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Ligand Hyperfine Interactions in Oxomolybdenum(V) and Oxochromium(V) Halide Complexes

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Ligand superhyperfine interactions have been observed in esr spectra of solutions, frozen glasses, and diamagnetically diluted single crystals of $MoOBr_5^{2-}$, $MoOI_5^{2-}$, and $CrOCl_5^{2-}$. The results indicate considerable covalency in metal–ligand bonding. In the molybdenum and chromium complexes the superhyperfine tensors indicate π bonding involving the metal d_{xy} orbital and p orbitals of the four equatorial ligands. In these d^1 complexes the ligand orbital involved in bonding possesses some s character.

Ligand superhyperfine interaction has been observed for fluoro-,[1-4] chloro-,[1,5] and bromooxomolybdate(V)[6,7] complexes. The presence of isotropic fluorine hyperfine splittings in a solution of CrO_3 dissolved in HF has been reported by Garifyanov[8] but the spectra were not analyzed in detail. Verbeek and Cornaz[9] have analyzed the spectrum of $CrOF_5^{2-}$ in 38% HF in the glassy state, by computer simulation, but values for ligand hyperfine splitting tensors were given by Manoharan and Rogers,[1] who also made single-crystal esr measurements.[1] A detailed single-crystal esr investigation of $MoOCl_5^{2-}$ has been made and the theory was given.[10] Similarly a careful esr study of $CrOCl_5^{2-}$ has been carried out by Kon and Sharpless.[11]

We have attempted to perform a complete analysis of ligand superhyperfine interactions in oxomolybdate(V) and oxochromate(V) halide complexes by studying the esr spectra under a wide range of conditions. An examination of single-crystal spectra is the most accurate method of obtaining all of the elements of the ligand superhyperfine tensors, and particular attention was paid to such studies.

Experimental Section

Preparation of Complexes.—Complexes of Mo(V) of the type M_2MoOX_5, where $M^+ = K^+$, NH_4^+ and $X^- = Br^-$, I^-, were prepared by the method of Allen, *et al.*[12] K_2CrOCl_5 was also made according to Weinland and Friederer.[13]

Growth of Single Crystals.—$(NH_4)_2MoOBr_5$ in $(NH_4)_2InBr_5 \cdot H_2O$ was prepared by the method of Wentworth and Piper.[14] Single crystals of $(NH_4)_2CrOCl_5$ in $(NH_4)_2InCl_5 \cdot H_2O$ were prepared in the manner used for the oxomolybdate(V)–chloro complex.

Instruments.—Spectra were taken at 9.2, 9.5, 35.0, and 35.5 GHz by using Varian X-band and Q-band esr spectrometers. Spectra were recorded at temperatures of 4.2, 77, and 300°K. Temperatures intermediate between 77 and 300°K were investigated by employing a Varian variable-temperature control apparatus with liquid nitrogen as coolant.

Particular care was taken to avoid saturation of the hyperfine and superhyperfine resonances at low temperature. Modulational amplitudes were kept to a minimum.

Diphenylpicrylhydrazyl (DPPH), pitch in potassium chloride, and peroxylaminedisulfonate were used as reference standards to facilitate the calculation of g values.[15]

Analysis of the Spectra.—A computer program was written to synthesize the spectra of crystals of rhombic symmetry. This program is similar to the spectrum generation program developed by Venable.[16]

The esr spectra of magnetically dilute powders, prepared from powdering single crystals, were simulated by summing spectra corresponding to particular orientations over all angles. Angular increments of approximately 1° were taken. We were not successful in simulating ligand hyperfine splittings, but since spin densities, calculated from metal and ligand hyperfine spectra agree well, we have confidence in the ligand hyperfine constants.

Results

$MoOBr_5^{2-}$.—We were unable to observe bromine superhyperfine interaction in solutions of the $MoOBr_5^{2-}$ complex; however, we were able to observe bromine superhyperfine structure for $MoOBr_5^{2-}$ in frozen acid glasses. The spectra did not appear to be particularly sensitive to the concentration of $MoOBr_5^{2-}$ or the acidity of the solution used to prepare the glass. A typical spectrum showed no detectable superhyperfine interaction of the molybdenum parallel hyperfine components on the $g_{\parallel}$ absorption; however, the $g_{\perp}$ absorption displayed a bromine superhyperfine structure consisting of 13 nearly equally spaced lines (see Figure 1). Dowsing and Gibson[7] suggested that the paramagnetic electron interacts with four equivalent bromines. However, in agreement with the interpretation of Manoharan and Rogers[1] for $MoOCl_5^{2-}$ and $MoOF_5^{2-}$, we believe the hyperfine interaction arises from two sets of two equivalent bromines. The

