D (in Table 3) are lower than those of Pt-catalysts without boron on the same supports (in Table 2), the both boron-promoted catalysts exhibit high tolerance against lead poisoning. The exact role of these base metals in the catalysis is not understood yet, but boron seems to be a promising candidate promoter for lead tolerant catalyst if the initial activity can be raised.

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Calculation of the Dipole Moments for Square Pyramidal Complexes

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Modified technique in calculating the dipole moments for square pyramidal complexes has been developed and then the dipole moments for bisacetylacetonato(oxo)vanadium(IV) complexes are calculated, adopting this approach. The calculated dipole moments for bisacetylacetonato(oxo)vanadium(IV) in benzene and bisacetylacetonato(oxo)vanadium in dioxane solutions are in agreement with the observed values. The calculated dipole moments of bisacetylacetonato(oxo)vanadium(IV) in dioxane solution is slightly higher than that of bisacetylacetonato(oxo)vanadium(IV) in benzene. Such a result may suggest that bisacetylacetonato(oxo)vanadium(IV) interact with dioxane molecule to form bisacetylacetonato(oxo)vanadium(IV)-dioxane adduct. This calculated dipole moments are also in agreement with the experimental results.

Introduction

Over the twenty years, a great deal of interest has been focussed on the measurement of the dipole moments for transition metal complexes in investigating their geometric structure in inert or aprotic solvent solutions.[1,2] A method for calculation of the electric dipole moments for molecules containing rotating polar groups has been proposed by Gilman,[3] modifying the vector method of Wilcox[4] and the mean square moments for organic molecules containing a single rotatable polar group as well as one or more fixed groups were calculated to obtain information for the absence of free rotation. Recently this method was applied to the calculation of the dipole moments for $CL_nSn(CH_2CL)_{4-n}$ type complexes.[5] The vector method of Wilcox and Gilman can only be applied to the calculation of the dipole moments for the molecules with both fixed and rotating polar groups. To overcome such the shortcoming, a new approach in calculating the dipole moments for transition metal complexes has been proposed. This approach was however applied to calculate the dipole moments for octahedral, square planar and tetrahedral complexes.

To determine the theoretical dipole moments for square pyramidal complexes such as bisacetylacetonato(oxo)vanadium(IV), we may modify the previous three assumptions,[6] which has been made to attempt to calculate the dipole moments for transition metal complexes, as follows;

(1) The only valence electrons of ligands, which take part in valence bond with the central metal ion, are assumed to be contributed to the nuclear part of the dipole moments for transition metal complexes.

(2) The atoms that bond directly with the metal ions and are located at the end of the ligands are assumed to be the dominant contribution to the dipole moment for transition metal complexes. We therefore adopt the modified linear combination of valence basis sets of the transition metal and ligands.

The purpose of this work is to perform example calculations of the dipole moments for square pyramidal complexes, adopting the modified two assumptions. As far as we are aware, no atempt has been made to determine the theoretical dipole moments for square pyramidal transition metal complexes.

Theory

For example calculation of the dipole moments for square pyramidal complexes, we choose bisacetylacetonato(oxo)-vanadium(IV). These complexes were known to interact with amines to form adducts in which the vanadium has a roughly octahedral coordination sphere.[7,8] It was however reported that with oxygen containing ligands, the evidence for such complexes formation is less certain though Nyburg *et al.*[9] isolated the complex $[VO(acac)_2]_2$ (dioxane) in which a dioxane molecule bridges two $VO(acac)_2$ groups.

In this work, we assume that bisacetylacetonato(oxo) vanadium(IV) interact with oxygen containing ligands to form adducts. This assumption may be justified by comparing the calculated dipole moments with the experimental values. We also assume that bisacetylacetonato(oxo)vanadium(IV) adducts with dioxane have C_{4v} symmetry. The transformation scheme of bisacetylacetonato(oxo)vanadium is listed in Table 1. As the transformation properties of the central metal ion and ligands are known, the valence basis sets of the central metal ion can be combined with the ligands basis sets having the same transformation properties.

