Preparation and Crystal Structure of Copper(I) Carbonyl Hydrogensulfate, obtained by Carbonylation in Sulphuric Acid

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Dedicated to Professor Joachim Strähle on the Occasion of his 65th Birthday

Abstract. The hydrogensulfato-carbonyl derivative [Cu(CO)- (SO_4H)]_n, as obtained from the Cu₂O/ H₂SO₄/CO system and recrystallized from H₂SO₄/(CH₃O)₂SO₂ has been shown to possess a crystal structure organised in infinite chains built up by corner sharing of {CuO₃(CO)} and {S(OH)O₃} tetrahedra. The chains are connected by hydrogen bonds in layers, with CO groups leaning

out on both sides. The absorption of CO by $CuSO_4/Cu$ or by Cu_2O in sulfuric acid was quantified as a function of concentration. The $CuSO_4/Cu$ system in water absorbs carbon monoxide (CO/Cu molar ratio = 1.0).

Keywords: Copper; Copper(I) carbonyls; Metal hydrogensulfates

Darstellung von Kupfer(I)-carbonyl-hydrogensulfat durch Carbonylierung in Schwefelsäure und die Kristallstruktur

Inhaltsübersicht. Das Hydrogensufato-carbonyl-Derivat [Cu(CO)- (SO_4H)]_n wurde aus dem Gemisch Cu₂O/H₂SO₄/CO erhalten und aus H₂SO₄/(CH₃O)₂SO₂ umkristallisiert. Es hat eine Kristallstruktur, die aus unendlichen Ketten von über Ecken verbrückten {CuO₃(CO)}- und {S(OH)O₃}-Tetraedern aufgebaut ist. Die Ket-

1 Introduction

Earlier some of us have used sulfuric acid to prepare and characterise silver hydrogensulfate $Ag(SO_4H)$) [1a]. On the track of our long-standing interest in carbonyl chemistry of late transition metals, which profited considerably from a lasting scientific collaboration with *Strähle* and his coworkers [1b-e], we measured the CO uptake by sulfuric acid solutions of Ag^+ at atmospheric pressure. In agreement with some earlier data [2], we observed a limited absorption of carbon monoxide corresponding to a CO/Ag molar ratio of 0.3. Furthermore, no solid compound different from $Ag(SO_4H)$ could be isolated from the solution [1].

Copper(I) sulfate which has been prepared and structurally characterized, was reported to be metastable [3]. The hypothesis that $Cu(SO_4H)$ might be stable had to be taken into consideration, as the single charge on the HSO_4^- anion could drastically modify the thermodynamics of the system with respect to Cu_2SO_4 . On the other hand, carbon monoxide can stabilise copper(I) derivatives, and the affinity of

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ten sind über Wasserstoffbrückenbindungen zu Schichten mit an beiden Seiten herausragenden CO-Gruppen verbunden. Die Absorption von CO durch $CuSO_4/Cu$ oder Cu_2O in der Schwefelsäure wurde als Funktion der Konzentration bestimmt. Das $CuSO_4/Cu$ -System in Wasser absorbiert CO (CO/Cu Molverhältnis = 1,0)

copper(I) for carbon monoxide was anticipated to be much higher than that of silver(I). These considerations suggested that copper(I) could be a good candidate for the isolation of the corresponding hydrogensulfato complex, with or without coordinated carbon monoxide, thus adding a new member to the series of the still limited family of hydrogensulfato metal complexes [4]. Further interest in this field was anticipated by the observation that the number of carbonyl complexes of copper(I) with oxygen donor ligands is still limited [5]. As the result of the reversible carbon monoxide absorption by Cu(ClO₄)₂/Cu in water, compounds analytically characterised as $Cu(ClO_4)(CO)(H_2O)_x$ have been reported [6]. Work from these Laboratories has shown that trifluoro- and trichloroacetato carbonyl derivatives are obtained by syn-proportionation between copper(II) trihaloacetate and copper in the presence of CO [7]. Moreover, carbon monoxide was found to be absorbed by suspensions of Cu₂O in Et₂O in the presence of sulfonic acids (added molecular sieves take care of the water formed in the reaction), giving carbonyl derivatives of formula $[Cu(SO_3R)(CO)]_n$ (with $R = CH_3$, C_2H_5 , CF_3 or p- $CH_3C_6H_4$) [8]. The crystal structure of the ethyl derivative has been determined, vide infra.

