## ESR spectra and electronic structure of the MoO<sup>3+</sup> complex with the dithiocarbamate ligand

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ESR spectra of liquid and frozen benzene solutions of isotope-enriched  $^{95,97,98}Mo^{VO}(dtc)_3$  complexes ([\*Mo] > 95%, dtc is the *N*,*N*-diethyl dithiocarbamate ligand) and their solid solutions in a matrix of tetraethylthiuram disulfide were studied in the X-range. Comparison of the experimental and calculated parameters of the ESR spectra shows that the axial symmetry of the magnetic tensors does not contradict the low symmetry of the complex, in which the "ylic" oxygen and five of six S atoms in three dithiocarbamate ligands form the coordination sphere of the metal.

Key words: molybdenum,  $MoO^{3+}$ , dithiocarbamate ligand, tetraethylthiuram disulfide, complex, ESR spectra, electronic structure.

S,S-Chelating ligands of the dithiocarbamate type can selectively interact with transition metals to form strong bonds with them. This provides wide use of dithiocarbamates in flotation and extraction, application of the corresponding complexes as the starting substances in the preparation of materials for electronics, and for studying the specific features of the electronic and geometric structure of compounds with a high degree of covalence of metal-ligand bonds.

The dithiocarbamate complexes of Mo<sup>V</sup>O have a relatively simple electronic structure with d<sup>1</sup>-configuration, which facilitates the interpretation of their ESR spectra.<sup>1-3</sup> ESR spectra of the MoO<sup>3+</sup> complexes with S,S-coordinating ligands are studied rather well (see, *e.g.*, Refs. 1, 3, and 4). However, according to the published data, tris(dithiocarbamates) have an almost isotropic g factor ( $g_{\parallel} \approx g_{\perp}$ ), which is unusual for the potentially low symmetry of these complexes. It is difficult to interpret the hyperfine structure (HFS) of complexes based on a natural mixture of molybdenum isotopes because of the low content of the two odd isotopes with nuclear spin. The present work is devoted to studying ESR spectra of isotope-enriched Mo<sup>V</sup>O(dtc)<sub>3</sub> complexes, where dtc is the *N*,*N*-diethyl dithiocarbamate ligand.

## Experimental

ESR spectra of liquid and frozen benzene solutions and solid solutions of  $MoO(dtc)_3$  in a matrix of tetraethylthiuram disulfide were recorded on a 70-02 XD/1 X-range radiospec-

trometer (Advanced Analytical Instruments, Minsk, Belarus'). The frequency was measured on a Ch3-46 microwave frequency meter, and g factors were determined relative to the signal of diphenylpicrylhydrazyl (DPPH).

Tetraethylthiuram disulfide was prepared by the oxidation of sodium diethyl dithiocarbamate with iodine in an aqueous solution followed by extraction with chloroform. To remove an iodine excess, the extract was washed with an aqueous solution of sodium thiosulfate, and tetraethylthiuram disulfide was crystallized from a CHCl<sub>3</sub> solution by slow evaporation of the solvent.

Isotope-enriched molybdenyl tris(N,N-diethyl dithiocarbamates),  $^{95,97,98}Mo^VO(dtc)_3$ , were prepared by the oxidation of metallic isotope-enriched molybdenum ([\*Mo] > 95%) with tetraethylthiuram disulfide in the presence of oxygen of the air.<sup>1-3</sup> The physicochemical constants of the complexes coincide with those available in the literature.

## **Results and Discussion**

All anisotropic spectra studied are similar (except for the shape of HFS, due to the monoisotopic composition) and only slightly differ in parameters. One of these spectra is presented in Fig. 1. Its shape is typical of  $MoO^{3+}$  complexes with d<sup>1</sup>-configuration and sulfide environment; therefore, identification of the composition of this complex with monobasic ligands by ESR spectra is rather reliable.

As follows from Fig. 1, a possible orthorhombic distortion of the complex does not appear, at least within the accuracy of the linewidth (-5 Oe), and the

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Fig. 1. ESR spectrum of a solid solution of  ${}^{97}Mo^{V}O(dtc)_3$  in a matrix of tetraethylthiuram disulfide at 295 K. The position of the signal of DPPH is shown by arrow (g = 2.0036), and the component due to an admixture of even isotopes is marked by an asterisk.

