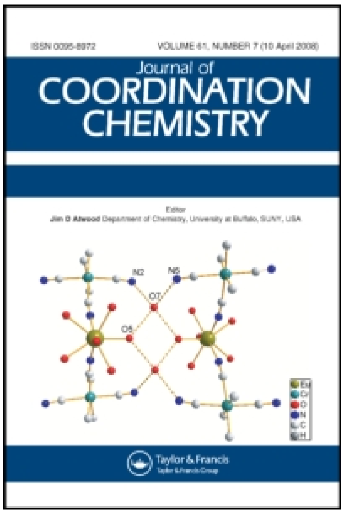

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Studies of Copper(II) Thiosemicarbazide Complexes and their Reactivities. X-Ray Structure of Two Unusual Reaction Products, [Cu(bpy)(H_2O)$_2$$SO_4$] and [(bpy)$_2$$Cu_2$($C_2O_4$)$Cl_2$]·$H_2O$

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STUDIES OF COPPER(II) THIOSEMICARBAZIDE COMPLEXES AND THEIR REACTIVITIES. X-RAY STRUCTURE OF TWO UNUSUAL REACTION PRODUCTS, $[Cu(bpy)(H_2O)_2SO_4]$* AND $[(bpy)_2Cu_2(C_2O_4)Cl_2] \cdot H_2O$

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A number of ternary complexes of Cu^{2+} with thiosemicarbazide (TSC) including $[Cu(bpy)(TSC)_2]Cl_2$, $[Cu(o\text{-phen})(TSC)_2]Cl_2$ and $[Cu(bpy)(TSC)_2][CuCl_4]$ $[Cu(o\text{-phen})(TSC)_2][CuCl_4]$ have been synthesised and characterized. Their reactivities in aqueous and DMF solutions were studied. It was observed that while on coordination to Cu^{2+} thiosemicarbazide is converted to thiocyanate in aqueous solution, in DMF solution the thiocyanate is further aerially oxidised to sulfate. In the presence of hydrogen peroxide, oxidation to sulfate is rapid and from the mother liquor we could isolate $[(bpy)_2Cu_2(C_2O_4)Cl_2] \cdot H_2O$ whose structure was determined by X-ray crystallography. X-ray crystal structure of $[Cu(bpy)(H_2O)_2SO_4]$ is also discussed.*

Keywords: Thiosemicarbazide; Cu^{2+} complexes; bpy; *o*-phen; Crystal structure

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*A preliminary report of the structure of $[Cu(bpy)(H_2O)_2SO_4]$ was published in Ref. [15].
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INTRODUCTION

Studies of complexes of thiosemicarbazides and thisemicarbazones have recently received much attention [1–7] due to their wide spectrum of biological activities. The presence of both hard (N) and soft (S) donor sites make the thiosemicarbazides and thiosemicarbazones versatile complexing agents and as a result, apart from their potential biological and medicinal applications, they are inherently chemically interesting. However, the chemical properties of such complexes are not so well documented. In this paper we report the results of a study on the reactivities of copper thiosemicarbazide complexes.

EXPERIMENTAL

All chemical were of reagent grade obtained from E. Merck (Germany), E. Merck (India) or Fluka AG. Elemental analyses were performed with a Perkin–Elmer 2400 C,H,N analyser. IR Spectra were recorded on a Perkin–Elmer 783 spectrophotometer using KBr pellets.

$[Cu(bpy)(TSC)_2]Cl_2$ and $[Cu(bpy)(H_2O)_2SO_4]$

$[Cu(TSC)Cl_2]$ was prepared by a previously described [8] procedure; 1 mmol (226 mg) of $[Cu(TSC)Cl_2]$ was dissolved in ~ 15 cm^3 of DMF and to it 1 mmol (156 mg) of 2,2′-bipyridine was added with stirring. Immediately a grass green compound separated out. Stirring was continued for 2 hours, then the solid was filtered off, washed several times with DMF and dried in a desiccator. The compound analysed as $Cu(bpy)(TSC)_2Cl_2$ (yield ~ 50%). *Analysis*: (found) (%): C, 30.7; N, 23.5; H, 4.1. calc. C, 30.5; N, 23.7; H, 3.8.

When the above reaction was carried out using identical amounts of the reactants but with four times the amount of solvent (*i.e.*, 60 cm^3 of DMF), only a small amount of the compound was precipitated. The filtrate on keeping for 12–16 weeks deposits needle-shaped blue crystals, which were filtered off, washed with a small amount of DMF and dried in a desiccator. The compound analysed as $[Cu(bpy)(H_2O)_2SO_4]$ (yield ~30%). *Analysis*: (found) C, 34.0; N, 7.9; H, 3.5. calc. C, 33.8; N, 7.9; H, 3.4; IR (in KBr, cm^{-1}): $\nu_3(SO_4^{2-})$: 1168, 1140–1118, 1060; $\nu_1(SO_4^{2-})$: 986; $\nu_4(SO_4^{2-})$: 620.

