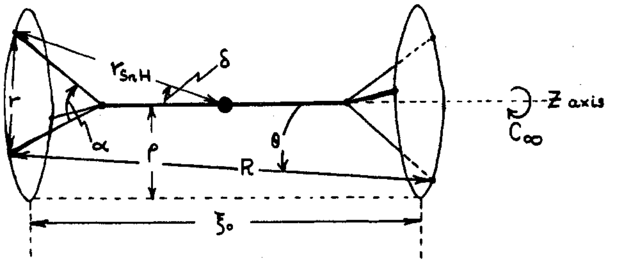

Figure 2. Geometric parameters appropriate for a discussion of the structure of the dimethyltin ion. On the nmr time scale the C–Sn–C bond direction is a C_∞ axis, denoted as the *z* axis. The methyl protons protons rotate freely on two circles displaced a distance ξ_0. The intramethyl proton–proton distance is "*r*." The instantaneous value of the intermethyl proton–proton distances is designated as "*R*;" this axis makes an angle θ with the *z* axis. "ρ" is the radius of the two circles swept out by the rotating methyl protons. "r_{SnH}" is the tin–proton distance and this vector makes an angle δ with the *z* axis. The H–C–H angles are given the symbol "α."

centrated micellar solution both lie in the expected range but indicate considerably different solvation of the dimethyltin ion. In what follows we shall be able to derive the actual value of the scalar coupling $^2J_{Sn-H}$ in the lyotropic nematic phase from analysis of the spectra in structural terms.

Analysis of Structural Details. The dimethyltin ion is known to be linear and Figure 2 depicts the geometric parameters necessary for discussion. Saupe[12] has treated a similar case and we shall adopt the same notation. Assuming that the methyl groups rotate freely and independently, the ratio of D_{12} to D_{11} is given by

$$\frac{D_{12}}{D_{11}} = \frac{-3\sqrt{3}}{\pi}\int_0^{2\pi} \frac{[(\beta-1)+\cos\phi]}{[(\beta+2)-2\cos\phi]^{5/2}}\,\mathrm{d}\phi \qquad (1)$$

for this particular linear arrangement.[12] ϕ is the relative rotational angle between the two methyl groups and $\beta = 3\xi_0^2/r^2 = \xi_0^2/\rho^2$. For free rotation, the value of $\beta = 21.348 \pm 0.002$ was obtained from the experimental values of D_{12} and D_{11} by use of a small computer program. If we now assume that $\rho = 1.033$ Å (from a tetrahedral carbon and a C–H bond distance of 1.097 Å) the value $\sqrt{\langle R^2\rangle}$ becomes 4.99 ± 0.01 Å (taking all errors from the present experiment).

It is possible, since the tin atom is a center of symmetry, to compute the partially averaged dipole–dipole coupling constant D_{SnH}[20]

$$D_{SnH} = \frac{-3\sqrt{3}\gamma_{Sn}D_{11}}{\gamma_H}\sin^3\delta(2-3\sin^2\delta) \qquad (2)$$

γ_{Sn} and γ_H are the mean magnetogyric ratios of tin-117 and tin-119 to that of the proton, respectively. The value of D_{SnH} obtained from (2) is 51.8 ± 0.1 Hz. The separation of the two experimental $A_3A'_3$ subspectra gave the value $|D_{SnH} + J_{SnH}| = 55.1 \pm 0.4$ Hz. The only acceptable value of $|J_{SnH}|$ becomes 106.9 ± 0.5 Hz which is that obtained from the micellar solution. By this argument we have been able to show that the solvent environment, from the point of view of the dimethyltin ion, in the lyotropic phase is essentially the same as that of the concentrated micellar solution. Aqueous dimethyltin nitrate has a significantly different solvation at the same concentrations. This result has significance for the study of sonicated membranes. It appears, at least from the point of view of the free ions, that sonicated vesicles dispersed in water provide the same ionic environment as in the original membrane. It is assumed that sonicated vesicles correspond to micellar solutions and the original superstructure of the membrane corresponds to the nematic phase.

Comparison of Data for the Dimethyltin Ion with Previous Determinations on Similar Structures. Englert[20] has investigated the structure of dimethylmercury in a thermotropic solvent. This is also a linear species. In Table I we have collected the structural data in the literature[12,13,20,21] for all related structures determined by nmr spectra of oriented molecules and compared them with those for dimethyltin. A similar assumption that $\rho = 1.033$ Å has been made in all cases and eq 1 was used to compute β under the conditions of free and independent rotation of the two methyl groups. It is interesting to note that the covalent radii of tin and mercury are in the right order and that the acetylenic group -C≡C- is intermediate in size.

Registry No. Dimethyltin ion, 34563-69-4.

