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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1086.

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Bonding Studies of Bis(tetramethylurea)dichlorooxovanadium(IV)

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The bonding in the X-ray-determined low-symmetry complex bis(tetramethylurea)dichlorooxovanadium(IV) was studied by optical and electron spin resonance spectroscopy and by molecular orbital calculations of the Wolfsberg-Helmholz type and compared with the bonding in high-symmetry complexes such as $VOCl_4^{2-}$. Assignments of the d–d optical transitions were made on the basis of calculated and experimental intensities as well as considerations of the expected effects of substituents and electrostatic terms. The molecular orbital calculations indicated a removal of all degeneracy in the vanadium d-orbital energy levels while the experimental optical spectra were ambiguous on this point. Of particular interest from the MO calculations is the finding of a bonding molecular orbital which is delocalized over the equatorial ligands and the vanadyl oxygen in $VO(tmu)_2Cl_2$. The esr data indicated that the overall average environment for the d_{xy} unpaired electron was very similar for $VO(tmu)_2Cl_2$ and $VOCl_4^{2-}$.

I. Introduction

A combined experimental and theoretical investigation of the electronic structure and chemical bonding of low-symmetry transition metal complexes is in progress in our laboratory in order to extend the knowledge of the dependence of bonding upon symmetry. This is considered important since many spectroscopic theories have been derived and/or tested mainly for cases of relatively high symmetry while many complexes of practical use such as industrial catalyst systems and biological complexes are of low symmetry. In previous papers we have studied the bonding of low-symmetry Cu(II) complexes.[1-3] Cu(II) was chosen since it has one unpaired electron which is normally involved in σ-type bonding to the ligands and can be easily studied by electron spin resonance spectroscopy. In order to extend this investigation to systems in which the unpaired electron is in the π system we have initiated similar studies of vanadyl complexes. The appearance of a three-dimensional X-ray structure determination[4] for bis(tetramethylurea)dichlorooxovanadium(IV), $VOCl_2 \cdot 2tmu$, made it an obvious choice for an initial study of this type.

II. Experimental Section

The complex was prepared according to the general method of du Preez and Sadie[5] and checked by comparison with their published ir data and elemental analysis. Digital electronic absorption spectra were obtained from a Cary 17 spectrophotometer and resolved into gaussian components by the use of the Fortran program BiGauss written by Cavell.[6] Esr studies were carried out on a Strand-Magnion, Varian hybrid spectrometer on 10^{-2}–10^{-3} M solutions of the complex dissolved in $CHCl_3$.

For the theoretical calculations the extended Huckel method was used. The calculation procedure used is different from what has been employed in previous studies. Rather than converging on a charge self-consistent solution based on either the theoretical charge dependence of the H_{ii} terms[7] or a scaled charge dependence for the metal ion with fixed ligand values,[8] we have chosen to calculate to charge self-consistency for the organic ligand and the vanadyl oxygen,[9] to use the neutral chloride H_{ii} values to correct for Madelung energy,[10] and empirically to adjust the vanadium 3d orbital H_{ii} value until a correct ground state is obtained and the esr, optical, and molecular orbital coefficient data are in general agreement with experiment. This is not a severe approximation since one adjustable parameter is being used simultaneously to fit a number of experimental parameters. The purpose of this approach is to see what the effect of the low-symmetry ligand environment is on the vanadium–ligand bonds, *i.e.*, what mixing and/or splitting of molecular orbitals occurs in this X-ray-determined low-symmetry complex which do not occur in high-symmetry classical complexes. The final values of the coulomb integrals, H_{ii}, are given in Table I (microfilm edition only). The orientation chosen for the calculations puts the vanadyl oxygen along the $+z$ direction, the vanadium at the origin, the chlorines in the general x and $-x$ directions, and the tmu ligands along the general y and $-y$ directions.

