

electron concentration = 4.5) in analogy with the stable phase SnSb (trigonally distorted B1); the atom sites in the new phase similarly form a rhombohedral primitive lattice. These results will be reported elsewhere.

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CHEMISTRY

Purification of Sodium Tungstate

SODIUM tungstate is used to provide charge compensation in neodymium-doped single crystals of calcium tungstate (scheelite) which are widely used as lasers¹. These crystals are generally grown by the Czochralski technique from melts which can contain up to 10 wt. per cent sodium. It is therefore desirable to remove impurities from the sodium tungstate which could lead to the formation of light-scattering centres in laser crystals incorporating this material². In this communication, a zone-refining method of purifying the readily available reagent grade of sodium tungstate is described.

The source material was 'AnalaR' grade material which corresponds to the composition Na₂WO₄·2H₂O. The water of crystallization was removed by heating this material in a vitreous carbon boat at a temperature of 400° C. The charge was afterwards compacted by slowly melting at a temperature of 700° C. Solidification at this stage yields a white opaque ingot. However, the passage of two molten zones, approximately 2.5 cm wide, along a 15-cm ingot produces transparent material for three-quarters of the ingot length, provided the movement rate of the zone does not exceed 1.5 cm h⁻¹. An atmosphere of argon, flowing at a rate of 200 c.c. min⁻¹, was used both for the compaction and for the zone-refining. Under these conditions the carbon remains chemically unattacked. The material produced in this manner is polycrystalline as expected for a substance which exhibits trimorphism³.

Samples of the transparent sodium tungstate, the impure end of an ingot and the source material have been analysed in an 'M.S. 7' mass spectrometer. The results of the analysis (Table 1) show that all the impurity elements detected, except molybdenum, have been reduced in concentration by the zone-refining process.

Table 1
Concentration (p.p.m. atomic)

Element	Source material	Impure end	Pure end
Mo	1,500	1,500	1,500
As	90	230	6
Ca	165	100	20
K	250	150	10
Cl	170	240	60
P	35	170	Not detected
Si	150	230	90
B	5	15	1

The reduction in the concentration of chlorine and silicon is particularly important since these elements are known to cause scatter in calcium tungstate single crystals⁴. The high molybdenum concentration is

unlikely to be detrimental, as sodium tungstate and sodium molybdate are isomorphous compounds which may both be used for charge compensation in scheelite structures.

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Magnetic Properties of Some N : N'-bis-Salicylidene-ethylenediamine Iron (III) Complexes

THE magnetic properties of some binuclear complexes of chromium (III) and iron (III) in which magnetic interaction was considered to occur through oxygen bridging groups were reported previously¹. In the cases discussed, it was not possible to fit the magnetic data very satisfactorily to a model for spin interaction between the metal ions. We report here a complex of iron (III) with N-N'-bis-salicylidene-ethylenediamine in which we have been able to establish a binuclear formulation and account for the magnetic properties satisfactorily in terms of spin interaction between the two metal ions.

The complex N-N'-bis-salicylidene-ethylenediamine iron (III)-μ-oxy-N-N'-bis-salicylidene-ethylenediamine iron (III) was first reported by Pfeiffer². In agreement with this formulation, the complex is a non-conductor in nitrobenzene and nitro-methane and the molecular weight in chloroform and nitrobenzene corresponds to the binuclear complex (C₁₆H₁₄O₂N₂Fe)₂O. The magnetic moment at 300° K was found to be 1.87 B.M., being appreciably lower than the value of 2.4 B.M. reported previously by Klemm and Raddatz³ and very dependent on temperature, falling to 0.60 B.M. at 80° K. Considerable care was taken to ensure that the susceptibility was independent of field strength.

The characteristics of the magnetic behaviour may be satisfactorily accounted for using the Hamiltonian $H = -2JS_1 \cdot S_2$, where J is the exchange interaction between the two ions and S_1 , S_2 are the spin vectors for the two ions. For $S = 5/2$, the susceptibility χ_A is given by:

$$\chi_A = \frac{3K}{T} \frac{[55 + 30 \exp(10x) + 14 \exp(18x) + 5 \exp(24x) + \exp(28x)]}{[11 + 9 \exp(10x) + 7 \exp(18x) + 5 \exp(24x) + 3 \exp(28x) + \exp(30x)]} + N(\alpha)$$

where $K = g^2 N \beta^2 / 3k$, $x = -J/kT$ and $N(\alpha)$ is a temperature-independent paramagnetic term. The figure gives the calculated curve for $J = -100$ cm⁻¹, $g = 2.07$ and $N(\alpha) = 0$; the values of g and $N(\alpha)$ are of the order anticipated for an iron (III) complex with a ⁶S ground-state. With the exception of binuclear copper (II) complexes, this is the first example of a binuclear complex with strong spin-spin interaction for which a satisfactory interpretation of the magnetic behaviour can be given.

We have also investigated the magnetic properties of the corresponding iron (III) bromide and chloride complexes over a temperature range. At room temperature the magnetic moments of the bromide and chloride are 5.41 and 5.36 B.M. respectively. These values are lower than the spin-free value of 5.92 B.M. expected for iron (III), which suggests the possibility of magnetic exchange interactions. The crystal structure of the chloride has been reported⁴ to consist of layers of N : N'-bis-salicylidene-ethylenediamine iron (III) groups separated by 3.4 Å. However, in adjacent layers, the iron atoms are