(ClO_4)$ (Figure 1) has two [Cu(DOHPN)(NCS)] complexes labeled A and B, a complex $[Cu(DOHPN)(H_2O)]^+$ labeled C and a perchlorate anion.

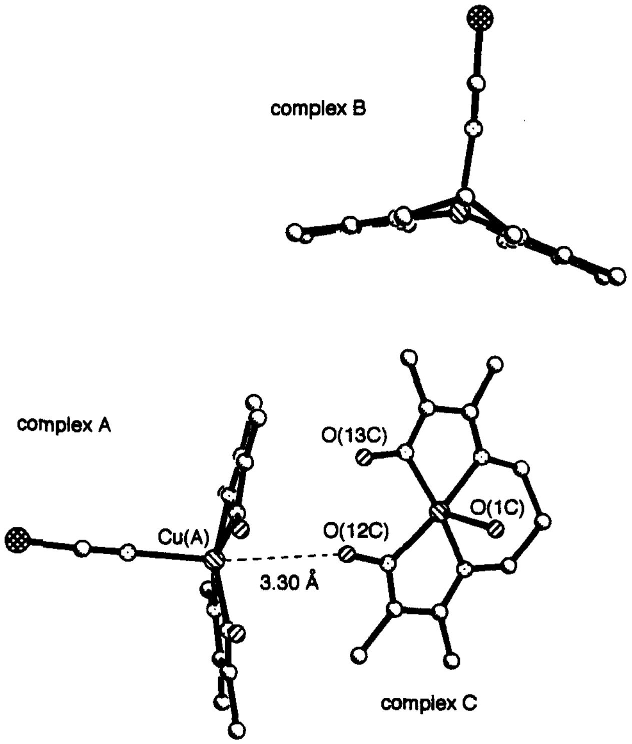

FIGURE 1 A view of the three complexes in the formula unit in the crystal of $[Cu(DOHPN)(NCS)]_2[Cu(DOHPN)(H_2O)](ClO_4)$ showing the intermolecular contact between the Cu(A) and O(12C). All hydrogen atoms and the carbon atoms C(6A1), C(6A2) and C(6C2) were omitted for clarity.

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† The hydrogen labels are the same as those used to identify the heavy atom that bears them, the last character of the label (1, 2 or 3) being used to distinguish between hydrogens bound to the same atom. As an example, the carbon atom C(15A) bears hydrogen atoms H(15A1), H(15A2) and H(15A3).

