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# The Synthesis and Electronic Structure of Oxoisothiocyanatomolybdates(V) and -Tungstates(V)

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*A number of complex salts containing the* $[MoO(NCS)_5]^{2-}$ *and* $[WO(NCS)_5]^{2-}$ *anions have been synthesized. The structure of these complex anions have been investigated by electronic, vibrational, and ESR spectra; magnetic studies were also carried out over a temperature range. The data obtained indicate, that the complex anions are mononuclear with* $C_{4v}$ *symmetry, and contain N-bonded* $NCS^-$*ligands.*

## Introduction

Mono-oxocomplexes of transition metal ions such as $V^{IV}$, $Nb^{IV}$, $Cr^{V}$, $Mo^{V}$, $W^{V}$, $Re^{(VI,V)}$, $Tc^{(VI,V)}$ are of interest in connection with the studies of the spectral and magnetic properties of the $d^1$ and $d^2$ electron configurations in strong fields of $C_{4v}$ symmetry. Investigations of Trzebiatowska *et al.*[1-4] have shown that in six-coordinate mono-oxocomplexes of $d^2$ metal ions the ground state is the orbital singlet $^1A_1$, resulting from the strong distortion of the octahedron along the z axis due to the oxo-ligand. This leads in general to the diamagnetism of such complexes. For the compounds with a $d^1$ electron configuration the magnetic moments differ only slightly from the spin-only value even for the 4d and 5d elements which usually have relatively large values of the spin-orbit coupling constants. This may be attributed to the relatively large separation, 12,000 $cm^{-1}$, between the orbitally nondegenerate ground state $^2B_2$ and the nearest excited term $^2E$.[5-7] In addition a very strong trans--effect due to the terminal oxygen atom was shown by X-Ray to be present in several oxocomplexes of $V^{IV}$, $Mo^{V}$, and $Re^{V}$.[8-12]

This paper reports the synthesis and the spectral and magnetic studies of a series of mononuclear oxoisothiocynatomolybdate(V) and -tungstate(V) complexes. The information available at present for such compounds is very limited. Some results of ESR spectral studies of the $Mo^V/SCN^-/H^+$ system in solution have been reported, but are strongly dependent on experimental conditions and may be variously interpreted.[13-15] The lack of data about well-defined oxoisothiocyanatomolybdates(V) and -tungstates(V), especially on their spectral and magnetic properties, is very likely due to a large extent to the difficulty of obtaining such complexes in a pure state. We found, that the method reported by Wardlaw[16] for the synthesis of $(PyrH)_2[MoO(NCS)_5]$ actually yields a mixture of different products. Since the purification of such compounds by crystallization is not feasable, we have worked out new routes for their syntheses.

## Experimental Section

All syntheses were carried out using p.a. grade reagents of « POCH » Gliwice-Poland.

### PREPARATION OF THE COMPLEX SALTS

*Pyridinium Oxoisothiocyanatomolybdate(V),* $(PyrH)_2[MoO(NCS)_5]$. Ammonium paramolybdate (6.0 g) was dissolved in 30 ml of water and 150 ml of conc. hydrochloric acid were added. The solution thus obtained was treated with 5 ml of 40% hydrazine hydrate an the mixture was heated at 80°C. After reduction had occured, 9 ml of pyridine were added. The reaction mixture was allowed to cool and 13.6 g of $NH_4SCN$ were added. A dark-green, viscous solid separated; after complete crystallization it was filtered off, washed twice with water and dried *in vacuo* over $P_2O_5$.

The corresponding oxoisothiocyanatomolybdate(V) salts of the α-picolinium. trimethylammonium, tetraethylammonium, quinolinium and oxyquinolinium cations were obtained in a similar manner. For the same quantities of all other reagents as given for $(PyrH)_2[MoO(NCS)_5]$, the following amounts of amines were used: 6 ml of α-picoline; 10 ml of $Me_3NHCl$ (50% aq. soln.); 18.8 g of $Et_4NBr$; 9.0 ml of quinoline; 9 g of 8-hydroxyquinoline in 9*M* HCl.