spectra are well described by the spin Hamiltonian (SH) for tetragonal symmetry<sup>3</sup>:

$$H = g_{\parallel}\beta S_{z}H_{z} + g_{\perp}\beta(S_{x}H_{x} + S_{y}H_{y}) + A_{\parallel}S_{z}I_{z} + A_{\perp}(S_{x}I_{x} + S_{y}I_{y}), \qquad (1)$$

where  $\beta$  is the Bohr magneton<sup>3</sup>;  $A_{\parallel}$  and  $A_{\perp}$  are the HFS constants from odd molybdenum isotopes, if any; and  $H_i$ ,  $S_i$ , and  $I_i$  are the projections of the external magnetic field, the operator of an electron spin, and the operator of a nuclear spin on the coordinate axis i = x, y, z, respectively. For liquid solutions, according to the published data,<sup>3</sup> SH (1) is simplified:

$$H = g_{s}\beta S_{z}H_{z} + a_{s}S_{z}I_{z}, \qquad (2)$$
  

$$g_{s} = (g_{\parallel} + 2g_{\perp})/3, \qquad (3)$$
  

$$a_{s} = (A_{\parallel} + 2A_{\perp})/3.$$

The ESR parameters obtained from the experimental spectra are presented in Table 1, from which it can be seen that, despite the almost isotropic g factor (which can have a random character), the strong anisotropy of the hyperfine coupling (HFC) constants unambiguously indicates a low symmetry of the complex.

The possible structures of the "ylic" tris(dithiocarbamate) complex are presented in Fig. 2. Structure **a** corresponds to a tetragonal pyramid; however, since the known complexes of  $MoO^{3+}$  with this structure have



Fig. 2. Models of the structures of the molybdenyl complexes with S-coordinating ligands that form a square (a), a pseudo-octahedron (b), a trigonal prism (c), and a distorted tetragonal pyramid (d). The direction of displacement of the Mo atoms from the center of sulfide polyhedra toward the "ylic" O atoms is shown by arrows.

 $g_{\parallel} > 2.000$ ,<sup>1</sup> it can be ruled out from consideration. Structure **b** is similar to the "ylic" complexes of a related metal (niobium), whose structure can often be presented as the result of incorporation of "ylic" oxygen into the initial regular octahedron<sup>5</sup> (in our case, the pseudo-octahedron of six S atoms of three chelating ligands). If the "ylic" oxygen is incorporated into a trigonal prism, the characteristic motif of the structure of molybdenum tris(dithiocarbamates),<sup>6</sup> we obtain structure **c**. Structure **d** is a strongly distorted octahedral complex.

Despite the superficial difference, structures **b** and **c** correspond to the close, trigonal symmetry of the complexes ( $C_3$  or higher). For this symmetry, the ground state of the complex with the d<sup>1</sup>-configuration is an orbital-degenerate doublet<sup>7</sup>

$$\begin{aligned} \psi_1 &= \alpha \langle x \rangle - \beta \langle y \rangle, \\ \psi_2 &= \alpha \langle x^2 - y^2 \rangle + \beta \langle x \rangle, \end{aligned} \tag{3}$$

the distortion of the octahedral crystalline field by the "ylic" oxygen (structure **b**) results in a decrease in  $\alpha$  to lower than  $1/\sqrt{3}$  (octahedron), and for a distorted trigo-

**Table 1.** Parameters of ESR spectra of  $^{95,97,98}$ Mo<sup>V</sup>O(dtc)<sub>3</sub> complexes in benzene solutions, in a matrix of tetraethylthiuram disulfide at 295 K, and in low-temperature (77 K) benzene glasses

Complex	Matrix*	gs (±0.003)	a <sub>s</sub> /Oe (±3)	<del>لا</del> ب (±0.003)	Aµ/Oe (±3)	<i>g</i> ⊥ (±0.003)	A⊥/Oe (±3)
<sup>97</sup> MoO(dtc) <sub>3</sub>	Benzene Tetraethylthiuram disulfide	1.980 1.980*	38.1 39.5*	1.979 1.977	62.4 61.3	1.982 1.981	27.6 28.7
<sup>95</sup> MoO(dtc) <sub>3</sub>	The same	1.980	38.7*	1.978	<b>60</b> .0	1.981	28.1
98MoO(dtc)3	The same	1.979*		1.977		1.980	

\* The values were obtained from the anisotropic parameters by Eqs. (2).

nal prism (structure c),  $\alpha$  is always equal to 0. Calculation by the SH method<sup>3</sup> shows that the following g factors correspond to this ground state:  $g_{\parallel} = 2 - 6\alpha^2$ ,  $g_{\perp} = 0$ , which strongly differ from the experimental values. Therefore, structures **b** and **c** should be excluded from consideration even if possible distortions are taken into account.

Thus, structure d corresponding to a distorted octahedron remains for consideration. Since the degree and character of distortion can be almost arbitrary, it is impossible to cover all variants by simulation; one should use reference data. The related dithiophosphate imido complex of Mo<sup>V</sup> was chosen as the reference structure.<sup>8</sup> The electronic structure of this complex (taking into account the nearest environment only) was calculated by the extended Hückel method (EHM) with the Mulliken approximation of non-diagonal matrix elements,  $H_{ij} = 1.75S_{ij}(H_{ii} + H_{jj})$ , and atomic parameters taken from the literature.<sup>9</sup> For comparison, we also calculated the scheme of one-electron levels for the model tetragonal complex with structure a with the Mo-S and Mo-O bond lengths equal to 1.40 and 1.65 Å, respectively, and the distance from the Mo atom to the plane formed by four S atoms  $\Delta = 0.5 \text{ Å}.^{6}$ 

Since EHM is, at best, appropriate for semiquantitative estimations, we do not present numerical results, but restrict our consideration only by qualitative analysis.