TABLE II Atomic coordinates [× 10^4] and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for the complex $[Cu(DOHPN)(NCS)_2)][Cu(DOHPN)(H_2O)](ClO_4)$. *U* (eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	*U* (eq)
CuA	7297 (2)	3996 (1)	3004 (1)	46 (1)
N (1A)	9137 (10)	3478 (7)	3398 (3)	46 (2)
C (2A)	9244 (13)	3958 (9)	3819 (4)	46 (2)
C (3A)	7896 (14)	4800 (9)	3935 (4)	55 (3)
N (4A)	6837 (11)	4901 (7)	3596 (3)	50 (2)
C (5A)	5364 (16)	5670 (11)	3638 (5)	76 (4)
C (6A1)	3614 (25)	4988 (17)	3370 (7)	42 (5)
C (6A2)	4719 (47)	5911 (28)	3207 (10)	99 (11)
C (7A)	3637 (15)	4811 (11)	2865 (5)	69 (4)
N (8A)	4953 (10)	4041 (7)	2690 (3)	45 (2)
C (9A)	4652 (12)	3344 (9)	2321 (4)	41 (2)
C (10A)	6088 (13)	2574 (9)	2180 (3)	43 (2)
N (11A)	7391 (10)	2739 (7)	2497 (3)	43 (2)
O (12A)	8775 (9)	2091 (6)	2444 (3)	61 (2)
O (13A)	10214 (9)	2676 (6)	3234 (2)	56 (2)
C (14A)	10576 (16)	3701 (11)	4172 (4)	77 (4)
C (15A)	7861 (17)	5385 (11)	4422 (4)	76 (4)
C (16A)	2979 (14)	3182 (10)	2008 (4)	61 (3)
C (17A)	6053 (15)	1740 (10)	1756 (4)	61 (3)
N (0A)	8915 (13)	5375 (10)	2702 (4)	73 (3)
C (0A)	9794 (14)	6061 (9)	2544 (4)	48 (3)
S (0A)	11190 (4)	6929 (3)	2276 (1)	68 (1)
CuB	8873 (2)	7613 (1)	712 (1)	39 (1)
N (1B)	8534 (10)	9286 (7)	790 (2)	39 (2)
C (2B)	9852 (13)	9992 (8)	688 (3)	41 (2)
C (3B)	11407 (13)	9419 (9)	524 (3)	44 (2)
N (4B)	11225 (10)	8278 (7)	504 (3)	44 (2)
C (5B)	12645 (14)	7576(9)	364 (4)	60 (3)
C (6B)	11928 (16)	6253 (11)	293 (5)	72 (4)
C (7B)	11340 (16)	5741 (10)	711 (4)	66 (3)
N (8B)	9675 (11)	6160 (7)	884 (3)	44 (2)
C (9B)	8735 (15)	5656 (9)	1174 (4)	50 (3)
C (10B)	7170 (14)	6265 (9)	1348 (3)	47 (3)
N (11B)	7076 (10)	7228 (7)	1170 (3)	42 (2)
O (12B)	5750 (9)	7882 (6)	1301 (2)	58 (2)
O (13B)	7030 (9)	9679 (6)	960 (3)	54 (2)
C (14B)	9825 (16)	11314 (9)	736 (4)	64 (3)
C (15B)	13090 (15)	10112 (11)	389 (4)	70 (3)
C (16B)	9050 (18)	4540 (9)	1357 (5)	76 (4)
C (17B)	5883 (16)	5818 (10)	1678 (4)	66 (3)
N (0B)	7374 (11)	7009 (8)	93 (3)	54 (2)
C (0B)	6502 (13)	6808 (8)	−231 (3)	38 (2)
S (0B)	5300 (5)	6498 (3)	−720 (1)	74 (1)
CuC	11430 (2)	10254 (1)	3329 (1)	42 (1)
N (1C)	11780 (11)	10330 (7)	2673 (3)	43 (2)
C (2C)	10426 (15)	9845 (9)	2399 (3)	48 (3)
C (3C)	8807 (14)	9439 (9)	2661 (4)	51 (3)
N (4C)	9027 (10)	9542 (8)	3094 (3)	50 (2)
C (5C)	7568 (15)	9201 (13)	3416 (4)	76 (4)
C (6C1)	8371 (25)	8909 (21)	3866 (8)	65 (6)
C (6C2)	7712 (43)	9880 (40)	3828 (12)	96 (14)
C (7C)	9390 (14)	9879 (11)	4201 (4)	60 (3)

TABLE II (*Continued*)

	x	*y*	*z*	*U* (eq)
N (8C)	11033 (10)	10405 (7)	3990 (3)	42 (2)
C (9C)	12360 (13)	10975 (9)	4240 (3)	42 (2)
C (10C)	13895 (12)	11454 (8)	3979 (3)	39 (2)
N (11C)	13683 (10)	11195 (7)	3550 (3)	41 (2)
O (12C)	14934 (9)	11585 (7)	3262 (2)	62 (2)
O (13C)	13334 (9)	10761 (6)	2511 (2)	56 (2)
C (14C)	10476 (17)	9729 (11)	1893 (4)	69 (3)
C (15C)	7096 (17)	8939 (13)	2386 (5)	92 (4)
C (16C)	12448 (16)	11185 (11)	4750 (3)	69 (3)
C (17C)	15528 (17)	12196 (12)	4218 (5)	88 (4)
O (1C)	12756 (10)	8480 (6)	3292 (3)	63 (2)
Cl	2641 (4)	7481 (3)	4496 (1)	58 (1)
O (1)	1640 (13)	7100 (9)	4081 (3)	96 (3)
O (2)	1537 (15)	7984 (11)	4827 (3)	122 (4)
O (3)	3347 (16)	6528 (9)	4657 (3)	114 (4)
O (4)	4038 (15)	8299 (11)	4401 (5)	144 (5)

Complexes A and B differ slightly in their structural parameters and are not related by symmetry. Table II has fractional atomic coordinates and Table III has selected bond distances, bond angles, distances from atoms to planes and dihedral angles between planes. The atomic labeling scheme of the Cu(DOHPN) fragment (Figure 2) of the three complexes differs only in the last character that indicates if it belongs to A, B or C (Table II). The atomic labeling of the isothiocyanate ligand of complexes A and B also differ only in the last character (Figure 2, Table II). The water oxygen atom of complex C was labeled O(1C).