The approximate molecular orbitals obtained may be represented, in general, using group theoretical notation by

$$\Phi_i(\mathrm{MO}) = N_i[\alpha_i \Gamma_i(\mathrm{M}) + \beta_i \Gamma_i(l)]$$
$$\Phi_i^*(\mathrm{MO}) = N_i^*[\alpha_i^* \Gamma_i(\mathrm{M}) + \beta_1^* \Gamma_i(l)] \tag{1}$$

where

$$N_i = [\alpha_i^2 + 2\alpha_i\beta_i < \Gamma_i(\mathrm{M}) | \Gamma_i(l) > + \beta_i^2 < \Gamma_i(l) | \Gamma_i(l) >]^{-\frac{1}{2}}$$
$$N_i^* = [\alpha_i^{*2} + 2\alpha_i^*\beta_i^* < \Gamma_i(\mathrm{M}) | \Gamma_i(l) > + \beta_i^{*2} < \Gamma_i(l) | \Gamma_i(l) >]^{-\frac{1}{2}} \tag{2}$$

Here it is necessary to mention that we adopt σ bonding ligand orbitals as a linear combination of ns and np_z orbitals of the same ligand atoms as

$$\sigma(l) = \sin\theta\,(\mathrm{ns}) \pm \cos\theta\,(\mathrm{np}_z) \tag{3}$$

where n = 2,3 or 4. The degree of hybridization is calculated by minimizing the quantity VSIP (θ)/S(θ), where S(θ) is the overlap integral of atomic orbitals of the central vanadium (IV) atom with ligand hybrid orbitals of varying values of θ, while VSIP (θ) is the valence state ionization potential of the same ligand hybrid orbital.[9] The angles at which the minimum of VISP (θ) occurred are listed in Table 2.

Table 1. Orbital Transformation scheme for the Distorted Square Pyramidal Bisacetylacetonate

Γ_i	Γ_M	Γ_l
$a_1(1)$	$3d_{z^2}+4s$	σ_5
$a_1(2)$	$4s-3d_{z^2}$	$\frac{1}{2}(\sigma_1+\sigma_2+\sigma_3+\sigma_4)$
$a_1(3)$	$4p_z$	σ_6
e	$3d_{xz}, 3d_{yz}$	$\pi_5(2p_x,\ 2p_y)$
	$4p_x,\ 4p_y$	$\frac{1}{\sqrt{2}}(\sigma_1-\sigma_3),\ \frac{1}{\sqrt{2}}(\sigma_2-\sigma_4)$
b_1	$3d_{x^2-y^2}$	$\frac{1}{2}(\sigma_1-\sigma_2+\sigma_3-\sigma_4)$
b_2	$3d_{xy}$	

The molecular orbital energies and the corresponding eigenvector are obtained by solving the following secular equation,

$$(H_{ij} - G_{ij}E) = 0 \tag{4}$$

where G_{ij} is the group overlap integral. Since we adopt two assumptions in calculating the dipole moments for square pyramidal complexes, the diagonal matrix elements for vanadium (IV) may be estimated from the negative values of the valence state ionization potential of valence orbitals in the following manner,

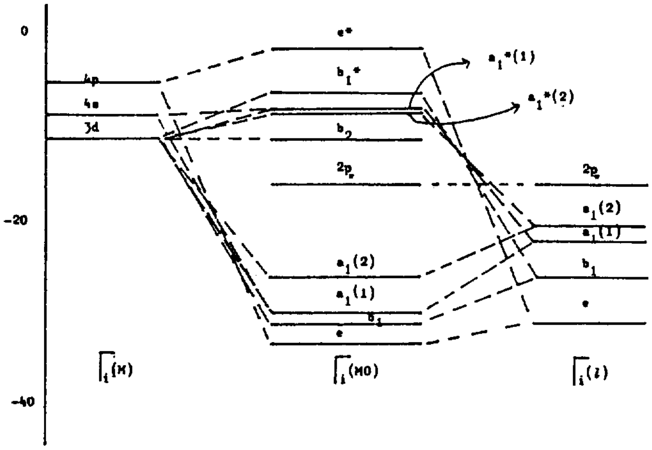
$$H_{ii} = N_i'^2 H_{ii}' \tag{5}$$

Here H_{ii}' is the negative value of the valence state ionization potential of valence orbital and N_i' is the normalization constant which can be calculated by