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Contribution from the Chemistry Department, University of Dortmund, D-46 Dortmund-Hombruch, West Germany

Transition Metal Complexes as Ligands. The Dioxodithiotungstate Ion $WO_2S_2^{2-}$ [1]

A. Mueller,* H.-H. Heinsen, and G. Vandrish

Received August 6, 1973

Recently, we reported novel transition metal complexes with the tetrathiotungstate (WS_4^{2-})[2,3] and monooxotrithiotungstate (WOS_3^{2-})[4a] ions as ligands (see also the review of Diemann and Mueller, where the chemistry of closed-shell transition metal chalkogen compounds has been reported,[4b] and the third edition of Cotton and Wilkinson[4c]). Since these bidentate ligands, in contrast to the thiosulfate[5] ion, coordinate only through sulfur, we have extended our studies to see whether this is also true for the dioxodithiotungstate ($WO_2S_2^{2-}$) ion and report here these results.

Experimental Section

General Information. Electronic absorption measurements were made on the chloroform or acetonitrile solutions of the compounds using a Perkin-Elmer EPS-3T recording spectrometer. Infrared spectra were recorded in Nujol mulls on a Perkin-Elmer Model 180 recording spectrometer.

Carbon, hydrogen, and sulfur were determined microanalytically and phosphorus was determined as ammonium molybdatophosphate

Materials. $(NH_4)_2WO_2S_2$ was prepared as previously described.[6]

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(1) The authors are grateful for the support of this research by Nato, Deutsche Forschungsgemeinschaft, the Fond der Chemischen Industrie, and the Minister fur Wissenschaft und Forschung des Landes Nordrhein-Westfalen.

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Table I. Infrared Frequencies (cm^{-1}) of Oxothiotungstate Complexes of Nickel and Cobalt

	Ref	ν(MS)	ν_t(W=S)[d]	ν_{br}(WS)[d]	$\nu(WS)_{av}$	ν(WO)	$\nu(WO)_{av}$
$[Ni(WS_4)_2]^{2-}$	3	328	490, 487	449 (447)	469		
$[Ni(WOS_3)_2]^{2-}$	4	325	496, 486	450	471[c]	921/908	914
$[Ni(WO_2S_2)_2]^{2-}$		322	(485)[e]	451		$\nu_s = 916$, $\nu_{as} = 883$	900
$[Co(WS_4)_2]^{2-}$	3	289	500, 491	442, 450	471		
$[Co(WOS_3)_2]^{2-}$	4	290	490, 485	445	466[c]	917/907	912
$[Co(WO_2S_2)_2]^{2-}$		287	(492)[e]	440		$\nu_s = 927$, $\nu_{as} = 892$	909
WS_4^{2-}	4a		$\nu_1(A_1) = 485$	$\nu_3(F_2) = 465$	470[b]		
WOS_3^{2-}	4a		$\nu_2(A_1) = 465$	$\nu_4(E) = 451$	456[a]	$\nu_1(A_1) = 870$	870
$WO_2S_2^{2-}$	4a		$\nu_2(A_1) = 454$	$\nu_8(B_2) = 442$	448	$\nu_1(A_1) = 886$ $\nu_6(B_1) = 848$	867

[a] $[{}^1/_3(\nu_2^2 + 2\nu_4^2)]^{1/2}$. [b] $[{}^1/_4(\nu_1^2 + 3\nu_3^2)]^{1/2}$. [c] $[{}^1/_4[\Sigma\nu_t^2(W{=}S) + 2\nu_{br}^2(WS)]]^{1/2}$. [d] Approximate assignment. [e] An extremely weak band indicates O coordination to a very small extent.

Table II. d→d Transitions (cm^{-1}) of Oxothiotungstato Complexes of Cobalt and Nickel

Complex	Ref	$\nu_1(A_{1g} \rightarrow A_{2g})$	$\nu_2(A_{1g} \rightarrow B_{1g})$	Δ_1[b]
$[Ni(WS_4)_2]^{2-}$	3	14,300	19,000	17,100
$[Ni(WOS_3)_2]^{2-}$[a]	4	14,500		17,300
$[Ni(WO_2S_2)]^{2-}$		15,150	22,200 ?	17,900

Complex	Ref	$\nu_3({}^4A_2 \rightarrow {}^4T_1(P))$	$\nu_2({}^4A_2 \rightarrow {}^4T_1(F))$	Δ[d]	B[d]	β[c]
$[Co(WS_4)_2]^{2-}$	3	12,400	8300 ?			
$[Co(WOS_3)_2]^{2-}$	4	14,000	7700	4610	525	0.54
$[CO(WO_2S_2)_2]^{2-}$		16,430	?			

[a] $[Ni(WOS_3)_2]^{2-}$ measured in $CHCl_3$, all others in CH_3CN solution. [b] $\Delta_1 = \nu_1 + 35F_4; F_2 = 10F_4 = 800$ cm^{-1}.[8] [c] $\beta = B/B_0$. [d] For equations used see ref 9.