$[Cu(bpy)_2(SCN)]Cl$

Some 2 mmol (~ 312 mg) of 2,2′-bipyridyl was dissolved in 15 cm^3 of distilled water and to it 1 mmol (~ 226 mg) of $[CuTSCCl_2]$ was added. After 15 minutes stirring the solution was filtered and the blue filtrate kept for slow evaporation. After about 12 weeks blue plates were obtained. These were filtered off, washed with a small amount of cold water and air dried. The compound analysed as $[Cu(bpy)_2(SCN)]Cl$ (yield ~ 38%). *Analysis*: (found) C, 53.8; H, 3.5; N, 14.8. calc. C, 53.7; H, 3.4; N, 14.9; IR (in KBr, cm^{-1}) ν_{SCN}: 2060, 2080(sh).

$[Cu(o\text{-phen})_2(SCN)Cl]$ and $[Cu(o\text{-phen})(H_2O)_2SO_4]$

One mmol (~ 198 mg) of *o*-phenanthroline monohydrate was dissolved in 15 cm^3 of DMF and to it 1 mmol (~ 226 mg) of $[CuTSCCl_2]$ was added slowly with continuous stirring. Stirring was continued for 2 hours then the solution was filtered. The deep green filtrate was allowed to stand for a week, when some green crystalline compound had separated out. This was filtered off, washed with a small amount of DMF and dried in a desiccator. It analysed for $[Cu(o\text{-phen})_2 (SCN)]Cl$ (yield ~ 20%). *Analysis*: (found) C, 58.2; N, 13.7; H, 3.1. calc. C, 58.0; N, 13.5; H, 3.1; IR (in KBr, cm^{-1}): ν_{SCN}: 2090. The filtrate on keeping for about 12 weeks deposited green needle-shaped crystals which analysed for $[Cu(o\text{-phen})(H_2O)_2SO_4]$ (yield ~ 28%). *Analysis*: (found) C, 38.6; N, 7.3; H, 3.4. calc. C, 38.3; N, 7.4; H, 3.2; IR (in KBr, cm^{-1}): $\nu_3(SO_4^{2-})$: 1160, 1145–1118, 1050; $\nu_1(SO_4^{2-})$: 982; $\nu_4(SO_4^{2-})$: 620.

$Cu_2(bpy)(TSC)_2Cl_4$ and $Cu_2(o\text{-phen})(TSC)_2Cl_4$

Ten mmol (0.9 g) of TSC was dissolved in 25–30 cm^3 of 2*N* HCl and cooled to 0°C. Ten mmol (1.7 g) of $CuCl_2 \cdot 2H_2O$ was dissolved in 20 cm^3 of water and to it 10 cm^3 of 2*N* HC1 was added, followed by ~ 10 mmol of bpy (1.6 g) or *o*-phen monohydrate (2.0 g) with stirring. After about 0.5 hr the cold TSC solution was gradually added drop by drop. A dirty green compound separated out. Stirring was continued for ~4 hrs. The solid was then filtered off, washed with 2*N* HCl, followed by dry alcohol, and dried over fused calcium chloride. *Analysis*: for $Cu_2(bpy)(TSC)_2Cl_4$ (yield ~65%) (found) C, 24.0; N, 18.2; H, 2.5. calc. C, 23.7; N, 18.4; H, 2.3; for $Cu_2(o\text{-phen})(TSC)_2Cl_4$ (yield ~60%) (found) C, 26.9; N, 17.7; H, 2.8. calc. C, 26.6; N, 17.7; H, 2.8.

$[(bpy)_2Cu_2(C_2O_4)Cl_2] \cdot H_2O$

About 200 mg of $[Cu(bpy)(TSC)_2]X_2$ ($X = Cl, CuCl_4$) was dissolved in DMF and to it about 35–40 cm^3 of H_2O_2 was added very slowly with continuous stirring. A vigorous reaction ensued with the evolution of oxygen. When the reaction subsided it was filtered, and the green mother liquor on slow evaporation at room temperature yielded green crystals (yield ~ 57%). *Analysis*: (Found) C, 42.6%; N, 9.2%; H, 3.0%. Calculated for $[(bpy)_2Cu_2(C_2O_4)Cl_2] \cdot H_2O$: C, 42.8; N, 9.1; H, 2.9.

