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Crystal Structures of Cu(II) Complexes of Pyridine-2,6-dithiocarbomethylamide

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The crystal structures of three copper(II) complexes of pyridine-2,6-dithiocarbomethylamide (*PDTA*) were determined by X-ray crystallographic methods. The structure of the bromide Cu*PDTA*$Br_2 \cdot H_2O$ (**2**) is isomorphous to the known crystal structure of the chloride Cu*PDTA*$Cl_2 \cdot H_2O$ (**1**). The iodide Cu*PDTA*$I_2 \cdot$ *DMF* (**3**) is non-isomorphous to the other two halogenides, but shows a very similar square-pyramidal 5-coordination of the copper atom. In contrast to the halogenides, the crystal structure of the nitrate Cu*PDTA* $(H_2O)_2 \cdot (NO_3)_2$ (**4**) shows a square planar metal coordination by the *PDTA* ligand and one water molecule. If one includes the second water molecule and one oxygen atom of a nitrate ion, the metal coordination becomes distorted octahedral.

(Keywords: Pyridine-2,6-dithiocarbomethylamide copper(II) bromide and iodide, crystal structure; Pyridine-2,6-dithiocarbomethylamide copper(II) nitrate, crystal structure)

Kristallstrukturen von Cu(II)-Komplexen von Pyridin-2,6-dithiocarbomethylamid

Die Kristallstrukturen von drei Cu(II)-Komplexen des Pyridin-2,6-dithiocarbomethylamids (*PDTA*) wurden mit der Methode der Röntgenstrukturanalyse bestimmt. Die Struktur des Bromids Cu*PDTA*$Br_2 \cdot H_2O$ (**2**) ist isomorph mit der bereits bekannten Kristallstruktur des Chlorids Cu*PDTA*$Cl_2 \cdot H_2O$ (**1**). Das Jodid Cu*PDTA*$I_2 \cdot$ *DMF* (**3**) zeigt — bei nicht isomorpher Kristallstruktur — eine den beiden anderen Halogeniden sehr ähnliche quadratisch-pyramidale 5-Koordination des Cu(II). Demgegenüber beobachtet man in der Kristallstruktur des Nitrats Cu*PDTA*$(H_2O)_2 \cdot (NO_3)_2$ (**4**) eine quadratisch planare Metallkoordination durch den *PDTA*-Liganden und ein Wassermolekül. Zählt man das zweite Wassermolekül und ein Sauerstoffatom eines Nitrations der Metallkoordination zu, so erhält man eine stark verzerrt-oktaedrische Koordination.

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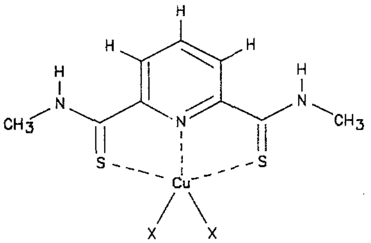
Introduction

The crystal structure of pyridine-2,6-dithio-carbomethylamide-copper(II) chloride Cu*PDTA*$Cl_2 \cdot H_2O$ **1** was recently reported[1], together with spectroscopic data for other members of the Cu*PDTA*-X_2 series. These data indicated considerable structural similarity between all compounds of the Cu-*PDTA*-X_2 type. We now report the crystal structures of Cu*PDTA*$Br_2 \cdot H_2O$ **2**, Cu*PDTA*$I_2 \cdot$ *DMF* **3** and Cu*PDTA* $(H_2O)_2 \cdot (NO_3)_2$ **4**.



1 : X=Cl , H_2O solvated
2 : X=Br , H_2O solvated
3 : X=I , DMF solvated
4 : X=H_2O, 2NO_3 counter ions

Upon heating, crystals of **4** loose two molecules of water at about 100 °C[7], leading to a complex with the nitrate ions coordinated directly to copper. While a stereochemistry similar to the Cu*PDTA*Cl_2 crystal structure was predicted for the water free nitrate complex, no definite prediction about compound **4** was ventured on the basis of the IR spectrum. The low temperature required for the removal of water from **2** (to be compared to 177 °C required to remove 1 molecule of non-coordinated water from crystals of **1**) would tend to argue in favour of weak or no coordination of water to Cu(II).