In this paper we report the study of the system Cu_2O/H_2SO_4 in the absence and in the presence of CO and the successful isolation and structural determination of $[Cu(SO_4H)(CO]_n]$.

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2 Experimental

All preparations were carried out in standard Schlenk tubes under dinitrogen or carbon monoxide, as indicated. Elemental analyses were performed in the house by standard procedures. IR spectra were measured with a Perkin-Elmer FT-IR mod.1725X spectrophotometer. Commercial H_2SO_4 96 % (J. T. Baker), Cu_2O (Janssen) and $(CH_3O)_2SO_2$ (Aldrich) have been used as received.

Preparation of $[Cu(SO_4H)(CO)]_n$

Copper(I) oxide Cu₂O (7.50 g, 52.4 mmol) was gradually added to concentrated H₂SO₄ (20 mL) under CO at room temperature. After 10 d the grey suspension was filtered and the solid was washed with dimethylsulfate (2 × 25 mL), dried *in vacuo* ($P = 10^{-2}$ Torr) at 25 °C for 22 h and stored under CO in sealed vials (0.972 g). Elemental analysis, found (calc.): Cu, 32.4 (33.7). From the filtrate, further product precipitated out at -18 °C as colourless leaflets, which were filtered, washed with dimethylsulfate and dried *in vacuo* (0.592 g). A third crop of the product (0.178 g) was similarly obtained from the previous mother liquor maintained at -18 °C. Crystals from the third crop were used for the X-ray diffractometric experiment. The total yield of the product was 9 %. IR spectrum (Nujol): v_{CO} 2120 cm⁻¹.

In a comparative experiment carried out in the absence of carbon monoxide, the deep red Cu₂O (11.60 g, 81.1 mmol) was added to concentrated H₂SO₄ (50 mL) under N₂ at room temperature and stirred for two days at room temperature. The resulting brown solid, filtered and washed with two portions of dimethylsulfate (2 × 20 mL) was dried *in vacuo* at T = 60 °C (14.31 g). An X-ray powder diffraction diagram showed peaks due to metallic copper, CuSO₄ and CuSO₄·5 H₂O (presumably originated from exposure to moisture during data collection).

Structure determination

A plate of $[Cu(SO_4H)(CO)]_n$ was sealed under a CO atmosphere in a glass capillary, together with a drop of its mother liquor and mounted on a Bruker-AXS P4 four-circle diffractometer. Diffraction data were collected at 293(2) K with graphite-monochromated Mo-K_a radiation operating at 50 kV and 40 mA. The cell parameters listed in Table 1 have been calculated using the XSCANS program [9] from the setting angles of 26 strong reflections with θ ranging between 11.34° and 14.96°. Due to the difficult sample handling, the very long specimen could not be cut and its longer edge (1.4 mm) overcame the diameter of the incident beam collimator (1.0 mm), thus introducing systematic errors in intensity evaluation which could not be completely corrected by the ψ -scan procedure. Data reduction was performed by SHELXTL [10]. The structure was solved by the direct method and difference Fourier map using SHELXS-97 [11] and refined on F^2 by full matrix leastsquares techniques using SHELXL-97 [11]. The hydrogen atom was located in the difference Fourier map and was refined without constraints.

The crystal data and the main reliability parameters of the structure refinement are listed in Table 1. The largest difference Fourier residual peak (0.775 e \cdot Å⁻³) is placed in the middle of the S–O(2) bond and is probably due to some inefficiency of the model in describing the electron density of the sulfur atom. The largest negative one (-1.294 e \cdot Å⁻³) placed at 0.86 Å from Cu may be attributed to a similar reason. Further details of the crystal structure investigation have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 176512. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code+(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk].