$$N_i' = [C_i^2 + \sum_{i \neq j} 2C_iC_jS_{ij}]^{-\frac{1}{2}} \tag{6}$$

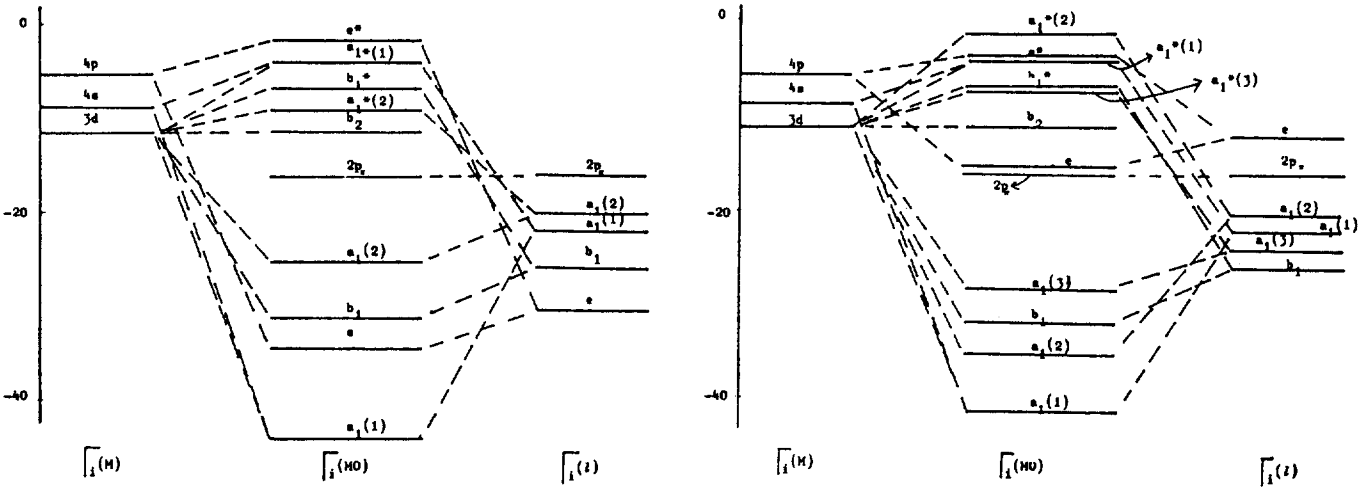
Table 2. Degree of Hybridization

Complexes	Γ_i	sin θ	cos θ	(degree)
$VO(acac)_2$ (planar)	a_1 (plane)	0.3746	0.9272	22
	a_1 (z axis)	0.3497	0.9397	20
$VO(acac)_2$ (distorted)	a_1	0.5726	0.8192	35
	b_1	0.7547	0.6561	49
	e	0.9744	0.2250	77
	a_1 (z axis)	0.5150	0.8572	31
$VO(acac)_2H_2O$	a_1 (z axis)	0.5592	0.8290	34
	a_1 (−z axis)	0.9135	0.4067	66
$VO(acac)_2Cl$	a_1 (z axis)	0.5150	0.8572	31
	a_a (−z axis)	1	0	90
$VO(acac)_2Br$	a_1 (z axis)	0.5150	0.8572	31
	a_1 (−z axis)	0.9703	0.2419	76
$VO(acac)_2 \cdot CH_3OCH_3$	a_1 (z axis)	0.5592	0.8290	34
	a_1 (−z axis)	0.9205	0.3907	67
$VO(acac)_2 \cdot C_4H_8O_2$	a_1 (z axis)	0.5150	0.8572	31
	a_1 (−z axis)	0.9135	0.4067	66