Experimental

All three structures were determined with the help of a modified STOE 4-circle diffractometer (MoK-radiation, graphite monochromator, $\lambda = 0.71069$ Å). Table 1 lists relevant experimental conditions and data for the three structures. Cell dimensions were determined by least-squares from the setting angles of 15-50 reflections, whose positions had been obtained from a peak search with subsequent reflection centering. Intensity data for all independent reflections within $2\theta \leq 50°$ ($\sin\theta/\lambda \leq 0.595$) were collected in the w/θ scan mode with fixed scan width and variable scan speed.

During data collection, several standard reflections were periodically monitored. While the standard intensities remained constant within ± 2% for **2** and **3**, they showed a decrease by about 20% for compound **4**.

Data reduction involved a correction for the standard intensity decrease (for compound **3**) and the usual derivation of *F*-values from raw intensities (LP-correction, no absorption correction).

Table **1**. *Summary of experimental conditions and crystal data for the structures of* **2**, **3** *and* **4**

Compound		**2**	**3**	**4**
chemical composition		$C_9H_{11}N_3S_2CuBr_2 \cdot H_2O$	$C_9H_{11}N_3S_2CuI_2 \cdot C_3H_7NO$	$C_9H_{11}N_3S_2Cu(H_2O)_2 \cdot (NO_3)_2$
space group		$P2_1/n$	$P2_1/a$	Cc
cell dimensions	a (Å)	9.292(2)	8.257(3)	8.383(1)
	b (Å)	9.153(2)	25.664(11)	11.024(1)
	c (Å)	17.929(6)	9.432(4)	18.036(3)
	β (°)	102.08 (1)	101.93 (2)	93.85 (1)
Z		4	4	4
d_m (d_x) (gcm^{-3}) a)		2.122 (2.08)	2.099 (2.091)	1.785 (1.793)
$\mu(MoK_\alpha)$ (cm^{-1})		75	45.6	16.6
scan width (°) b)		1.5	1.8	1.2
Nr. of independent reflections		2615	3459	1572
Nr. of significant reflections c)		1611	2547	1537
weighting system coefficients a/b d)		2.25 / 0.00112	1 / 0.00442	3.5 / 0.000068
Nr. of parameters e)		199	160	226
Nr. of observations e)		1607	2546	1532
R (R_w) e)		0.077 (0.070)	0.074 (0.082)	0.038 (0.044)
P_{max} ($eÅ^{-3}$) f)		0.6	1.7	0.6

a) observed (calculated) density ; observed density by flotation in $CCl_4/CHBr_3$

b) scan width for data collection (ω/θ scan)

c) $|F_o|>3\sigma(F_o)$

d) $w_i=a/(\sigma^2(F_o)+bF_o^2)$

e) last refinement cycle

f) highest peak in final difference *Fourier* synthesis

Table 2. *Fractional atomic coordinates and isotropic or equivalent isotropic tensor components* (·10^4, *U values in* Å^2) *for the crystal structures of* **2** (**A**), **3** (**B**) *and* **4** (**C**). The isotropic temperature factor has the form: $T = \exp(-8\pi^2 U \sin^2\theta/\lambda^2)$. For anisotropically refined atoms (see exp. section), the equivalent isotropic tensor components Ueq were calculated as one third of the trace of the orthogonalized Uij tensor. Standard deviations are in units of the last digit