Table 1 Crystal data and structure refinement.

Empirical formula	CHCuO ₅ S
M	188.62
Colour	Colourless
Crystal size / mm	$1.40 \times 0.34 \times 0.18$
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
a/Å	8.5900(7)
b / Å	4.8980(6)
c / Å	12.027(1)
βl°	95.193(9)
Z	4
$D_c / (g \cdot cm^{-3})$	2.486
μ/mm^{-1}	4.672
$V/Å^3$	503.96(9)
<i>F</i> (000)	368
θ range / °	2.38 - 31.99
Max., min. transmission	0.1535, 0.0744
No. reflections collected	2461
No. independent reflections	1753
R _{int}	0.0148
No. observed reflections, $I > 2\sigma$	1271
Data / restraints / parameters	1753 / 0 / 78
Extinction coefficient	0.010(3)
$\rho_{\rm min}, \rho_{\rm max} / (e \cdot {\rm \AA}^{-3})$	-1.294, 0.775
Completeness to $\theta = 31.99^{\circ}$	100.0 %
$R_1 = \Sigma \ F_0 - F_c / \Sigma F_0 , I > 2\sigma(I)$	0.0436
$wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[w(F_0^2)^2]\}^{1/2}$	0.1248
Goodness-of-fit, $GooF = S =$	1.042
$\{\Sigma[w(F_0^2 - F_c^2)^2] / (n - p)\}^{1/2}$	

Reaction of copper(I) with H_2SO_4 under CO. Gasvolumetric measurements

In a series of experiments carried out under CO (T = 26 °C; P 756÷770 Torr) and monitored gas-volumetrically, Cu₂O was progressively added to 10 mL of concentrated H₂SO₄ (96%): the experimental CO/Cu molar ratio was 1.3 with 5.55 mmol of Cu₂O, and decreased to 1.0 when further Cu₂O (17.5 mmol) was introduced. The addition of Cu₂O to H₂SO₄ corresponds to a dilution of the acid (from 96% to 86% with 5.55 mmol of Cu₂O, and to 58% with 23.05 mmol of Cu₂O).

In another experiment carried out in 50 % H₂SO₄, 0.04 g of Cu₂O (0.28 mmol) absorbed CO (T = 26 °C; P = 752 Torr) up to a CO/ Cu molar ratio of 1.0. Comparable results were obtained in experiments [12] where the CO uptake by the system CuSO₄/Cu/H₂SO₄ was measured. In a typical experiment CuSO₄ ·5 H₂O (0.260 g, 1.04 mmol) and a slight excess of Cu (0.070 g, 1.10 mmol) were individually introduced in sealed glass ampoules and then contacted with concentrated H₂SO₄ (96 %, 10 ml) under CO at 26 °C and P = 766 Torr. A volume of carbon monoxide corresponding to a CO/Cu molar ratio of 1.3 was found to be absorbed in 2.5 h. The system was treated *in vacuo* for 1 h and then supplied again with CO: the absorption of CO, after appropriate correction for the known volume of the reactor, corresponded to a CO/Cu molar ratio of 0.3. IR: v_{CO} 2182, 2144 cm⁻¹.

Reaction of copper(II) sulfate and metallic copper with CO in H_2O

Gas-volumetric experiment. Two sealed fragile ampoules individually containing $CuSO_4$ ·5 H_2O (0.070 g, 0.28 mmol) and an excess

of Cu (0.070 g, 1.10 mmol) were introduced into a reactor together with deionized H₂O (10 mL) under CO at 26 °C and P = 751 Torr. After breakage of the ampoules, a CO uptake corresponding to a CO/Cu molar ratio of 1.0 was measured. IR: v_{CO} 2111 cm⁻¹. The addition of an excess of Na(BPh₄) caused the complete evolution of CO.

Solid Cu₂O or suspensions of Cu₂O in water did not absorb CO.

