and Gholami[5] as log $K_{DO}^{Cr} = -4.4$ at 25 °C ($I = 3.0$M) (see eq 1).

$$\mathrm{Cr_2(OAc)_4(aq)} \overset{K_{DO}^{Cr}}{\rightleftharpoons} \mathrm{2Cr(OAc)_2(aq)} \tag{1}$$

Gerding[6] has studied copper(II) acetate equilibria with variation of copper concentration and found no change in the formation numbers over the range $[\mathrm{Cu}]_T = 0.02$–0.08 M. From a consideration of the precision of the experiments, we have calculated a lower limit log $K_{DO}^{Cu} \geq 0.2$ at 25 °C ($I = 3.0$ M) (see eq 2). Actual values of K_{DO}^{Cu} can be estimated

$$\mathrm{Cu_2(OAc)_4(aq)} \overset{K_{DO}^{Cu}}{\rightleftharpoons} \mathrm{2Cu(OAc)_2(aq)} \tag{2}$$

roughly by two independent methods. The solubility of copper(II) acetate hydrate in water is 0.38 M at 25 °C.[7] Estimating concentrations of monomer complexes in the saturated solution, with appropriate stability constants,[8] we obtain log $K_{SD}^{Cu} = -1.4$ (see eq 3).

$$\mathrm{Cu_2(OAc)_4(OH_2)_2(s)} \overset{K_{SD}^{Cu}}{\rightleftharpoons} \mathrm{2Cu(OAc)_2(aq)} \tag{3}$$

Chromium(II) acetate is much less soluble,[5] and in view of the structural similarity of the two solids,[1,2] it seems reasonable to assume that, in the absence of the dissociation reaction (2), the copper complex would have had the same solubility, i.e., that log $K_{SO}^{Cu} = -2.7$ (see eq 4). Combining eq 3 and 4 then

$$\mathrm{Cu_2(OAc)_4(OH_2)_2(s)} \overset{K_{SO}^{Cu}}{\rightleftharpoons} \mathrm{Cu_2(OAc)_4(aq)} \tag{4}$$

gives log $K_{DO}^{Cu} = 1.3$.

In acetic acid–water media, equilibrium 5 has been directly

$$\mathrm{Cu_2(OAc)_4 + 4H_2O} \overset{K_D'}{\rightleftharpoons} \mathrm{2Cu(OAc)_2(OH_2)_2} \tag{5}$$

observed,[10] with log $K_D' = -5.0$ at 25 °C. The experimental data cover the range $[\mathrm{H_2O}] = 0$–10 M only, but on extrapolating to aqueous solution by substituting $[\mathrm{H_2O}] = 55.5$ M, we obtain log $K_{DO}^{Cu} = 2.0$. Thus both estimates are consistent with the lower limit given above, though the agreement between them must be fortuitous.

The greater stability of the chromium complex must be due to a stronger metal–metal bond. Metal–oxygen bonding is important in both complexes but is expected to act in the opposite sense, since complexes of copper(II) are characteristically more stable than those of chromium(II). This effect can be roughly quantified by noting that the dimers $\mathrm{M_2(OAc)_4}$ contain eight cation–anion "half-bonds", while the monomers $\mathrm{M(OAc)_2}$ contain two full bonds. Taking the gross stability constants log $\beta_2^{Cr} = 1.9$[5] and log $\beta_2^{Cu} = 2.7$[6] suggests that metal–oxygen bonding destabilizes the chromium(II) dimer relative to the copper(II) dimer by about 2(2.7 − 1.9) = 1.6 units in the logarithm of the equilibrium constant. Hence the true difference between the Cr–Cr and Cu–Cu bonds is of the order of 4.4 + 2.0 + 1.6 = 8.0 units.

For the copper dimer, magnetic[11-13] and spectroscopic[14,15] data are generally interpreted in terms of a very weak Cu–Cu interaction, a δ bond formed by overlap of the metal $d_{x^2-y^2}$ orbitals. For the chromium dimer, the interaction is accepted to be stronger and more complex. It is usually described as a quadruple bond, with one σ, two π, and one δ component,[11,16] though admittedly[17] not so strong as the interaction in the isoelectronic Mo–Mo[3] and Mo–Cr[4] compounds. What the present calculations show is that, in spite of a difference of three units in bond order, the Cr–Cr bond in the acetate system is stronger than the Cu–Cu bond by only about 45 kJ mol^{-1}.

Registry No. $\mathrm{Cr_2(OAc)_4}$, 15020-15-2; $\mathrm{Cu_2(OAc)_4}$, 23686-23-9.