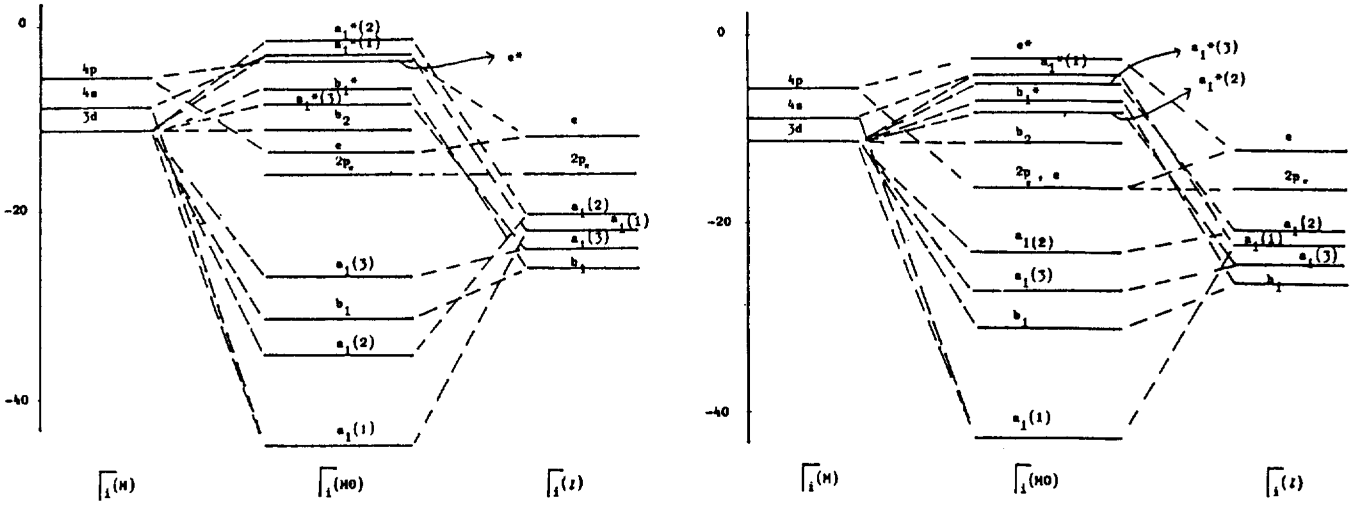


a) $VO(acac)_2$

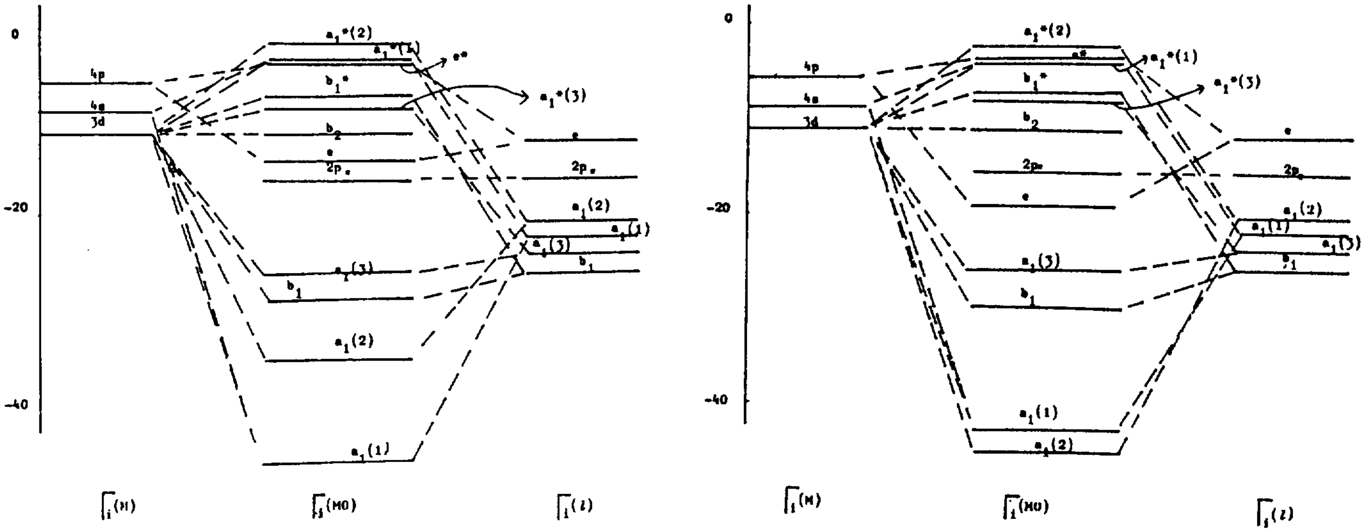
Figure 1. The energy level diagram for bisacetylacetonato-(oxo)vanadium(IV).



b) distorted VO(acac)$_2$ e) VO(acac)$_2$·C$_4$H$_8$O$_2$



c) VO(acac)$_2$·CH$_3$OCH$_3$ f) VO(acac)$_2$·Cl



d) VO(acac)$_2$·H$_2$O g) VO(acac)$_2$·Br

Figure 1. Continued.

