

and/or  $K_2[Rh(C_2O_4)_2(H_2O)(Cl)]$ . For the anions of the latter complex salts one would expect spectral shifts toward longer wavelengths relative to the corresponding isomers of  $Rh(C_2O_4)_2(H_2O)_2^-$ .

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### Covalency in Cesium Vanadyl Chloride Monohydrate as Measured by Nuclear Quadrupole Resonance Spectroscopy

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Oxyhalides of transition elements, of the type  $MO^{n+}$  where  $M^{(n+2)+}$  is  $Cr^{5+}$ ,  $W^{5+}$ , or  $V^{4+}$ , containing a  $d^1$  configuration, have been of much recent interest. The relatively simple optical and magnetic properties which arise from a single unpaired electron have made these systems particularly appealing for electron spin resonance studies. The halide complexes of these ions have been studied and it is well established that there is substantial  $\pi$  bonding between the metal and oxygen atoms.<sup>1-5</sup> Such studies have also shown that in chloride systems there is delocalization of unpaired spin density into the ligand chloride  $\sigma$  and  $\pi$  atomic orbitals. This can be confirmed in favorable cases where chlorine hyperfine splittings have given similar results for spin densities.<sup>1</sup> Nuclear quadrupole resonance data, as interpreted in terms of p-electron covalency, have also been used in evaluating metal-halogen covalency.<sup>6</sup> The similarity in the relationship of the spectroscopic observables in esr and nqr spectra<sup>7</sup> to electron orbital population prompts a comparison of the data obtained for complexes which have been studied by both methods.<sup>8</sup>

#### Theoretical Section

The bonding and molecular orbitals of interest in oxyhalide systems have been discussed in detail by various authors.<sup>1-5</sup> In a complex with  $C_{4v}$  symmetry where  $\pi$  bonding between the metal and ligand is considered, the molecular orbitals are antibonding in character and of the forms

(1) L. A. Dalton, R. D. Bereman, and C. H. Brubaker, Jr., *Inorg. Chem.*, **8**, 2477 (1969).

(2) (a) P. T. Monoharan and M. T. Rogers, *J. Chem. Phys.*, **49**, 3912 (1968); (b) P. T. Monoharan and M. T. Rogers, *ibid.*, **49**, 5519 (1968).

(3) H. Kon and N. Sharpless, *J. Phys. Chem.*, **70**, 105 (1966).

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

(5) B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).

(6) T. L. Brown, W. G. McDugle, and L. G. Kent, *J. Amer. Chem. Soc.*, **92**, 3645 (1970), and references therein.

(7) R. Bersohn and R. G. Shulman, *J. Chem. Phys.*, **45**, 2298 (1966).

(8) This correlation check is not possible for a  $d^1$  complex with pure  $O_h$  symmetry since data are not available for such systems.

$$|B_2\rangle^* = N_{\pi_2}(d_{xy} - \lambda_{\pi_2}\phi^L_{\pi_2}) \quad (1)$$

$$|B_1\rangle^* = N_{\sigma_2}(d_{x^2-y^2} - \lambda_{\sigma_2}\phi^L_{\sigma_2}) \quad (2)$$

$$|E\rangle^* = N_{\pi_1}((d_{xz} \text{ or } d_{yz}) - \lambda^e_{\pi_1}\phi^e_{\pi_1} - \lambda^a_{\pi_1}\phi^a_{\pi_1}) \quad (3)$$

where

$$\phi^L_{\pi_2} = 1/2(p_x(1) + p_y(2) + p_y(3) + p_x(4)) \quad (4)$$

$$\phi^L_{\sigma_2} = 1/2(\sigma(1) + \sigma(2) + \sigma(3) + \sigma(4)) \quad (5)$$

