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ESR Spectra of Hexaaquamolybdenum(III) Ions in Cesium Indium Alum

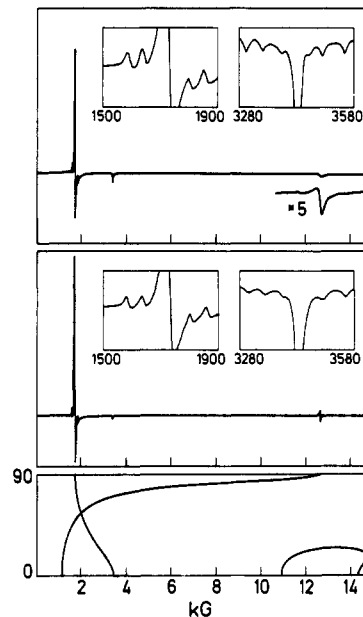Claus J. H. Jacobsen[1,2] and Erik Pedersen*,[2]

The isolation and characterization of transition-metal aqua ions is an area of considerable interest. Hexaaquachromium(III) ions are well characterized[3] and have been known for a long time, but it was not until 1986 that a convenient route to the congeneric hexaaquamolybdenum(III) ions was published[4] and still hexaaquatungsten(III) ions are unknown. When the coordination chemistry of chromium(III) and molybdenum(III) is compared, it is immediately conspicuous that only relatively few classical Werner-type molybdenum(III) complexes are known. Consistent with this, several reports concerning the ESR spectrum of hexaaquachromium(III) ions diluted in diamagnetic alums have appeared.[5] In 1977, the ESR spectrum of hexaaquamolybdenum(III) ions diluted in ammonium aluminum alum was reported.[6] Unfortunately, this report seems to be erroneous, and we decided, therefore, to undertake this study.

Experimental Section

Synthesis. All operations were carried out under dinitrogen using Schlenk equipment and standard vacuum techniques. The chemicals used were of analytical grade and were used without further purification.

Hexaaquamolybdenum(III) ions obtained directly from cesium molybdenum alum as well as from hydrolyzed sodium hexakis(formato)-molybdate(III) were diluted in cesium indium alum by the following procedure: 16.8 mg of sodium hexakis(formato)molybdate(III) or 24.2 mg of cesium molybdenum alum[4] (38.6 μmol) was added with stirring to a solution of 1.00 g (1.93 mmol) of In$_2$(SO$_4$)$_3$ in 10 mL of 1 M sulfuric acid. Immediately thereupon 0.70 g (1.93 mmol) of Cs$_2$SO$_4$ was added, and within a few seconds the molybdenum(III)-doped cesium indium alum precipitated. This was washed twice with 10 mL of 96% ethanol and dried in vacuum. Molybdenum-doped ammonium aluminum alum was prepared by an analogous procedure. The molybdenum content was not analyzed but assumed to be approximately 1%.

ESR Spectra. X-band spectra of powdered samples at 6 and 70 K were recorded with a Bruker ESP 300 spectrometer equipped with an Oxford ESR-900 continuous-flow cryostat and operating at 9.37 GHz. All spectra were obtained by averaging 10 scans using a modulation

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Figure 1. Top: Powder ESR spectrum of 1% hexaaquamolybdenum(III) ions diluted in cesium indium alum measured at 6 K. Detailed spectra showing the hyperfine structure of both the *xy* transition at approximately 1740 G and the *z* transition at 3425 G are included. The signal appearing as a shoulder at 3463 G in the spectrum of the *z* transition is due to an unidentified impurity. Middle: Result of simulating the ESR spectra with the spin-Hamiltonian parameters given in Table I and line widths of 10 G. Bottom: Angular dependence of the line positions as a function of the angle between the molecular *z* axis and the magnetic field. For clarity the isotopes with nonzero nuclear spin have been excluded.

Table I

$g_\parallel$	$g_\perp$	$\lvert D\rvert$/cm^{-1}	$10^4\lvert A_\parallel\rvert$/cm^{-1}	$10^4\lvert A_\perp\rvert$/cm^{-1}
1.954	1.950	1.15	50.5	47.3

frequency of 100 kHz with an amplitude of 2.88 G. The magnetic field range was 50–15 050 G.

