

Alternative Routes to the Synthesis of Chevrel's Salt, $\text{Cu}^{\text{II}}[\text{Cu}^{\text{I}}(\text{SO}_3)]_2 \cdot 2\text{H}_2\text{O}$

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Received 9 November 1987; revised and accepted 16 December
1987

Yellow Etard's salt ($\text{Cu}^{\text{I}}_2\text{SO}_3 \cdot 1/2\text{H}_2\text{O}$) and red Chevrel's salt ($\text{Cu}^{\text{II}}[\text{Cu}^{\text{I}}\text{SO}_3]_2 \cdot 2\text{H}_2\text{O}$) have been synthesised by the reaction of cupric acetate or freshly prepared $\text{Cu}(\text{OH})_2$ with $\text{SO}_2(\text{g})$ in aqueous medium. Characterisation of the compounds is based on the results of elemental analyses, IR spectral and magnetic moment studies and chemical reactions.

The literature¹⁻³ methods of preparation of Chevrel's salt (cupric cuprosulphite, $\text{Cu}^{\text{II}}[\text{Cu}^{\text{I}} - \text{SO}_3]_2 \cdot 2\text{H}_2\text{O}$) involves either the use of KHSO_3 in a considerably high amount or the prior synthesis of Etard's salt ($\text{Cu}^{\text{I}}_2\text{SO}_3 \cdot 1/2\text{H}_2\text{O}$). The latter method always yields impure product containing an equimolar mixture of metallic copper and $\text{Cu}[\text{CuSO}_3]_2 \cdot 2\text{H}_2\text{O}$. In view of the current interest⁴ in mixed valence metal complexes, we have reinvestigated the sulphito-chemistry of copper and have developed two new straight-forward methods for the synthesis of the title compound. The chosen reaction strategies also enabled us to obtain Etard's salt in a pure form, as an intermediate product.

Reagent grade chemicals were used. Copper(II) hydroxide was precipitated from $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, centrifuged and washed several times to make it free from chloride and alkali. IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer. Magnetic susceptibility measurements were made by Guoy method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant.

Total copper content in the compounds was estimated iodometrically⁵ after oxidation with H_2O_2 and removal of excess peroxide. In Chevrel's salt, $\text{Cu}[\text{CuSO}_3]_2 \cdot 2\text{H}_2\text{O}$, the percentage of cupric copper was determined by direct iodometric titration. The difference between the total copper content and that of cupric ion, directly afforded the percentage of cuprous ion in the compound. Sulphur was estimated⁶ as BaSO_4 after conversion of sulphite to sulphate by boiling with H_2O_2 .

Synthesis of Chevrel's salt ($\text{Cu}^{\text{II}}[\text{Cu}^{\text{I}}\text{SO}_3]_2 \cdot 2\text{H}_2\text{O}$)

Method I: Through an aqueous suspension of freshly prepared copper(II) hydroxide was bubbled SO_2 gas for ~ 10 min. The suspended hydroxide

slowly went into solution, the colour of which gradually turned to light blue with simultaneous appearance of some yellow precipitate. On bubbling the gas for further 5 min, the precipitate redissolved resulting in a clear, transparent light blue solution. The bubbling of SO_2 was stopped at this stage, and the solution was heated on a steam-bath for 15 min whereupon a red crystalline compound which analysed for $\text{Cu}^{\text{II}}[\text{Cu}^{\text{I}}\text{SO}_3]_2 \cdot 2\text{H}_2\text{O}$ separated out. The compound was washed thrice with acetone and dried *in vacuo*.

Method II: Through an aqueous solution of hydrated cupric acetate [$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$], SO_2 gas was bubbled for ~ 20 min to obtain a clear light blue solution. The rest of the procedure, including isolation of the compound was similar to that described under method-I.

(Found: Cu, 49.1; S, 16.2. Calc for $\text{Cu}_3\text{S}_2\text{O}_8\text{H}_4$; Cu, 49.3; S, 16.6%; μ_{eff} (298 K), 1.82 B.M.; IR (cm^{-1}): 1030 m, 995s, 980m, 915m, 860w, 638m, 580m and 485 (SO modes).

Isolation of intermediate yellow product. Etard's salt ($\text{Cu}_2\text{SO}_3 \cdot 1/2\text{H}_2\text{O}$)

The yellow precipitate obtained in the preparation of $\text{Cu}[\text{CuSO}_3]_2 \cdot 2\text{H}_2\text{O}$ (vide method-I) was filtered off, and the filtrate was treated with ethanol taken in an amount equal to half the volume of the filtrate. The mixture was allowed to stand for 5 min in a deep freeze when an additional amount of yellow precipitate was obtained. Both the lots of the yellow products were purified by separately washing with ethanol and finally dried *in vacuo*. Each of the products analysed for $\text{Cu}_2\text{SO}_3 \cdot 1/2\text{H}_2\text{O}$ (Found: 58.6; S, 14.4. Calcd. for $\text{Cu}_2\text{SO}_3 \cdot 1/2\text{H}_2\text{O}$: Cu, 58.8; S, 14.8%; IR (cm^{-1}): 980m, 892m, 661s, 490sh and 480s (SO modes).