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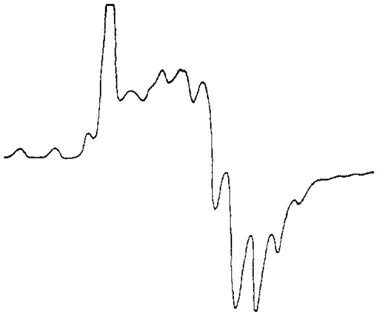

Figure 1.—Spectrum of $MoOBr_5^{2-}$ in frozen acid glass.

13 lines arise from the near degeneracy of the molybdenum perpendicular hyperfine components and the bromine superhyperfine components. The values of the magnetic tensor elements measured from solution and frozen glass spectra are given in Tables I and II.

TABLE I

ESR SPECTRA AND DERIVED QUANTITIES FOR THE COMPLEXES[a] STUDIED (METAL NUCLEAR HYPERFINE CONSTANTS)

Complex	$\langle g\rangle$	$g_\parallel$	$g_\perp$	$\langle a\rangle$	$A_\parallel$	$A_\perp$
$(NH_4)_2[MoOBr_5]$ in $(NH_4)_2[InBr_5\cdot H_2O]$ (single crystal)	+1.993	+2.090	+1.945	+41.7	+66.0	+30.0
$(NH_4)_2[MoBr_5]$ in $(NH_4)_2[InBr_5\cdot H_2O]$ (powder)		+2.090	+1.945			
$MoOBr_5^{2-}$ in solution and frozen glasses	+1.994	+2.09	+1.944	+41.5	+66.0	+30.0
$MoOI_5^{2-}$ in solution	+2.508					
$CrOCl_5^{2-}$ solution	+1.9877			+18.2		
$CrOCl_5^{2-}$ (single crystal)		+2.008	+1.977		+36.1	+9.7
$CrOCl_5^{2-}$ (frozen glass)		+2.008	+1.977		+36.1	+9.7

[a] A values are given in $cm^{-1} \times 10^{-4}$.

$MoOI_5^{2-}$.—Although ligand superhyperfine interaction was observed for the $MoOI_5^{2-}$ complex in acid solution, the separation of the molybdenum hyperfine components was smaller than for other oxomolybdate(V) halide complexes and resulted in considerable overlap of the superhyperfine components, thus making quantitative measurements of either the molybdenum hyperfine interaction or iodine superhyperfine interaction impossible at present.

Crystal and Polycrystalline Spectra.—The Zeeman and metal hyperfine interaction tensors can be thought of as having their origin at the molybdenum nucleus. To calculate the theoretical expressions for the elements of the Zeeman and hyperfine interaction tensors from molecular orbital theory it is convenient to take the z axis along the M═O bond. The x and y axes are located in the plane formed by the four equatorial halide ligands. This coordinate system permits unambiguous specification of Zeeman and metal hyperfine tensor elements but not the ligand superhyperfine tensor elements.

To consider ligand superhyperfine interaction a coordinate system which has its origin at the ligand nucleus rather than the metal nucleus is considered. A local coordinate system is chosen on an equatorial halide[17] with the x axis along the Mo—X bond, z parallel to the symmetry axis of the complex (the M═O bond), and y chosen to form a right-handed coordinate system.

The electronic Zeeman and metal hyperfine tensors obey the relationships

$$g = (g_z^2 \cos^2 \theta + g_x^2 \sin^2 \theta \cos^2 \phi + g_y^2 \sin^2 \phi)^{1/2} \quad (1)$$

$$gA(\text{metal}) = (A_z^2 g_z^2 \cos^2 \theta + A_x^2 g_x^2 \sin_x^2 \theta \cos^2 \phi + A_y^2 g_y^2 \sin^2 \theta \sin^2 \phi)^{1/2} \quad (2)$$

The spherical polar angles θ and ϕ relate the external magnetic field vector $\vec{H}$ to the z and y axes, respectively. The orientation for which $\theta = 0$ gives rise to the spectrum corresponding to g_z and A_z while those for which $\theta = \pi/2$ and $\phi = 0$ give rise to the spectra corresponding to (g_x, A_x) and (g_y, A_y), Table I.