Formation of Cu[BPh₄]

Copper sulfate CuSO₄·5 H₂O (1.43 g, 5.72 mmol) and an excess of Cu (3.092 g, 48.66 mmol) were introduced in a reactor containing deionized H₂O (30 mL) under CO at room temperature. The mixture was stirred until the CO uptake ceased (about 4 h). The suspension was filtered and the filtrate was treated with a solution of Na(BPh₄) (3.840 g, 11.22 mmol) in water (60 mL). An immediate gas evolution was observed and a colourless solid precipitated out. The suspension was filtered and the solid was washed with two portions of deionized water (2 x 20 mL) and dried *in vacuo* (2.790 g, 65 % yield). Elemental analysis, found (calc.): Cu, 16.6 (16.6). IR spectrum (PCTFE, most intense bands): 3044, 1574, 1556, 1475, 1423 cm⁻¹.

Reaction of copper(II) sulfate and metallic copper with CO in CH_3OH

Copper sulfate CuSO₄·5 H₂O (0.110 g, 0.44 mmol) and an excess of Cu (0.510 g, 8.03 mmol) were introduced into a reactor containing CH₃OH (9.2 mL) under CO at 27.2 °C. The CO uptake corresponded to a CO/Cu molar ratio of 1.0. IR spectrum of the solution: $\nu_{\rm CO}$ 2101 cm⁻¹.

3 Results and Discussion

At the onset of this work the preparation of Cu(SO₄H) was attempted by the route successfully applied for Ag(SO₄H) [1]. The addition of Cu₂O to sulfuric acid in a dinitrogen atmosphere at room temperature results in a brown suspension of metal copper and copper(II) sulfate. On the other hand, Cu₂O was reported [2] to absorb CO in concentrated sulfuric acid forming solutions of copper(I) carbonyl complexes, $[Cu(CO)_n]^+$ ($n = 1 \div 3$, depending on temperature, sulfuric acid concentration and CO pressure).

In our hands, Cu₂O in concentrated sulfuric acid (96 %, *initial* concentration) under CO gave a colourless solution or a suspension of a light grey solid, depending on the relative amounts of Cu₂O and sulfuric acid. The solid analyses as Cu(SO₄H)(CO), but the structure of the product could only be established by X-ray crystallography, *vide infra*. The nature of the carbonylated species in solution depends on the final sulfuric acid concentration. Other species beside Cu(SO₄H)(CO) may be present in solution, since carbon monoxide was absorbed up to a CO/Cu molar ratio of 1.3, observed at concentrations of H₂SO₄ as high as 86 %.

$$1/2 Cu_2O + H_2SO_4 + CO \rightarrow 1/n [Cu(SO_4H)(CO]_n + 1/2 H_2O (1)]$$

The solid of composition $Cu(SO_4H)(CO)$, as a dispersion in Nujol, shows a strong absorption at 2120 cm⁻¹, similar

to what observed for $Cu(SO_3C_2H_5)(CO)$ at 2117 cm⁻¹ [8] and for $Cu(ClO_4)(CO)(H_2O)_2$ at 2130 cm⁻¹ [6]. On the other hand, in concentrated sulfuric acid, i. e. under conditions of CO absorption corresponding to a CO/Cu molar ratio of 1.3, a weak band at 2182 cm^{-1} and a rather intense one at 2144 cm^{-1} were observed. We suggest that the band at 2144 cm⁻¹ is due to a monocarbonyl-copper derivative, while the band at 2182 cm⁻¹ is related to a dicarbonyl derivative, by analogy with similar compounds described in the literature, namely Cu[1-Et-CB₁₁F₁₁](CO)₂ (v_{CO} : 2184, 2166 cm⁻¹, OC-Cu-CO 124.1°) [13a] and Cu- $[N(SO_2CF_3)_2](CO)_2$ (v_{CO}: 2184, 2158 cm⁻¹, OC-Cu-CO 122.0°) [13b]. The second band expected for a dicarbonyl derivative having a bent OC-Cu-CO group could be responsible for the observed broadening (at about 2150 cm^{-1}) of the most intense absorption. In agreement with the literature [14], the equilibrium (see eq. 2) between the two species in solution is displaced to the left under a reduced partial pressure of CO, while the monocarbonyl complex is stable. As already observed by Souma et al. [2], we found that the position of the band attributed to the monocarbonyl species depends on the sulfuric acid concentration (2144 or 2120 cm^{-1} in 96 % or 50 % H₂SO₄, respectively). In addition, when the sulfuric acid concentration decreases, the band at high energy (2182 cm^{-1}) disappears. The solvent may influence both the equilibrium between the dicarbonyland the monocarbonyl-copper complexes (see eq. 2), and the degree of solvation of the monocarbonyl-copper species. In less concentrated sulfuric acid, the greater availability of the solvent for complexation to the copper atom causes the C=O stretching to shift to lower wavenumbers. In aqueous solution hydrated species such as $[Cu(CO)(H_2O)_m(SO_4H)]_n$ may exist, the degree of complexity n and the number of co-ordinated H₂O groups depending on the concentration of the acid medium. As a matter of fact, the CO/Cu molar ratio established gas-volumetrically corresponds to about 1.3 in 96 % H_2SO_4 , decreases by dilution of the acid and reaches 1.0 in about 60 % H₂SO₄, while further dilution does not affect this value.