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**Table I.** Analytical Data for Oxopentaisothiocyanatomolybdates(V) and -Tungstates(V).

| | Colour | % C Calcd. | % C Found | % N Calcd. | % N Found | % S Calcd. | % S Found | % Me Calcd. | % Me Found |
|---|---|---|---|---|---|---|---|---|---|
| $(PyrH)_2[MoO(NCS)_5]$ | dark-green | 32.03 | 31.79 | 17.43 | 17.48 | 28.50 | 28.43 | 17.06 | 17.05 |
| $(\alpha\text{-picH})_2[MoO(NCS)_5]$ | dark-green | 34.46 | 34.41 | 16.55 | 16.78 | 27.06 | 26.93 | 16.20 | 16.31 |
| $(Met_3NH)_2[MoO(NCS)_6]$ | dark-green | 25.29 | 25.07 | 18.77 | 18.79 | 30.68 | 30.81 | 18.37 | 18.27 |
| $(Met_4N)_2[MoO(NCS)_5]$ | red | 28.37 | 28.16 | 17.82 | 17.83 | 29.12 | 29.17 | 17.43 | 17.42 |
| $(Et_4N)_2[MoO(NCS)_5]$ | red | 38.07 | 37.93 | 14.80 | 14.63 | 24.20 | 24.12 | 14.48 | 14.70 |
| $(QuinH)_2[MoO(NCS)_5]$ | brown | 40.18 | 40.18 | 14.80 | 14.76 | 24.20 | 24.17 | 14.48 | 14.52 |
| $(OxineH)_2[MoO(NCS)_5]$ | red-brown | 38.33 | 38.17 | 14.12 | 14.04 | 23.08 | 23.17 | 13.87 | 13.60 |
| $(\alpha\text{-picH})_2[WO(NCS)_5]$ | dark-green | 30.01 | 29.93 | 14.41 | 14.38 | 23.56 | 23.46 | 27.03 | 27.15 |
| $(Met_4N)_2[WO(NCS)_5]$ | light-green | 24.46 | 24.49 | 15.36 | 15.41 | 25.11 | 25.16 | 28.81 | 28.71 |

*Tetramethylammonium oxoisothiocyanatomolybdate (V), $(Met_4N)_2[MoO(NCS)_5]$.* A solution of 4 g of tetramethylammonium oxochloromolybdate (V) in 10 ml of water was added to a hot solution of 2.8 g of $NH_4SCN$ in 10 ml of water. The resulting fine, red crystalline precipitate was filtered off, washed and dried as the corresponding pyridinium salt.

*α–picolinium oxoisothiocyanatotungstate(V), $(\alpha\text{–}picH)_2[WO(NCS)_5]$,* was obtained as described by Funk et al.[17] The synthesis of $(Met_4N)_2[WO(NCS)_5]$ was carried out in a similar manner except that 0.6 g of $Met_4NOH$ (30% aq.soln.) were added to 30 ml of the stock solution of $W^V$.

The analytical data of the compounds obtained are listed in Table I.

## PHYSICAL MEASUREMENTS

Magnetic susceptibility measurements were carried out by the Gouy method in the temperature range 77-300°K. Electronic spectra in acetone and ethanol solutions were recorded on a Unicam SP 700 spectrophotometer. Vibrational spectra in the region 200-4000 $cm^{-1}$ were recorded with a Perkin Elmer Model 321 and a Carl-Zeiss Jena UR-20 spectrophotometer using Nujol and hexachlorobutadiene mulls. ESR spectra of polycrystalline samples and of acetone or acetone-benzene (1:9) solutions were measured at 77 and 295°K, using a JEOL JES-ME-3x spectrometer.

The temperature dependence of the magnetic moments for some of the complexes is given below:

$(PyrH)_2[MoO(NCS)_5]$:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| T °K | 77.0 | 90.0 | 103.0 | 118.0 | 133.0 | 146.5 | 160.0 | 175.0 |
| $\mu_{eff}$ BM | 1.59 | 1.64 | 1.61 | 1.63 | 1.63 | 1.63 | 1.63 | 1.66 |
| T °K | 192.0 | 204.5 | 220.0 | 231.0 | 248.0 | 265.0 | 285.5 | 297.0 |
| $\mu_{eff}$ BM | 1.67 | 1.67 | 1.67 | 1.65 | 1.68 | 1.71 | 1.68 | 1.69 |