In order to check whether the final calculated organic ligand charge distributions and energy levels are realistic, CNDO2,[11] MINDOII,[12] and CNDO-CI[13] calculations were performed on the tetramethylurea. The charge distributions and energies calculated by the various methods for tmu are given in Table II (microfilm edition only).

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Table III (microfilm edition only) gives the calculated energy levels and molecular orbital coefficients for $VOCl_2$ and $VOCl_4^{2-}$. They will be used for comparison purposes.

The theoretical oscillator strengths were calculated using the method of Cotton and Wise.[14]

III. Results and Discussion

Optical Spectra. The gaussian analysis of the visible portion of the optical spectrum in methanol-free chloroform yielded peaks at 12.4 ± 0.1, 15.2 ± 0.1, and 25.1 ± 0.1 kK with oscillator strengths of $(2.0 \pm 0.9) \times 10^{-4}$, $(10.2 \pm 0.2) \times 10^{-4}$, and $(3.0 \pm 0.4) \times 10^{-4}$, respectively (see Figure 1). du Preez and Gibson[15] obtained similar data in a CH_2Cl_2-CH_3CN mixed solvent. Since our molecular orbital calculations predicted a transition at lower energy we also examined the infrared region from 4.5 kK up (see Figure 2). A broad peak was found at 9.8 ± 0.2 kK with an oscillator strength of $(1.4 \pm 0.2) \times 10^{-4}$. This broad peak is expected because a clear low-energy tail is observed in the experimental spectrum. A similar tail has been reported by Valek, *et al.*,[16] for vanadyl keto enolates and by Wentworth and Piper[17] for $VOCl_5^{3-}$. Both groups did not consider it to be a separate peak but attributed it to the coupling of the vanadyl and/or in-plane vibration modes to the $xy \rightarrow xz, yz$ transitions. Usually, we would also reject the possibility that it is a separate peak on the basis that the line width is considerably different from the other peaks in the spectrum.[18] This similarity in line width "rule" was expected to be particularly applicable when comparing the $xy \rightarrow xz$ and $xy \rightarrow yz$ line widths; however, inspection of our molecular orbital calculations revealed that the lower energy xz symmetry molecular orbital has chlorine atomic p orbital coefficients of 0.17 for each of the two chlorines while the yz symmetry molecular orbital has chlorine p orbital coefficients of only 0.01. Thus, it seems possible that the two transitions could have appreciably different line widths. The next step is to determine whether this possibility is consistent with the other information available. If the in-plane vibronic coupling broadening mechanism is the predominant one, then the difference in line widths could be explained by a much higher V-Cl in-plane stretching frequency than a V-tmu in-plane stretching frequency. The V-Cl stretching frequency has been tentatively assigned to the 400-cm^{-1} region by du Preez and Gibson.[15] Since this is the same region in which in-plane V-O stretching frequencies appear, the hypothesis that the V-Cl stretching frequency is ≫V-tmu is not supported by the available quantitative data. Another check on the original hypothesis that the transition involving the Cl would be much broader than the transition involving the tmu, and one that is not dependent on a model, is to compare the line width found for $VOCl_4^{2-}$ by Piovesana and Selbin[19] with their other vanadyl line widths and those reported by other authors such as Spessard.[20] Both the 10-20 and the 20-28-kK bands in $VOCl_4^{2-}$ are appreciably broader than the bands of the other complexes. Other examples of very broad $VOCl_4^{2-}$ spectra have been reported by Drake, *et al.*,[21] Kilty and Nicholls,[22] and Feltz.[23] It appears that although one cannot build a strong case for the existence of the 9.8-kK band as a separate $d_{xy} \rightarrow d_{xz}$ transition, it would be risky to reject completely this possibility on the basis of the available evidence. If we *assume* that the band is real, a possible assignment for the four expected d-d transitions would be $d_{xy} \rightarrow d_{xz}$ at 9.8 kK, $d_{xy} \rightarrow d_{yz}$ at 12.4 kK, $d_{xy} \rightarrow d_{x^2-y^2}$ at 15.2 kK, and $d_{xy} \rightarrow d_{z^2}$ at 25.1 kK. If the band is not real the only change required is to assign both the $d_{xy} \rightarrow d_{xz}$ and $d_{xy} \rightarrow d_{yz}$ bands to 12.4 kK. The most controversial part of this assignment is the assignment of the 25.1-kK band to the z^2 transition rather than to a charge-transfer transition as has often been done for other vanadyl complexes. For example, Wentworth and Piper[17] placed the z^2 level at ~50 kK above the xy for $VOCl_5^{3-}$. Wentworth and Piper's principal argument for the high $xy \rightarrow z^2$ transition energy is that the axial crystal field must be stronger than the equatorial; *i.e.*, the vanadyl oxygen dominates the crystal field. There are two possible objections to this model. The first is that a survey of published molecular orbital calculations[21,24-27] indicates that the final charge on the vanadyl oxygen is somewhere between 0.1- and 0.8-.