A

Atom	X/a	Y/b	Z/c	Ueq or U
CU	805 *2*	1801 *2*	4107 *1*	370 *10*
BR-1	961 *2*	1827 *2*	2602 *1*	454 *9*
BR-2	2216 *2*	3887 *1*	4619 *1*	503 *9*
S-1	-1369 *4*	3040 *4*	3984 *3*	488 *23*
S-2	2703 *4*	224 *4*	4533 *2*	506 *22*
N-1	-3895 *12*	1871 *13*	3302 *7*	417 *69*
N-2	2510 *13*	-2562 *12*	4178 *7*	399 *68*
N-3	-440 *12*	9 *11*	3875 *6*	341 *62*
C-1	-2483 *14*	1649 *14*	3613 *8*	325 *72*
C-2	1837 *14*	-1326 *14*	4200 *7*	287 *69*
C-3	-1904 *15*	142 *15*	3624 *7*	344 *77*
C-4	190 *16*	-1334 *14*	3928 *7*	332 *73*
C-5	-2804 *15*	-1092 *16*	3392 *8*	373 *76*
C-6	-637 *15*	-2582 *15*	3754 *8*	367 *81*
C-7	-2146 *15*	-2456 *17*	3484 *8*	401 *81*
C-8	-4625 *20*	3294 *18*	3283 *11*	647 *111*
C-9	4114 *15*	-2736 *17*	4447 *11*	554 *102*
O	3954 *11*	397 *12*	2308 *7*	580 *69*
H -N1	-4596 *158*	1019 *127*	3058 *88*	975 *633*
H -N2	1844 *136*	-3147 *135*	3729 *53*	627 *456*
H1-O	3252 *105*	899 *116*	2579 *60*	302 *329*
H2-O	2986 *130*	197 *242*	2100 *124*	1783 *911*

B

Atom	X/a	Y/b	Z/c	Ueq or U
CU	1308 *2*	965 *1*	6188 *2*	402 *9*
I-1	3472 *1*	1228 *0*	9001 *1*	479 *6*
I-2	2734 *1*	1414 *1*	4317 *1*	588 *7*
S-1	2558 *5*	191 *1*	5916 *4*	495 *21*
S-2	-598 *5*	1614 *1*	6054 *4*	476 *20*
N-1	2235 *16*	-614 *5*	7611 *12*	485 *30*
N-2	-3207 *16*	1555 *5*	7288 *13*	469 *28*
N-3	-214 *13*	544 *4*	7157 *10*	321 *23*
C-1	1628 *19*	-145 *6*	7091 *16*	481 *36*
C-2	-1864 *15*	1311 *5*	7000 *13*	314 *27*
C-3	170 *17*	48 *5*	7532 *13*	368 *30*
C-4	-1579 *16*	765 *5*	7477 *13*	351 *29*
C-5	-825 *.16*	-243 *5*	8234 *13*	351 *28*
C-6	-2600 *20*	483 *6*	8180 *16*	511 *36*
C-7	-2187 *21*	-26 *6*	8590 *16*	514 *37*
C-8	3672 *24*	-866 *7*	7077 *19*	641 *46*
C-9	-3600 *22*	2098 *6*	6846 *18*	591 *41*
C1S	4089 *24*	3254 *7*	1559 *20*	652 *46*
O1S	3894 *18*	3634 *5*	787 *14*	719 *34*
N1S	4698 *17*	2818 *5*	1308 *13*	536 *33*
C2S	5316 *27*	2721 *8*	51 *22*	753 *52*
C3S	5316 *27*	2721 *8*	51 *22*	753 *52*
H-N1	1695 *141*	-913 *31*	8050 *115*	1 *335*
H-N2	-2961 *133*	1434 *41*	8353 *28*	798 *265*