$(\alpha\text{-picH})_2[MoO(NCS)_5]$:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| T °K | 77.0 | 97.0 | 107.5 | 121.5 | 135.0 | 150.0 | 163.5 | 177.5 |
| $\mu_{eff}$ BM | 1.77 | 1.79 | 1.82 | 1.81 | 1.83 | 1.83 | 1.83 | 1.83 |
| T °K | 191.5 | 204.5 | 217.5 | 233.0 | 248.5 | 264.5 | 275.0 | 285.0 |
| $\mu_{eff}$ BM | 1.83 | 1.82 | 1.83 | 1.82 | 1.82 | 1.83 | 1.83 | 1.83 |

$(Met_3NH)_2[MoO(NCS)_5]$:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| T °K | 77.0 | 94.0 | 107.5 | 121.5 | 135.5 | 149.5 | 163.0 | 177.0 |
| $\mu_{eff}$ BM | 1.62 | 1.67 | 1.69 | 1.71 | 1.72 | 1.74 | 1.75 | 1.76 |
| T °K | 191.0 | 204.5 | 218.0 | 231.4 | 248.0 | 261.0 | 272.5 | 293.0 |
| $\mu_{eff}$ BM | 1.77 | 1.77 | 1.77 | 1.78 | 1.79 | 1.75 | 1.80 | 1.83 |

$(Met_4N)_2[MoO(NCS)_5]$:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| T °K | 77.0 | 90.5 | 102.5 | 117.0 | 134.0 | 148.0 | 162.0 | 175.5 |
| $\mu_{eff}$ BM | 1.68 | 1.67 | 1.67 | 1.68 | 1.67 | 1.67 | 1.66 | 1.64 |
| T °K | 192.5 | 206.0 | 232.0 | 248.5 | 261.0 | 280.5 | 293.0 | |
| $\mu_{eff}$ BM | 1.67 | 1.68 | 1.65 | 1.66 | 1.67 | 1.70 | 1.71 | |

$(Et_4N)_2[MoO(NCS)_5]$:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| T °K | 77.0 | 94.0 | 107.5 | 121.5 | 135.0 | 149.0 | 163.0 | 179.0 |
| $\mu_{eff}$ BM | 1.44 | 1.54 | 1.53 | 1.56 | 1.58 | 1.60 | 1.60 | 1.62 |
| T °K | 193.0 | 206.5 | 217.5 | 231.5 | 250.0 | 263.0 | 276.5 | 293.5 |
| $\mu_{eff}$ BM | 1.61 | 1.63 | 1.63 | 1.67 | 1.66 | 1.65 | 1.65 | 1.67 |

$(\alpha\text{-picH})_2[WO(NCS)_5]$:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| T °K | 77.0 | 94.0 | 107.5 | 122.0 | 136.5 | 151.5 | 173.0 | 183.5 |
| $\mu_{eff}$ BM | 1.51 | 1.52 | 1.51 | 1.51 | 1.47 | 1.46 | 1.55 | 1.49 |
| T °K | 194.0 | 212.0 | 224.5 | 257.0 | 269.0 | 280.5 | 293.0 | |
| $\mu_{eff}$ BM | 1.50 | 1.55 | 1.54 | 1.56 | 1.54 | 1.57 | 1.58 | |

$(Met_4)_2[WO(NCS)_5]$:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| T °K | 77.0 | 94.0 | 104.5 | 116.0 | 129.5 | 143.0 | 157.5 | 172.5 |
| $\mu_{eff}$ BM | 1.38 | 1.39 | 1.40 | 1.38 | 1.33 | 1.40 | 1.42 | 1.45 |
| T °K | 186.5 | 199.0 | 213.0 | 224.5 | 241.0 | 255.5 | 292.5 | |
| $\mu_{eff}$ BM | 1.43 | 1.41 | 1.41 | 1.40 | 1.41 | 1.40 | 1.39 | |