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Microwave Spectrum, Dipole Moment, and Conformation of Vinyldifluorophosphine

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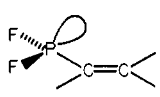
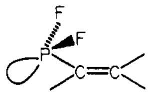
The synthesis of vinyldifluorophosphine ($\mathrm{PF_2C_2H_3}$) was reported by Centofanti and Lines.[1] A molecular symmetry of C_s would be expected for it since this is often found in $\mathrm{PF_2}$ derivatives such as $\mathrm{PF_2NH_2}$[2] and $\mathrm{PF_2OCH_3}$.[3] It is more difficult to anticipate whether the predominant conformer is I or II. We report the assignment of the microwave spectrum and find that the rotational constants are consistent with I.



I



II

Experimental Section

Sample. The compound was prepared according to the literature synthesis.[1] It was difficult to handle the starting material $\mathrm{Hg(C_2H_3)_2}$ and to avoid its vile odor during transfer and clean up. Consequently, enriched syntheses were not attempted.

Spectrometers. A conventional 80-kHz Stark modulated spectrometer with klystron sources and a Hewlett-Packard 8460A spectrometer system[4] were employed to record the spectra at −78 °C. Transition frequencies are believed to be accurate to ±0.1 MHz.

Spectra. A μ_a-type spectrum was observed with clustering of transitions at intervals of about 5 GHz. The regions between these intervals were generally sparse. A clear set of 2 or 3 vibrational satellite lines were observed on the high-frequency side of each strong ground-state line. The assignment of transitions was based on their Stark effects and the frequency fit. Only μ_a transitions could be found indicating that μ_b and μ_c were very small.

Several of the assigned transitions and the rigid rotor rotational constants derived from them are listed in Table I. A complete list of observed transitions for the ground state and first three vibrational states is given in Tables S1 and S2 (available as supplementary material). The complete set of frequencies was fit with use of a first-order centrifugal distortion analysis program, provided by Thomas.[5] The effective semirigid rotor constants derived from this set (Table S3, available as supplementary material) differed from

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Table I. Transitions and Rotational Constants for $PF_2C_2H_3$[a]

transition	ν(obsd), MHz	$\Delta\nu$, MHz[b]	transition	ν(obsd), MHz	$\Delta\nu$, MHz
3_{13}–4_{14}	20 905.99	−0.05	5_{15}–6_{16}	31 162.40	−0.05
3_{03}–4_{04}	21 613.91	0.24	5_{05}–6_{06}	31 695.21	0.11
3_{12}–4_{13}	23 106.43	0.18	5_{14}–6_{15}	34 323.77	−0.07
4_{14}–5_{15}	26 053.57	0.04	6_{06}–7_{07}	36 625.43	−0.06
4_{04}–5_{05}	26 708.71	0.18	6_{16}–7_{17}	36 235.64	−0.15
4_{13}–5_{14}	28 763.08	0.02	6_{15}–7_{16}	39 757.63	−0.20

[a] $A = 7158.3$ (10) MHz, $B = 3041.28$ (2) MHz, $C = 2486.57$ (1).
[b] $\Delta\nu = \nu(\text{obsd}) - \nu(\text{calcd, rigid rotor assumption})$.

the values in Table I by less than the estimated uncertainties.

The vibrational satellites appeared to be successively higher excited states of a single vibrational mode. Relative intensity measurements of the $v = 0$, $v = 1$, and $v = 2$ states gave a vibrational energy level spacing of 110 ± 30 cm^{-1}. The low-lying mode is probably the A'' torsion about the P–C bond.[2,6]

Dipole Moment. Second-order Stark coefficients (frequency shift vs. electric field) were measured for five transitions. They are given in Table S4 (available as supplementary material). These were used to determine the values of μ_a, μ_b, and μ_c by the standard procedure.[7] Four possible combinations of nonzero dipole components were tried in the analysis. Fits assuming $(\mu_a,\mu_c) \neq 0$ or $(\mu_a,\mu_b,\mu_c) \neq 0$ gave somewhat better agreement to the observed Stark coefficients than fits assuming $(\mu_a) \neq 0$ or $(\mu_a,\mu_b) \neq 0$. All four fits indicated that $|\mu_a| = 2.42$ D while $|\mu_b|$ and $|\mu_c|$ were estimated to be ≤ 0.090 D. In essence, these latter components were too small to be reliably estimated from the data. If μ_b is set to zero as required by symmetry for I or II, the result was $|\mu_a| = 2.42$ (3) D, $|\mu_c| = 0.08$ (5) D, and a total molecular dipole moment of 2.42 (3) D. This interpretation is preferred for reasons given below.