In the course of our studies on fluoro(sulphato)cuprates(II)⁷, attempts were made to synthesise the aforesaid compounds from a reaction mixture containing $\text{Cu}(\text{OH})_2$, alkali metal fluoride, $\text{SO}_2(\text{g})$ and H_2O_2 . However all attempts led to a red compound, which analysed for $\text{Cu}[\text{CuSO}_3]_2 \cdot 2\text{H}_2\text{O}$. This prompted us to study the behaviour of copper(II) ion in the presence of SO_2 under different experimental conditions. Accordingly, reactions of copper(II) with SO_2 gas in aqueous as well as organic media were carried out. Reaction of either an acidified (dil. H_2SO_4) aqueous solution of cupric sulphate or that of a suspension of it in acetonitrile, with SO_2 gas resulted in the total reduction of copper(II) to copper(I). Similar observation was also made when cupric acetate or freshly prepared cupric hydroxide was treated with SO_2 gas in

acetonitrile. On the contrary, when the reaction of cupric acetate or a suspension of freshly prepared cupric hydroxide with SO_2 gas was performed in an aqueous medium (see preparation of Chevreul's salt) the colour of the solution was still observed to be blue although partial conversion of copper(II) to copper(I) was not discounted. The reduction in the intensity of the blue colour of the solution supported this contention. The resultant solution obtained at this stage, on being warmed on a steam-bath, afforded Chevreul's salt. It is to be noted that if bubbling of SO_2 gas is stopped at a stage when the yellow product just begins to appear and the mother liquor is treated with ethanol to obtain another crop of the yellow product, the compound obtained under this condition is identified as similar to that of Etard's salt ($\text{Cu}_2\text{SO}_3 \cdot 1/2\text{H}_2\text{O}$). This, therefore, provides evidence that reaction proceeds through the formation of Etard's salt as an intermediate.

Thus it is imperative to emphasise, in accord with our experimental conditions and findings, that the reaction of copper(II) with SO_2 should not be conducted with a pre-acidified solution. From the course of reactions, as monitored by the isolation of products at different stages (Etard's salt and Chevreul's salt, respectively), it may be concluded that SO_2 only partly reduces copper(II) to copper(I). Thus SO_2 plays at least two important roles, viz. as a controlled reducing agent for copper(II) and also to produce SO_3^{2-} in the reaction medium which coordinates with copper centre permitting isolation of the products. Another significant aspect of the present methods of synthesis is that the mixed valence cupric cuprosulphite compound prepared by either method is obtained in a very pure form, which is evident from the results of chemical analyses, IR spectrum, magnetic moment and chemical reactions.

For example, treatment of the red $\text{Cu}[\text{CuSO}_3]_2 \cdot 2\text{H}_2\text{O}$ with aqueous ammonia dissolves the copper compound completely in the form of soluble ammine complexes producing a clear transparent blue solution and leaves no residue of metallic copper. This implies that no impurity of metallic copper is present in the compound, as opposed to that of Rogojski's salt³. The above mentioned chemical reaction is considered crucial for checking the purity of the product. Further, the results of direct iodometric titration of the mixed valence compound showed electron-transfer corresponding to one-third of the total

copper content in the compound, which is in accord with the formulation.

The analytical data and physical properties of both the compounds, reported herein, are in conformity with those reported earlier^{3,8}. $\text{Cu}[\text{CuSO}_3]_2 \cdot 2\text{H}_2\text{O}$ is only sparingly soluble in water. $\text{Cu}_2\text{SO}_3 \cdot 1/2\text{H}_2\text{O}$, as expected, showed diamagnetic behaviour³. The room temperature (298 K) magnetic moment of the mixed-valence $\text{Cu}[\text{CuSO}_3]_2 \cdot 2\text{H}_2\text{O}$ is found to be 1.82 B.M. This value, of course, is slightly higher than that of Rogojski's salt (1.76 B.M.)³, which, however, is an equimolar mixture of $\text{Cu}[\text{CuSO}_3]_2 \cdot 2\text{H}_2\text{O}$ and copper powder. The appearance of νSO modes at higher wave number regions as compared to those of the free SO_3^{2-} ion as well as the strong band at 995 cm^{-1} in the IR spectrum of Chevreul's salt imply that the pyramidal sulphite group is bonded to metal centre through sulphur^{9,10}. Moreover, the appearance of a moderate intensity band at 915 cm^{-1} causes^{10,11} us to infer that there also exists an appreciable interaction between an oxygen atom of SO_3^{2-} and copper centre, in agreement with the crystal structure of the compound, reported earlier¹². This indicates that the pyramidal C_{3v} symmetry of the SO_3 group may not be absolutely preserved in this compound¹¹. The IR spectrum of $\text{Cu}_2\text{SO}_3 \cdot 1/2\text{H}_2\text{O}$ is straightforward and compares very well with earlier reports³.

One of the authors (NMB) is thankful to the Principal, Shillong College, Shillong for his permission to carry out the work. The award of a SRF to MD by CSIR is gratefully acknowledged.

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