C

Atom	X/a	Y/b	Z/c	Ueq or U
CU	9506 *fix*	3480 *1*	8818 *fix*	352 *4*
O-1	7714 *7*	1460 *5*	8405 *3*	460 *30*
O-2	10916 *7*	2733 *6*	9599 *3*	537 *34*
S-1	7555 *2*	3815 *2*	9591 *1*	364 *8*
S-2	11440 *2*	3315 *2*	7972 *1*	438 *10*
N-1	4911 *7*	4925 *6*	9131 *3*	372 *32*
N-2	10737 *8*	3630 *6*	6552 *3*	379 *32*
N-3	8140 *6*	4167 *5*	8010 *3*	279 *27*
C-1	6284 *8*	4475 *6*	8950 *3*	302 *13*
C-2	10255 *9*	3730 *6*	7228 *4*	351 *15*
C-3	6681 *8*	4576 *6*	8158 *3*	299 *13*
C-4	8614 *8*	4205 *6*	7318 *4*	283 *13*
C-5	5862 *9*	5043 *6*	7601 *4*	374 *15*
C-6	7647 *9*	4692 *7*	6735 *4*	421 *16*
C-7	6170 *9*	5126 *7*	6880 *4*	387 *16*
C-8	4403 *11*	4876 *8*	9884 *5*	499 *19*
C-9	12314 *11*	3228 *7*	6377 *5*	486 *18*
N -nit1	6323 *8*	1632 *6*	6518 *3*	470 *36*
O1-nit1	5771 *9*	1734 *8*	7128 *4*	828 *50*
O2-nit1	7728 *8*	1468 *7*	6478 *4*	796 *49*
O3-nit1	5376 *8*	1693 *8*	5973 *3*	943 *58*
N -nit2	9492 *7*	6412 *5*	9598 *3*	418 *32*
O1-nit2	8895 *7*	6642 *5*	10205 *3*	608 *37*
O2-nit2	10712 *7*	6800 *6*	9584 *4*	673 *38*
O3-nit2	8772 *8*	6798 *6*	9029 *3*	689 *39*
H1-O1	6864 *76*	1226 *73*	8761 *35*	961 *231*
H2-O1	7021 *114*	1672 *84*	7920 *29*	997 *315*
H1-O2	10892 *162*	2897 *113*	10158 *21*	1253 *401*
H2-O2	12120 *33*	2627 *99*	9545 *59*	773 *362*
H-N1	4336 *106*	5390 *86*	8702 *42*	727 *321*
H-N2	10056 *107*	3875 *89*	6081 *37*	838 *332*

The structures of **3** and **4** were solved by direct methods and subsequent F_0 and F_0—F_c *Fourier* syntheses. Structure **2** was fount to be isomorphous to the Cu*PDTA*$Cl_2 \cdot H_2O$ (**1**) crystal structure, whose coordinates were therefore used as a starting point. The conditions of the least-squares refinement were chosen with regard to the size and quality of the three data sets and differed slightly between the three structures:

- Compound **2**: all non-hydrogen atoms refined with anisotropic temperature factors; the 4 strongest reflections were excluded due to suspected extinction.
- Compound **3**: only Cu, I and S refined with anisotropic temperature factors, all other atoms isotropic.
- Compound **4**: all carbon atoms refined with isotropic temperature factors, N, O, S and Cu with anisotropic temperature factors. An empirical extinction correction (Program SHELX[3]) was applied, and the 5 strongest reflections were excluded.

For all three structures, hydrogen atoms were treated alike: an individual isotropic temperature factor was refined for each H-atom, methyl groups were refined as rigid groups and the other H-atom positions were subjected to a bond-length constraint (C—H 1.08, N—H 1.05, O—H 1.00 Å).

Atomic coordinates and isotropic tensor components are given in Table 2 A-C. Hydrogen atom coordinates are not given, with the exception of protons with potential involvement in hydrogen bonds. The following computer programs were used: MULTAN[2], SHELX[3], XRAY[4], PLUTO[5] (some programs in locally modified versions).

Results and Discussion

Fig. 1 shows projections of the Cu*PDTAX*$_2$ moieties into the *PDTA* plane for the structures of **3** and **4**; packing diagrams for these two structures are given in Fig. 2. Intramolecular bond-lengths and -angles for all three structures are presented in Fig. 3.

The crystal structure of the bromide **2** is isomorphous to the previously reported structure of the chloride **1**[1]; both structures consist of pairs of antiparallel molecules, which are crosslinked by hydrogen bonds involving the solvated water molecule. We refrain from giving a projection of the Cu*PDTA*Br_2 moiety or a packing diagram for the crystal structure of **2**, and refer to the detailed description of structure **1**.