Infrared Spectrum

Selected infrared frequencies of the spectrum of $[Cu(DOHPN)(NCS)]_2[Cu(DOHPN)(H_2O)](ClO_4)$ are presented in Table IV with the ranges for known thiocyanate and isothiocyanate complexes.

DISCUSSION

Crystal Structure

On each complex the copper(II) ion has a distorted square pyramidal environment. The axial ligand bound to the copper(II) ion is an isothiocyanate anion in the neutral complexes A and B and is a water molecule in complex C (Figure 1).

TABLE III Selected bond distances (Å), bond angles (degree), distances from atoms to planes (Å), dihedral angles between planes (degree) and mean deviation from the least-squares planes (Å) (degree) for $[Cu(DOHPN)(NCS)]_2[Cu(DOHPN)(H_2O)](ClO_4)$ and [Cu(DOHPN)(SCN)] (esd's in parantheses)[a]

	Complex A[a] *[Cu(DOHPN)(NCS)]*	*Complex B*[a] *[Cu(DOHPN)(NCS)]*	*Thiocyanate isomer*[e] *$[Cu(DOHPN)(SCN)]^+$*	*Complex C*[a] *$[Cu(DOHPN)(H_2O)]^+$*	*Ref.* [17g] *$[Cu(DOHPN)(H_2O)]^+$*
Distances (Å)					
Cu-axial ligand	2.172(11)	2.093(10)	2.521(2)	2.366(8)[b]	2.355(7)
Cu–N(1)	1.965(8)	1.961(8)	1.956(3)	1.946(7)	1.945(7)
Cu–N(4)	1.959(8)	1.973(8)	1.970(3)	1.953(8)	1.960(8)
Cu–N(8)	1.964(8)	1.964(8)	1.965(3)	1.946(8)	1.972(7)
Cu–N(11)	1.941(8)	1.968(8)	1.974(3)	1.940(8)	1.950(6)
N(0)–C(0)	1.121(12)	1.118(12)	1.129(8)	—	—
C(0)–S(0)	1.642(12)	1.643(11)	1.613(7)	—	—
O(12)–O(13)	2.497	2.504	2.530(4)	2.489	2.49
Cu-tetraaza-plane[c]	0.3112	0.4077	0.336(2)	0.1400	0.10
Angles (degree)					
Cu–N(0)–C(0)	177.7(10)	172.0(9)	—	—	—
Butterfly angle[c,d]	163.2	149.9	161.8	172.9	—
Mean deviation from the least-squares planes (Å)					
Tetraaza plane[c]	0.036	0.010	0.0113	0.011	—
Butterfly wing 1[c]	0.002	0.000	0.0138	0.018	
Butterfly wing 2[c]	0.014	0.003	0.0001	0.008	

[a] The complexes A, B and C are shown in the view of the formula unit, Figure 1;

[b] $CuC-O1C(H_2O)$;

[c] Least-squares planes: tetraaza plane = N1N4N8N11; butterfly wing 1 = N1N4C2C3; butterfly wing 2 = N8N11C9C10;

[d] Dihedral angle between butterfly wing 1 and butterfly wing 2;

[e] Refer footnote on p. 261.