X-Ray Analysis

A blue needle-shaped crystal of $[Cu(bpy)(H_2O)_2SO_4]$ of dimensions $0.2 \times 0.3 \times 0.4$ mm was chosen for X-ray crystallography. The crystals are triclinic, space group $P\ \bar{1}$, with $a = 6.963(1)$, $b = 9.804(1)$, $c = 9.819(1)$ Å; $\alpha = 78.90(1)$, $\beta = 77.68(1)$, $\gamma = 78.05(1)°$, $V = 632.9(5)$ Å^3, $Z = 2$, $\mu = 1.918$ mm^{-1}, $F(000) = 358$. Crystal data were collected at 291 K on a Siemens R3m/v diffractometer, using MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å) from a highly oriented graphite crystal monochromator; scan mode $\omega - 2\theta$, 2θ range 7.0 to 45.0°, scan speed 3.00 to 45.00°/min in ω, scan range (ω) 0.60, covering indices $-1 \le h \le 9$, $-12 \le k \le 12$, $-12 \le l \le 12$. Crystal stability was monitored by 3 check reflections after every 97 reflections. A total of 3350 reflections was collected of which 2809 were independent reflections ($R_{int} = 0.022$); 2306 observed reflections ($F > 4.0\sigma(F)$). The structure was solved by direct methods, using full-matrix least-squares refinement and a riding model for H-atoms; weighing scheme $w^{-1} = \sigma^2(F) + 0.0015F^2$; $R = 0.051$, $R_w = 0.065$; R values using all data 0.073, $R_w = 0.081$; goodness of fit 1.27; largest and mean $\Delta/\sigma = 0.167$ and 0.015 respectively, largest difference peak 0.99 eÅ^{-3}, largest difference hole -1.57 eÅ^{-3}.

A blue plate of $[(bpy)_2Cu_2(C_2O_4)Cl_2] \cdot H_2O$ of dimensions $0.02 \times 0.10 \times 0.16$ mm was chosen for X-ray crystallography, Crystals were monoclinic, space group $C2/c$, with $a = 18.899(4)$, $b = 6.848(1)$, $c = 18.348(4)$ Å, $\beta = 95.24(3)°$, $V = 1182.4(4)$ Å^3, $Z = 4$, $F(000) = 1232$. Data was collected on a Siemens R3m/v diffractometer using graphite-monochromated MoK$_\alpha$ radiation ($\lambda = 0.71073$ Å); ω scan type was used with scan range 0.60° below K$_{\alpha 1}$ to 0.60° above K$_{\alpha 2}$ having a collection range $-20 \le h \le 20$, $0 \le k \le 7$, $-20 \le l \le 14$ and $2\theta_{max} = 44°$. Full-matrix least-squares refinement of the model based on 1756 unique reflections and 748 observed data ($F > 4\sigma F$) converged to a final $R = 0.053$ and $R_w = 0.051$ ($w^{-1} = [\sigma^2 F_0]$); goodness of fit $S = 1.25$; largest and mean $\Delta/\sigma = 0.00$. The residual extrema in the final difference map are $+0.63$ to -0.49 eÅ^{-3}. The structure was solved by direct methods, using a riding model for H atoms. All calculations were carried out on a DEC Microvax-II computer using the SHELTXL – plus programme [9] package. Analytical expressions of neutral

TABLE I Atomic coordinates (× 10^5 for Cu; × 10^4 for other atoms) and equivalent isotropic displacement coefficients ($Å^2 \times 10^4$) for $[Cu(bpy)(H_2O)_2SO_4]$

	x/a	*y/b*	*z/c*	*U(eq)**
Cu(1)	25000 (7)	27435 (4)	22566 (4)	231 (1)
S(1)	7498 (1)	3461 (1)	1539 (1)	261 (2)
O(1)	8864 (4)	3148 (3)	2550 (3)	417 (5)
O(2)	6313 (4)	4912 (2)	1583 (3)	326 (4)
O(3)	8684 (4)	3413 (3)	87 (2)	321 (4)
O(4)	6135 (4)	2457 (3)	1849 (3)	421 (5)
N(1)	2721 (4)	641 (3)	2596 (3)	239 (5)
N(2)	2276 (4)	2408 (3)	4357 (3)	237 (4)
C(1)	2961 (5)	– 180 (3)	1602 (3)	323 (5)
C(2)	3132 (5)	– 1618 (3)	1919 (4)	360 (5)
C(3)	3029 (5)	– 2236 (3)	3316 (4)	373 (5)
C(4)	2781 (5)	– 1413 (3)	4352 (3)	333 (5)
C(5)	2619 (4)	35 (3)	3960 (3)	241 (5)
C(6)	2368 (4)	1050 (3)	4958 (3)	239 (5)
C(7)	2232 (5)	643 (4)	6404 (3)	344 (5)
C(8)	1969 (5)	1682 (4)	7246 (3)	391 (5)
C(9)	1862 (5)	3086 (4)	6616 (3)	373 (5)
C(10)	2035 (5)	3404 (3)	5168 (3)	319 (5)
O(1W)	2473 (4)	2894 (2)	227 (2)	261 (4)
O(2W)	2530 (4)	4779 (2)	2108 (2)	261 (4)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE II Atomic coordinates (10^4) and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) for $[(bpy)_2Cu_2(C_2O_4)Cl_2] \cdot H_2O$

