

Communications

Low temperature synthesis and inter-conversions of copper sulphides using acetonitrile

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Low temperature preparation of crystalline covellite, chalcocite and digenite from the constituent elements is promoted by acetonitrile. Interconversion of digenite and chalcocite is also possible by addition of the appropriate constituent element in acetonitrile. Factors which determine the phase of the copper chalcogenide formed have been elucidated. Evidence is presented for the involvement of molecular intermediates in their formation.

Transition metal chalcogenides have attracted considerable attention in the recent past¹, due to the interesting properties they possess². Some of them are battery materials, catalysts, and even superconductors. As a result, there is considerable interest in the synthesis of these materials through novel routes. Of the many unconventional routes to solid state materials, the most interesting are those that allow for designed synthesis of the material. The guiding principle for such investigations is the increasing awareness that the relationship between coordination chemistry and the solid state chemistry^{3,4} could be exploited for synthetic gains. Transition metal sulphides are excellent candidates for exploring such relationships since the bridging nature of sulphides leads to a wide variety of polynuclear complexes. In fact, it has been pointed out that polynuclear metal thiolates have marked structural properties, justifying their being referred to as molecular fragments of solid sulphides⁴. We report here a low temperature molecular route to crystalline covellite, digenite and chalcocite from the elements under extremely mild conditions. Furthermore, facile interconversion between covellite and digenite has also been accomplished.

Experimental

Our serendipitous discovery of this synthesis resulted from our efforts to synthesize polysulphide copper complexes with diphosphines. We reacted the elements, copper metal powder and sulphur in

acetonitrile in the presence of 1,2-bis-diphenylphosphinoethane (dppe), expecting to make a $\text{Cu}_x\text{S}_y(\text{dppe})$ complex⁶. Instead, we obtained covellite in excellent yield. Omission of dppe from the reaction mixture was of no consequence to the formation of covellite. A summary of the results obtained under various conditions is given in Table 1.

Results and discussion

Pure and crystalline covellite could be obtained when the elements, copper metal powder and freshly recrystallised sulphur were mixed in 1:1 ratio and refluxed for four hours in dry acetonitrile under an atmosphere of nitrogen (S.No.1, Table 1). However, the reaction at room temperature under similar conditions yielded only amorphous material. When the reaction was carried out in air, powder X-ray diffraction (XRD) pattern of the solid obtained contained peaks other than those due to covellite (S. No. 2).

Surprisingly, on just increasing the ratio of copper to sulphur (2:1) in acetonitrile, chalcocite-M was formed (S.No.3). When the reaction was carried out in air, chalcocite-Q and digenite were formed (S.No.4). Prolonged reaction in air led to the formation of digenite only (S. No. 5).

When pure covellite was mixed with copper metal (powder) in the ratio 1:1 in acetonitrile as solvent, chalcocite-Q and digenite were formed (S.No.6). Only digenite was formed when the reaction was carried out in the presence of air (S. No. 7). However, such a reaction with covellite resulted in the formation of digenite when pyridine was used as the solvent (S. No.12). Cu_2S could be converted to CuS in acetonitrile as well as in pyridine (S. Nos. 8,9,10 & 11).

The interconversions of the various phases of Cu_xS at such low temperatures is quite interesting and suggests the formation of a molecular species which decomposes to give CuS when Cu_2S is dissolved in the presence of excess sulphur. The consistently high yields in the reactions carried out in acetonitrile (>95%) require transient intermediacy of any species that is formed. The difference between this work and that of Rauchfuss *et al.*⁶ is that the species obtained by them is sulphur-rich and hence could only decompose to CuS , the most stable low temperature phase. The formation of Cu_2S from CuS would require the formation of a copper-rich

Table 1—Summary of experimental results

S.No.	Reactants ratio	Solvent (a)	Reaction condition		Product (b)
			Time (hr)	Atm	
1	Cu ₂ S(1:1)	CH ₃ CN	4	N ₂	CuS (Covellite)
2	Cu ₂ S(1:1)	CH ₃ CN	12	Air	CuS
3	Cu ₂ S(2:1)	CH ₃ CN	16	N ₂	Cu ₂ S (Chalcocite-M)
4	Cu ₂ S(2:1)	CH ₃ CN	16	Air	Cu _{17.96} S (Chalcocite-Q), Cu _{1.8} S (Digenite)
5	Cu ₂ S	CH ₃ CN	48	Air	Cu _{1.8} S
6	CuS,Cu(1:1)	CH ₃ CN	48	N ₂	Cu _{1.96} S, Cu _{1.8} S
7	CuS,Cu(1:1)	CH ₃ CN	48	Air	Cu _{1.8} S
8	Cu ₂ S,S(1:1)	CH ₃ CN	12	N ₂	CuS
9	Cu ₂ S,S(1:1)	CH ₃ CN	12	Air	CuS
10	Cu _{1.8} S,S(1:1)	CH ₃ CN	12	Air	CuS
11	Cu ₂ S,S(1:1)	C ₅ H ₅ N	12	Air	CuS
12	CuS,Cu(1:1)	C ₅ H ₅ N	48	N ₂	Cu _{1.8} S
13	CuS,Cu(1:1)	C ₅ H ₅ N	48	Air	(c)
14	Cu ₂ S(2:1)	C ₅ H ₅ N	16	N ₂	Cu _{1.96} S
15	Cu ₂ S(2:1)	C ₅ H ₅ N	16	Air	Cu _{1.8} S