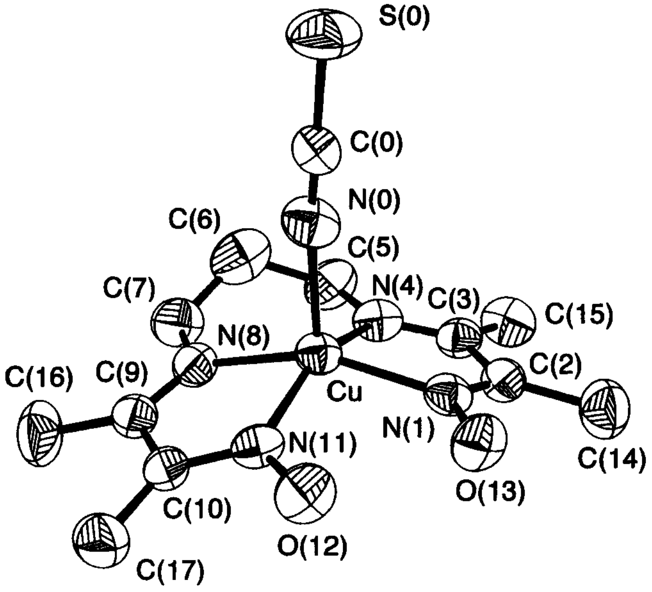

FIGURE 2 ORTEP view of complex B, [Cu(DOHPN)(NCS)], present in the crystal of $[Cu(DOHPN)(NCS)]_2[Cu(DOHPN)(H_2O)](ClO_4)$. The hydrogen atoms have been omitted for clarity. The thermal ellipsoids were drawn at the 50% probability level. The label scheme of the Cu(DOHPN) macrocycle is the same for all three complexes being the last character of each label in Table II used to distinguish between the complexes A, B or C. The labels for the NCS fragment is the same for complexes A and B being the last character of each label in Table II used to distinguish between the complexes A and B.

TABLE IV Infrared frequencies for the title complex, $[Cu(DOHPN)(NCS)_2][Cu(DOHPN)(H_2O)](ClO_4)$, and the mean values for other thiocyanate and isothiocyanate complexes described in the literature, cm^{-1}

	Title complex	*S-bonded*	*N-bonded*	*"Free" SCN*
ν(CS)	798(w)	690–720	780–860	748
δ(NCS)	448(w), 475(w)	420	480	486, 471
ν(CN)	2024(sh), 2082(s)	≈2100	2050–2080	2053
Ref.	This work	30, 31	30, 31	30, 31

The copper(II)–N(NCS) bond distances found in complexes A and B are characteristic of an isothiocyanate axially bound to a central metal atom with coordination number five.[10] The four nitrogen atoms of the DOHPN ligand in complexes A, B and C are reasonably coplanar with the maximum deviation from the least-square plane being lower than 0.036 Å (Table III). The N–C and the C–S bond distances of the isothiocyanate ligand in complexes A and B (Table III) are in accord with published values for related NCS complexes.[17f,18,26,25] The hydrogen bond between the oxime oxygen atoms is quite strong in complexes A, B and C as shown by the short O(12)–O(13) distance of about 2.50 Å. Other bond lengths and angles observed in A, B and C are as expected from earlier studies of related complexes.[12,17,18,25–27]

In complexes A, B and C, the four Cu–N (tetraaza) bond lengths are very similar regardless of the nitrogen being part of an oxime or of an imine group (Table III).

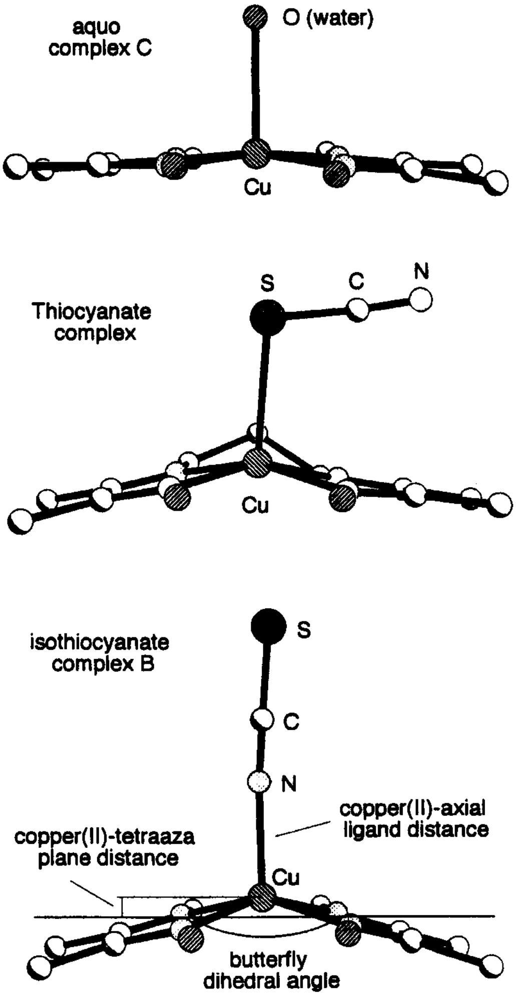

FIGURE 3 View of the crystal structure of complexes $[Cu(DOHPN)(H_2O)]^+$ (top), [Cu(DOHPN)(SCN)] (middle) and [Cu(DOHPN)(NCS)] (bottom). The three structural parameters related to the copper(II) square pyramidal environment were drawn over the bottom structure. The tetraaza and butterfly wing planes are defined in Table III.