All complexes were prepared by the following method. A 30 ml aqueous solution containing either 140 mg of $Ni(NO_3)_2 \cdot 6H_2O$ or $CoSO_4 \cdot 7H_2O$ and either 370 mg of Ph_4PCl or 410 mg of Ph_4AsCl was quickly added to 20 ml of freshly prepared aqueous solution containing 320 mg of $(NH_4)_2WO_2S_2$. The resulting precipitate was quickly filtered under nitrogen and dried under vacuum over phosphorus pentoxide. The resulting cobalt complexes were blue green in color while the nickel complexes were light olive green to brown.

Tetraphenylphosphonium Bis(dioxodithiotungstato)nickelate(II). *Anal.* Calcd for $(Ph_4P)_2Ni(WO_2S_2)_2$: C, 44.41; H, 3.08; P, 4.77; S, 9.89. Found: C, 44.05; H, 3.17; P, 4.70; S, 9.45.

Tetraphenylphosphonium Bis(dioxodithiotungstato)cobaltate(II). *Anal.* Calcd for $(Ph_4P)_2Co(WO_2S_2)_2$: C, 44.41; H, 3.08; P, 4.77; S, 9.89. Found: C, 43.2; H, 3.17; P, 4.62; S, 9.55.

Tetraphenylarsonium Bis(dioxodithiotungstato)nickelate(II). *Anal.* Calcd for $(Ph_4As)_2Ni(WO_2S_2)_2$: C, 41.88; H, 2.97; S, 9.26. Found: C, 41.90; H, 2.99; S, 8.95.

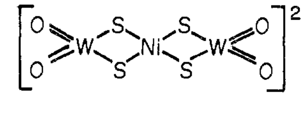
Tetraphenylarsonium Bis(dioxodithiotungstato)cobaltate(II). *Anal.* Calcd for $(Ph_4As)_2Co(WO_2S_2)_2$: C, 41.88; H, 2.97; S, 9.26. Found: C, 41.10; H, 3.00; S, 9.00.

Results and Discussion

Vibrational spectroscopic data for the nickel and cobalt complexes are presented in Table I. Data for the corresponding WOS_3^{2-} and WS_4^{2-} complexes are included for purposes of comparison.

It is readily seen (Table I) that a terminal W=S group is characterized by one or two vibrational frequencies between 480 and 500 cm^{-1} and a bridging WS group by bands between 440 and 450 cm^{-1}. Since the upper frequency band is missing in the $WO_2S_2^{2-}$ complexes, no terminal W=S group is present. Furthermore, the WO stretching frequency (as expected when WO is terminal) shifts to higher wave numbers compared to the average ν(WO) frequency of $WO_2S_2^{2-}$. Hence the $WO_2S_2^{2-}$ ligand behaves like the WOS_3^{2-} ligand and coordinates through sulfur. This interesting conclusion differs when thiosulfate is the ligand, since the latter forms isomers.[5] It is also noteworthy that the average ν(WS) stretching frequency is similar (Table I) in the free and complexed oxothiotungstate ions.

Electronic absorption spectral data are presented in Table II. It is easily shown from these data and from magnetic measurements that nickel forms square planar (the complex is diamagnetic) and cobalt tetrahedral ($\mu_{eff} = 4.2$ BM, T 25°) complexes. Furthermore, the d-d transitions lie in the region expected for sulfur-containing ligands (*e.g.*, for a NiS_4 or CoS_4 chromophor).[7] Hence, the following structure (*e.g.*, for the Ni complexes) with approximate D_{2h} symmetry is proposed (pseudo D_{4h} for the NiS_4 group).



The WO_2 planes should be perpendicular to the WS_2 planes because W is tetrahedrally surrounded. The calculated ligand field strengths, Δ_1 (Table II),[8] for the nickel complexes are in the order ($\Delta_1 = E(d_{x^2-y^2}) - E(d_{xy})$) $WS_4^{2-} < WOS_3^{2-} < WO_2S_2^{2-}$. Although ν_2 and therefore the ligand field parameter could be determined only for the $[Co(WOS_3)_2]^{2-}$ (see Table II) complex, a similar order of ligand field strength toward cobalt is deduced from the variation of the ν_3 frequency. The calculated Δ (ligand field parameter) and β (nephelauxetic parameter) for the $[Co(WOS_3)_2]^{2-}$ complex indicates that the WOS_3^{2-} ion has an extremely high nephelauxetic effect[9] ($\beta = 0.54$).

The ligand internal charge transfer transitions partly overlap with cation internal bands and are not so interesting. For a general discussion of the electronic spectra of isolated thio- and selenoanions and of complexes with these ligands see the review of Mueller, *et al.*[10]

Registry No. $(Ph_4P)_2Ni(WO_2S_2)_2$, 50450-04-9; $(Ph_4P)_2Co(WO_2S_2)_2$, 50306-59-7; $(Ph_4As)_2Ni(WO_2S_2)_2$, 50306-60-0; $(Ph_4As)_2Co(WO_2S_2)_2$, 50306-61-1.

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