	x/a	*y/b*	*z/c*	*U(eq)*
Cu(1)	991 (1)	2305 (2)	3578 (1)	34 (1)
Cl(1)	1246 (2)	– 1192 (4)	3693 (2)	60 (1)
O(1W)	0	– 3405 (5)	2500	102 (1)
O(1)	– 71 (3)	2253 (4)	3447 (3)	34 (1)
O(2)	– 908 (3)	2378 (5)	2512 (3)	43 (1)
N(1)	1928 (3)	3555 (5)	3660 (3)	30 (1)
N(2)	1014 (3)	3128 (5)	4601 (3)	31 (1)
C(1)	– 276 (4)	2267 (5)	2767 (4)	34 (1)
C(2)	2372 (4)	3624 (5)	3124 (4)	44 (1)
C(3)	3044 (4)	4540 (5)	3216 (4)	64 (1)
C(4)	3245 (4)	5288 (5)	3905 (4)	59 (1)
C(5)	2803 (4)	5263 (5)	4471 (4)	44 (1)
C(6)	2143 (4)	4335 (5)	4326 (4)	37 (1)
C(7)	1601 (4)	4074 (5)	4875 (4)	32 (1)
C(8)	1708 (4)	4740 (5)	5585 (4)	44 (1)
C(9)	1177 (4)	4423 (5)	6047 (4)	58 (1)
C(10)	576 (4)	3492 (5)	5781 (4)	55 (1)
C(11)	497 (4)	2869 (5)	5049 (4)	43 (1)

* *U(eq)* is defined as one third of the trace of the orthogonalized *U* tensor.

atom scattering factors were employed and dispersion corrections were applied. Final atomic coordinates are listed in Tables I and II.

RESULTS AND DISCUSSION

Description of the Structure of [Cu(bpy)(H_2O)$_2$$SO_4$]

An ORTEP diagram of [Cu(bpy)(H_2O)$_2$$SO_4$] is shown in Figure 1 and the corresponding packing diagram in Figure 2. Some important bond length and bond angles are given in Table III. From the figures it is evident that Cu(II) has square pyramidal coordination environment, where the two nitrogen atoms (N(1) and N(2)) of 2,2′-bipyridyl and two aqua ligands (O(1W) and O(2W)) constitute the basal plane, while the sulfato oxygen atom (O(4a)) occupies the axial position. All bond lengths are quite normal. In addition, there are strong intramolecular hydrogen bonds between the coordinated water molecules and the sulfate oxygen atoms. Of the four sulfato oxygen atoms, coordinated oxygen O(4) along with O(1) do not participate in hydrogen bonding. The O(2) oxygen is involved in one intramolecular hydrogen bond along with an intermolecular hydrogen bond with an adjacent molecule. The O(3) oxygen on the other hand is involved in two intramolecular hydrogen bonds, one with the same complex molecule