$$\phi^e_{\pi_1} = (1/\sqrt{2})(p_y(1) + p_x(3)) \quad (6)$$

$$\sigma^a_{\pi_1} = (1/\sqrt{2})(-p_x(5) + p_y(6)) \quad (7)$$

and  $\lambda^e_{\pi_1}$  and  $\lambda^a_{\pi_1}$  are the  $|E\rangle^*$  molecular orbital coefficients for the equatorial and axial ligands, respectively. The ligand orbitals of the chlorine and oxygen involved in  $\pi$  bonds are pure p orbitals while the  $\sigma$  ligand orbitals are usually taken as  $sp_z$  hybrids. However, as noted by Bersohn and Shulman,<sup>7</sup>  $sp$  hybridization is not necessary to explain the observed results for the quadrupole coupling constants for I and Cl in ICl. For the discussion here, therefore, the  $\sigma$  orbitals on the halogens will be taken as pure  $p_z$  in character.

If we follow the convention of Townes and Dailey<sup>9</sup> that the p-orbital electron contribution to the quadrupole interaction dominates, then the quadrupole coupling constant for the chloride,  $eQq_{\text{mol}}$ , can be related to the quadrupole coupling constant for the free halogen atom,  $|eQq|_{\text{atomic}}$ ,<sup>6</sup> as in

$$|eQq|_{\text{mol}} = U_p |eQq|_{\text{atomic}} \quad (8)$$

where

$$U_p = 1/2[N_{p_x} + N_{p_y}] - N_{p_z} \quad (9)$$

and the  $N$ 's refer to the electron populations in the chlorine 3p orbitals. The  $p_z$  orbital is directed along the bond axis; the  $p_x$  and  $p_y$  orbitals are normal to it. Thus,  $U_p$  is a measure of the *difference* in p-orbital population. The orbital populations can be expressed as

$$N_{p_x} = 2 - \pi_x \quad (10)$$

$$N_{p_y} = 2 - \pi_y \quad (11)$$

$$N_{p_z} = 2 - \sigma_z \quad (12)$$

For the equatorial halides in a paramagnetic complex with  $C_{4v}$  symmetry, the terms  $\sigma_z$ ,  $\pi_x$ , and  $\pi_y$  can be related directly to the unpaired spin density in each ligand p orbital. Thus, making use of Mulliken's population analysis<sup>10</sup>

$$\sigma_z \equiv \frac{N_{\sigma_2}^2 \lambda_{\sigma_2}^2 - N_{\sigma_2}^2 \lambda_{\sigma_2} S_{b_2}}{4} \quad (13)$$

$$\pi_x \equiv \frac{N_{\pi_2}^2 \lambda_{\pi_2}^2 - N_{\pi_2}^2 \lambda_{\pi_2} S_{b_2}}{4} \quad (14)$$

$$\pi_y \equiv \frac{N_{\pi_1}^2 \lambda_{\pi_1}^2 - N_{\pi_1}^2 \lambda_{\pi_1} S_e}{4} \quad (15)$$

where  $S_{b_2}$ ,  $S_{b_1}$ , and  $S_e$  are the group overlap terms for the respective molecular orbitals. Following the method of Bersohn and Shulman,  $U_p$  may then be evaluated as

(9) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

(10) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

$$U_p = \frac{|eQq|_{\text{mol}}}{|eQq|_{\text{atomic}}} = \frac{\eta_{\sigma}(N_{\sigma_2}^2\lambda_{\sigma_2}^2 - N_{\sigma_2}\lambda_{\sigma_2}S_{b_1})}{4} - \frac{\eta_{\pi_x}(N_{\pi_2}^2\lambda_{\pi_2}^2 - N_{\pi_2}\lambda_{\pi_2}S_{b_2})}{4} - \frac{\eta_{\pi_y}(N_{\pi_1}^2\lambda_{\pi_1}^2 - N_{\pi_1}^2 - N_{\pi_1}\lambda_{\pi_1}S_e)}{4}$$

where  $\eta_{\sigma}$ ,  $\eta_{\pi_x}$ , and  $\eta_{\pi_y}$  are the numbers of holes in the metal d orbitals with the appropriate symmetry (and would be 2, 1, and 2, respectively, here).