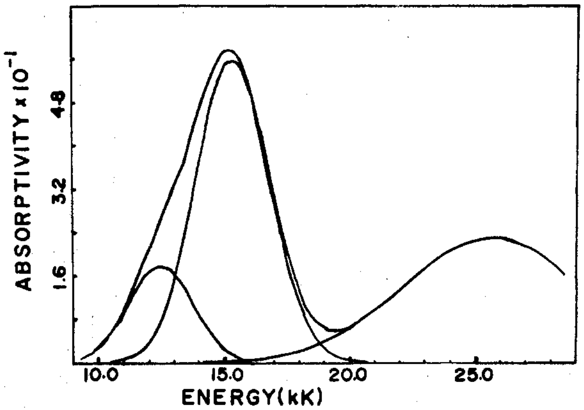

Figure 1. Gaussian analysis of the visible portion of the optical spectrum of the $VOCl_2 \cdot 2tmu$ in chloroform.

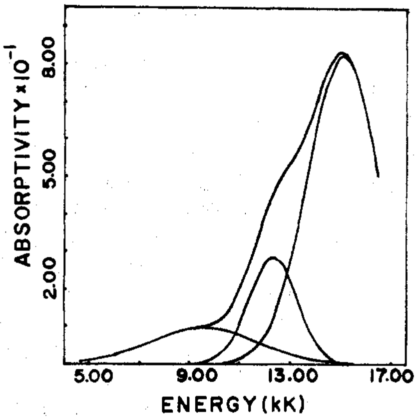

Figure 2. Gaussian analysis of the infra-red region of the optical spectrum of $VOCl_2 \cdot 2tmu$ in chloroform.

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Table IV. Electronic Spectral Bands (kK) for $VOCl_2 \cdot 2X$ Type Complexes

Compd	Medium	$xy \rightarrow xz, yz$	$xy \rightarrow x^2 - y^2$	$xy \rightarrow z^2$	Ref for exptl spectrum
$VOCl_2 \cdot 2$tmu	$CHCl_3$	9.8? (4),[d] 12.4 (13)	15.2 (56)	25.1 (17)	*e*
$VOCl_2 \cdot 2$HMPA[a]	CH_2Cl_2	11.9	13.6 (31)	25.6	*f*
$VOCl_2 \cdot 2(C_6H_5)_3PO$	CH_2Cl_2	13.5 (34.8)		25.0 (9.7)	*g*
$VOCl_2 \cdot 2N(CH)_3)_3$	C_6H_6	12.9 (10)	16.1	26.3 (8)	*h*
$VOCl_2 \cdot 2NH(CH_3)_2$	C_6H_6	12.5 (12)	15.9	26.3 (10)	*h*
$VOCl_2 \cdot 2S(CH_3)_2$	$(CH_3)_2S$	12.2, 13.3 (15)	16.5	24.1 (5)	*h*
$VOCl_2 \cdot 2S(C_2H_5)_2$	$(C_2H_5)_2S$	12.2, 13.3 (12)	16.5	24.4 (5)	*h*
$VOCl_2 \cdot$(substituted pyridine 1-oxides)[b]					*i*
$VOCl_2 \cdot EBDPP \cdot H_2O$[c]	CH_2Cl_2	12.9	14.6	23.8	*j*
$VOCl_2 \cdot$(series of P, As, and S ligands)	CH_2Cl_2 CH_3CN	10.5–13.6	13.5–14.8	23.8–26.3	*k*