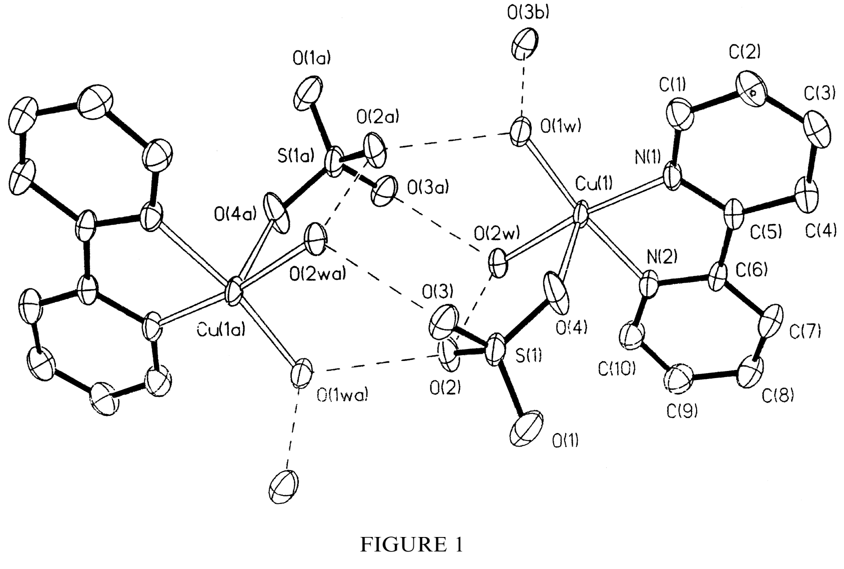

FIGURE 1

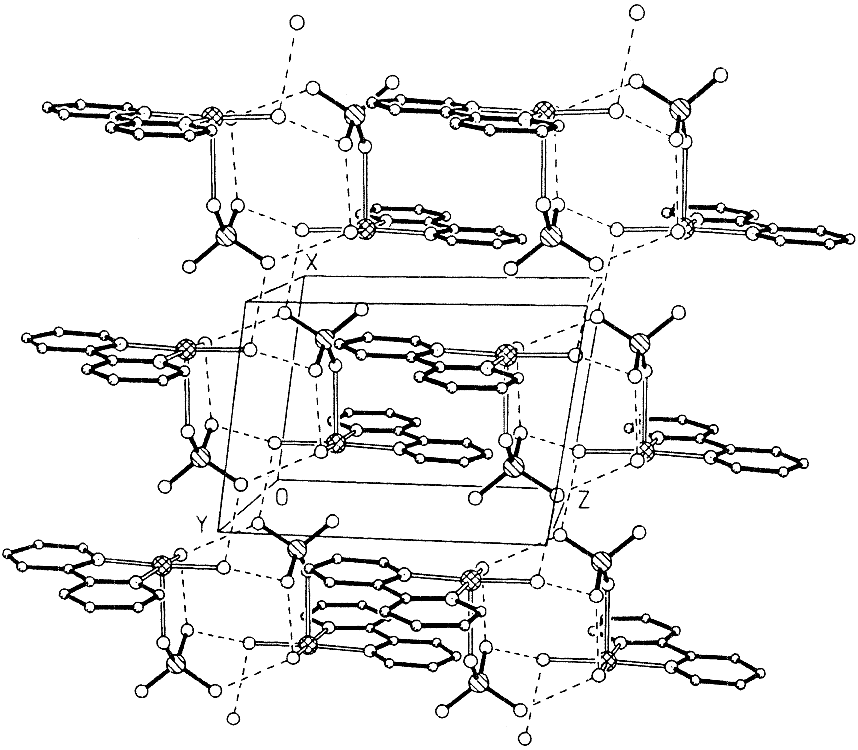

FIGURE 2

(linked to O(2)), another with a complex unit situated above it. Thus a pair of adjacent complex units (see Fig. 1) are linked by intra-dimer hydrogen bonds formed by the sulfato O(3) and O(2) atoms of one molecule with O(2W) and O(1W) of the aqua ligands of the other molecule. Such dimers are then interlinked by hydrogen bonding to form, ultimately, a three-dimensional supramolecular network. It is possibly due to this extensive hydrogen bonding network that the compound is insoluble in water and most common organic solvents including DMF.

Description of the Structure of $[(bpy)_2Cu_2(C_2O_4)Cl_2] \cdot H_2O$:

An ORTEP plot of the compound along with the atom labelling scheme is shown in Figure 3. Some important bond length and bond angles are given in Table IV. The copper atom has square pyramidal coordination, with oxalate ion acting as a μ_2–bridge. Two nitrogen atoms of one 2,2′-bipyridyl with two *syn* oxygen atoms of the oxalate moiety form a square plane. The

TABLE III Bondlengths (Å) and bond angles (°) for [Cu(bpy)$(H_2O)_2SO_4$]

Cu(1)–N(1)	2.002 (3)	Cu(1)–N(2)	2.002 (3)
Cu(1)–O(1W)	1.973 (2)	Cu(1)–O(2W)	1.977 (2)
S(1)–O(1)	1.466 (3)	S(1)–O(2)	1.493 (2)
S(1)–O(3)	1.492 (2)	S(1)–O(4)	1.452 (3)
N(1)–C(1)	1.344 (5)	N(1)–C(5)	1.350 (4)
N(2)–C(6)	1.343 (4)	N(2)–C(10)	1.338 (5)
C(1)–C(2)	1.370 (5)	C(2)–C(3)	1.382 (5)
C(3)–C(4)	1.378 (5)	C(4)–C(5)	1.385 (4)
C(5)–C(6)	1.487 (5)	C(6)–C(7)	1.388 (4)
C(7)–C(8)	1.391 (5)	C(8)–C(9)	1.391 (5)
C(9)–C(10)	1.380 (5)	O(1W)···O(2a)	2.673 (6)
O(1W)···O(3b)	2.610 (6)	O(2W)···O(3a)	2.680 (6)
O(2W)···O(2c)	2.599 (6)		
N(1)–Cu(1)–N(2)	81.2 (1)	N(1)–Cu(1)–O(1W)	93.3 (1)
N(2)–Cu(1)–O(1W)	172.3 (1)	N(1)–Cu(1)–O(2W)	172.2 (1)
N(2)–Cu(1)–O(2W)	93.1 (1)	O(1W)–Cu(1)–O(2W)	92.9 (1)
O(1)–S(1)–O(2)	109.8 (2)	O(1)–S(1)–O(3)	109.1 (1)
O(2)–S(1)–O(3)	108.1 (1)	O(1)–S(1)–O(4)	111.4 (2)
O(2)–S(1)–O(4)	108.9 (2)	O(3)–S(1)–O(4)	109.5 (2)
Cu(1)–N(1)–C(1)	125.9 (2)	Cu(1)–N(1)–C(5)	115.0 (2)
C(1)–N(1)–C(5)	119.1 (3)	Cu(1)–N(2)–C(6)	114.7 (2)
Cu(1)–N(2)–C(10)	125.8 (2)	C(6)–N(2)–C(10)	119.5 (3)
N(1)–C(1)–C(2)	122.4 (3)	C(1)–C(2)–C(3)	118.4 (3)
C(2)–C(3)–C(4)	120.2 (3)	C(3)–C(4)–C(5)	118.5 (3)
N(1)–C(5)–C(4)	121.4 (3)	N(1)–C(5)–C(6)	114.1 (3)
C(4)–C(5)–C(6)	124.5 (3)	N(2)–C(6)–C(5)	115.0 (3)
N(2)–C(6)–C(7)	121.8 (3)	C(5)–C(6)–C(7)	123.2 (3)
C(6)–C(7)–C(8)	118.6 (3)	C(7)–C(8)–C(9)	119.3 (3)
C(8)–C(9)–C(10)	118.7 (3)	N(2)–C(10)–C(9)	122.2 (3)
O(3b)···O(1W)···O(2a)	100.2 (4)	O(3a)···O(2W)···O(2c)	100.7 (4)