$$[Cu(CO)]^{+} + CO \rightleftharpoons [Cu(CO)_{2}]^{+}$$
⁽²⁾

Analogous results were obtained starting from equimolar mixtures of copper(II) sulfate and metallic copper under CO. A syn-proportionation reaction was observed accompanied by CO uptake with CO/Cu molar ratios depending on sulfuric acid concentration, similar to the results obtained with Cu₂O. In water the reaction proceeds up to CO/Cu molar ratio of 1.0, the IR spectrum of the solution showing a band at 2111 cm^{-1} , a value to be compared with the previous ones, recorded in 96 % and 50 % H_2SO_4 , which confirms the tendency of v_{CO} 's to shift towards lower values with increasing donating power of the solvent. The aqueous solution thus obtained was treated with Na(BPh₄) in an attempt to precipitate the hypothetical $Cu(CO)(H_2O)_m(BPh_4)$ arising from the cationic complex in solution. However, complete evolution of CO was observed with formation of the colourless sparingly soluble

Cu(BPh₄), whereby presumably an aromatic ring of the anion displaces carbon monoxide from the coordination sphere of the metal through its π -electron density. Although Cu(BPh₄) is known, its structure has not been reported. It was prepared from CuBr₂ and Li(BPh₄) [15a], or by acidification of Cu(BPh₄)py₄ [15b], or from CuPh and BPh₃ in diethylether [15c].

The carbonyl species of copper(I) obtained in H₂SO₄ are well soluble in sulfuric acid and copper(I) concentrations up to 5 M can be obtained. A solution prepared from Cu₂O, CO and initially 96 % H₂SO₄, after addition of dimethylsulfate, was stored at low temperature (-18 °C) giving colourless plates of [Cu(SO₄H)(CO]_n, very sensitive to moisture, which were used for the X-ray diffraction study. The structure of $[Cu(SO_4H)(CO]_n]$ is shown in Fig. 1, where the atoms of the asymmetric unit together with those directly connected to it are labelled. In the structure may be distinguished chains, growing along b, made by the condensation of eight-membered rings $\{Cu_2O_4S_2\}$. Two types of rings, both possessing an inversion centre are present, and, although crystallographically distinct, they are very similar. Each ring shares three atoms: Cu, O, S, with the preceding one and three with the following one in the chain.



Fig. 1 View of a chain present in the structure of $Cu(CO)HSO_4$ projected down c. Primed atoms are related to unprimed ones by the symmetry operations given in Table 1. The **b** translation and the inversion operators are also drawn.