The structural parameters of the aquo-complex C are in close agreement with those determined in the same complex present in a different crystal environment as seen in Table III.

In Figure 3 the structures, of the aquo, thiocyanate and isothiocyanate[‡] DOHPN copper(II) complexes are presented. On going from the S-bonded to the N-bonded isomer the butterfly wings close, and the copper(II) moves toward the axial ligand, away from the tetraaza plane. The trends in these three parameters indicate a weaker copper(II)–axial ligand interaction in the S-bonded than in the N-bonded isomer. A similar trend is observed on going from complex C to complex B and from complex A to complex B (Table III).

The stronger copper(II)–axial (NCS) interaction in complex B than in complex A is due to the intermolecular interaction between the copper(II) of complex A and the oxime oxygen O(12) of complex C, which are 3.30 Å apart (Figure 1). The copper(II) ion of complex B does not experience an analogous interaction.

Anderson[27,28–30] has reported the preparation and structure of $[Cu(CYCLOPS)]^+$ (CYCLOPS = difluoro-3,3′-(trimethylenedinitrilo) bis-(2-butanone oximato)borate – a ligand prepared from the DOHPN ligand by replacement of the oxime hydrogen bond with a BF_2 bond) containing several different axial ligands. In the [Cu(CYCLOPS)(I)][29] complex, the flexible macrocycle allows a copper(II) displacement of 0.38 Å from the equatorial plane, while the Cu(II)–N(equatorial) bond distances are Cu(II)–(N1) 1.959(8); Cu(II)–(N2) 1.966(11); Cu(II)–(N3) 1.936(8); Cu(II)–(N4) 1.964(11). In $[Cu(CYCLOPS)(H_2O)]ClO_4$, the copper(II) is 0.32 Å above the tetraza plane, and the Cu–N(equatorial) bond lengths are Cu(II)–(N1) 1.949 (9); Cu(II)–(N2) 1.954(10); Cu(II)–(N3) 1.938 (10); Cu(II)–(N4) 1.917 (9).[30] While the length of the bonds to the axial ligand vary (similar to the values found for complex A and B in our work, namely, 0.31 and 0.40 Å respectively, see Table III) the Cu–N(tetraaza) bonds appear to be of approximately equal length in these compounds.

Other workers have also studied copper–CYCLOPS complexes. Gagné[19] reported that the four-coordinate copper(I)–CYCLOPS complex forms very stable five-coordinate copper(I) complexes with ligands such as carbon monoxide. The spectroscopic and electrochemical properties of a series of monomeric $[Cu(II)(CYCLOPS)(L)]^{n+}$ complexes involving varying apical

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[‡] The molecular plot in Figure 3, packing diagrams and the calculated structural parameters listed in Table III were obtained by manipulating an instruction like SHELXL-93 file built from the crystal atomic coordinates given in Ref. [17f].

substitution have been investigated by Addison and Wicholas.[31] The energies of the d-d bands of these complexes were used to assign a "spectrochemical series" for apical ligands, L. The spectrochemical series obtained in this manner was $H_2O \ll$ pyridine < imidazole < $I^- < Cl^- < NCS^- \ll NCO^-$. The authors pointed out that the placement of neutral ligands such as water, imidazole and pyridine relative to the halides in this series was highly unusual and demanded, based on crystal field arguments, a large variation in the apical displacement of the copper(II) and unusually strong bonds to anionic ligands in the apical position. In other words, anionic ligands induce larger Cu(II)-out-of-plane displacements and stronger axial binding in comparison to neutral ones.

The range of Cu-out-of-plane displacements observed in the crystal structures and suggested by the spectroscopic investigation of the parent Cu(II)–CYCLOPS system, implies that the copper(II) has considerable geometric flexibility with respect to its static position in the macrocyclic ligand.

Because of the structural similarity between the CYCLOPS and the DOHPN ligands, there is no reason to believe that the same arguments cannot be applied to the Cu-DOHPN analogous complexes.

The relation between the copper(II)–(axial ligand) strength and the changes in the three structural parameters of DOHPN, as seen in Table III, were also observed in the analogous CYCLOPS complex as described above.

It might be argued that the copper–axial bond length is influenced mainly by the "butterfly" geometry adopted by the macrocycle ligand. However, it is likely that copper-to-axial ligand π-bonding is also operative in this case.