[a] HMPA = hexamethylphosphoramide. [b] The 25-kK bands were obscured for the Cl complexes; however, for $VOBr_2 \cdot 2X$ a linear correlation between the band position and the substituent Hammett type parameter was found (the more electronegative the substituent the lower the energy). [c] EBDPP = ethylenebis(diphenylphosphine). [d] Values in parentheses are approximate extinction coefficients. [e] This paper. [f] Reference 5. [g] S. M. Horner, S. Y. Tyree, and D. L. Venezky, *Inorg. Chem.*, 1, 844 (1962). [h] K. L. Baker, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J. Inorg. Nucl. Chem.*, 29, 1881 (1967). [i] R. G. Garvey and R. O. Ragsdale, *ibid.*, 29, 745 (1967). [j] J. Selbin and G. Vigee, *ibid.*, 30, 1644 (1968). [k] Reference 15.

Our molecular orbital calculations for this particular compound yield a charge of 0.33–. The low charge is consistent with the chemical behavior of the vanadyl group. Thus, it is best thought of as a very covalent bond not as a highly ionic bond. If we place our actual calculated charges into Wasson and Stoklosa's computer program[28] for calculating the electronic spectra from crystal field theory, we obtain the incorrect ground state (the d_{yz}) when the theoretical values for $\langle r^2 \rangle$ and $\langle r^4 \rangle$ are used. If we adjust $\langle r^2 \rangle$ and $\langle r^4 \rangle$ to values similar to those used by Wasson and Stoklosa,[28] the calculated ground state is correct but the transition energies are too small: $xy \rightarrow yz$ at 0.28 kK, $xy \rightarrow xz$ at 0.38 kK, $xy \rightarrow x^2 - y^2$ at 1.1 kK, and $xy \rightarrow z^2$ at 1.8 kK. This brings up the second objection against Wentworth and Piper's argument for the position of the $xy \rightarrow z^2$ transition. Crystal field theory has been historically rejected since it has failed as a quantitative theory.[29] Thus, we feel that the position of the z^2 orbital must be based on considerations other than quantitative crystal field theory. Piovesana and Selbin,[19] in a paper that appears to be the most recent from Selbin's group on this controversy, summarized the available evidence that supports the assigning of the 20-30-kK band as a charge-transfer band. We choose to take exception to their correlation between the VSIP values for F^- (16.13 kK), Cl^- (20.97 kK), and H_2O (101.7 kK) with the position of the band in question since the VSIP values for the neutral Cl and F vary in the opposite direction: F (151 kK), Cl (111 kK), and Br (101 kK);[30] and experimentally, as reviewed by Jorgensen,[31] the charge-transfer bands for F are at higher energy than for Cl. Their point that ligand to metal charge-transfer bands are observed in other vanadium compounds is indeed a valid one. For example, $VOCl_3$, in which vanadium is in the +5 state and has no d electrons, is found to have a transition at 29 kK[32] with an extinction coefficient of ~8000 and VCl_4 has a transition at ~24.5 kK with an extinction coefficient of ~2000.[33] For $VOCl_4^{2-}$ the 25-kK band has an experimental extinction coefficient of ~15.[22,23] The lowest energy chlorine to d_{xy} charge-transfer transition in $VOCl_4^{2-}$ has a calculated energy of 22.5 kK with an extinction coefficient of 510. Both of these values should be considered as lower limits due to the approximations involved. The large difference in extinction coefficients between our experimental 25-kK band and the "known" charge-transfer bands rules out the comparison for the specific compounds mentioned. Also, for our specific case the ~25-kK band remains within 1 kK of its original position if the Cl is replaced by Br.[5] A comparison with the literature would lead one to expect a large change in going from Cl to Br if the band was a halogen to metal charge-transfer band. For example,[31] for $TiCl_4$ the transition is at 35.6 kK while for $TiBr_4$ it is at 27.75 and 29.4 kK; for $TiCl_6^{2-}$ it is at 25.0 kK, and for $TiBr_6^{2-}$ it is at 17.7 kK. The molar extinction coefficients are all around 1000. Thus, the lack of dependence of our 25-kK band on halide used and its low extinction coefficient can be used to rule out the possibility that it is a chloride to metal charge-transfer band. The next question is whether it can be a tmu oxygen to metal charge-transfer band. The spectral bands of a number of $VOCl_2 \cdot 2X$ complexes are given in Table IV. The band in question remains relatively constant for O, N, P, S, and As ligands. Also, the linear correlation reported for the substituted pyridine 1-oxides is in the wrong direction for a charge-transfer assignment. Electron-donating groups should lower the transition energy if the band were of ligand to metal charge-transfer origin. Thus, the present study is consistent with our previous optical assignments for vanadyl complexes[34] which placed the z^2 level at low energy for ionic vanadyl complexes and in the 20-30-kK region for more covalent vanadyl complexes. It is worth noting that Spessard[20] studied VO^{2+} in the ionic medium phosphoric acid and also concluded that the z^2 level was at low energy (14.8 kK) rather than at 50-70 kK.