For paramagnetic complexes with  $C_{4v}$  symmetry, the experimental electron spin resonance parameters can be related to the molecular orbital coefficients by<sup>11</sup>

$$g_{||} - 2.0023 = \frac{-8\zeta N_{\pi_2}^2 N_{\sigma_2}^2}{\Delta(b_2 - b_1)} \times [1 - \frac{1}{2}(\lambda_{\pi_2}\lambda_{\sigma_2})T(n) - 2\lambda_{\sigma_2}S_{b_1} - 2\lambda_{\pi_2}S_{b_2}] \quad (16)$$

$$g_{\perp} - 2.0023 = \frac{-2\zeta N_{\pi_2}^2 N_{\pi_1}^2}{\Delta(b_2 - e)} [1 - (1/\sqrt{2})(\lambda_{\pi_1}\lambda_{\pi_2}) - 2\lambda_{\pi_2}S_{b_2} - \sqrt{2}\lambda_{\pi_1}^e S_{b_2} - \lambda_{\pi_1}^a S_e] \quad (17)$$

$$A_{||} - \langle a \rangle = \frac{4N_{\pi_2}^2 P}{7} - \frac{8\zeta N_{\pi_2}^2 N_{\sigma_2}^2 P}{\Delta(b_2 - b_1)} - \frac{6\zeta N_{\pi_2}^2 N_{\pi_1}^2 P}{7\Delta(b_2 - e)} \quad (18)$$

where  $\Delta(b_2 - b_1)$  and  $\Delta(b_2 - e)$  are the experimental optical transitions between the ground state  $|B_2\rangle^*$  molecular orbital and the higher energy  $|B_1\rangle^*$  and  $|E\rangle^*$  molecular orbitals, respectively.  $\zeta$  is the spin-orbit coupling constant and  $P = 2.0023g_N\beta_e\beta_N\langle r^{-3} \rangle_{av}$ , where  $\beta_e$  and  $\beta_N$  are the Bohr and nuclear magnetons, respectively, and  $g_N$  is the nuclear  $g$  factor.  $S_{b_1}$ ,  $S_{b_2}$ , and  $S_e$  are the metal-ligand overlap integrals.  $T(n)$  is defined by Kivelson and Lee<sup>12</sup> as

$$T(n) = n - (1/3)^{1/2}(1 - n^2)^{1/2}R \times \int_0^{\infty} r^2 R_{31}(r) \frac{d}{dr} [R_{30}(r)] dr \quad (19)$$

where  $R$  is the vanadium-ligand distance and  $R_{31}(r)$  and  $R_{30}(r)$  are the normalized radial 3p and 3s functions, respectively.  $N_{\pi_2}$  and  $\lambda_{\pi_2}$  are related by the normalization requirement

$$N_{\pi_2}^2 = [1 + \lambda_{\pi_2}^2]^{-1}$$

#### Experimental Section

**Preparation of  $Cs_2VOCl_4 \cdot H_2O$ .**—Both cesium chloride (18 g) and 6 ml of vanadium tetrachloride (Research Organic-Inorganic Chemical Corp.) were dissolved in a minimal amount of concentrated hydrochloric acid and these solutions were mixed and cooled while saturating the mixture with HCl gas. The precipitate was filtered and dried under vacuum. *Anal.* Calcd for  $Cs_2VOCl_4 \cdot H_2O$ : Cl, 28.79; V, 10.36. Found: Cl, 28.58; V, 10.36.

**Preparation of  $Cs_2MoOCl_5$ .**—Both cesium chloride and a stoichiometric amount of molybdenum pentachloride (Research Organic-Inorganic Chemical Corp.) were dissolved in a minimal amount of concentrated hydrochloric acid and these solutions were mixed and cooled. The precipitate was washed with concentrated hydrochloric acid and ethyl ether and dried under vacuum. *Anal.* Calcd for  $Cs_2MoOCl_5$ : Cl, 31.94. Found: Cl, 31.64.