$MoOBr_5^-$.—For $(NH_4)_2MoOBr_5$ in $(NH_4)_2InBr_5\cdot H_2O$, as for the chloride complex,[1] ligand superhyperfine structure was not observed at room temperature and the best resolution of the bromine superhyperfine structure was obtained near 77°K. The spectra observed for single crystals of the bromide complex in $(NH_4)_2InBr_5\cdot H_2O$ (Figure 2) were very similar to those observed[1] for the chloride complex.

At $\theta = 0$ no bromine superhyperfine structure was observed which indicates $A_z(Br) \cong 0$ G. At $\theta = \pi/2$ and $\phi = 0$ the spectrum consisted of 7 equally spaced lines while at $\theta = \pi/2$ and $\phi = \pi/4$ the spectrum consisted of 13 equally spaced lines and, together with the intensity ratios and the observed splittings, indicates that $A_z(Br) \cong 0$ G, $A_y(Br) = 40 \pm 1$ G, and $A_x(Br) = 0$ G.

Pentachloro(oxo)chromate(V).—The esr spectrum of $K_2{}^{53}CrOCl_5$ in acetic acid has been studied by Kon and Sharpless.[11] In our experiments $CrOCl_5^{2-}$ was doped in single crystals of $(NH_4)_2InCl_5\cdot H_2O$. The crystals were grown in aqueous HCl. The esr parameters obtained from measurements at low temperatures on these single crystals and powders, obtained by crushing the crystals, are shown in Tables I and II. Superhyperfine interactions due to ^{35}Cl and ^{37}Cl were observed.

Discussion

Ligand Superhyperfine Interactions.—If we assume that electron–nuclear dipolar interaction accounts for the anisotropic parts of the ligand superhyperfine interaction tensors, the anisotropic part of the superhyperfine interaction tensor may be expressed as

$$A_p = {}^2/_5 g_\perp \beta_e g_n \beta_n \langle r^{-3}\rangle |\rho|$$

and the spin density in the halide orbitals may be calculated (Table III), where they are compared with the results of Manoharan and Rogers.[1]

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[17] We restrict ourselves at this time to considering only superhyperfine interaction involving the four equatorial ligands.

TABLE II

LIGAND SUPERHYPERFINE CONSTANTS

		A_x	A_y	A_z	A_s	A_{xx}	A_{yy}	A_{zz}	$A_{p\sigma}$	$A_{p\pi}$		
Complex	Ligand	Cm^{-1} × 10^{-4}									% f_σ	% f_π
$MoOBr_5^{2-}$	Eq Br	0	36	0	12	−12	24	−12	0	24	0	4.8
$CrOCl_5^{2-}$	Eq Cl	0	7.8	0	2.6	−2.6	5.2	−2.6	0	5.2	0	5.2
$MoOF_5^{2-}$ [a]	Eq F	−20.1	53.1	3.7	(11.1)	−32.33	40.83	−8.33	−15.59	32.88	1.64	3.4
$CrOF_5^{2-}$ [a]	Eq F	−22.97	36.76	3.65	(5.87)	−28.11	30.87	−2.74	−16.83	22.42	1.7	2.25
$MoOCl_5^{2-}$ [a]										6.0	0	6

[a] From ref 1. A_x, A_y, A_z, and A_s are ligand hyperfine isotropic and isotropic splittings. A_{xx}, A_{yy}, and A_{zz} are calculated by subtracting the isotropic part from the ligand hyperfine constants A_x, A_y, and A_z. $A_{p\sigma}$ and $A_{p\pi}$ have been calculated from corrected dipolar interactions of the unpaired electrons in the in-plane p_x and p_y orbitals of the halide ligands.[1]

Spin density in the ligand p_y orbital can most logically be thought of as arising from in-plane π bonding involving the molybdenum b_2 (primarily d_{xy}) and ligand b_2 (primarily p_y) orbitals. Since the paramagnetic electron would be thought to be localized primarily in the ground-state $b_2(d_{xy})$ orbital, it is reasonable that a fairly large paramagnetic density would be expected to reach the ligand $b_2(p_y)$ orbital.

The explanation of spin density in the ligand p_x orbital is not so straightforward. The ground-state b_2 orbital is of the wrong symmetry to overlap appreciably with the ligand p_x orbitals and configurational interaction involving an excited molybdenum $b_1(d_{x^2-y^2})$ orbital must be considered. σ bonding would be considerably less effective than in-plane π bonding involving the metal and ligand b_2 orbitals and it would be less effective for the chloride and bromide ligands than for the fluoride[1] ligands. There is not very much evidence for any significant amount of out-of-plane π bonding.