As far as the stereochemistry of the Cu*PDTAX*$_2$ complex is concerned (see below) the crystal structure of the iodide **3** is similar to the other two halogenides **1** and **2** (Fig. 1 *A*). However, the solvated *DMF* molecule in the crystals of **3** offers less hydrogen bonding capacity than the water molecule in **1** and **2**, leading to only one significant intermolecular H-bond in structure **3** [between H2 and the carbonyl oxygen O1S at $-x + 1/2$, $y - 1/2$, $-z + 1$; $d = 1.74$ (10) Å].

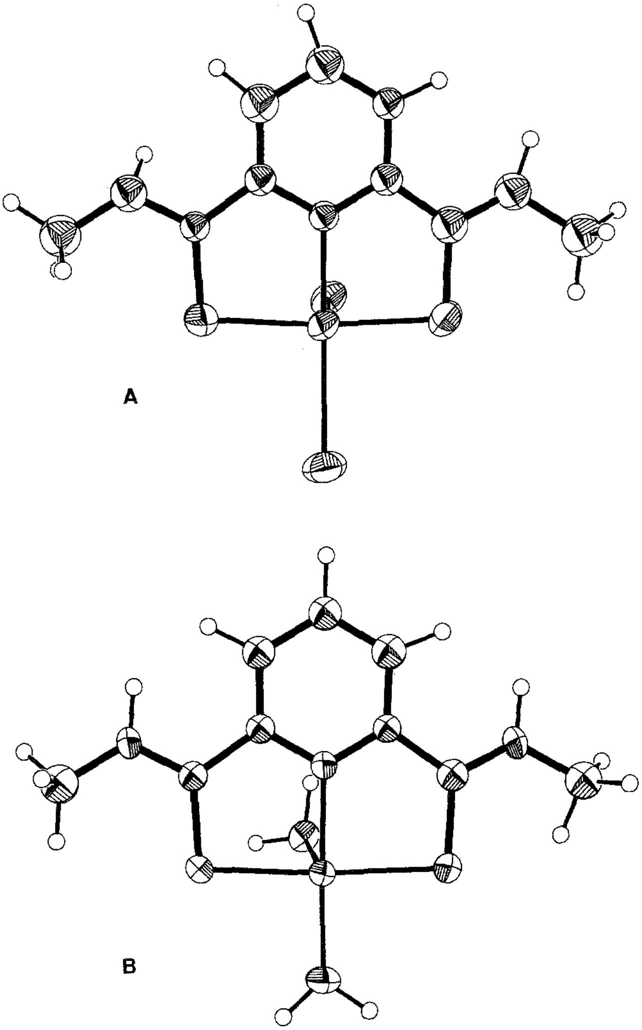


Fig. 1. Projection of the Cu*PDTAX*$_2$ moiety into the molecular plane. Atoms are represented with their observed temperature ellipsoids (50% probability), with the exception of hydrogen atoms, which were drawn as spheres with a radius of 0.1 Å. **A**: X = I (compound **3**); **B**: X = H_2O (compound **4**)

Although Fig. 1 *B* might suggest a large degree of similarity in the Cu-coordination between structure **4** and the halogenides **1**, **2** and **3**, there are significant differences to be discussed in the next paragraph. The packing of structure **4** (Fig. 2 *B*) appears to be dominated by numerous hydrogen bonds involving the amide protons, the water molecules and the nitrate ions: H—N 1...O 1 $(-1/2+x, 1/2+y, z)$, 1.85 (9) Å; H—N 2...O 1—nit 2 $(x, 1-y, -1/2+z)$, 1.89 (7) Å; H 1—O 1...O 2—nit 2 $(-1/2+x, -1/2+y, z)$, 1.88 (7) Å; H 2—O 1...O 1—nit 1 (x, y, z), 1.71 (7) Å; H 1—O 2...O 3—nit 1 $(1/2+x, 1/2-y, 1/2+z)$, 1.63 (7) Å; H 2—O 2...O 3—nit 2 $(1/2+x, -1/2+y, z)$, 1.95 (8) Å.