**Preparation of  $Cs_2CrOCl_5$ .**—Chromium trioxide in anhydrous

acetic acid saturated with hydrogen chloride and cesium chloride in hydrochloric acid were mixed and cooled. The precipitate was washed with anhydrous acetic acid saturated with hydrogen chloride and dried under vacuum. *Anal.* Calcd for  $Cs_2CrOCl_5$ : Cl, 34.68. Found: Cl, 34.03, 33.84.

**Nqr Spectra.**—The nuclear quadrupole resonance spectra were obtained with a Wilkes Scientific NQR-1A spectrometer. Frequency measurements were made with the use of a Drake Model R-4A receiver fitted with a frequency converter which permitted continuous tuning of the receiver over a wide range of frequencies by selection of a suitable crystal. The receiver was equipped with a 100-kHz calibrator and the dial was scribed in units of kilohertz. Using this arrangement, it was possible to place calibration markers on the recorder chart paper with an event marker at convenient intervals.

**Temperature Control.**—Variable-temperature measurements were carried out using a dual-pass cold cell, which provides for passage of nitrogen (obtained either from boiling off liquid nitrogen or by heating a stream of nitrogen) over the sample. Temperatures were monitored with a thermocouple fastened to the sample vial and 1 hr was allowed for the sample to reach an equilibrium temperature.

#### Results and Discussion

Two  $^{35}Cl$  resonances of approximately equal intensity and the corresponding  $^{37}Cl$  resonances were obtained for  $Cs_2VOCl_4 \cdot H_2O$ . This agrees with a recent crystal structure of the same salt by Atovmyan and Aliov<sup>13</sup> where two sets of equivalent chlorines were found giving the ion  $C_{2v}$  symmetry. A phase transition must occur between  $-103$  and  $-130^\circ$  since each resonance splits into a pair at the lower temperature. Table I lists the

TABLE I  
NQR FREQUENCIES FOR  $Cs_2VOCl_4 \cdot H_2O$

Temp, °C	NQR Frequencies (kHz)		Temp, °C	NQR Frequencies (kHz)	
-130	9.640, 9.700	10.090, 10.130	-4	9.603	10.004
-103	9.635	10.100	+33	9.586	9.987
-73	9.620	10.050	+68	9.568	9.925
-25	9.610	10.021			

experimentally determined frequencies at the various temperatures. The temperature dependence of the resonance ( $\partial\nu/\partial t$ ) is approximately the same for each line and equal to 0.30 kHz/deg.

The electron paramagnetic resonance parameters for  $VOCl_4 \cdot H_2O^{2-}$ , determined by Kon and Sharpless<sup>3</sup> from a solution study, are given in Table II. The

TABLE II  
ESR PARAMETERS FOR  $VOCl_4 \cdot H_2O^{2-}$

$g_{  }$	= 1.944	$A_{  }^a$	= 172.9
$g_{\perp}$	= 1.979	$A_{\perp}^a$	= 66.2
$\langle g \rangle$	= 1.969	$\langle a \rangle^a$	= 101.4

<sup>a</sup> Hyperfine splittings are given in  $10^{-4} \text{ cm}^{-1}$ .

other parameters needed to evaluate eq 13-18 are given in Table III.<sup>4,5,14,15</sup> The molecular orbital coefficients obtained by an iterative treatment of eq

TABLE III  
QUANTITIES USED IN CALCULATING BONDING COEFFICIENTS

Quantity	Value	Quantity	Value
$\Delta(b_2 - b_1)^a, \text{ cm}^{-1}$	12,000	$S_e^b$	0.139
$\Delta(b_2 - e)^a, \text{ cm}^{-1}$	13,800	$\zeta^c, \text{ cm}^{-1}$	170
$S_{b_2}^b$	0.099	$P^d, \text{ cm}^{-1}$	$128 \times 10^{-4}$
$S_{b_1}^b$	0.165	$T(n)^e$	0.25

<sup>a</sup> Reference 14. <sup>b</sup> Those values calculated for  $VOCl_5^{3-}$  in ref 4 were used. <sup>c</sup> Reference 15. <sup>d</sup> Reference 5.