Molecular Orbital Calculation. The d-d transitions are calculated at 8.25 kK ($xy \rightarrow xz$), 10.0 kK ($xy \rightarrow yz$), 17.3 kK ($xy \rightarrow x^2 - y^2$), and 25.0 kK ($xy \rightarrow z^2$) with oscillator strengths of 5.4×10^{-6}, 1.1×10^{-4}, 7.3×10^{-4}, and 5.5×10^{-4}, respectively. The final charge calculated for the vanadium is 1.07+. A value of between 0.2+ and 2+ is expected based on previous molecular orbital calculations of vanadyl complexes.[24-27] The charge can be lowered by using more stable values for the vanadium H_{ii} terms but this results in an increase in the xy to $x^2 - y^2$ and xy to z^2 transition energies and finally to a change in the ground-state configuration.

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Table V. Calculated Energies and Molecular Orbital Coefficients for $VOCl_2 \cdot 2tmu$

		Energy, kK						
Atom	Atomic orbital	−18.75	−52.69	−60.34	−67.65	−69.34	−77.67	−79.65
V	z^2		0.91	0.09				0.05
	xz	−0.02				0.86		
	x^2-y^2		0.07	−0.88			−0.01	−0.14
	yz	−0.04			−0.81	−0.01		
	xy		0.01	−0.02			−0.90	−0.06
	4s		−0.03	0.01			−0.01	
	$4p_z$		−0.09	0.01				0.01
	$4p_x$	0.15				0.01		
	$4p_y$	−0.09			−0.02			
O(1)	s		−0.22	−0.04				−0.01
	p_z		0.61	0.09				0.05
	p_x	−0.01				−0.62		
	p_y	0.03			0.52	0.01		
Cl	s	−0.08	0.03	0.09		0.04		0.01
	p_z	0.01	0.11	0.09		−0.03		0.04
	p_x	0.01	−0.08	−0.27		−0.17		
	p_y	−0.06	−0.01	0.01			0.08	0.03
Cl′	s	0.08	0.03	0.09				
	p_z	0.01	0.11	0.09		0.03		0.04
	p_x	0.01	0.08	0.27		−0.17		
	p_y	−0.06	0.01	−0.01	0.01		−0.08	−0.03
O(2)	s	0.02	0.07	−0.13	−0.05		−0.03	−0.02
	p_z	−0.08	0.12	−0.07	0.18	−0.01	0.05	−0.60
	p_x	−0.31	−0.04	0.04	0.02	−0.01	0.27	−0.02
	p_y	0.23	−0.11	0.34	0.29		−0.03	−0.30
O(2′)	s	−0.02	0.07	−0.13	−0.05		−0.03	−0.02
	p_z	0.08	0.12	−0.07	−0.18	0.01	0.05	−0.60
	p_x	−0.31	0.04	−0.04	0.02	−0.01	−0.27	0.02
	p_y	0.23	−0.11	−0.34	0.29		0.03	0.30

