doped in the cubic lattice $(NH_4)_2SnBr_6$ at several temperatures between 300 and 10°K. Note first that the strongest band in solution (14,500 cm^{-1}) is in fact the weakest in the 300°K crystal spectrum indicating a substantial contribution to the observed intensity from solvent perturbations. As the temperature is lowered, this band undergoes a striking reduction in intensity while the ϵ_{max} of the other two bands (13,000 and 13,600 cm^{-1}) increases markedly. Gaussian fitting and numerical integration of the data indicates that the oscillator strength of the 14,500-cm^{-1} band in the crystal is reduced by a factor of ~5.5 while the sum of the oscillator strengths of the 13,000- and 13,600-cm^{-1} bands actually shows a monotonic increase[9] of ~40–50% upon cooling to 10°K.

Using intensity data at 300, 210, 166, 143, 130, 79, and 10°K for the 14,500-cm^{-1} band assuming a single activating vibration, one obtains a quite reasonable fit of eq 1 with $\nu \sim 80$ cm^{-1}. Only the two t_{1u} fundamentals of $IrBr_6^{2-}$ appear to have been reported[10] ($\nu_3 \sim 230$ cm^{-1}, ν_4 82 cm^{-1}), but in analogy with $ReBr_6^{2-}$,[11] $PtBr_6^{2-}$,[12] and WBr_6^{2-},[13] the t_{2g} (ν_5) and t_{2u} (ν_6) fundamentals probably also occur in this region as well as several lattice modes. Furthermore, there is no *a priori* reason for assuming a single activating frequency,[2] and we make no attempt here to decide which vibrations are involved.

The $(NH_4)_2SnBr_6$ lattice has the cubic K_2PtCl_6 structure at room temperature[14] with the Sn (and hence presumably the substituted Ir) at a site of O_h symmetry. It is known from the nuclear quadrupole resonance data[15] that this structure persists at least down to 201°K, but no quadrupole resonance signal at all was observed at liquid nitrogen temperature,[15] and it is known from heat capacity measurements[16] that there is a λ point at 145°K and some sort of phase transition covering a range of ~90°. However, our intensity data for the 14,500-cm^{-1} band vary smoothly with temperature through this region and there seems no doubt that we are observing the behavior characteristic of a vibronically allowed transition.

We have also studied the system K_2SnBr_6–Ir^{4+} where the K_2SnBr_6 lattice is a slight tetragonal modification of the K_2PtCl_6 structure.[17] The behavior of this same band system is very similar, the sum of the intensities of the two lower frequency components increasing by about 10% and the intensity of the vibronically allowed component decreasing by about a factor of 5 as the temperature is lowered to 11°K. We shall discuss the absorption and MCD spectra of the $IrBr_6^{2-}$ ion in detail at a later date.[18]

These experiments indicate that absorption bands in the intermediate intensity range must be approached with a considerable degree of caution. We have clearly demonstrated that a forbidden transition may have substantial oscillator strength at room temperature. Our example also shows that these bands of intermediate intensity may be allowed transitions, and we feel that it is very desirable to differentiate by experiment rather than to rely heavily on the agreement of band positions with a crystal field calculation. In addition, it should be emphasized that vibronically allowed bands can arise from forbidden charge-transfer transitions as well as from d → d transitions.

Finally, Table I emphasizes the sensitivity of eq 1 to the numerical value of the activating frequency. We see that a given vibronically allowed transition at room temperature may vary in intensity over a sizable range depending upon the frequency of the activating vibration (or vibrations). Thus for metals with heavy ligands (and hence low vibrational frequencies) it may be very difficult on the basis of room-temperature intensity measurements alone to distinguish forbidden vibronic transitions from fully allowed charge-transfer transitions, particularly in solution where solvent interactions may also enhance the intensity. In the example cited in this note, a band with $\epsilon_{max} \sim 3000$ in solution at room temperature has been shown rather conclusively to be due to a forbidden (vibronically allowed) transition.