Symmetry transformations: a, $(1-x, 1-y, -z)$; b, $(-1+x, y, z)$; c, $(2-x, 1-y, -z)$.

chloride ion occupies the axial position, the Cu—Cl bond being relatively long. Cu—O bond distances are marginally longer than those reported [10] for $[Cu_2(bpy)_2(H_2O)_2C_2O_4]X_2$ ($X = NO_3$, BF_4, ClO_4), but are considerably longer when compared to the mononuclear compounds [10, 11] [Cu(bpy)(C_2O_4)] and $(ImzH)_2[Cu(C_2O_4)_2]$ (ImzH = imidazolium cation). Cu—N bond distances in the present compound are however closer to those of the mononuclear compound [Cu(bpy)(C_2O_4)], rather than those in the dimers $[Cu_2(bpy)_2(H_2O)_2C_2O_4)]X_2$. Another important feature of the structure is that the two axial chlorides in the dimeric unit are *syn* to each other, where as in $[Cu_2(bpy)_2(H_2O)_2C_2O_4)]X_2$, the axial water molecules are *anti* to each other.

Chemical Reactivity

Thiosemicarbazide on coordination to copper(II) undergoes facile deprotonation, often followed by ligand to metal electron transfer to produce a

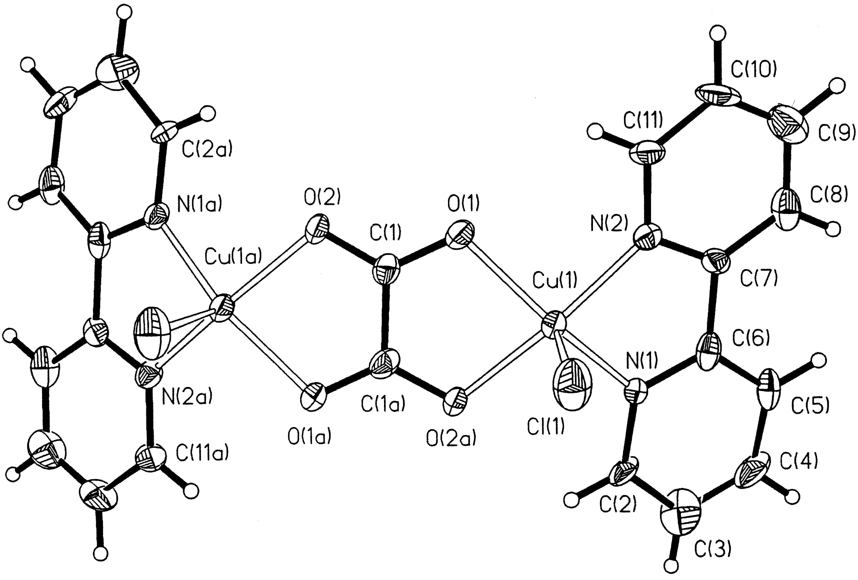

FIGURE 3

Cu(I) species. Thus the preparation of stable Cu(II) complexes of thiosemicarbazide often requires a strongly acidic medium. Previously we have reported [8] the synthesis of [CuTSCCl$_2$] in cold 2*N* HCl. Though the compound is stable in the solid state for several months, it gradually decomposes even in strongly acidic solution. A solution of [CuTSCCl$_2$] in 2*N* HCl exhibits a broad, Jahn-Teller distorted band with a maximum of ~ 725 nm. However [CuTSCCl$_2$] in water exhibits two broad bands of similar intensity at ~ 675 nm and ~ 540 nm. The later band rapidly gains intensity with time and after 6 hours the 540 nm band becomes the dominant feature with a shoulder at 625 nm. The band at 725 nm corresponds to d–d transitions of [CuTSCCl$_2$], [12] whereas that at ~ 675 nm probably corresponds to $[Cu(TSC)Cl(H_2O)]^+$ and the 625 nm band is due to $[Cu(TSC)(H_2O)_2]^{2+}$. The 540 nm band is a charge transfer band which may arise [13, 14] due to a S(thiolate) → Cu(II) LMCT transition. In neutral aqueous solution the decomposition is fast and within a few days CuSCN is deposited. In the presence of 2,2′-bipyridyl or 1,10-phenanthroline one obtains [Cu(N-N)$_2$SCN)Cl from aqueous solution. In concentrated DMF solution [CuTSCCl$_2$] reacts