Table 3. Group Overlap Integrals and Molecular Orbital Energies

(a) VO(acac)$_2$

Γ_i(MO)	G_{ij}	E_i(ev)	α_i	ß$_i$	E_i^* (ev)	α_i^*	ß$_i^*$
a_1 (1)	0.1271	-30.52	-0.2576	0.9747	-8.21	0.9340	0.3795
a_1 (2)	0.1137	-26.99	0.3688	0.9365	-8.43	0.9724	-0.2599
b_1	0.1971	-31.41	0.5386	0.8662	-6.63	0.9554	-0.3573
e_π	0	-11.60	0	0			
e (x)	0.2842	-33.53	0.5557	0.8826	-1.73	1.0042	-0.2819
e (y)	0.2842	-33.53	0.5557	0.8826	-1.73	1.0042	-0.2819
b_2	0	-11.60	0	0			

(b) distorted VO(acac)$_2$

Γ_i(MO)	G_{ij}	E_i(ev)	α_i	ß$_i$	E_i^* (ev)	α_i^*	ß$_i^*$
a_1 (1)	0.3060	-44.26	-0.3976	0.9722	-4.16	0.8039	0.6761
a_1 (2)	0.0938	-25.06	0.2351	0.9765	-9.35	0.9942	-0.1428
b_1	0.1789	-30.38	0.5114	0.8784	-7.19	0.9557	-0.3460
e_π	0	-11.60	0	0			
e (x)	0.2793	-33.42	0.5489	0.8851	-1.82	1.0032	-0.2798
e (y)	0.2793	-33.42	0.5489	0.8851	-1.82	1.0032	-0.2798
b_2	0	-11.60	0	0			

(c) VO(acac)$_2$CH$_3$OCH$_3$

Γ_i(MO)	G_{ij}	G_{ik}	E_i(ev)	α_i	ß$_i$	γ_i	E_i^* (ev)	α_i^*	ß$_i^*$	γ_i^*
a_1 (1)	0.3331		-45.91	-0.4039	0.98065		-3.36	0.7901	0.7075	
a_1 (2)	0.2852		-35.24	-0.2966	1.0029		-1.57	0.8742	0.5696	
a_1 (3)	0.1137		-26.87	0.3670	0.9370		-8.32	0.9730	-0.2576	
b_1	0.1969		-30.86	0.5297	0.8716		-6.92	0.9589	-0.3477	
e_π	0		-11.60	0	0					
e (x)	0.0511	0.0649	-13.74	-0.0930	0.1811	0.9737	-3.5758	-0.1410	0.9765	-0.1275
e (y)	0.0511	0.0649	-13.74	-0.0930	0.1811	0.9737	-3.5758	-0.1410	0.9765	-0.1275
b_2	0		-11.60	0						

(d) VO(acac)$_2$H$_2$O

Γ_i(MO)	G_{ij}	G_{ik}	E_i(ev)	α_i	ß$_i$	γ_i	E_i^* (ev)	α_i^*	ß$_i^*$	γ_i^*
a_1 (1)	0.3331		-46.24	-0.4035	0.9808		-3.38	0.7904	0.7072	
a_1 (2)	0.2852		-35.45	-0.3011	0.9990		-1.71	0.8716	0.5735	
a_1 (3)	0.1137		-26.79	0.3563	0.9413		-8.48	0.9757	-0.2470	
b_1	0.1969		-31.06	0.5336	0.8693		-7.07	0.9573	-0.3520	
e_π	0		-11.60	0	0					
e (x)	0.0511	0.0649	-13.91	-0.0890	0.1812	0.9741	-3.61	-0.1430	0.9763	-0.1270
e (y)	0.0511	0.0649	-13.91	-0.0890	0.1812	0.9741	-3.61	-0.1430	0.9763	-0.1270
b_2	0		-11.60	0	0					

(e) VO(acac)$_2$C$_4$H$_8$O$_2$

Γ_i(MO)	G_{ij}	G_{ik}	E_i(ev)	α_i	ß$_i$	γ_i	E_i^* (ev)	α_i^*	ß$_i^*$	γ_i^*
a_1 (1)	0.3060		-43.77	-0.3948	0.9734		-4.05	0.8059	0.6737	
a_1 (2)	0.2852		-35.49	-0.2951	1.0007		-1.53	0.8750	0.5683	
a_1 (3)	0.1137		-28.63	0.4439	0.9034		-7.27	0.9480	-0.3383	
b_1	0.1969		-30.93	0.5286	0.8723		-6.91	0.9593	-0.3465	
e_π	0		-11.60	0	0					
e (x)	0.0511	0.0649	-14.02	-0.1116	0.2184	0.9641	-3.55	-0.0833	0.9779	-0.1628
e (y)	0.0511	0.0649	-14.02	-0.1116	0.2184	0.9641	-3.55	-0.0833	0.9779	-0.1628
b_2	0		-11.60	0	0					