The final electronic energies for the five molecular orbitals that are predominantly vanadium d atomic orbitals and for the orbitals of next higher and next lower energy are given in Table V. Also given are the molecular orbital coefficients for the vanadium and the five nearest neighbor atoms. Of particular interest is the removal of the xz, yz degeneracy with the xz mixing with the vanadyl oxygen and the chlorines and the yz mixing with the vanadyl oxygen and the tmu ligands. The amount of mixing of the x^2-y^2 orbital into the z^2 is small and of the same magnitude as the $4p_z$ mixing into the z^2. The molecular orbital directly below the five orbitals with predominant vanadium character is predominantly of tmu oxygen π character. Its energy position (only 2 kK lower than the d_{xy}) requires additional comment since the small energy difference suggests that there would be low-energy charge-transfer transitions. For a $\pi \rightarrow d_{xy}$ charge-transfer transition one must add the effects of interelectronic repulsion to the difference in molecular orbital energies, E_π and $E_{d_{xy}}$, *i.e.*

$$\Delta E_{\text{obsd}} = E_{d_{xy}} - E_\pi + J(\text{d,d}) - J(\text{d},\pi)$$

where $J(\text{d,d})$ is the average coulomb integral between two d_{xy} electrons and $-J(\text{d},\pi)$ is the attraction between the hole produced in the π orbital and the new d_{xy} electron supplied by optical excitation.[31] Jorgensen[31] estimated $J(3\text{d},3\text{d})$ as around 60 kK and $J(\text{d},\pi)$ when a halogen is the ligand, as around 30 kK. For a delocalized tmu electron $J(\text{d},\pi)$ would be smaller so a large (30 kK or above) net ΔE_{obsd} can still be consistent with a small $E_{d_{xy}} - E_\pi$ value. We must emphasize that the above discussion is not meant to be a justification of our quantitative energy level positions but is only meant to show that repulsion energy terms may be the predominant terms. We say "may be" because the estimation of repulsion energies is very qualitative. For example, Ballhausen and Gray[24] estimated the repulsion energy for this transition in $VO(H_2O)_5^{2+}$ as 11.7 kK, a factor of at least 3 lower than mentioned above. Yet, Vanquickenborne and McGlynn[27] considered the 11.7-kK value "exceedingly high." We can place a lower bound on the tmu to metal charge-transfer states by noting at what experimental energy the first intense band appears and then checking the calculations to see which is the lowest energy theoretical band with a high intensity and adjusting its calculated value to the experimental value. The transition from the highest energy tmu orbital to the d_{yz} is calculated to have an oscillator strength of 0.12. The experimental uv spectrum reveals only a slowly rising peak which has its maximum above the solvent cutoff point, 41.6 kK. The calculated energy level difference for this transition is only 12 kK. The difference between the actual energy, ~41.6 kK, and 12 kK is too large to be accounted for by the $J(d_{xy},d_{yz})$ term since the $J(d_{xy},d_{yz})$ term will be appreciably smaller than $J(d_{xy},d_{xy})$ (Zerner and Gouterman[25] estimated a value of 3.9 kK). Assuming that the $J(\text{d},\pi)$ term can be considered relatively constant, we will approximate the actual minimum position of the other charge-transfer states by