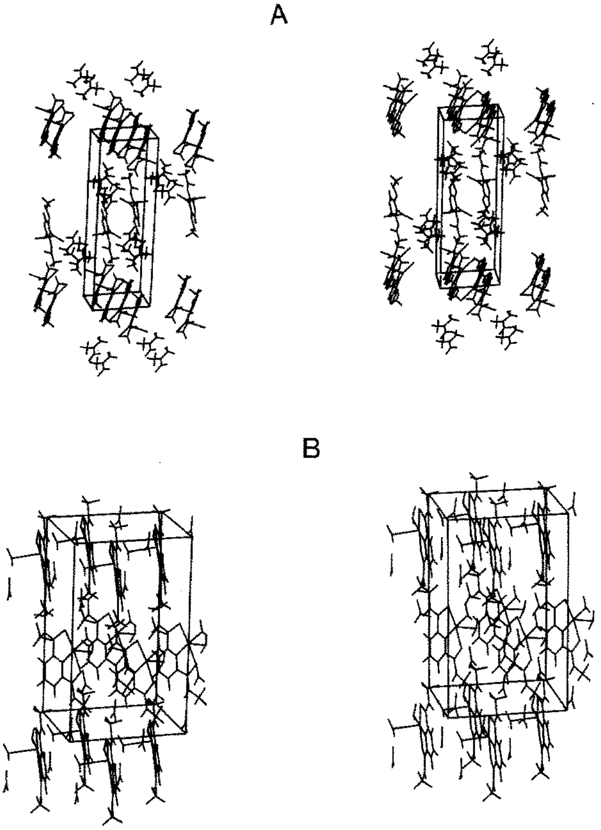


Fig. 2. Stereoscopic packing diagrams for the crystal structures of **3** (**A**) and **4** (**B**)