Analysis and Discussion

The presence of a plane of symmetry containing the phosphorus and vinyl group is indicated from several considerations. (1) Since $I_a + I_b - I_c = 33.53$ $\mu\text{Å}^2$, totally planar configurations are ruled out. Moreover, $I_a + I_c - I_b = 2\sum m_i b_i^2 = 53.832$ $\mu\text{Å}^2$ is similar to that in other PF_2X species such as PF_2H (54.99 $\mu\text{Å}^2$)[8] and PF_2CN (54.00 $\mu\text{Å}^2$).[6] This indicates that only the out of plane F···F interatomic distance contributes to $I_a + I_c - I_b$. (2) The observed values of μ_b and $\mu_c \simeq 0$ make some low-symmetry forms unlikely such as a conformation with C_1 symmetry which occurs in going from I to II by rotating the vinyl group about the P–C bond. As the vinyl moiety is rotated, one or both of these components must become sizeable due to the reorientation of the principal axes, even if the vinyl fragment has a low group moment. On the other hand, rough estimates of the components from assumed bond dipoles for a C_s conformation predict $\mu_a > \mu_c$ and $\mu_b = 0$ for either I or II. (3) The moments of inertia agree reasonably well with calculated values for I with assumption of plausible internal parameters. Conformer II and C_1 conformations do not appear to fit these moments unless unreasonable values for the internal coordinates are assumed.

Inspection of the preliminary moments of inertia which were predicted for I or II from an initial set of assumed internal parameters illustrates the basis for the assignment of the observed spectra to I. This model[9] predicted rotational constants of 6250, 3510, and 3020 MHz for II and 7300, 3010, and 2484 MHz for I. The discrepancies from the observed values of 13–18% for II cannot readily be corrected without some large and implausible changes in the initial structural parameters. However, it is a straightforward procedure to modestly alter these preliminary parameters and arrive at a reasonable structure for conformer I which agrees with the experimental moments of inertia. Such a structure will not be unique since only three equations are available which are functions of the 12 internal structural parameters. One solution has values for the vinyl moiety similar to other monosubstituted alkenes[10] and is consistent with the following parameters involving the PF_2 moiety: $d(\text{PF}) = 1.577$ Å, $d(\text{PC}) = 1.805$ Å, $\angle\text{FPF} = 97.9°$, $\angle\text{FPC} = 98.0°$, $\angle\text{PCC} = 120.5°$.[11] There is good reason to believe from comparison with other species that the true structure is within 0.02 Å and 3° of these values. For example, $d(\text{PF})$ and $\angle\text{FPF}$ are usually between 1.567–1.591 Å and 95–99° in PF_2–R compounds.[6] This range of PF_2 parameters would be consistent with a range for $d(\text{PC})$ between 1.78–1.82 Å. This is somewhat shorter than in $P(CH_3)_3$ (1.843 (3) Å),[13] but it is similar to the value in PF_2CN (1.815 (5) Å)[6] and the estimated value for PF_2CH_3 (1.82 (2) Å).[3]

The possibility of II being present in low concentrations in the gas phase cannot be completely eliminated. Its spectrum, if present at all, is certainly less intense. This lower intensity would imply that II is higher in energy since its spectrum should be comparable in intensity to I apart from this Boltzmann factor.

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Registry No. $PF_2C_2H_3$, 51130-03-1.

Supplementary Material Available: Table S1, complete set of assigned frequencies for the ground state, Table S2, assigned frequencies for excited vibrational states, Table S3, rotational constants for the ground and excited states, and Table S4, Stark coefficients (6 pages). Ordering information is given on any current masthead page.

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(10) This model consists of $d(\text{CH}) = 1.078$ Å, $d(\text{CC}) = 1.337$ Å, $\angle\text{CCH}_t = 119.8°$, $\angle\text{CCH}_c = 122.0°$, and $\angle\text{CCH}_g = 121.6°$, where H_t, H_c, and H_g refer to cis, trans, or geminal to the phosphorus.

(11) Values close to these (within 0.006 Å and 0.6°) were also obtained by a fitting procedure called the method of predicate observables. In this procedure, the rotational constants and plausible structural parameters (with an uncertainty range) are treated as weighted data points to be fit by least squares. The details are described elsewhere.[7,12]

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Oxidative Cleavage of Ditartrate-Bridged Binuclear Chromium(III) Complexes. A Stereochemical Correlation

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Gillard and Price have reported the oxidative cleavage by permanganate of vicinal diols in bridging tartrate groups in two diastereomers of the monotartrate-bridged complex μ-(d-tartrato(4−))-tetrakis(ethylenediamine)dicobalt(III), $[Co_2(tart)(en)_4]^{2+}$, to give (oxalato)bis(ethylenediamine)cobalt(III), $[Co(en)_2(ox)]^+$, enriched in one or the other enantiomer.[1] We report here a similar stereochemical correlation for the dibridged tartrate complexes of chromium(III) $[H_2Cr_2(tart)_2L_2]$ and $[HCr_2(tart)_2L_2]^-$ (L = 2,2′-bipyridyl or 1,10-phenanthroline) (**1**). Unlike the monobridged cobalt

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