(f) $VO(acac)_2Cl$

Γ_i(MO)	G_{ij}	G_{ik}	E_i(ev)	α_i	$ß_i$	γ_i	E_i^* (ev)	α_i^*	$ß_i^*$	γ_i^*
a_1 (1)	0.3060		-42.54	-0.3867	0.9766		-3.74	0.8114	0.6670	
a_1 (2)	0.0401		-22.99	-0.0622	0.9989		-4.31	0.9956	0.1022	
a_1 (3)	0.1137		-26.66	0.3442	0.9458		-7.99	0.9788	-0.2344	
b_1	0.1969		-30.91	0.5280	0.8727		-6.89	0.9596	-0.3458	
e_π	0		-11.60	0	0					
e (x)	0.1434	0.1547	-16.78	-0.1867	0.4090	0.8847	-2.28	-0.2031	0.9266	-0.2915
e (y)	0.1434	0.1547	-16.78	-0.1867	0.4090	0.8847	-2.28	-0.2031	0.9266	-0.2915
b_2	0		-11.60	0	0					

(g) $VO(acac)_2Br$

Γ_i(MO)	G_{ij}	G_{ik}	E_i(ev)	α_i	$ß_i$	γ_i	E_i^* (ev)	α_i^*	$ß_i^*$	γ_i^*
a_1 (1)	0.3060		-43.03	-0.3883	0.9766		-3.90	0.8064	0.6740	
a_1 (2)	0.4078		-45.98	-0.5013	0.9738		-2.50	0.6847	0.8548	
a_1 (3)	0.1137		-26.59	0.3522	0.9429		-8.27	0.9768	-0.2427	
b_1	0.1969		-30.79	0.5297	0.8717		-6.90	0.9589	-0.3477	
e_π	0		-11.60	0	0					
e (x)	0.1365	0.1746	-19.93	-0.4254	0.2867	1.1144	-3.57	-0.3979	1.1049	-0.3547
e (y)	0.1365	0.1746	-19.93	-0.4254	0.2867	1.1144	-3.57	-0.3979	1.1049	-0.3547
b_2	0		-11.60	0	0					

Table 4. The Calculated Dipole Moments for Square Pyramidal Complexes

Complexes	R	R'	μ^b (calcd.)	μ^b (expl.)
$VO(acac)_2$	1.56		3.337	3.10,[9] 3.24,[10] 3.31
$VO(acac)_2$ (distorted)	1.67	1.97[a]	2.938	
$VO(acac)_2\cdot CH_3OCH_3$	1.56	2.40	3.819	
$VO(acac)_2\cdot {}^5H_2O$	1.56	2.40	1.916	
$VO(acac)_2\cdot C_4H_8O_2$	1.67	2.40	3.704	3.75,[9] 3.89[10]
$VO(acac)_2Cl$	1.67	2.215	2.989	
$VO(acac)_2Br$	1.67	2.362	2.775	

[a] The bond distance for V–O in equatorial bonds for the square pyramidal vanadyl bisacetylacetonate. Here R is the bond distance of V–O bond for z axis, and R′ is the those of V–X for z axis. [b] The unit of the dipole moment is debye.

and the off-diagonal matrix elements are calculated by using Wolfsberg and Helmholtz approximation.[10]

$$H_{ij}=\frac{1}{2}F\,G_{ij}\,(N_i'^2H_{ii}'+N_j'^2H_{jj}') \qquad (7)$$

where F = 1.80. Therefore, for hybrid orbitals of ligands, the diagonal matrix elements are estimated from[11]

$$H_{ij} = -\{\sin^2\theta\,(N_i'^2\cdot\text{VSIP of ns})+\cos^2\theta\,(N_j'^2\cdot\text{VSIP of np}_z)\} \qquad (8)$$

Group overlap integrals and molecular orbital energies for square pyramidal complexes are listed in Table 3. The energy level diagrams for bisacetylacetonato(oxo)vanadium(IV) complexes are also represented in Figure 1.