The copper atom presents a pseudo-tetrahedral coordination, being connected to one carbonyl group and to three oxygens, belonging to three different hydrogensulfato ligands. The distortion from the ideal tetrahedral geometry is due, beside the difference in length between Cu–O and Cu–C bonds, to the wide C–Cu–O angles (mean value 121.5°) with respect to the O–Cu–O' ones (mean value 95.2°). Such an angular difference is normally observed in Cu(I) carbonyl derivatives with O-ancillary ligands and is consistent with the greater Cu–O distance and the greater electronegativity of oxygen which removes negative charge from the copper allowing the O–Cu–O' angles to close. Hydrogensulfato groups show their usual tetrahedral structure [4] with a marked lengthening of the S–OH (1.555 Å) bond with respect to the S–O ones (mean value 1.453 Å). Each hydrogensulfato anion uses its non-protonated oxygens to bonding three different copper centres. A list of the bond distances and angles is shown in Table 2. The Cu-CO and C–O bond distances of 1.807 and 1.104 Å, respectively, compare well with the corresponding distances observed in metal carbonyl derivatives of copper(I) with oxygen donor ligands [5].

Table 2 Bond lengths/A and angles/° for Cu($(CO)HSO_4$	4.

Cu-C	1.807(3)	S-O(4)	1.446(2)
Cu = O(3')	2.062(2)	S-O(3)	1.448(2)
Cu = O(4'')	2.070(2)	S - O(5)	1.464(2)
Cu-O(5)	2.145(2)	S-O(2)	1.555(2)
C-O(1)	1.104(4)		
C-Cu-O(3')	125.5(1)	O(4) - S - O(5)	111.5(1)
C-Cu-O(4'')	122.2(1)	O(3) - S - O(5)	113.2(1)
C-Cu-O(5)	116.7(1)	O(4) - S - O(2)	107.6(1)
O(3) - Cu - O(4'')	94.32(8)	O(3) - S - O(2)	104.1(1)
O(3') - Cu - O(5)	93.76(9)	O(5) - S - O(2)	106.5(1)
O(4') - Cu - O(5)	97.54(8)	S-O(3)-Cu'	130.9(1)
O(1)-C-Cu	175.8(4)	S-O(4)-Cu''	127.5(1)
O(4) - S - O(3)	113.2(1)	S-O(5)-Cu	128.4(1)

Symmetry transformations used to generate equivalent atoms: ' = -x, -y + 1, -z; '' = -x, -y, -z

As it can be seen in Fig. 1, the CO groups are almost parallel, leaning out of the chain in two opposite directions, up and down; on the other hand, the OH groups stick out also in two opposite directions, forward and backward. The structure of the chain and the positions of the carbonyl groups are reminiscent of those found in $[Cu(SO_3Et)(CO)]_n$, where the ethyl and the carbonyl groups are bent approximately in the same direction [8]. In the structure of $[Cu(SO_3Et)(CO)]_n$ the chains are held together by *van der*



Fig. 2 Projection down \mathbf{a} of a layer of hydrogen bonded chains with the screw helix 2_1 relating two neighbouring ones.

Waals interactions. Further stabilisation of the solid-state structure of our compound may arise from the fact that the OH groups can behave as donors towards the O(5) atoms, establishing a network of hydrogen bonds, which organize the chains in layers spreading in the yz plane. A section of one of these planes is shown in Fig. 2.

The layers have both faces covered by CO groups lodging within the corresponding CO's of neighbouring ones. The joining of two adjacent layers is shown in Fig. 3 together with the symmetry operators relating the layers.



Fig. 3 Two neighbouring layers in the structure of $Cu(CO)HSO_4$ viewed along *b*.

The carbonyl derivative $[Cu(SO_4H)(CO)]$ is the first example of a structurally characterized hydrogensulfatocarbonyl derivative of copper. It belongs to the family of noble-metal carbonyl complexes studied in solution by *Souma* and co-workers [2, 14, 16]. This paper has pointed out that carbonyl groups are compatible with the hydrogensulfato ligand.

A limited number of hydrogensulfato complexes of transition *d* elements, namely those of Mn^{II} and Cr^{III} (electronic configurations $3d^5$ and $3d^3$, respectively) have already been reported [17]. As carbon monoxide is a typical ligand of transition *d* metals, the results of the present paper suggest that complexes containing the CO/SO₄H ligand combination may become available for relatively low oxidation states of these elements.

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