**Table II.** Electronic Spectra of Oxoisothiocyanatomolybdates(V) and -Tungstates(V).

| Compound | Absorption Bands, $cm^{-1}$, and ε Values (in parentheses) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $(PyrH)_2[MoO(NCS)_5]$ | 39,600<br>(12,480) | 31,500<br>(3,950) | 29,800<br>(18,370) | 24,500 sh | 21,500<br>(17,800) | 18,600 sh | 12,700<br>(76) | |
| $(\alpha\text{-picH})_2[MoO(NCS))_5]$ | 38,000<br>(20,400) | 30,100<br>(25,400) | 29,500<br>(25,350) | 24,500 sh | 21,600<br>(25,060) | 18,400 sh | 12,700<br>(76) | |
| $(Met_3NH)_2[MoO(NCS)_5]$ | 38,400<br>(9,760) | 31,400<br>(7,430) | 29,500<br>(23,190) | | 21,300<br>(22,560) | 18,500 sh | 12,800<br>(116) | |
| $(Et_4N)_2[MoO(NCS)_5]$ | | 31,000<br>(22,680) | 29,800<br>(24,160) | 24,400 sh | 21,500<br>(22,880) | | 12,500<br>(80) | |
| $(Met_4N)_2[MoO(NCS)_5]$ | | | 29,800<br>(24,060) | 24,400 sh | 21,600<br>(22,240) | 18,400 sh | 12,500<br>(104) | |
| $(QuinH)_2[MoO(NCS)_5]$ | 36,000<br>(10,360) | 32,600<br>(12,830) | 29,600<br>(14,860) | 24,400 sh | 21,600<br>(9,330) | 18,400 sh | 12,900<br>(67) | |
| $(\alpha\text{-picH})_2[WO(NCS)_5]$ | 38,000<br>(20,900) | 31,600<br>(6,940) | 28,000<br>(1,765) | | 24,900<br>(22,300) | 22,400 sh | 17,600 sh | 13,400<br>(201) |
| $(Met_4N)_2[WO(NCS)_5]$ | 37,300<br>(2,030) | 32,600<br>(1,590) | 30,800<br>(3,620) | | 25,100<br>(17,670) | 22,800 sh | 17,400 sh | 13,800<br>(172) |

## Results and Discussion

*Electronic Spectra.* The electronic spectra of the monomeric oxoisothiocyanatomolybdates(V) and -tungstates(V) complex ions reported in this work (Table II) are generally characteristic of the $d^1$ electronic configuration in a strong tetragonal field. Of the observed absorption bands, those arising essentially from d-d type electronic transitions can be assigned with confidence on the basis of the energy levels reported by Gray[5,6] for tetragonal oxo-complexes of $d^1$ metal ions. The weak, lowest-energy absorptions observed at *ca.* 12,600 $cm^{-1}$ for the $[MoO(NCS)_5]^{2-}$ ion, an dat 13,600 and 17,500 $cm^{-1}$ for the $[WO(NCS)_5]^{2-}$ ion, are assigned to the $^2B_2 \rightarrow {}^2E(I)$ transition from the $b_2^*$ metal orbital to the antibonding $e_\pi^*$ $(d_{xz}, d_{yz})$ orbital. The energy of this transition determines the tetragonal splitting parameter δ.[5] The absorptions observed at 18,400 $cm^{-1}$ and 21,800 $cm^{-1}$ for the $[MoO(NCS)_5]^{2-}$ and $[WO(NCS)_5]^{2-}$ ions, respectively, are assigned to the $^2B_2 \rightarrow {}^2B_1$ transitions from the $b_2^*$ $(d_{xy})$ metal orbital to the antibonding $b_1^*$ $(d_{x^2-y^2})$ orbital. The energy of this transition determines the 10 Dq parameter. It is interesting to point out that the 10 Dq values of the $[MoO(NCS)_5]^{2-}$ and $[WO(NCS)_5]^{2-}$ complex ions are appreciably lower than those of the corresponding oxopentachloro- and oxopentabromo-complexes (10 Dq in $cm^{-1}$: $[MoOCl_5]^{2-}$, 21,600; $[MoOBr_5]^{2-}$, 21,700; $[WOCl_5]^{2-}$, 25,400; $[WOBr_5]^{2-}$ 26,000), thus indicating the presence of rather weak M-N bonds in the equatorial plane of the oxoisothiocyanatocomplexes.

A splitting of the absorption band corresponding to the $^2B_2 \rightarrow {}^2E(I)$ transition has been observed by Brisden et al.[18] and Rudolf[19] in the reflectance and solution spectra of oxohalomolybdates(V) and -tungstates(V), whereas no splitting is detectable in the spectra of corresponding complexes of chromium (V), $[CrOX_5]^{2-}$. The isothiocyanato-complexes studied in this work show a similar trend, the splitting of the $^2B_2 \rightarrow {}^2E(I)$ transition being considerably greater for the oxoisothiocyanatotungstates(V) (1,300-3,000 $cm^{-1}$, depending on the ligand) than for the oxoisothiocyanatomolybdates(V) (0-1,200 $cm^{-1}$). It may therefore be assumed that the observed splitting of this band arises from spin-orbital interaction which would lift the degeneracy of the orbital doublet $^2E$ (Figure 1).