The general formulas of the electric dipole moment matrix elements for bonding and antibonding molecular orbitals are

$$<\Phi_i\,(\text{MO})\,|\underset{\sim}{r}|\,\Phi_i(\text{MO})>=N_i^2\,[2\alpha_i\beta_i<\Gamma_i\,(\text{M})\,|\underset{\sim}{r}|\,\Gamma_i\,(l)>+\beta_i^2<\Gamma_i\,(l)\,|\underset{\sim}{r}|\,\Gamma_i\,(l)>]$$
$$<\Phi_i^*\,(\text{MO})\,|\underset{\sim}{r}|\,\Phi_i^*\,(\text{MO})>=N_i^{*2}\,[2\alpha_i^*\beta_i^*<\Gamma_i\,(\text{M})\,|\underset{\sim}{r}|\,\Gamma_i\,(l)>+\beta_i^{*2}<\Gamma_i\,(l)\,|\underset{\sim}{r}|\,\Gamma_i\,(l)>] \qquad (9)$$

Now we apply the coordinate transformation scheme to the molecular orbitals of square pyramidal complexes and then calculate the dipole moments for bisacetylacetonato(oxo)-vanadium(IV) complexes using the following formula,

$$\mu=-2e\sum_i<\Phi_i\,(\text{MO})\,|\underset{\sim}{r}|\,\Phi_i\,(\text{MO})>+e\sum_k n_kR_k \qquad (10)$$

where R_k is the distance from the central metal ion to Kth nucleus, and n_k the number of valence electrons. The calculated dipole moments for bisacetylacetonato(oxo)vanadium-(IV) complexes are listed in Table 4.

Results and Discussion

Bisacetylacetonato(oxo)vanadium(IV) complexes have increasingly been investigated experimentally and particular interests were on the electronic spectral studies to interpret the optical and other data.[12] The detailed molecular orbital treatments for square pyramidal oxovanadium (IV) complexes has been suggested that these complexes may have C_{4v} symmetry.[13-16]

As shown in Table 4, the calculated dipole moments for $VO(acac)_2$ complex in benzene solution, using equation (10), is in agreement with the experimental dipole moments. Small difference between the theoretical dipole moment and the observed value may however be due to the solvent effect on the dipole moments[17] but the experimental value in dioxane solution is slightly higher than that of benzene solution. Table 4 also shows that the calculated dipole moments for adducts of bisacetylacetonato(oxo)vanadium(IV) with dioxane in dioxane solution is in agreement with the observed values. This calculated results may suggest that bisacetylacetonato(oxo)-vanadium(IV) interact with oxygen-containing ligand to form adducts and the results of Table 4 may also suggest that this calculation method of the dipole moments for square pyramidal complexes is more superior than other approaches we have adopted in calculating the dipole moments for transition metal complexes as far as the calculation of the dipole moments of square pyramidal complexes is concerned. This work may be applied to calculate the dipole moments for square pyramidal complexes and may predict the geometric structure in inert or aprotic solvent solutions.

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Phase Transition and Approximated Integral Equation for Radial Distribution Function

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A reduced condition for liquid-gas phase transition from the singularity of compressibility is derived using diagrammatic approach and is examined in the hard sphere system. The condition turns out that the Percus-Yevick and the Hyper-Netted-Chain approximation never conceive the idea of phase transition, and explains that the liquid-gas transition does not exist in hard sphere system. The solid-fluid transition is considered on the viewpoint of correlation function and diagrammatic analysis.

Introduction

Knowledge of the radial distribution function $g(r)$ is the essential prerequisite for a complete static description of homogeneous classical liquids whose molecules are taken to interact through effective two-body forces. The radial distribution function is expressed from the diagrammatic analysis[1] of density expansion with three unknowns, as is given by

$$g(r)=e^{-\beta u(r)}\{1+N(r)\}+e^{-\beta u(r)}Z(r) \tag{1-a}$$

$$Z(r)=e^{N(r)+E(r)}-\{1+N(r)\} \tag{1-b}$$

where $N(r)$ is analyzed from the nodal group of which elements have at least one nodal point, $E(r)$ is from the cross-bridged group which has no nodal point, β is $1/kT$ and $u(r)$ is the pair potential. These functions also satisfy following equations