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Abstract

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MAGNETIC SUSCEPTIBILITY AND STEREOCHEMISTRY OF COMPLEX COMPOUNDS OF Mo(III) WITH UREA, THIOUREA, AND THEIR DERIVATIVES

Trivalent molybdenum contains three unpaired electrons and therefore it was to be expected that its complex compounds [Mo(III)] should be paramagnetic, with an effective magnetic moment close to the "spin-only" value of 3.87 μ_B for three unpaired electrons. Indeed, complex compounds are known, for example $(NH_4)_3[MoCl_6]$, $K_3[MoCl_6]$, as well as phenanthroline complexes $[Mo(Phen)_3]Cl_3$, with "normal" magnetic moments (^{1}). Complex compounds of trivalent molybdenum with urea, thiourea, and their derivatives were synthesized. Depending on the conditions of synthesis, two types of compounds are obtained. The first comprises complexes of composition MoA_3Cl_3, where A is urea, thiourea, phenylthiourea, diphenylthiourea, as well as $[Mo(NH_2CONH_2)_6]Br_3 \cdot 2H_2O$ and $[Mo(NH_2CSNH_2)_4Br_2]Br$. The second group should include the compounds $[Mo_2(NH_2CSNH_2)_3Cl_6]$, $[Mo_2(NH_2NHCSNH_2)_3Cl_6]$, and $[Mo_2(C_6H_5NHCSNH_2)_3Cl_6]$.

A study of the magnetic susceptibility of these nine compounds confirmed this division, since the compounds of the first group proved to be paramagnetic, and their effective magnetic moments lie within the range 3.66–3.85 μ_B. The compounds of the second group are only weakly paramagnetic, which indicates the absence of unpaired electrons.

The magnetic susceptibility and effective magnetic moments are given in Table 1.

Table 1

Compound	$\chi_g \cdot 10^6$	$\chi_{mol} \cdot 10^6$	$\chi_{Mo(III)} \times 10^6$	T, °K	μ_{eff}, μ_B
$[Mo(NH_2CSNH_2)_3Cl_3]$	13,20	5640	5838	293	3,71
$[Mo(NH_2CSNHC_6H_5)_3Cl_3]$	7,99	5265	5660	295	3,66
$[Mo(C_6H_5NHCSNHC_6H_5)_3Cl_3]$	6,11	5420	5960	295	3,76
$[Mo(NH_2CONH_2)_3Cl_3]$	15,08	5760	5850	293	3,72
$[Mo(NH_2CONH_2)_6]Br_3 \cdot 2H_2O$	8,23	6020	6270	293	3,85

schematic structure of $[MoA_3Cl_3]$ with Mo at the center and ligands Cl and A

Figure 1: schematic structure of $[MoA_3Cl_3]$ with Mo at the center and ligands Cl and A

Compound	$\chi_g \cdot 10^6$	$\chi_{mol} \cdot 10^6$	$\chi_{Mo(III)} \times 10^6$	T, °K	μ_{eff}, μ_B
$[Mo(NH_2CONH_2)_4Br_2]$ Br	10,08	5805	6065	293	3,78
$[Mo_2(NH_2CSNH_2)_3Cl_6]$	−0,268	−169	150	293	0,59
$[Mo_2(NH_2CSNHCH_3)_3Cl_6]$	−0,292	−177	154	295	0,60
$[Mo_2(C_6H_5NHCSNH_2)_3Cl_6]$	−0,401	−345	140	293	0,57

The effective magnetic moments presented in Table 1 were calculated on the assumption that the susceptibility of all the complex compounds studied obeys the Curie law.

It is known, however, that for complexes of composition $[MoA_3Cl_3]$ the Curie-Weiss law is better obeyed, although the Weiss constants θ do not exceed several degrees. Therefore it does not appear possible to discuss, in rigorous form, the deviations of the μ_{eff} values found by us from the theoretical value. But there is no doubt that some spin-orbital interaction takes place here.

The spin-orbit interaction constant for Mo(III) is $\lambda = +267$ cm^{-1}; hence a certain decrease in μ_{eff} in comparison with the "spin-only" value becomes understandable, since the theoretical effective moment, taking spin-orbit interaction into account, calculated from the equation $\mu_{eff} = \mu_{t.sp}(1 - 2\lambda/\Delta)$, where $\Delta = 20\,000$ cm^{-1}, is equal to $3.84\,\mu_B$.

Thus, μ_{eff} of hexaureamolybdenum bromide almost coincides with the theoretical magnetic moment. For the other complexes the deviations can apparently be explained by the fact that they obey the Curie–Weiss law, and not Curie' s law.

On the basis of the study of magnetic susceptibility, for compounds of the type $[MoA_3Cl_3]$ one should assume an octahedral structure with d^2sp^3 hybridization:

The specific magnetic susceptibility of the compounds of the second group is negative. Only by introducing corrections for intrinsic diamagnetism does a small paramagnetism appear. A characteristic feature of these complex compounds is their bridging character, owing to which they have a dimeric structure $[Mo_2A_3Cl_6]$. The presence of two paramagnetic ions (in the free state) in the molecule of the complex is also the cause of such small paramagnetism. It is known that diamagnetic W(III) compounds of the compositions $Me_3[W_2Cl_9]$ (^{2}) and $[W_2A_3Cl_6]$ (^{3}) have an octahedral structure with three common chlorine ions, which corresponds to one common trigonal face. Schematically this looks as follows:

schematic structure of two face-sharing octahedra labeled W

Figure 2: schematic structure of two face-sharing octahedra labeled W

two possible schematic binuclear structures for [$Mo_2A_3Cl_6$], joined by "or," with labels Cl, A, and Mo

Figure 3: two possible schematic binuclear structures for [$Mo_2A_3Cl_6$], joined by "or," with labels Cl, A, and Mo

The presence of a common face in two octahedra causes a decrease in the distance between tungsten ions to 2.46 Å. Such a small distance between W atoms allowed Pauling (^{4}) to suggest that the bond between them is multiple, with the bond order apparently approaching two.

Since complex compounds of the type [$Mo_2A_3Cl_6$] are diamagnetic, it may be assumed that they are also binuclear and have a structure analogous to that of the tungsten compounds:

The diamagnetism of these binuclear compounds of trivalent molybdenum can be explained as follows. Since we have assumed that the complexes have an octahedral structure with a common trigonal face, the stereochemistry of the σ-bonds must correspond to d^2sp^3-hybridization. Nine ligands ($3A$ and $6Cl^-$) form twelve σ-bonds with two molybdenum ions. Two d-orbitals of the molybdenum ion participate in the formation of σ-bonds (dx^2-y^2 and dz^2). According to Hund' s rule, three unpaired electrons must occupy the three remaining d_ε-orbitals (d_{xy}, d_{yz}, and d_{xz}). Because of the very small Mo—Mo distance, partial overlap of their d-orbitals is possible.

According to Orgel (^{5}), as a result of such interaction of the d-orbitals (d_{xy}—d_{xy}, d_{yz}—d_{yz}, d_{xz}—d_{xz}), two π-bonds and one δ-bond may be formed. Although these bonds are considerably weaker than σ-bonds, the indicated interaction leads to complete pairing, which is the reason for such small paramagnetism.

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