

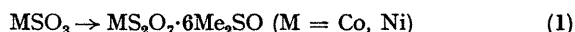
An Unusual Oxidation of Cobalt(II) and Nickel(II) Sulphites involving Sulphur Dioxide in a Non-aqueous Medium

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Summary The oxidation of anhydrous cobalt(II) and nickel(II) sulphites to the corresponding pyrosulphates with sulphur dioxide and dimethyl sulphoxide is described.

FOLLOWING the preparation of CoSO_3 and NiSO_3 from the corresponding metal iodides and tetramethylammonium pyrosulphite,¹ we have discovered that a mixture of sulphur dioxide and dimethyl sulphoxide oxidizes these transition-metal sulphites to the corresponding pyrosulphates, according to reaction (1). Neither cobalt nor nickel



sulphite dissolves in liquid sulphur dioxide or in dimethyl sulphoxide alone. It is important, therefore, to consider the steps involved in the conversion of sulphite into pyrosulphate.

The properties of CoSO_3 and NiSO_3 suggest that they are essentially covalent compounds. The i.r. spectra of both compounds are shown in the Table. No bands are present

I.r. bands of cobalt sulphite and nickel sulphite (cm^{-1})

CoSO_3 : 465w, 532w, 648s, 950vs, 1020s, 1200w.

NiSO_3 : 465w, 532w, 650s, 948vs, 1020s, 1195w.

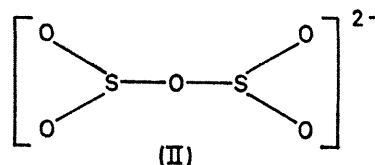
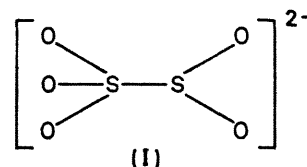
The spectra are recorded in Nujol. All bands are broad or very broad.

which might be associated with an ionic metal sulphite.² The general insolubility of the compounds in a wide range of solvents has so far prevented molecular weight and conductivity measurements from being made. In particular, the nature of the bonding of the sulphite group to cobalt in CoSO_3 may be complicated, since both the sulphur and the oxygen atoms may be involved.

Since both SO_2 and Me_2SO are required before CoSO_3 is brought into solution, a likely process seems to be the initial conversion of CoSO_3 into CoS_2O_5 , a species thought to exist in ethanolic solution,¹ and which probably exists in Me_2SO as a solvated molecule. The next step is probably a direct oxidation to the pyrosulphate.

The pyrosulphite group was considered originally to have one of two possible structures (I) and (II) and most recent evidence³ favours structure (I). The oxidation of

CoSO_3 and NiSO_3 to the corresponding pyrosulphates on treatment with SO_2 and Me_2SO is to be contrasted with the reaction of Na_2SO_3 with SO_2 and Me_2SO . In the latter case, no oxidation occurs, and Na_2SO_3 is converted only into the pyrosulphite. The different reactions may be attributed to the difference in bonding between sulphite and an alkali metal, and sulphite and a transition metal, which in the latter case is likely to be more covalent. Covalent bonding



of sulphite to cobalt or nickel will lead to an increase in the electropositive character of the sulphur atom in comparison with ionic sulphite, irrespective of whether sulphite is covalently bound to the transition metal through oxygen, or sulphur, or both. Should this be the case, then it would seem that in the presence of sulphur dioxide, the transition-metal sulphites probably form transition-metal pyrosulphites by complexation with sulphur dioxide, involving pyrosulphites having structure (II). These are sufficiently covalent to be oxidized by Me_2SO to the corresponding transition-metal pyrosulphates, which are ionic, and the Me_2SO is reduced to dimethyl sulphide. Our evidence suggests that pyrosulphite is oxidized by Me_2SO to pyrosulphate, only when it is covalently bound to a transition-metal ion. It is thought that pyrosulphite having structure (II) may be involved, since oxidation of structure (I) to pyrosulphate would involve the insertion of an oxygen atom into an S-S linkage.

The oxidation products, $\text{CoS}_2\text{O}_7 \cdot 6\text{Me}_2\text{SO}$ and $\text{NiS}_2\text{O}_7 \cdot 6\text{Me}_2\text{SO}$, were obtained as crystalline compounds from Me_2SO solutions. Their solid reflectance spectra were similar to those observed for their solutions in Me_2SO , and they, together with magnetic moment measurements, indicated

that the metal was in each case octahedrally co-ordinated by Me_2SO , and that the compounds are ionic. Satisfactory elemental analyses were obtained and qualitative tests for pyrosulphate were all positive.

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¹ R. Maylor, J. B. Gill, and D. C. Goodall, *J. Inorg. Nuclear Chem.*, 1971, in the press.

² K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd edn., Wiley, 1970, p. 94, and references therein.

³ A. W. Herlinger and T. V. Long, *Inorg. Chem.*, 1969, 8, 2661.