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Periodate Oxidation of Cu(II) and Cu(0) in Alkaline Medium

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Vrtis, Malabrade, Malatesta, Beck, Lister and Jensovsky [1–7] reported the formation of Cu(III) complexes by oxidising highly alkaline solutions of Cu(II), either by peroxydisulfate or by hypochlorite, in the presence of periodate. Electrolytic oxidation [4] of Cu(II) also resulted in the formation of Cu(III) complexes.

In all the above cases periodato complexes of Cu(III) with a reddish brown colour, possessing highly oxidising properties in alkaline medium, were obtained. It has been suggested by Lister [5] that in the formation of these Cu(III) complexes, peroxydisulfate or hypochlorite acts as oxidising agent while periodate stabilizes the Cu(III) state forming a complex.

During the course of the present work, it was observed that the formation of periodate complex of Cu(III) is possible even in the presence of periodate alone. Presence of oxidising agents like peroxydisulfate or hypochlorite is not at all necessary, indicating thereby that the periodate is acting both as an oxidising agent and a stabilizing agent.

Secondly, it is not only the Cu(II) which is oxidised to Cu(III) in highly alkaline medium, but copper metal, in the form of fine turnings, also undergoes oxidation to Cu(III). In this case, presence of peroxydisulfate appears to be essential for the complete conversion to Cu(III). The complex obtained on oxidation of copper metal also possesses the same reddish brown colour and similar oxidising properties as those possessed by the complexes obtained by the oxidation of Cu(II).

Experimental

The periodate complexes of Cu(III) were prepared in this laboratory by the following methods:

A. Cu(II) and periodate in the presence of highly alkaline solutions (no peroxydisulfate or hypochlorite).

B. Copper metal (fine turnings) in the presence of periodate and peroxydisulfate (for complete conversion) in highly alkaline medium.

Synthesis of diperiodato cuprate(III)

A. Copper sulfate pentahydrate (2.0 g), KOH (8.0 g) and 6.5 g of potassium periodate (all the reagents were AR or GR grade) were transferred to a litre round bottom flask (Corning) containing 200 ml of twice distilled water and fitted with a reflux condenser. The order of the addition of the reagents is not important. The mixture was refluxed slowly but continuously. A greenish blue precipitate was obtained which dissolved after being refluxed for about an hour giving a reddish brown solution. The solution was allowed to cool to room temperature. 100 ml of this solution were transferred to a 500 ml beaker (Corning) and treated with 200 ml of 5% sodium nitrate solution and kept apart for about 48 h for crystallisation. The dark brown needle shaped crystals were filtered through a sintered glass crucible, washed free of sodium and potassium salts with twice distilled water, dried and stored in a dessicator.

Detailed investigations were carried out to find out the effect of the concentration of various reagents used in the synthesis. As a result of these investigations, the following optimum conditions were obtained:

TABLE I.

No.	Reagents	Optimum concentrations
1	Cu^{2+}	$\geqslant 2 \times 10^{-5}$ *M*
2	Alkali	0.15 to 0.2 *M*
3	Periodate	0.1 *M*

Best results are, however, obtained when the concentrations of Cu^{2+}, KOH and KIO_4 are 4×10^{-4} *M*, 0.2 *M* and 0.1 *M*, respectively.

B. One gram of very fine copper turnings (AR), 10.0 g of KOH (GR), 2.5 g of potassium periodate (AR) and 4.5 g of potassium peroxydisulfate (GR) were transferred to a litre round bottom flask containing 200 ml of twice distilled water and refluxed for about three hours as indicated above. The turnings were dissolved completely. The dark brown needle shaped crystals of Cu(III) complex were obtained on treatment with 5% sodium nitrate solution as above.

Spectrophotometric Studies of the Complexes

The dark reddish brown diperiodato cuprate (III) complexes were studied spectrophotometrically in the UV visible and infrared regions. A Backman-36 type spectrophotometer was used for UV and visible studies. Solutions (0.05%) for this purpose were made by dissolving the pure crystals of the complex in twice distilled water. The results obtained agree very well with those reported by Jensovsky [8] and Balikungeri *et al.* [9]. We observed a band at 418 nm in the visible spectrum. The same band was reported by Jensovsky [8] at 415 nm and by Balikungeri *et al.* [9] at 421 nm. A further two bands at 208 and 258 nm in the UV spectrum of the complex were observed, while Jensovsky [8] and Balikungeri *et al.* [9] reported the former at 208 nm and the latter at 265 nm.

For infrared spectroscopic study of the complexes, pellets were prepared by pressing well-dried complex crystals with potassium bromide in 1:100 ratio and the spectra were recorded using a Backman DGB type infrared spectrophotometer. The periodato complex of Cu(III) gave three bands at 1650 cm^{-1}, 2250 cm^{-1} and a broad band with a shoulder at 3200 cm^{-1}. Balikungeri *et al.* [9] also reported three bands at 1690 cm^{-1}. 2210 cm^{-1} and a broad band between 3600 and 2900 cm^{-1}.

Our spectroscopic data together with those reported by previous workers are summarised in Table II.

Conclusion

In the light of the results obtained, it is evident that the reddish brown complex synthesized according to the procedures indicated in this paper is diperiodato cuprate(III) [1–9].

TABLE II.

	Visible region (nm)	UV region (nm)		Infrared region (cm^{-1})		
Procedure A	418	208	258	1650	2250	3200
Procedure B	418	208	258	1650	2250	3200
J. Jensovsky	415	208	265	–	–	–
A. Balikungeri *et al.*	421	208	262	1690	2210	3600–2900

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References

1 M. Vrtis, *Rec. Trav. Chim., 44,* 425 (1925).
2 L. Malaprade, *Compt. Rend., 204,* 979 (1937).
3 L. Malatesta, *Gazz. Chim. Ital., 71,* 467 (1941).
4 M. W. Lister, *Can. J. Chem., 31,* 638 (1953).
5 M. W. Lister, *Can. J. Chem., 39,* 2330 (1961).
6 G. Beck, *Mikro Chemie, 40,* 258 (1953).
7 L. Jensovsky, *Z. Anorg. Allg. Chem., 307,* 208 (1961).
8 L. Jensovsky, *Coll. Czech. Chem. Comm., 22,* 1996 (1967).
9 A. Balikungeri, M. Pelletier and D. Monnier, *Inorg. Chim. Acta, 22,* 7 (1977).