TABLE I

RATIO OF ROOM-TEMPERATURE TO LOW-TEMPERATURE (0–10°K) OSCILLATOR STRENGTH AS A FUNCTION OF ACTIVATING FREQUENCY (ν)

ν, cm^{-1}	f(300°K)/f(0–10°K)	ν, cm^{-1}	f(300°K/f(0–10°K)
≥1250	1.00	200	2.24
700	1.07	100	4.25
500	1.20	80	5.28
300	1.62	40	10.5

Acknowledgments.—This work was supported by a grant from the National Science Foundation.

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(9) Similar behavior has been noted recently for several bands of $OsBr_6^{2-}$: B. D. Bird, P. Day, and E. A. Grant, *J. Chem. Soc., A*, 100 (1970). We shall argue elsewhere that the two strong bands (13,000 and 13,600 cm^{-1}) in $IrBr_6^{2-}$ are Jahn–Teller components of the first $E_g'' \rightarrow U_u'$ charge-transfer transition.

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New Chromyl Compounds

BY J. N. GERLACH AND G. L. GARD[1]

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New chromyl compounds, CrO_2X_2 (where X = CF_3CO_2, $ClCF_2CO_2$, and $CF_3CF_2CF_2CO_2$) have been

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prepared and characterized. When chromium trioxide and trifluoroacetic anhydride react at room temperature in the absence of light, chromyl trifluoroacetate is formed in yields greater than 90% according to

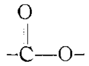
$$CrO_3 + (CF_3CO)_2O \longrightarrow CrO_2(CF_3COO)_2 \qquad (1)$$

Chromyl trifluoroacetate is a yellow-brown crystalline solid which is extremely hygroscopic and upon exposure to the atmosphere fumes, forming red chromium trioxide and presumably trifluoroacetic acid. In a large excess of water the reaction appears to be

$$CrO_2(CF_3COO)_2 + 2H_2O \longrightarrow H_2CrO_4 + 2CF_3COOH \qquad (2)$$

The trifluoroacetate is soluble in CCl_4, $ClCF_2CFCl_2$, and $(CF_3CO)_2O$.

The infrared spectrum of $CrO_2(CF_3COO)_2$ measured between NaCl windows (see Table I) showed the characteristic


$$-\overset{O}{\overset{\|}{C}}-O-$$

asymmetric stretch at 1690 cm^{-1}. Sharp, *et al.*,[2] have found this stretch occurring at 1660–1710 cm^{-1} in anhydrous metal trifluoroacetates.

TABLE I

INFRARED SPECTRA (CM^{-1})

$CrO_2(CF_3COO)_2$		$CrO_2(ClCF_2COO)_2$	
1690 s, b	960 s, b	1720 s	980 s, b
1400 m, b	855 w	1340 m	925 m
1180 vs, vb	790 m	1150 vs, vb	735 m
	730 m		

On the basis of the results of Sharp and coworkers,[2] the following absorption bands for $CrO_2(CF_3COO)_2$ at 1400, 1180, 855, 790, and 730 cm^{-1} are due respectively to COO symmetric stretch, C–F asymmetric stretch, C–C stretch, CF_3 symmetric stretch, and CCO_2 in-plane bend. The remaining absorption band at 960 cm^{-1} represents the stretching frequency of the two Cr–O groups. In CrO_3, this band is found at 960 cm^{-1}.[3] This is the general region assigned for Cr–O stretching in CrO_2F_2 and CrO_2Cl_2.[4,5]

The ^{19}F nmr spectrum of $CrO_2(CF_3COO)_2$ in excess $(CF_3CO)_2O$ has a single peak in the region for fluorine bound to carbon at a chemical shift of 76 ppm from fluorine in CCl_3F (internal standard). With CCl_4 as the solvent, the ^{19}F spectrum of $CrO_2(CF_3COO)_2$ gave a single peak at 75 ppm from CCl_3F (internal standard). The CF_3 resonance in $CrO_2(CF_3COO)_2$ appears to be very close to that found in $(CF_3CO)_2O$ or CF_3COOH.[6]

The ultraviolet and visible spectra of the chromyl compounds synthesized in this work contain two major absorption peaks which lie between the absorption for CrO_2F_2 and CrO_2Cl_2.