In all copper(II) complexes, the main bonding is σ-type, and with $[Cu(NH_3)X_2]$[32] and $[Cu(en)_2X_2]$,[33,34] it is the only bonding in the equatorial plane. However, with these σ-bonding ligands, a strict square coplanar stereochemistry does not occur and some further capacity for bonding is required for stability. In the above complexes, this is supplied by the weak bonding of the semi-coordinating anions, X. In these complexes, the most likely π-bonding is out-of-plane, using the copper d_{xz} and d_{yz} orbitals.

This potential for bonding above four-coordination could also be satisfied by formation of a five-coordinate complex. The copper(II) ion can form both trigonal-bipyramidal and square-based pyramidal complexes, especially the latter.[35]

Crystal-structure[36] data for the square-based pyramidal stereochemistry are much more extensive. In this, the fifth ligand is bonded at a distance of 0.2–0.6 Å greater than the in-plane ligands and, in most cases, the copper(II) ion is not strictly coplanar with the equatorial ligands but is lifted ca. 0.2 Å towards the fifth ligand.

Of the three complexes of Figure 3, and in accord with the trend in the copper(II)-(tetraaza plane) distance and "butterfly" angle discussed above, the aquo ligand has the weaker axial interaction with the copper(II) ion. On the other hand the copper(II)–axial (SCN) distance is longer than the copper(II)–axial O(water) distance. The same behavior was also observed for the complexes [Cu(CYCLOPS)(I)][29] and [Cu(CYCLOPS)(H_2O)]ClO_4.[30] We believe that the copper(II)–axial (SCN) interaction is stronger than that of copper(II)–axial O(water) even having a bond distance some 0.16 Å longer, due to the more negative charge and the higher radius of the sulfur atom in the SCN ligand when compared to the oxygen in the aquo ligand.

In the isothiocyanate complexes A and B the Cu–NCS group is almost linear with an Cu–N–C angle around 175° (Table III). The analogous Cu–N–C angle observed in [Cu(3-acetylamino-1,2,4-triazole)$(NCS)_2$] is 118.1°.[18] This wide variation in Cu–N–C angle is rationalized by the intermolecular interactions in both systems. In the crystal of the latter complex the sulfur atom is hydrogen bonded to the acetyl OH group whereas in the former the sulfur does not experience such an interaction. In contrast, the Cu–S–C angle of about 99° observed in the respective thiocyanato complexes[17f,18] seems to be independent of hydrogen bonding. In the 3-acetylamino-1,2,4-triazole complex,[18] the nitrogen atom of SCN is hydrogen bonded to a trizole NH group whereas in the DOHPN the nitrogen atom does not have such an interaction.

It is important to realize that all the structural data: Cu-axial ligand, Cu–N(equatorial), Cu-tetraaza-plane distances and the "butterfly" angle, here reported for our work and related systems are a result of a synergistic effect which includes electronic and stereochemical aspects, not to mention crystal packing effects. Any attempt to make an isolated analysis must be taken with caution.

Infrared Spectrum

The IR regions corresponding to the ν(CN), δ(NCS) and ν(CS) vibrational frequencies of thiocyanate have been used to determine its coordination mode in complexes, the ν(CN) is the most reliable diagnostic.[37,38] The three frequencies (Table IV) in the spectrum of the compound [Cu(DOHPN)(NCS)$]_2$[Cu(DOHPN)(H_2O)](ClO_4) are close to the range of the isothiocyanate coordination mode in agreement with the crystal data (Table IV).

As in [Cu(DOHPN)(NCS)$]_2$[Cu(DOHPN)(H_2O)](ClO_4) there are two ν(CN) frequencies in complexes [Ni(diamine)$(NCS)_2$][39] and [Cu(3-acetylamino-1,2,4-triazole)$_2(NCS)_2$][18] the nature of this phenomenon is still unknown. In the former compound the presence of the two bands is probably not due to an energy splitting of states but a necessary consequence of the two different crystal environments for the isothiocyanate ligand (complexes A and B in Figure 1). The absorptions at 328(s) and 411(s) cm^{-1} have been assigned as Cu–N(tetraaza) by comparison with the corresponding values of 326(w) and 406(w) cm^{-1} found in $[Cu(en)_2(NCS)](ClO_4)$.[40]

Thiocyanate–Isothiocyanate Isomers

According to Pearson's classification, copper(II) occupies an intermediate position between hard and soft and does not display a sharp preference between the hard N atom and the soft S atom. In most copper(II)–isothiocyanate complexes described in the literature the N-bonding mode is preferred, although S-bonded complexes have been reported.[10,18] Some *ab initio* VHF-SCF-MO calculations conducted by Ferrer *et al.*[18] on both isomers of the Cu-(3-acetylamino-1,2,4-triazole) system, based on crystal data, showed that the S-bonded isomer is the most stable with the lowest total energy.