$$\Delta E = E_{\text{d}} - E_{\text{L}} + J(\text{d,d}) + 29.0$$

We will use $J(d_{xy},d_{xy}) = 11$ kK and $J(d_{xy},\text{d}) = 4$ kK. The scaled values using the above equation are given in Table VI. In order to determine the approximate energy positions of the predominantly tmu molecular orbitals, the experimental uv spectrum of tmu was obtained and compared with the predicted spectrum as calculated by the use of a CNDO-CI program. The experimental spectrum is given in Figure 3. The peak at 30.5 ± 0.1 kK has an oscillator strength of $(2.7 \pm 2.2) \times 10^{-7}$ and the peak at 34.0 ± 0.5 kK has an oscillator strength of $(4.2 \pm 4.0) \times 10^{-7}$. The calculation predicted singlet transitions at 28.0 kK (6.3×10^{-5} oscillator strength), 50.7 kK (5.1×10^{-2}), and 52.6 kK (0.22) and triplet transitions at 27.7, 32.7, and 47.4 kK. Oscillator strengths cannot be calculated for triplet transitions but they are usually of low oscil-

Table VI. Calculated Energies and Intensities for Charge-Transfer Transitions of $COCl_2 \cdot 2tmu$[a]

Lower MO	Higher MO	$E_d - E_L$, kK	Scaled ΔE, kK	Oscillator strength	Polarizn
tmu π, p_z	d_{xy}	2.0	38.0	2.3×10^{-5}	z
tmu π, p_z	d_{xy}	2.4	38.4	4.3×10^{-3}	y
=O p_y				3.0×10^{-4}	x
tmu π, p_z	d_{xy}	3.5	39.5	1.2×10^{-2}	y
tmu π, p_z	d_{xy}	5.5	41.5	1.6×10^{-3}	x
				1.3×10^{-2}	z
tmu π, p_x	d_{xy}	5.6	41.6	4.8×10^{-2}	y
tmu π, p_x	d_{xy}	8.1	44.1	1.3×10^{-3}	x
				1.0×10^{-2}	z
=O π, p_x	d_{xy}	13.3	49.3	2.3×10^{-4}	y
=O π, p_y	d_{xy}	13.9	49.9	4.7×10^{-3}	y
=O σ, p_z	d_{xy}	15.5	51.5	3.2×10^{-3}	z
Cl[a] π, p_y	d_{xy}	28.5	64.5	2.8×10^{-4}	y
				1.4×10^{-4}	x
Cl π, p_y	d_{xy}	29.8	65.8	1.6×10^{-2}	z

[a] There are four additional orbitals below the last tmu orbital listed and the first Cl orbital.

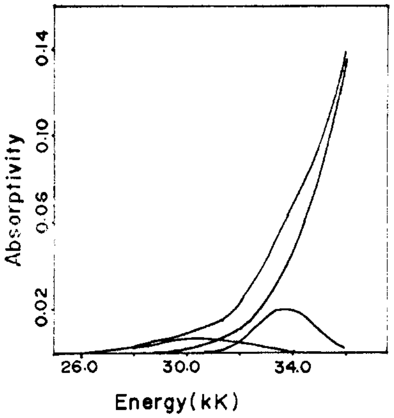

Figure 3. Gaussian analysis of the uv spectrum of tmu in chloroform.

lator strength (around 10^{-5}). Thus the CNDO-CI program appears to underestimate the transition energies by about 2-6 kK.

The change in energy of the predominantly tmu molecular orbitals caused by coordination is of interest in determining why the neutral tmu bonds to the neutral $VOCl_2$ molecule. It appears that the predominant change is a delocalization of the least stable tmu O_{p_z} electrons into the trans tmu groups with very little vanadium or vanadyl oxygen participation in one case and with considerable vanadyl oxygen p_y orbital participation in the other; see Table VII. The second mode of delocalization (through the vanadyl oxygen) was unexpected. We expected either the two tmu molecular orbital sets to be relatively localized or, if they mixed, to have a node at the vanadium or to have a sizable vanadium atomic orbital contribution. To see whether the same type of mixing would occur in a high-symmetry vanadyl complex, we looked at $VOCl_4^{2-}$. The $VOCl_4^{2-}$ had one molecular orbital with equal $Cl_{p_{y,x}}$ character and nodes at both the vanadium and the oxygen, but there was no molecular orbital with appreciable Cl_p and O_p character.