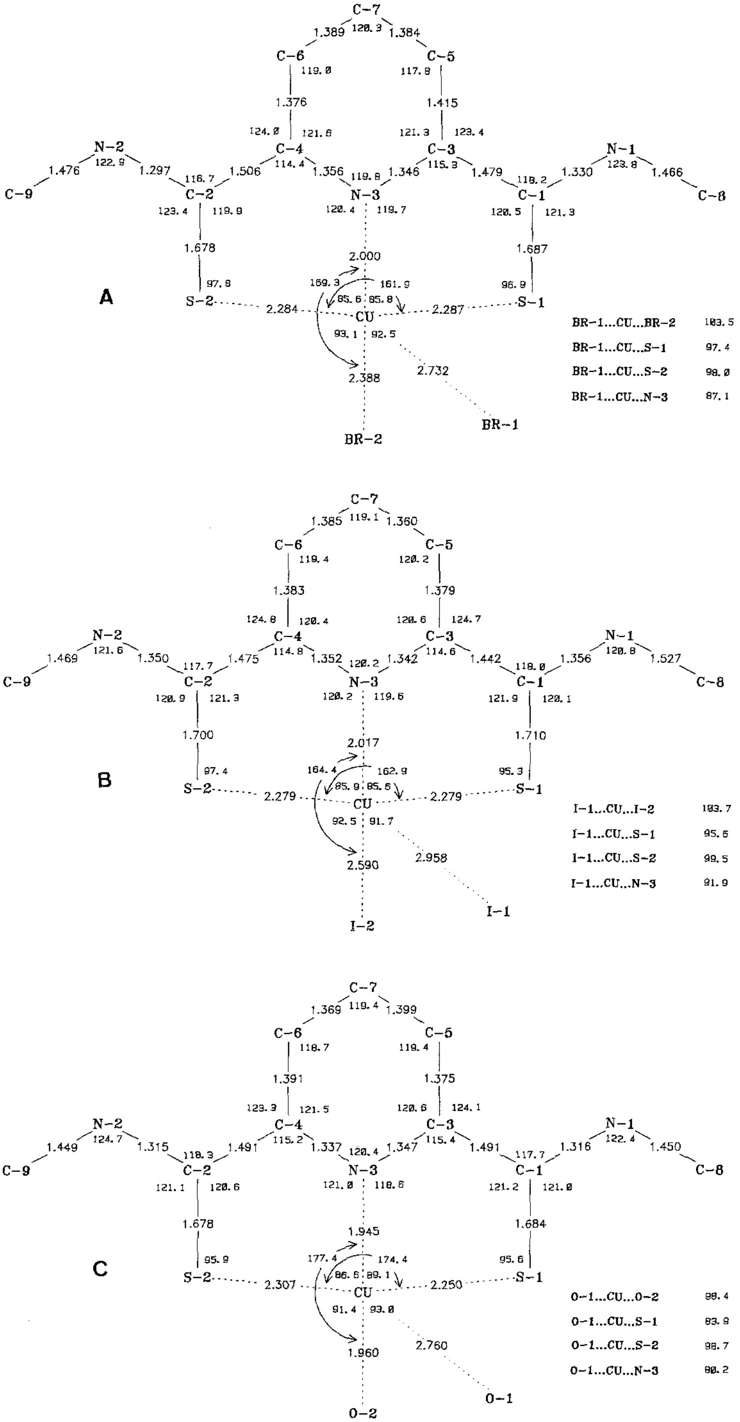


Fig. 3. Bond lengths and bond angles for the crystal structures of **2** (**A**), **3** (**B**) and **4** (**C**). Standard deviations (from the least squares refinement) are as follows: Compound **4**: Cu—O: 0.006; Cu—S: 0.002; Cu—N: 0.005; C—S: 0.007; C—C, C—N: 0.01 Å; angles: 0.3-0.7°. For compounds **2** and **3**, the standard deviations are about twice as large; Cu—Br, Cu—I: 0.002 Å

Coordination Around Cu(II)

In each of the three halogenide structures, a square pyramidal coordination of the copper atom by the two thioamide sulfur atoms, the pyridine nitrogen atom and the two halogenide atoms is observed. The distance from the copper to the equatorial halogenide atom X_2 is about 0.35 Å shorter than the distance to the apical halogenide X_1. The copper atom is displaced by about 0.3 Å from the base plane (formed by X, S 1, S 2 and N 3) towards X_1 (**1**, 0.28; **2**, 0.27; **3**, 0.31 Å).

Structure **4**, which has two water molecules instead of the halogenide atoms ($X = H_2O$) displays a metal coordination which appears similar to the 5-coordination of the halogenides (Fig. 1 *B*). However, the difference in the coordination distance between apical and equatorial water molecule is more than twice as large (0.8 Å), and the displacement of the Cu-atom from the plane of the four equatorial ligand atoms is practically zero (0.02 Å). The metal coordination should therefore be more appropriately termed square planar or—if the nearest nitrate oxygen atom is included (Cu ... O 2—nit 2, 3.05 Å)—distorted octahedral.

Both types of metal coordination are quite common for Cu(II) complexes, which have been classified in terms of the tetragonal distortion T[6]. T should be smallest for the square planar complex **4**. This agrees with the observation, that the equatorial bonds are slightly longer for the halogenides than for the hydrate: $<$ Cu ... S $>$ (**1**, **2**, **3**), 2.286; $<$ Cu ... S $>$ (**4**), 2.279; $<$ Cu ... N $>$ (**1**, **2**, **3**), 2.007; Cu ... N (**4**), 1.96 Å. A similar conclusion is deductible from the IR band positions.

Intramolecular bond-lengths and -angles (Fig. 3) agree between the three structures and show few significant differences to the structures of the free ligand[8] and its nickel complex[9]. The only exceptions are the thioamide bonds, where a lengthening of C=S and a shortening of C—N was noted[1] for the coordination to Cu(II).

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