(11) H. A. Kuska and M. T. Rogers, "Radical Ions," E. T. Kaiser and L. Devans, Ed., Interscience, New York, N. Y., 1968, Chapter 13.  
(12) D. Kivelson and S. Lee, *J. Chem. Phys.*, **41**, 1896 (1964).

(13) L. O. Atovmyan and Z. G. Aliov, *Zh. Strukt. Khim.*, **11**, 728 (1970).  
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13–18 for the  $\text{VOCl}_4 \cdot \text{H}_2\text{O}^{2-}$  ion are  $N_{\pi_2^2} = 0.981$ ,  $N_{\sigma_2^2} = 0.582$ , and  $N_{\pi_1^2} = 0.988$ . The calculations were carried out with aid of a desk calculator.

$U_p$  is evaluated as 0.177 from the nqr data at 33° using an average of the two frequencies. The MO parameters based on esr data give a value of 0.167.

This treatment could allow the estimation of the nqr frequencies for the equatorial chlorines in other oxyhalides for which molecular orbital parameters are available. Table IV lists the parameters for the Mo-

	$\text{MoOCl}_5^{2-}$ <sup>a</sup>	$\text{CrOCl}_5^{2-}$ <sup>b</sup>		$\text{MoOCl}_5^{2-}$ <sup>a</sup>	$\text{CrOCl}_5^{2-}$ <sup>b</sup>
$N_{\pi_2^2}$	0.905	0.886	$S_{b_2}$	0.12	0.12
$N_{\sigma_2^2}$	0.754	0.592	$S_{b_1}$	0.12	0.16
$N_{\pi_1^2}$	0.901	0.958	$S_e$	0.20	0.20

<sup>a</sup> Reference 2a. <sup>b</sup> Reference 1.

$\text{OCl}_5^{2-}$  and  $\text{CrOCl}_5^{2-}$  ions. These lead to predicted <sup>35</sup>Cl resonance frequencies of 3.20 and 8.91 MHz, respectively. Extensive searching between 2 and 15 MHz at room temperature and -140° has been unsuccessful to date in locating the resonances for the cesium salts of both ions.

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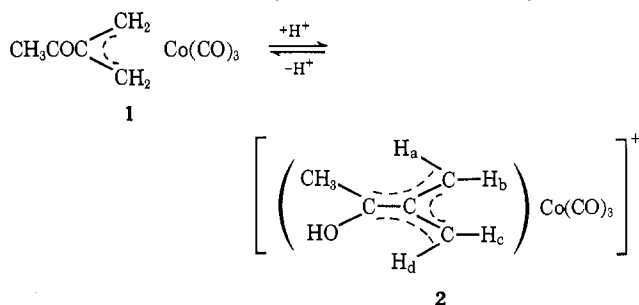
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## 1-Methyl-1-hydroxy(trimethylenemethane)-cobalt Tricarbonyl Cation and Its Derivatives

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Metal complexes of trimethylenemethane, an interesting  $4\pi$ -electron system, have been limited mainly to iron carbonyl derivatives.<sup>1–6</sup> We found protonation of 2-acetyl- $\pi$ -allylcobalt tricarbonyl (1) leads to a novel, cationic trimethylenemethanecobalt system (2).



(1) G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **88**, 3172 (1966).

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(6) R. Pettit and J. S. Ward, *ibid.*, 1419 (1970).