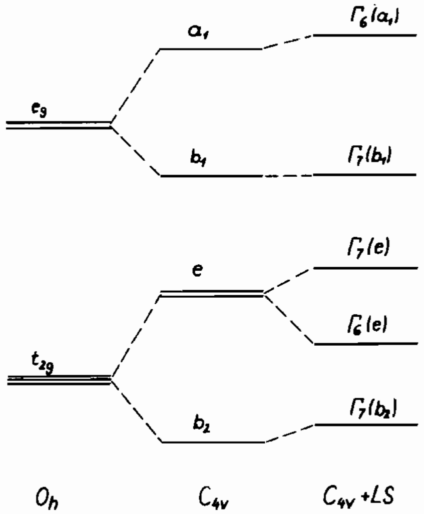

Figure 1. Energy levels scheme of the $^2D$ term in tetragonal fields including spin-orbit interaction.

The approximate solutions of the appropriate secular equations[20] result in the following energy levels:

$$E'(\Gamma_6) = -4Dq - Ds + 4Dt - \frac{\xi}{2} - \frac{3}{2}\,\frac{\xi^2}{10Dq + Ds - 10Dt + \frac{\xi}{2}} \qquad (e)$$

$$E''(\Gamma_6) = 6Dq - 2Ds - 6Dt + \frac{3}{2}\,\frac{\xi^2}{10Dq + Ds - 10Dt + \frac{\xi}{2}} \qquad (a_1)$$

$$E'(\Gamma_7) = -4Dq + \frac{1}{2}Ds + \frac{3}{2}Dt + \frac{\xi}{4} - \frac{1}{2}\sqrt{\frac{9}{4}\xi^2 + \xi\delta + \delta^2} \qquad (b_2)$$

$$E''(\Gamma_7) = -4Dq + \frac{1}{2}Ds + \frac{3}{2}Dt + \frac{\xi}{4} + \frac{1}{2}\sqrt{\frac{9}{4}\xi^2 + \xi\delta + \delta^2} \qquad (e)$$

$$E'''(\Gamma_7) = 6Dq + 2Ds - Dt \qquad (b_1)$$

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Finally:

$$\Delta E(^2E) = E''(\Gamma_7) - E''(\Gamma_6) \cong -\frac{\delta}{2} + \frac{3}{4}\xi + \frac{1}{2}\sqrt{\frac{9}{4}\xi^2 + \xi\delta + \delta^2}$$

where

$$\delta = -3Ds + 5Dt$$

Thus the magnitude of the splitting of the $^2B_2 \rightarrow {}^2E(I)$ band depends directly on the tetragonal splitting parameter $\delta$ and on the spin-orbit coupling constant, which for oxoisothiocyanatotungstates(V) is about 1,000 cm$^{-1}$, as discussed below.

In the spectra of oxoisothiocyanatomolybdate(V) complexes, a weak shoulder was observed on the low frequency side of the strong C-T band at 21,500 cm$^{-1}$. This shoulder, which is assigned to the $^2B_2 \rightarrow {}^2A_1$ transition, has not been previously observed in the spectra of other oxomolybdate (V) complexes. The remaining absorptions in the electronic spectra of oxopentaisothiocyanatomolybdate(V) and -tungstate(V) complexes are assigned to C-T transitions of the ligand→metal type. Gray[5] has interpreted the spectrum of the $[MoOCl_5]^{2-}$ ion on the assumption, that all the observed C-T bands arise from oxygen-to-metal transitions. In the reported calculations the $p_\pi$ orbital system of the equatorial ligands was neglected and a simplified MO scheme was obtained. Recently, Drake et al.[21] have shown, that for the $[VOCl_5]^{3-}$ ion the weakly bonding and non-bonding $\pi$-orbitals of the chloroligands have higher energy than the $e_\pi^b$ orbital of the vanadyl oxygen. A similar situation is likely to be present in the oxomolybdates (V) and -tungstate (V), as is also indicated by the MO calculations reported by one of us[22] for the $[Mo_2O_4Cl_4(H_2O)_2]^{2-}$ ion. These considerations change the assignment of the C-T bands for the $[MoOCl_5]^{2-}$ ion given by Gray. If the model proposed by Gray were correct, the first C-T transition, $^2B_2 \rightarrow {}^2E(II)$, should be independent on the kind of ligands in the equatorial plane of the complex. Actually, however, this band shifts markedly toward lower energies in the order $Cl^- > Br^- > NCS^-$, in good agreement with the trend expected from the optical electronegativities of these ligands:[23,24]