with 2,2′-bipyridyl to precipitate [Cu (bpy)(TSC)$_2$]Cl$_2$. However in more dilute solutions, which prevents precipitation of [Cu(bpy)(TSC)$_2$]Cl$_2$, one could ultimately obtain [15] [Cu(bpy)(H$_2$O)$_2$SO$_4$] from the reaction medium. Using *o*-phenanthroline in place of 2,2′-bipyridyl, we do not obtain [Cu(phen)(TSC)$_2$]Cl$_2$ (probably

TABLE IV Bond lengths (Å) and bond angles (°) for $[(bpy)_2Cu_2(C_2O_4)Cl_2]\cdot H_2O$

Cu(1)–Cl(1)	2.448 (3)	Cu(1)–O(1)	2.000 (5)
Cu(1)–N(1)	1.960 (6)	Cu(1)–N(2)	1.957 (6)
Cu(1)–O(2a)	1.992 (5)	O(1)–C(1)	1.271 (8)
O(2)–C(1)	1.243 (8)	N(1)–C(2)	1.351 (9)
N(1)–C(6)	1.362 (8)	N(2)–C(7)	1.342 (8)
N(2)–C(11)	1.346 (9)	C(1)–C(1a)	1.497 (14)
C(2)–C(3)	1.414 (9)	C(3)–C(4)	1.384 (10)
C(4)–C(5)	1.389 (11)	C(5)–C(6)	1.403 (9)
C(6)–C(7)	1.511 (10)	C(7)–C(8)	1.377 (9)
C(8)–C(9)	1.389 (11)	C(9)–C(10)	1.354 (9)
C(10)–C(11)	1.403 (9)		
Cl(1)–Cu(1)–O(1)	100.4 (1)	Cl(1)–Cu(1)–N(1)	104.6 (1)
O(1)–Cu(1)–N(1)	155.0 (2)	Cl(1)–Cu(1)–N(2)	102.2 (1)
O(1)–Cu(1)–N(2)	93.1 (2)	N(1)–Cu(1)–N(2)	81.9 (2)
Cl(1)–Cu(1)–O(2a)	96.2 (1)	O(1)–Cu(1)–O(2a)	83.8 (2)
N(1)–Cu(1)–O(2a)	93.1 (2)	N(2)–Cu(1)–O(2a)	161.5 (2)
Cu(1)–O(1)–C(1)	109.4 (4)	C(1)–O(2)–Cu(1a)	111.2 (5)
Cu(1)–N(1)–C(2)	125.2 (4)	Cu(1)–N(1)–C(6)	115.7 (5)
C(2)–N(1)–C(6)	119.0 (6)	Cu(1)–N(2)–C(7)	116.3 (5)
Cu(1)–N(2)–C(11)	126.5 (4)	C(7)–N(2)–C(11)	117.2 (6)
O(1)–C(1)–O(2)	124.5 (7)	O(1)–C(1)–C(1A)	118.3 (7)
O(2)–C(1)–C(1A)	117.1 (7)	N(1)–C(2)–C(3)	122.6 (6)
C(2)–C(3)–C(4)	116.2 (7)	C(3)–C(4)–C(5)	123.0 (6)
C(4)–C(5)–C(6)	116.7 (6)	N(1)–C(6)–C(5)	122.3 (7)
N(1)–C(6)–C(7)	112.7 (5)	C(5)–C(6)–C(7)	125.0 (6)
N(2)–C(7)–C(6)	113.3 (6)	N(2)–C(7)–C(8)	124.0 (7)
C(6)–C(7)–C(8)	122.7 (6)	C(7)–C(8)–C(9)	118.2 (6)
C(8)–C(9)–C(10)	118.9 (6)	C(9)–C(10)–C(11)	120.0 (7)
N(2)–C(11)–C(10)	121.6 (6)		

Symmetry transformation: a, $(-x, y, 0.5-z)$.

due to its high solubility in DMF). However, on standing, we could isolate $[Cu(phen)(H_2O)_2SO_4]$. The conversion of the thioketone sulfur (of thiosemicarbazide) to sulfate under such mild conditions (aerial oxidation in DMF medium at room temperature) is a very interesting observation and this is probably the first report of this kind. Though the aerial oxidation in DMF takes about two weeks, oxidation of TSC to sulfate by H_2O_2 is rapid ($\sim$15 minutes) in water, methanol or DMF.