The ultraviolet and visible spectrum of $CrO_2(CF_3COO)_2$ in CCl_4 has strong absorption peaks at 410 and at 286 mμ. This spectrum is very similar to that reported for $CrO_2(CH_3COO)_2$[7] where the two peaks are at 400 and 283 mμ in CCl_4. It is of interest that chromyl fluoride also has these two peaks at 383 and 278 mμ in CCl_4,[8] and CrO_2Cl_2 has two major peaks at 415 and 298 mμ with a shoulder at 280 mμ in CCl_4.[8,9]

$CrO_2(ClCF_2COO)_2$, prepared by the reaction

$$CrO_3 + (ClCF_2CO)_2O \xrightarrow{25^\circ} CrO_2(ClCF_2COO)_2 \qquad (3)$$

has a visible and ultraviolet spectrum with (two major peaks at 400 and 281 mμ in CCl_4. It is a brown solid which is less stable toward decomposition than $CrO_2(CF_3COO)_2$ but has a similar infrared spectrum (see Table I) and a similar X-ray powder pattern (see Table II).

TABLE II

X-RAY POWDER SPECTRA

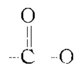
$CrO_2(CF_3COO)_2$		$CrO_2(ClCF_2COO)_2$		
11.27 s	3.38 s		3.58 m	
7.30 m	3.03 w	11.59 s	3.49 vw	2.26 vw
6.72 w	2.49 w	7.61 m	3.42 vw	2.19 w
5.64 m	2.34 w	6.79 m	3.10 w	2.09 vw
4.92 s	2.27 vw	5.88 s	2.87 vw	2.05 vw
4.24 m	2.08 w	4.96 s	2.73 vw	1.94 vw
3.88 vs	1.91 w	4.29 m	2.60 w	1.86 vw
3.60 m	1.81 w	3.98 vs	2.45 w	1.66 vw
		3.67m		

$CrO_2(CF_3CF_2CF_2COO)_2$, a brown solid soluble in $(C_5F_7CO)_2O$ and CCl_4 was prepared by the reaction

$$CrO_3 + (C_3F_7CO)_2O \xrightarrow{25^\circ} CrO_2(C_3F_7COO)_2 \qquad (4)$$

It is unstable and in the dark at room temperature decomposes. The ultraviolet and visible spectrum in CCl_4 has two peaks—278 and ~380 mμ. Further characterization of this compound was not attempted due to its instability. These new chromyl compounds appear to be light sensitive but do not explode with handling or heating even above room temperature.

$CrO_2(CF_3COO)_2$, $CrO_2(ClCF_2COO)_2$, and $CrO_2(C_3F_7COO)_2$ were reduced with excess anhydride and heat in order to prepare the corresponding chromium(III) fluoroacetates. With $(CF_3CO)_2O$, a green, stable amorphous solid, $Cr(CF_3COO)_3$, is formed which is readily soluble in acetone and insoluble in benzene and which will only slowly dissolve in water. Its infrared spectrum agrees quite well to that previously reported[3] except for the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asymmetric stretch which was at 1620 cm^{-1}. The absorption in this region is broad (1670–1620 cm^{-1}) and

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(2) M. J. Bailie, D. H. Brown, K. C. Moss, and D. W. A. Sharp, *J. Chem. Soc., A*, 3110 (1968).

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(6) Perfluoroacetic anhydride gives a ^{19}F chemical shift of 76 ppm from CCl_3F (internal standard). In CF_3COOH the CF_3 resonance is 76.55 ppm from CCl_3F. See J. J. Burke and T. R. Krugh, "A Table of ^{19}F Chemical Shifts of a Variety of Compounds," Mellon Institute, Pittsburgh, Pa.