As could be expected, the sequence of antibonding orbitals  $|xy\rangle$ ,  $|xz,yz\rangle$ ,  $|z^2\rangle$ ,  $|x^2 - y^2\rangle$  corresponds to the tetragonal model complex with structure **a**. It is nontrivial that for the previously described<sup>8</sup> dithiophosphate imido complex, orbitals with almost the same composition were obtained due to pivoting of the initial system of coordinates (with the z axis along the short metal metal bond) by three Euler angles.<sup>10</sup> Therefore, in the rough ionic model for structures **a** and **c**, the parameters of the ESR spectra are described by the same equations<sup>3</sup>:

$$g_{\parallel} = g_{e} - 3\alpha_{1};$$

$$g_{\perp} = g_{e} - 2\alpha_{2};$$

$$A_{\parallel} = |P(-\kappa - 4/7 - 8\alpha_{1} - 3/7 \cdot 2\alpha_{2})|;$$

$$A_{\perp} = |P(-\kappa + 2/7 - 11/14 \cdot 2\alpha_{2})|,$$
(4)

where  $\alpha_1 = \xi/\Delta E(xy - x^2 - y^2)$ ;  $\alpha_2 = \xi/\Delta E(xy - xz,yz)$ ;  $\xi$  is the parameter of spin-orbital interaction, which is reduced by delocalization effects to a factor of -0.5 as compared with the "purely ionic" value of 900 cm<sup>-1</sup> <sup>3</sup>;  $\kappa = 0.751$  is the parameter of contact interaction; and  $P = -50.3 \cdot 10^{-4}$  cm<sup>-1</sup> is the dipole HFC constant for a free ion,<sup>3</sup> which is also reduced in the complex. The orthorhombic distortion should result in splitting of the doublet  $|xz,yz\rangle$  and modification of Eqs. (4) corresponding to the appearance of two nonequivalent directions in the "perpendicular" region. In the low-symmetry dithiophosphate imido complex<sup>8</sup> that models Mo<sup>V</sup>O(dtc)<sub>3</sub>, the  $|xz\rangle$  and  $|yz\rangle$  orbitals are not degenerate, but  $|\Delta E(xz - yz)/\Delta E(xy - xz,yz)| <$ 0.1. Even for the g tensor, this corresponds to experimentally undetectable orthorhombic anisotropy. The  $g_{\parallel} \approx g_{\perp}$  ratio in the ESR spectrum of Mo<sup>V</sup>O(dtc)<sub>3</sub>, according to the published data,<sup>5</sup> corresponds to  $\alpha_1/\alpha_2 \approx$ 1/4. This condition can really be fulfilled from the results of EHM calculations and does not contradict the qualitative analysis of the scheme of levels in the model of point charges or in the model of angular overlapping,<sup>11</sup> especially when a higher degree of localization of the  $|x^2 - y^2\rangle$  orbitals (than that of  $|xz,yz\rangle$ ) is taken into account.

Let us consider the reasons for the difference of the Mo<sup>V</sup>O(dtc)<sub>3</sub> complex from the tetragonal systems with  $g_{\parallel} > 2.000$ . The possibility of g > 2.000 for d<sup>n</sup>-complexes with n < 5 is explained (see, e.g., Ref. 1) by the effect of bonding orbitals, which make a contribution of the  $\alpha_1$  type, but with the opposite sign, to  $g_{\parallel}$ . In the tetragonal complexes (structure a), the Mo-S bond lengths are close to the sum of covalent radii,<sup>6</sup> so that  $\Delta E(xy - x^2 - y^2)$  is high,  $\alpha_1$  is low, and the contribution of bonding orbitals to  $g_{\parallel}$  predominates. In systems of the  $Mo^{V}O(dtc)_3$  type and in the previously described dithiophosphate imido complex,<sup>8</sup> due to steric hindrances, the Mo-S distances are ~0.1 Å higher,  $\Delta E(xy - x^2 - y^2)$  is lower, and the contributions of bonding and antibonding orbitals are opposite. Of course, this consideration is valid if, in both cases, the values of splitting between the orbital of a lone electron and the bonding orbitals are close. The results of calculations confirm this assumption.

Since for Mo<sup>V</sup>O(dtc)<sub>3</sub>  $\Delta g \ll 1$ , it should be expected that  $A_{\perp}/A_{\parallel} \approx |(-\kappa + 2/7)/(-\kappa - 4/7)| \approx 0.35$ . Taking into account that this estimate is approximate, we may believe that the value obtained agrees well with the experimental value of -0.43. The parameters of the ESR spectrum of MoO(dtc)<sub>3</sub> will be analyzed in more detail after the complete X-ray diffraction study of this complex.

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