The copper(II) complexes of 3-acetylamino-1,2,4-triazole are the first example where the thiocyanate and isothiocyanate isomers have been characterized by X-ray crystallography; the crystals of each isomer could be obtained from the same mother liquor due to packing differences.[18]

Recently Tahirov and Lu[17f] reported the crystal structure of the thiocyanate isomer of the isothiocyanate complex reported in the present work. Factors such as the nature of the metal, its oxidation state, the presence of other ligands, steric effects and physical state may influence the mode of coordination.[38] These factors are common in both isomers except for the synthetic procedures. While the thiocyanate isomer was prepared in water at room temperature in the presence of excess NaSCN, the isothiocyanate isomer was prepared in hot (~50°C) methanol with a Cu(DOHPN)/NCS molar ratio of 2/1 in ca 20 min. From the comparison between the two synthetic routes it seems that the isothiocyanate isomer is thermodynamically favored over the thiocyanate isomer.

CONCLUSIONS AND FUTURE WORK

The product synthesized as described in the experimental section was initially formulated as the dimer $[Cu(DOHPN)_2(\mu\text{-}N)(NCS)](ClO_4)$, where the

NCS would bridge two Cu(DOHPN) moieties. The dimer formulation is in agreement with the elemental analysis and infrared spectra. The crystal structure surprised us and the compound had to be reformulated as $[Cu(DOHPN)(NCS)]_2[Cu(DOHPN)(H_2O)](ClO_4)$, illustrating the importance of the crystallographic characterization along with other analytical techniques.

We have prepared and characterized $[Cu(DOHPN)(NCS)]_2[Cu(DOHPN)(H_2O)](ClO_4)$ by X-ray crystallography and IR spectroscopy. The formula unit of the crystal has two non-equivalent [Cu(DOHPN)(NCS)] complexes, a third complex $[Cu(DOHPN)(H_2O)]^+$ and a perchlorate anion. The first of the isothiocyanate complexes is bound to an oxime oxygen atom of the aquo complex whereas the second is not and this intermolecular interaction is responsible for their structural differences. The bond distances and angles of all three complexes are within the ranges expected for similar complexes. The infrared spectroscopic data collected in the solid state were found to be in agreement with the crystal structure and are comparable to those of related complexes.

The strength of the copper(II)–(axial ligand) interaction is associated with the length of the copper(II)–(axial ligand) bond, the copper(II)–(tetraaza plane) distance and the dihedral angle between the butterfly wing planes. Again we emphasize that any rationalization of the structural data reported here must consider that a cooperative effect of electronic, steric and crystallographic packing properties is involved.

Our findings, along with Tarivov's[17f] work, illustrate a new case of structurally characterized thiocyanate–isothiocyanate linkage isomers. From comparison between the synthetic conditions used to prepare the isothiocyanate and the thiocyanate complexes we suggest that the N-bonded isomer is thermodynamically favored, but kinetically not favored, over the S-bonded isomer. This proposition will be the target of future investigations in our laboratories and will be reported in Part-II of this work with electronic and EPR spectral studies. The electronic origin of the strong copper(II)–(axial ligand) interaction, first seen in [Cu(CYCLOPS)(NCO][28] and now in [Cu(DOHPN)(NCS)] is not fully understood. It would be interesting to compare the copper(II) apical displacement from the square plane and the strength of the copper(II)–(axial ligand) interaction observed in the present study with those of a neutral axial ligand which is similar to the isothiocyanate-ligand in the observed spectrochemical series.[41] The preparation and characterization of such a complex is under way in our laboratories.

Supplementary Material

A CIF file containing full details of crystal data collection, structure solution, structure refinement, hydrogen atom coordinates, anisotropic thermal parameters, was deposited in the Cambridge Crystallographic Data Base and are available upon request.

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