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(8) W. V. Rochat and G. L. Gard, unpublished work done in this laboratory.

(9) L. Helmholz, H. Brennan, and M. Wolfsberg, *J. Chem. Phys.*, **23**, 853 (1955).

could be related to the amorphous nature of the product.

With $(ClCF_2CO)_2O$ and $(C_3F_7CO)_2O$ the reduced products were mixtures which could possibly contain the chromium(III) fluoroacetate. They were green amorphous solids with no oxidizing power toward acidic KI. Further characterizations of these mixtures were not attempted.

Experimental Section

1. **Chemicals and Equipment.**—The chromium trioxide used was reagent grade. It was dried at 120° *in vacuo* for 4 hr. The anhydrides were dried over P_4O_{10} and distilled prior to use. An infrared spectrum confirmed their purity. The infrared spectra were recorded on a Perkin-Elmer 137 infrared spectrophotometer. The fluorine spectra were obtained with a Varian Model HA-100 analytical nmr spectrometer operating at 94.1 mcps. For the spectrum of $CrO_2(CF_3COO)_2$ with $(CF_3CO)_2O$ in excess and with CCl_3F as an internal standard, the solution composition (by weight) was 23.6% $CrO_2(CF_3COO)_2$, 57.1% $(CF_3CO)_2O$, and 19.3% CCl_3F. For the spectrum of $(CF_3CO)_2O$, with CCl_3F as an internal standard, the solution composition (by weight) was 34.6% CCl_3F and 65.4% $(CF_3CO)_2O$.

X-Ray powder spectra were obtained using an XRD-5 General Electric camera. Nickel-filtered copper radiation (Cu Kα radiation) was used. The procedure was standardized using known compounds (CrO_3, Cr_2O_3, $CrF_3 \cdot 3H_2O$) in which the calculated d values agreed with the published ASTM values.

The ultraviolet spectra were recorded using a Cary Model 14 recording ultraviolet spectrophotometer. The samples were dissolved in gas chromatographic spectrophotometric quality CCl_4 (Mallinckrodt). Path length of cells was 1.00 cm.

2. **Chemical Analyses.**—The chromium content was determined iodometrically, after hydrolysis, by quantitatively reducing chromic acid to trivalent chromium. The acidity was determined by titration with a standard base solution using phenophthalein indicator.

3. **Preparation of $CrO_2(CF_3COO)_2$.**—The fused silica reaction vessel (~100 ml) equipped with a Kontes Teflon stopcock and Teflon stirring bar was evacuated and dried. Chromium trioxide (7.83×10^{-3} mol), previously dried, was added in a drybox and redried *in vacuo*. A slight excess of trifluoroacetic anhydride, 9.54×10^{-3} mol, was vacuum transferred. The vessel was then removed from the liquid nitrogen bath and warmed to room temperature. At room temperature, in the dark, reaction was completed in 5–7 hr. The volatile materials [only $(CF_3CO)_2O$ and traces of COF_2 and CF_3COF] were removed under reduced pressure and the remaining solid was maintained at reduced pressure until it achieved a constant weight. The product [7.40×10^{-3} mol if $CrO_2(CF_3COO)_2$] is a yellow-brown solid (yield *ca.* 95% based on CrO_3); mp 47.5–49.5°; uv (CCl_4) peaks at 286 and 410 mμ. *Anal.* Calcd: Cr, 16.77. Found: Cr, 16.30, 16.25, *via* iodometry; Cr, 16.35, 16.71, *via* acidity (based on eq 2).

