The Bis(tetrathiotungstato)nickelate(II) Ion, a Novel Complex with the WS$_4^{2-}$ Ion as a Ligand†

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Summary The preparation and properties of the bis(tetrathiotungstato)nickelate(II) ion are reported.

WE have prepared the bis(tetrathiotungstato)nickelate(II) ion [Ni(WS$_4$)$_2$]$^{2-}$ (I) by a simple method. On mixing aqueous solutions of NiCl$_2$ and (NH$_4$)$_2$WS$_4$ (slightly acidified with dilute acetic acid) the ion (I) is formed instantaneously. On addition of aqueous solutions of the respective cations, the reddish brown tetraphenylarsonium salt (II) and tetraphenylphosphonium salt (III) are precipitated.‡ Earlier attempts to prepare heavy-metal tetrathio-molybdates and -tungstates[1] gave black NiS if the mixture was not acidified.

The salts (II) and (III) were characterised by elemental analysis, and i.r. and electronic spectra. They are soluble in nitromethane, acetonitrile, and chloroform, slightly soluble in ethanol, and insoluble in water. The i.r. spectrum up to 200 cm^{-1} shows bands due to the cations, and, in addition the following strong absorptions: 490 [ν_s(W=S)], 487 [ν_{as}(W=S)], and 449 and 447 cm^{-1} [ν (ring)]. The first two bands are assigned to the stretching modes of the terminal WS groups, which are, as expected, shifted to higher wavenumbers as compared with the ν(WS) modes $\nu_1(A_1)$ and $\nu_3(F_2)$ in the WS$_4^{2-}$ ion (*cf.* ref. 2). The other both vibrations have predominantly ν(W–S) character. On the basis of the diamagnetism of (I), the Ni atom is considered to have square-planar geometry (Figure). The electronic spectrum is consistent with this view, showing charge-transfer bands of the type π(S) $\rightarrow$ d(W) at 23,800 (ϵ 12,000) and 26,300 cm^{-1} (ϵ 14,000). The longest-wavelength absorption of WS$_4^{2-}$ occurs at 25,500 cm^{-1} (*cf.* ref. 3) and is split because of the lower symmetry in the complex. In the case of the d^8-configuration and pseudo-D_{4h}-symmetry of the NiS$_4$ group the following three spin allowed $d \rightarrow d$ transitions are expected[4,5]: $^1A_{1g} \rightarrow {}^1A_{2g}$ (which is $^1A_{1g} \rightarrow {}^1B_{1g}$ for D_{2h} symmetry); $^1A_{1g} \rightarrow {}^1B_{1g}$, and $^1A_{1g} \rightarrow {}^1E_g$. The spectrum shows two bands in the expected range: ν_1 *ca.* 14,300 and ν_2 *ca.* 19,000 cm^{-1}. The values for Ni(dtp)$_2$, for which the square-planar geometry has been confirmed by *X*-ray studies,[6] are ν_1 = 14,500 and ν_2 = 19,100 cm^{-1},[5] indicating that the ligand-field strength of WS$_4^{2-}$ and the diethyldithiophosphate ligand are similar. Using the approximation of Gray *et al.*[4] with Slater–Condon parameters $F_2 = 10\ F_4 = 800$ cm^{-1} the ligand field splitting parameter Δ_1 = 17,100 cm^{-1} was calculated; for Ni(dtp)$_2$ Δ_1 was 17,300 cm^{-1}.[7] The third expected $d \rightarrow d$ transition of (I) is not observed, since it is in the same region of the spectrum as charge-transfer bands.

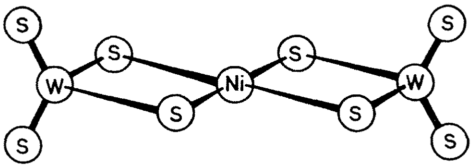

FIGURE. *Suggested structure for* [Ni(WS$_4$)$_2$]$^{2-}$ (*probable symmetry* D$_{2h}$).

Note added in proof. The corresponding complexes of Co$^{\text{II}}$ and Zn$^{\text{II}}$ have also been prepared (*Chem. Ber.*, submitted for publication.

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‡ They were purified by recrystallisation from nitromethane.

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