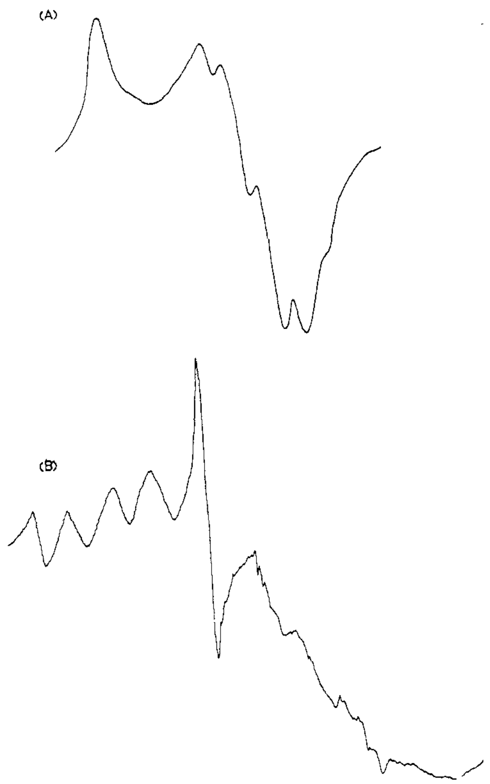

Figure 2.—Polycrystalline spectra of $(NH_4)_2MoOBr_5$ in $(NH_4)_2InBr_5 \cdot H_2O$.

TABLE III

SPIN DENSITIES IN HALIDE ORBITALS[a]

Complex	Ligand	% f_s	% f_π	% f_σ
$MoOF_5^{2-}$ [b]	Eq ^{19}F	0.9	4.2	1.3
$MoOCl_5^{2-}$ [b]	Eq ^{35}Cl, ^{37}Cl	0.1	5.9	0.0
$MoOBr_5^{2-}$	Eq ^{79}Br, ^{81}Br		4.8	
$CrOCl_5^{2-}$	Eq ^{35}Cl, ^{37}Cl	0.1	5.2	0.0
$CrOF_4^{-}$ [b]	Eq ^{19}F	0.5	1.0	0.5
$CrOF_5^{2-}$ [b]	Eq ^{19}F	0.5	1.0	0.5
	Ax ^{19}F	0.1		

[a] The values of f_π and f_σ were calculated by using the measured values of A_p and the values of $\langle r_{np}^{-3} \rangle$ tabulated by R. G. Barnes and W. V. Smith, *Phys. Rev.*, **93**, 95 (1954); A. J. Freeman and R. E. Watson, *ibid.*, **123**, 521 (1961); and R. Bersohn and R. G. Shulman, *J. Chem. Phys.*, **45**, 2298 (1966). The values of f_s were calculated by using the observed values of A_s and the atomic or ionic values of $\psi_{ns}(0)$ tabulated by G. W. Chantry, A. Horsfield, J. R. Morton, J. R. Rowlands, and D. H. Whiffen, *Mol. Phys.*, **5**, 233 (1962); E. Clementi, C. C. J. Roothaan, and M. Yoshimine, *Phys. Rev.*, **127**, 1618 (1962); R. J. Cook, J. R. Rowlands, and D. H. Whiffen, *Proc. Chem. Soc.*, 252, (1962); R. E. Watson and A. J. Freeman, *Phys. Rev.*, **123**, 521 (1961); R. Bersolm and R. G. Shulman, *J. Chem. Phys.*, **45**, 2298 (1966); G. L. Gardner, *ibid.*, **46**, 2991 (1967). [b] From ref 1.

The results appear to be consistent with this analysis. Metal–ligand overlap integrals of 0.01–0.20 could easily account for the observed distribution of electron density.