2-Acetyl- $\pi$ -allylcobalt tricarbonyl [<sup>1</sup>H nmr in  $\text{C}_6\text{H}_6$ :  $\delta$  1.76 (2 H), 1.89 (3 H), and 3.41 (2 H) ppm] was dissolved in concentrated sulfuric acid with a drastic change in its nmr spectrum giving rise to well-defined signals which are best interpreted in terms of the expected 1-methyl-1-hydroxytrimethylenemethane complex (2). Thus, two broad doublets at  $\delta$  3.72 and 2.85<sup>7</sup> ppm ( $J = 3$  Hz) are assigned<sup>8</sup> to two nonequivalent mutually coupled protons,  $\text{H}_a$  and  $\text{H}_d$ , and two singlets at  $\delta$  2.81 and 2.53 are assigned to  $\text{H}_b$  and  $\text{H}_c$  protons. The highest field signal (sharp singlet, 3 H,  $\delta$  1.75 ppm) is then ascribed to  $\text{CH}_3$  protons. Upon dilution with a small amount of water, only three singlets appeared at  $\delta$  2.60, 1.85, and 1.75 ppm (each with half-height width of 8 Hz). The singlet at  $\delta$  2.60 is apparently due to an averaging between protons,  $\text{H}_a$  and  $\text{H}_d$ , and also the singlet at  $\delta$  1.85 to that between  $\text{H}_b$  and  $\text{H}_c$ . The averaging appears to be accounted for in terms of a rapid equilibrium between the protonated and the deprotonated species. Recovery of the starting material on dilution with a large amount of water indicated deprotonation without skeletal change. Further evidence of the protonation was obtained by the comparison of the electronic spectra of 2-acetyl- $\pi$ -allylcobalt tricarbonyl and its derivatives in ethanol and in concentrated sulfuric acid.

The result is shown in Table I for positions of ab-

TABLE I  
COMPARISON OF ELECTRONIC SPECTRA FOR  $\text{CH}_3\text{COC}(\text{CH}_2)_3\text{Co}(\text{CO})_2\text{L}$

	Absorption max, nm	
	In ethanol ( $\epsilon$ )	In concd sulfuric acid
CO	353 ( $3.34 \times 10^3$ ) 305 sh	307 380 sh
PPh <sub>3</sub>	379 ( $2.45 \times 10^3$ ) 305 sh	300 sh
<i>tert</i> -BuNC	377 ( $4.18 \times 10^3$ ) 298	365 sh

sorption maxima only. Blue shift occurred with decrease in intensity when protonated with concentrated sulfuric acid. The formation of a positively charged species 2 was also confirmed by the ir CO stretching pattern in concentrated sulfuric acid. Thus, the solution placed between thin polyethylene films showed two strong bands at 2125 and 2084  $\text{cm}^{-1}$ . The high-frequency shift from the unprotonated complex (*cf.*  $\nu_{\text{C=O}}$  at 2045 and 1983  $\text{cm}^{-1}$ ) is consistent with the formation of a cationic complex 2. The ketonic carbonyl region was covered with heavy absorption of sulfuric acid to inhibit a reliable conclusion. Attempts to isolate the protonated species 2 (a) by addition of concentrated aqueous  $\text{NaBF}_4$  into a sulfuric acid solution of 1 or (b) by introduction of dry hydrogen chloride into a hexane solution of 1 have failed. Also attempts to alkylate 1 with trimethyloxonium<sup>9</sup> or triphenylmethyl tetrafluoroborate have been fruitless. It is worth noting that the ketone carbonyl frequencies of unprotonated 1 (1669  $\text{cm}^{-1}$ ) and of the benzoyl derivative (1650  $\text{cm}^{-1}$ ) rule out any significant bonding between cobalt and the carbonyl carbon before protonation.

(7) This peak is partly overlapped with the  $\delta$  2.81 singlet.

(8) The assignment may be exchanged. The long-range coupling via a W-shaped route has been observed in (trimethylenemethane)iron complexes.<sup>3,4</sup>

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