(a) Reactions were carried out at the reflux temperature of the solvent.

(b) The products were identified by their powder X-ray diffraction data.

(c) The product was not chalcocite, but could not be identified from the XRD pattern alone.

molecular species if a similar intermediate was involved in the interconversion process. Such a species has indeed been characterised recently⁷.

Removal of the solvent from the supernatant solution after formation of CuS yielded a colorless crystalline compound⁸ which decomposed rapidly to give black amorphous CuS. UV-VIS spectrum of the supernatant solution revealed the presence of a species other than sulphur. In order to verify if more than one molecular species are present in solution depending on the ratios of Cu and S present, we obtained the UV-VIS spectra of the various solutions in equilibrium with the solids. These spectra clearly indicate the presence of different species in solution (Fig. 1). While the complexes are stable in solution, they decompose to give CuS or Cu₂S on removal of acetonitrile.

Two different mechanisms have been discussed for these metal dissolving reactions⁹. One of them involves a sulphidation of the surface followed by dissolution of the tarnished layer by the solvent and the other involves interaction of the donor solvent with the metal making it a better reductant. The dissolution of the metal in the presence of acetonitrile and sulphur cannot be ascribed to the latter process since acetonitrile is not a good donor. However, it is a good ligand for Cu(I) and stabilises it. It also dissolves ionic complexes with great

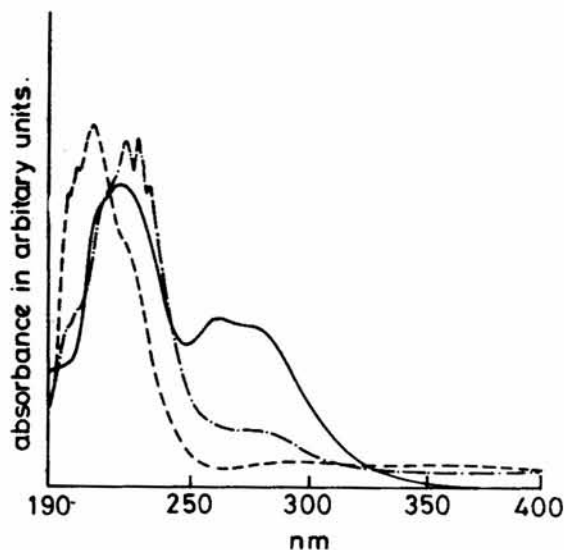


Fig. 1—UV-visible spectra of acetonitrile solutions in equilibrium with S (—), Cu₂S (—●—), and CuS (---).

facility. Hence, the former mechanism is indicated by these observations.

The formation of molecular intermediates helps one to understand the formation of different phases in pyridine and acetonitrile when the ratio of Cu/S is > 1. When the solvent does not stabilise the Cu(I) state preferentially, as in the case of pyridine, which

forms complexes with copper(I) and copper(II) with equal facility, partial oxidation takes place resulting in the formation of phases such as chalcocite-Q and digenite rather than chalcocite-M (S.Nos.14,15). However, the presence of oxygen leads to partial oxidation even in acetonitrile (S.Nos.4-7). Thus, if the metal dissolving reactions are carried out in an oxidising environment, in the presence of air or pyridine, partial oxidation results in the formation of digenite. Digenite has 10% of the Cu(I) sites replaced by Cu(II)¹⁰. The formation of different phases is thus dependent only on the ratios of the elements and the oxidising nature of the environment. This suggests that conditions under which Cu_xS minerals were formed could be determined by examining the phases present in the mineral.

The present study shows that acetonitrile is a convenient solvent for preparing covellite and chalcocite from their constituent elements at low temperatures. The results also show that metal dissolving reactions observed with Cu and S do not necessarily need donor solvents as originally suggested⁹. The sulphur-rich species initially formed are soluble and stable in donor solvents such as pyridine. On the other hand, acetonitrile, which is a good solvent for Cu(I) complexes, is also capable of dissolving the species formed, promoting the metal dissolving reaction. But unlike pyridine, it

accelerates the conversion of these species to CuS or Cu₂S.

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