Measurement of the spectra of single crystals and of polycrystalline powders has greatly facilitated the interpretation of the frozen glass spectra of $MoOBr_5^{2-}$. Results are listed in Tables I–III, and the following quantities were calculated as in our previous work:[15] $-K = 41.0 \times 10^{-4}$ cm^{-1}, $-\chi = 5.24$ au, $\rho = 48.9 \times 10^{-4}$ cm^{-1}, $\beta^2 = 0.890$

As can be seen in the present results and those of Manoharan and Rogers,[1] the large changes in the values of the Zeeman and metal hyperfine interaction tensors with changes in halide ligand do not apparently arise from changes in metal–ligand bonding and probably arise from changes in the exchange polarization of the ground-state d_{xy} and inner s orbitals of molybdenum. The theory of exchange polarization applicable to molybdenum d^1 complexes has recently been extensively reviewed.[18]

We have also employed the molecular orbital treatment of Manoharan and Rogers[1] and calculated the bonding coefficients for $MoOBr_5^{2-}$ and $CrOCl_5^{2-}$ by use of the quantities given in Table IV and the coefficients

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TABLE IV
QUANTITIES USED IN CALCULATING BONDING COEFFICIENTS

Quantity	$MoOBr_5$[a]	$CrOCl_5$[a]
λ_M, cm^{-1}	820[b]	275[c]
λ_L, cm^{-1}	2460[d]	587[b]
$\Delta E(b_2 - b_1)$, cm^{-1}	21,800.0[d]	23,200.0[e]
$\Delta E(b_2 - e)$, cm^{-1}	14,290.0[d]	13,200.0[e]
S_{b_2}	0.12[b]	0.12
S_e	0.16	0.16
S_{b_1}	0.20	0.20
K	0.9[b]	0.6[e]
P, cm^{-1}	−0.0055[b]	−0.00397[f]

[a] Reference 2. [b] Reference 1. [c] T. M. Dunn, *Trans. Faraday Soc.*, **57,** 1441 (1961). [d] Reference 6. [e] Reference 11. [f] Reference 18.

are $\beta_2 = 0.932$, $\epsilon = 0.844$, and $\beta_1 = 0.596$ for $MoOBr_5^{2-}$ and 0.886, 0.958, and 0.952 for $CrOCl_5^{2-}$. Although no trend is noted in the coefficients for $\beta_2(d_{xy})$, regular decreases in ϵ and β_1 are recorded in passing from fluoride[1] to chloride[1] to bromide.

By use of Mulliken population analysis one can then calculate spin densities and we find 3.3% for equatorial halide in $MoOCl_5^{2-}$ and 5.3% for $CrOCl_5^{2-}$.

TABLE V
BONDING COEFFICIENTS

Coefficient	$MoOBr_5^{2-}$	$CrOCl_5^{2-}$
β_2	0.932	0.886
ϵ	0.844	0.958
β_1	0.596	0.592

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The Preparation and Optical and Electron Spin Resonance Spectra of Some Hexachloro- and Pentachloroalkoxovanadates(IV)

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Several compounds of the type $[R_4N]_2V(OR')Cl_5$ have been prepared from $[(CH_3)_4N]_2VCl_6$ and $[(CH_3CH_2)_4N]_2VCl_6$. All compounds show normal, spin-only paramagnetism for a d^1 ion at room temperature. The magnetic moments for the alkoxo complexes vary little with temperature. Electronic, infrared, and electron spin resonance spectra have been measured. Bonding coefficients for the pertinent molecular orbitals have been calculated. $N_{\pi_2}^2$ and $N_{\sigma_2}^2$ decrease with increasing length of alkoxo chain while $N_{\pi_1}^2$ increases. Spin densities have been calculated for the equatorial Cl atoms from the bonding parameters.

Much recent interest has centered on the investigation of d^1 transition elements involving oxy ions of the type MO^{n+} where $M^{(n+2)+}$ is Cr^{5+}, Mo^{5+}, or V^{4+}. The halide complexes of these ions have been studied carefully and it is well established that there is substantial π bonding between the metal and oxygen atom.[1-5] Recent work in this laboratory has concerned the preparation and characterization of d^1 transition element alkoxides and complexes containing alkoxides as ligands.[6-12] It was decided that vanadium(IV) chloride alkoxides would be of interest because of the large amount of work which has been done with the vanadyl systems. The monoalkoxide species ought to be six-coordinate anions where the metal to oxygen bond is formally a single bond. A study of these compounds should show the effect on the bonding parameters of changing the donating strength of the oxygen by varying the alkoxide group. The effect of changing the halogen from F^- to Cl^- to Br^- has been shown in the case of $MoOX_5^{2-}$.[1,2]

Bradley and Mehta[13] and Thomas[14] have prepared a number of vanadium alkoxides of the type $V(OR)_4$. Various investigators have isolated substances of the general form $V(OR)_2Cl_2 \cdot ROH$ from alcoholic solutions.[15-17] Several salts of the hexachlorovanadate ion

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