| | $[MoOCl_5]^{2-}$ | $[MoOBr_5]^{2-}$ | $[MoO(NCS)_5]^{2-}$ |
|---|---|---|---|
| First C-T Band (in cm$^{-1}$) | 25,000 | 24,500 | 21,500 |

| | $[WOCl_5]^{2-}$ | $[WOBr_5]^{2-}$ | $[WO(NCS)_5]^{2-}$ |
|---|---|---|---|
| First C-T Band (in cm$^{-1}$) | 33,200 | 28,800 | 25.000 |

It may be concluded, that the first C-T band really arises from a transition of the $\pi$-ligand(equat.)→metal type. For the oxohalo-complexes the first C-T bands are relatively weak, and so they are probably due to the orbitally forbidden $^2B_2 \rightarrow {}^2B_1$ transition from the $b_1$ or $a_2$ orbitals of the halo-ligands to the $b_2^*$ metal orbital. On the other hand, in the oxoisothiocyanates the first C-T band is very intense, and thus may reasonably be assumed to arise from the $^2B_2 \rightarrow {}^2E$ ($e_\pi^* \rightarrow b_2^*$) or $^2B_2 \rightarrow {}^2B_2$ ($b_2 \rightarrow b_2^*$) transitions which are orbitally allowed. For the remaining C-T bands a detailed assignment would of necessity be only speculative.

*Magnetic Properties.* The magnetic moments of the oxoisothiocyanatomolybdates(V) and -tungstates (V) are much higher than the values expected for $O_h$ symmetry, which should be *ca.* 0.9 BM for $Mo^V$ ($\lambda$ = 1,025 cm$^{-1}$) and *ca.* 0.5 BM for $W^V$ ($\lambda$ = 2,500 cm$^{-1}$) respectively. As shown by Gray et al.,[5] the replacement of one Cl ligand of $[MoCl_6]^-$ by a $\pi$-bonding oxo-ligand tends to remove the orbital degeneracy of $^2T_{2g}$ term. According to Figgis[25] it is possible to fit the temperature dependence curve of magnetic moments of systems with $^2T_{2g}$ ground terms in tetragonal fields to the values of the orbital reduction factor *K*, of the spin-orbit coupling constant, and of the $\mathbf{V} = \delta/\lambda$ parameter. For the $[MoO(NCS)_5]^{2-}$ and $[WO(NCS)_5]^{2-}$ complexes, since the experimental curves can be fitted to a wide range of values of these parameters, accurate values of the latter cannot be obtained. However, it is significant that the tetragonal splitting parameters determined in this way are one order of magnitude lower than the values determined from spectral data - as is the case for the oxohalomolybdate(V) and -tungstate(V) complexes.[18] The spin-orbit coupling constants for $[MoO(NCS)_5]^{2-}$ and $[WO(NCS)_5]^{2-}$, determined independently from ESR spectra, are 245 cm$^{-1}$ and 965 cm$^{-1}$ respectively. A slight admixing of higher energy terms into the ground term resulting from spin-orbit interaction seems to be responsible for the reduction of the magnetic moments in the case of the oxoisothiocyanatotungstate(V).

**Table III.** ESR Data for Oxoisothiocyanatomolybdates(V) and -Tungstates(V) [a]

| Compound | <g> | $A \times 10^4$(cm$^{-1}$) |
|---|---|---|
| $(PyrH)_2[MoO(NCS)_5]$ | 1.938 | 45 |
| ($\alpha$-picH)$_2[MoO(NCS)_5]$ | 1.938 | 44 |
| $(Et_4N)_2[MoO(NCS)_5]$ | 1.938 | 44 |
| $(QuinH)_2[MoO(NCS)_5]$ | 1.939 | 44 |
| $(OxineH)_2[MoO(NCS)_5]$ | 1.950 | 44 |
| ($\alpha$-picH)$_2[WO(NCS)_5]$ | 1.803 | |
| $(Met_4N)_2[WO(NCS)_5]$ | 1.803 | |

[a] ESR spectra were recorded in acetone-benzene (1:9) solution.