Results and Discussion

The ESR spectrum of hexaaquamolybdenum(III) ions diluted in cesium indium alum measured at 6 K is shown in Figure 1 together with the computer-simulated spectrum and a diagram showing the angular dependence of the line positions. We chose the cesium indium alum as a diamagnetic matrix since this is known to be a β-alum[7] just as the cesium molybdenum alum.[8] Furthermore, the ionic radii of the hexaaqua complexes of indium(III) and molybdenum(III) are expected to be similar. In an alum the site symmetry of the hexaaquamolybdenum(III) ions is S_6, i.e. a trigonally distorted environment. In accordance with this the spectrum can be interpreted in terms of the conventional spin Hamiltonian for a d^3 ion in axial symmetry, i.e. a quartet ground state:

$$\hat{H} = \mu_B \mathbf{H} \cdot \mathbf{g} \cdot \hat{\mathbf{S}} + \hat{\mathbf{S}} \cdot \mathbf{A} \cdot \hat{\mathbf{I}} + D(\hat{S}_z^2 - \tfrac{1}{3}S(S+1)) =$$
$$\mu_B(g_\parallel H_z \hat{S}_z + g_\perp(H_x \hat{S}_x + H_y \hat{S}_y)) + A_\parallel \hat{S}_z \hat{I}_z + A_\perp(\hat{S}_x \hat{I}_x +$$
$$\hat{S}_y \hat{I}_y) + D(\hat{S}_z^2 - \tfrac{1}{3}S(S+1)) \quad (1)$$

Naturally occurring molybdenum consists of several isotopes of which ^{95}Mo (15.72%) and ^{97}Mo (9.46%) are the only ones having a nonzero nuclear spin ($I_{Mo} = {}^5/_2$). These two nuclides have slightly different magnetic moments, but the difference is too small to be observed in our ESR data. This means that an ESR spectrum of monomeric molybdenum(III) in ideal cases will consist of one or more groups of lines, each group having one relatively strong center line and six hyperfine lines, the intensities

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being dictated by the isotope distribution.

A first estimate of the spin-Hamiltonian parameters was obtained by considering only the line positions of the signals stemming from molybdenum(III) without nuclear spin. The hyperfine coupling constants were estimated from the distances between the hyperfine lines. These parameters were used to simulate the spectrum and then slightly adjusted until agreement between the measured and the simulated spectrum was obtained. It was not possible to obtain the sign of the zero-field splitting by a comparison of the intensities of the lines in the spectra measured at 6 and 70 K because of line broadning at the higher temperature.

Altogether we obtained the spin-Hamiltonian parameters listed in Table I.

In 1977, single-crystal ESR spectra of Mo^{3+} in ammonium aluminum alum were reported. The procedure was the following: The so-called Mo(III) ions were diluted into the alum by slowly evaporating a saturated solution of the alum dissolved in moderately concentrated hydrochloric acid to which $(NH_4)_2MoOCl_5$ was added. With the present knowledge of molybdenum chemistry it seems doubtful that this procedure should yield any trace of molybdenum(III). This is first of all based on the fact that no reduction of $MoOCl_5^{2-}$ is to be expected upon dissolution in hydrochloric acid. At the same time it is worth remembering that the hexaaquamolybdenum(III) ion is very sensitive to oxidation by the atmospheric dioxygen.[4] Furthermore, if we look at the published spectra, the mean g value of 1.985, the D value of 0.506 cm^{-1}, and the absence of hyperfine structure lead us to believe that the ESR signal is due to a hexaaquachromium(III)[5] impurity, perhaps introduced with the alum.

We also measured the ESR spectrum of $Mo(H_2O)_6^{3+}$ diluted in ammonium aluminum alum, which is an α–alum.[9] At 80 K our spectrum contained only two lines at $g_\perp = 1.96$ and $g_\perp =$

3.78 in terms of a spin Hamiltonian for $S = \frac{1}{2}$. This observation clearly demonstrates that the spectrum obtained by Radhakrishna et al.[6] is not due to hexaaquamolybdenum(III).

Comparing the spin-Hamiltonian parameters of molybdenum(III) compounds with those of the analogous chromium(III) compounds, an increase in the zero-field splitting often by more than 1 order of magnitude and a decrease in the mean g value is observed. Our data are consistent with both of these effects, which are partly due to the larger spin–orbit coupling constant of Mo^{3+} ($\zeta_{Mo(III)} = 820$ cm^{-1} and $\zeta_{Cr(III)} = 273$ cm^{-1} for the free ions).

Concluding Remarks

Only very few ESR spectra of molybdenum(III) complexes have been reported,[10] and most of these are not very rich in details. This is due to the often rather large zero-field splittings and the fact that the hyperfine structure is only seldomly resolved. To our knowledge, the ESR spectrum of hexaaquamolybdenum(III) ions diluted in cesium indium alum is the first example of a classical molybdenum(III) complex that contains enough features to allow determination of all the parameters in the spin-Hamiltonian (1).

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