Electron Spin Resonance. The esr data are given in Table VIII. The data will be treated more completely in another paper. Of interest here is the lack of detectable splitting of the $A_\perp$ and/or $g_\perp$ terms. A splitting would be expected if the Cl and tmu bonding were appreciably different. The data are similar to the data reported for $VOCl_4^{2-}$ by Flowers, *et al.*,[35] and the data for $VOCl_5^{3-}$ by DeArmond, *et al.*,[36] indicating, within the resolution available, similar electronic environments for the three.

Table VII. Energy Levels and Coefficients of Predominantly tmu Molecular Orbitals in $VOCl_2 \cdot 2tmu$

Atom	Atomic orbital	Energy, kK					
		−79.65	−80.08	−81.15	−83.24	−83.29	−85.76
V	z^2	0.05			−0.04		
	xz		−0.01	0.01		−0.45	−0.20
	$x^2 - y^2$	−0.14			−0.14		
	yz		−0.19	0.01		−0.12	0.34
	xy	−0.06			−0.16		
=O	s	−0.01					
	p_z	0.05			−0.07		
	p_x		0.02			−0.73	−0.28
	p_y		0.42	0.10		−0.21	0.57
O_y	s	−0.02	−0.01	−0.02	−0.03	−0.04	0.09
	p_z	−0.60	−0.49	−0.32	0.16	−0.09	0.19
	p_x	−0.02	−0.12	0.20	−0.10	0.07	−0.18
	p_y	−0.30	−0.25	0.04	−0.07	0.07	−0.14
O_{-y}	s	−0.02	0.01	0.02	−0.03	0.04	−0.09
	p_z	−0.60	0.49	0.32	0.16	0.09	−0.19
	p_x	0.02	−0.12	0.20	0.10	0.07	−0.18
	p_y	0.30	−0.25	0.04	0.06	0.07	−0.14

Table VIII. Esr Data for Vanadyl–Chlorine Complexes

	$A_\parallel$, cm^{-1}	$A_\perp$, cm^{-1}	$g_\parallel$	$g_\perp$	Ref
$VOCl_4^{2-}$	0.01688	0.00628	1.9478	1.9793	*c*
$VOCl_5^{3-}$	0.01730	0.00638	1.9450	1.9847	*d*
$VOCl_2 \cdot 2tmu$	0.01749[a]	0.00641[a]	1.941[b]	1.983[b]	*e*

[a] ±0.00006. [b] ±0.003. [c] J. M. Flowers, J. C. Hempel, W. E. Hatfield, and H. H. Dearman, *J. Chem. Phys.*, 58, 1479 (1973). [d] K. DeArmond, B. B. Garrett, and H. S. Gutowsky, *ibid.*, 42, 1019 (1965). [e] Present work.

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Registry No. $VOCl_2 \cdot 2TMU$, 51017-59-5.

Supplementary Material Available. Table I, final values of Coulomb integrals, H_{ii}, and orbital exponents used (for $VO(tmu)_2Cl_2$), Table II, tmu calculated charge distributions and MO energy levels, and Table III, calculated energy levels and MO coefficients for $VOCl_2$ and $VOCl_4^{2-}$, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy of $2.00 for microfiche, referring to code number INORG-74-1090.

(35) J. M. Flowers, J. C. Hempel, W. E. Hatfield, and H. H. Dearman, *J. Chem. Phys.*, 58, 1479 (1973).

(36) K. DeArmond, B. B. Garrett, and H. S. Gutowsky, *J. Chem. Phys.*, 42, 1019 (1965).