*Vibrational Spectra.* The vibrational spectra of the oxoisothiocyanatomolybdates(V) and -tungstates (V) confirm their monomeric structure and also afford additional information on the character of the metal-ligand bonds.

A single absorption band, arising from the stretching vibration of the $Mo{\equiv}O^{3+}$ group, is observed in the region 946-979 cm$^{-1}$. This frequency range agrees with that usually observed for mono-oxocomplexes of the transition metal ions, indicating the presence of two strong metal-oxygen $d_\pi$-$p_\pi$ bonds in addition to the metal-oxygen $\sigma$-bond.

In regard to the $NCS^-$ ligands, their characteristic absorption frequencies clearly indicate coordination through the N atom. The central band resulting from

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**Table IV.** Characteristic Frequencies[a] of Some Oxoisothiocyanatomolybdates(V) and -Tungstates(V).

| Compound | $\nu$Me-N | $\delta$NCS | $\nu$C-S | $\nu$Me-O$_t$ | $\nu$C$\equiv$N |
|---|---|---|---|---|---|
| (PyrH)$_2$[MoO(NCS)$_5$] | 306 s | 476 m | 870 w | 950 s, 970 sh | 2025 vs,b, 2090 vs |
| ($\alpha$-picH)$_2$[MoO(NCS)$_5$] | 317 s | 469 sh, 478 m | 877 w | 960 vs | 2025 vs, 2060 sh, 2080 vs |
| (Met$_3$NH)$_2$[MoO(NCS)$_5$] | 308 s | 473 m | | 980 s | 2000 vs |
| (Met$_4$N)$_2$[MoO(NCS)$_5$] | 321 s | 457 w, 488 m | 830 vw | 950 vs, 956 vs | 2030 vs,b, 2090 vs |
| (Et$_4$N)$_2$[MoO(NCS$_5$] | 312 s | 486 sh, 492 m | | 946 vs | 2020 vs, 2080 vs, 2090 sh |
| (QuinH)$_2$[MoO(NCS)$_5$] | 304 s | 470 w, 482 m, 490 m | | 970 vs | 2010 vs, 2085 vs |
| (OxineH)$_2$[MoO(NCS)$_5$] | 309 s | 403 vw, 487 m | | 979 vs | 2020 vs, 2070 vs |
| ($\alpha$-picH)$_2$[WO(NCS)$_5$] | 280 s | 460 w, 480 m | 890 w | 955 s | 2000 vs, 2095 vs |
| (Met$_4$N)$_2$[WO(NCS)$_5$] | 285 s | 460 w, 473 m, 490 s | 833 w | 945 s, 959 s | 2030 vs, 2095 vs |

[a] Frequencies are in cm$^{-1}$

the C$\equiv$N stretching mode occurs in the range 2000-2030 cm$^{-1}$, much lower than the value observed for the free NCS$^-$ ligand in KNCS. This frequency lowering is characteristic for the N-bonded NCS$^-$ ligand. Also, the C-S stretching vibration occurs at relatively high frequencies, 830-890 cm$^{-1}$ - a typical feature for isothiocyanates.[26-28] The N-coordination of the thiocyanate ligand is further confirmed by the NCS$^-$ deformation mode, which appears in the region 457-492 cm$^{-1}$, as reported for other isothiocyanates.[28-30] The small splittings of this band observed in the spectra of some of the complexes very likely arise from the tetragonal distortion of the ligand field and from the strong trans-effect of the oxo-ligand. Finally the intense absorption bands observed at about 311 cm$^{-1}$ and 283 cm$^{-1}$ for the [MoO(NCS)$_5$]$^{2-}$ and [WO(NCS)$_5$]$^{2-}$ ions, respectively, are assigned to the metal-nitrogen stretching vibrations. The values of these frequencies are relatively low compared with those of other isothiocyanates and support the conclusion drawn from the electronic spectra, that the metal-ligand equatorial bonds are relatively weak.

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