$Cu_2(bpy)(TSC)_2Cl_4$ is obtained by reaction of $CuCl_2\cdot 2H_2O$ with 2,2′-bipyridyl and thiosemicarbazide in 2*N* HCl. So far, we have been unsuccessful in obtaining single crystals of the compound, and in the absence of X-ray data it is difficult to predict the actual structure of the compound. However the e.p.r. spectrum of the compound considered along with that of $[Cu(bpy)(TSC)_2]Cl_2$ throws some interesting light on its structure. The powder e.p.r. spectrum (at RT) of $[Cu(bpy)(TSC)_2]Cl_2$ consists of three signals corresponding to $g_1 = 2.03$, $g_2 = 2.04$, and $g_3 = 2.11$. For $Cu_2(bpy)(TSC)_2Cl_4$ the e.p.r. spectrum under identical conditions is made up of two sets of signals corresponding to $g_1 = 2.03$, $g_2 = 2.06$, $g_3 = 2.13$ and $g_{\|} = 2.25$ $g_{\perp} = 2.02$. While the rhombic signal of the binuclear complex is very similar to that of $[Cu(bpy)(TSC)_2]Cl_2$, the axial signals are similar to those observed [16, 17] for the D_{4h} ion $CuCl_4^{2-}$ with $g_{\|} \approx 2.23$ and $g_{\perp} = 2.04$. Thus it is tempting to formulate the binuclear species $Cu_2(bpy)(TSC)_2Cl_4$ as $[Cu(bpy)(TSC)_2][CuCl_4]$, containing the D_{4h} $CuCl_4^{2-}$ ion. The formation of $CuCl_4^{2-}$ from $CuCl_2$ in concentrated hydrochloric acid is chemically quite logical. Similarly the compound $Cu_2(phen)(TSC)_2Cl_4$ exhibits two sets of g values at $g_1 = 2.03$, $g_2 = 2.06$, $g_3 = 2.13$ and $g_{\|} = 2.25$, $g_{\perp} = 2.03$ and may be formulated as $[Cu(phen)(TSC)_2][CuCl_4]$.

The complexes $[Cu(bpy)(TSC)_2]X_2$ ($X = Cl$, $CuCl_4$] were found to catalytically decompose hydrogen peroxide. Though we are yet to fully understand the course of the reaction and the nature of the products to which the parent complex is ultimately converted, we obtained from the reaction medium the unexpected compound $[(bpy)_2Cu_2(C_2O_4)Cl_2]\cdot H_2O$, which was identified by X-ray crystallography. A probable reaction pathway for the formation of the above product is given in Scheme 1. It may be noted that formation of an organic radical as envisaged in step (4) of the scheme followed by C—C bond formation leading to the formation of $C_2O_4^{2-}$ in step (5) is akin to observations [18] made of the reaction of thioacetic acid with V(II), leading to the formation of succinic acid.

$$[(bpy)Cu(\mathbf{N}H_2NHC({=}\mathbf{S})NH_2)_2]X_2 \rightleftharpoons [(bpy)Cu(\mathbf{N}H_2NHC({=}\mathbf{S})NH_2)]X_2 + NH_2NHC({=}S)NH_2 \tag{1}$$

$$[(bpy)Cu(\mathbf{N}H_2NHC({=}\mathbf{S})NH_2)]X_2 + 3H_2O_2 \rightarrow [(bpy)(Cl)Cu(\mathbf{N}H_2NHC({=}O)\mathbf{O})] + SO_2 + NH_4^+ + 2H_2O \tag{2}$$

$$[(bpy)(Cl)Cu(\mathbf{N}H_2NHC({=}O)\mathbf{O})] + H_2O_2 \rightarrow [(bpy)(Cl)Cu(\mathbf{N}H{=}NC({=}O)\mathbf{O})] + 2H_2O \tag{3}$$

$$[(bpy)(Cl)Cu(\mathbf{N}H{=}NC({=}O)\mathbf{O})] + 1/2H_2O_2 \rightarrow [(bpy)(Cl)(H_2O)Cu(\mathbf{O}{-}\dot{C}{=}O] + N_2 \tag{4}$$

$$2[(bpy)(Cl)(H_2O)Cu(\mathbf{O}{-}\dot{C}{=}O] \rightarrow [(bpy)_2(Cl)_2Cu(C_2O_4)] + 2H_2O \tag{5}$$

SCHEME 1 Bold letters correspond to the donor atoms of chelating ligands.

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