4. **Preparation of $Cr(CF_3COO)_3$ from $CrO_2(CF_3COO)_2$.**—To 4.05×10^{-3} mol of CrO_3 in a fused-silica vessel (~100 ml), a tenfold excess of $(CF_3CO)_2O$ was added. The reactants were heated at ~40° for 5 days. The volatile materials (CO_2, CF_3COF, and COF_2) were removed leaving a green solid whose weight corresponded to 3.96×10^{-3} mol of $Cr(CF_3COO)_3$. *Anal.*[10] Calcd for $Cr(CF_3COO)_3$: C, 18.5; F, 43.7; Cr, 13.3. Found: C, 16.5; F, 40.1; Cr, 16. Some chromium(IV) oxyfluoroacetate was present.

5. **Preparation and Reaction of $CrO_2(ClCF_2COO)_2$.**—The reaction of CrO_3 with $(ClCF_2CO)_2O$ was carried out in essentially the same way as it was with $CrO_2(CF_3COO)_2$. To 1.19×10^{-2} mol of CrO_3, 1.19×10^{-2} mol of $(ClCF_2COO)_2O$ was added. After 7 hr the volatile materials (COF_2, CF_3COF, CrO_2Cl_2) were pumped away until a constant weight loss was achieved. The product [1.05×10^{-2} mol of $CrO_2(ClCF_2COO)_2$] is a yellow-brown solid (yield *ca.* 88% based on CrO_3); mp 64–66°; uv (CCl_4) peaks at 281 and 400 mμ. *Anal.* Calcd: Cr, 15.2. Found: Cr, 14.4, *via* iodometry; Cr, 14.6, *via* acidity.

With excess anhydride (2.7×10^{-2} mol) and CrO_3 (4.9×10^{-3} mol) at 21° for 5 hr and then at 60–70° for 24 hr, a dark green solid was formed (1.442 g, compared to the calculated value for $Cr(ClCF_2COO)_3$ of 1.688 g) along with CrO_2Cl_2, CO_2, and COF_2. The product is not entirely $Cr(ClCF_2COO)_3$; the weight is too low. An infrared spectrum gave the following absorption peaks in cm^{-1}: 1610 (s, b), 1440 (m), 1150 (vs, b) 975 (s), 827 (m), 730 (m). This spectrum is closely analogous to that of $Cr(CF_3COO)_3$. The green solid is slightly soluble in water and soluble in acetone. It is an amorphous solid with no oxidizing power toward acidic KI.

6. **Preparation and Reaction of $CrO_2(CF_3CF_2CF_2COO)_2$.**—To 8.38×10^{-3} mol of CrO_3, 11.9×10^{-3} mol of $(C_3F_7CO)_2O$ was added in a fused-silica reaction vessel. After 4 hr at room temperature the volatile materials (C_3F_7COF, C_2F_5COF, COF_2, and CO_2) were pumped away at 0° leaving a brown solid [8.16×10^{-3} mol of $CrO_2(C_3F_7COO)_2$] (yield *ca.* 97% based on CrO_3); uv (CCl_4) peaks at ~380 and 278 mμ. The solid was unstable and could not be handled further at room temperature without decomposition. Analysis of hydrolyzed samples gave satisfactory but tentative results. *Anal.* Calcd: Cr, 10.2. Found: Cr, 10.3, *via* iodometry; Cr, 10.5, *via* acidity. With excess $(C_3F_7CO)_2O$ at 90° for 17 hr a green amorphous product [whose weight corresponded to the empirical composition $Cr(C_{3.2}F_{5.4}O_2)_3$] was formed. The structure of this solid is unknown.

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Cyanatopentaamminecobalt(III). Preparation from Urea and Kinetics of Acid-Catalyzed Decomposition

BY R. J. BALAHURA AND R. B. JORDAN

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Linhard and Flygare[1] found that the reaction of NCO^- with $(NH_3)_5CoOH_2^{3+}$ gave the carbamato complex $(NH_3)_5CoO_2CNH_2^{2+}$ as product. In a more recent study Sargeson and Taube[2] have confirmed this result and have shown that the reaction occurs without cleavage of the Co–O bond in $(NH_3)_5CoOH_2^{3+}$. Ablov, Popova, and Samus[3] have reported the dimethylglyoxime (DMG)–cobalt(III) complexes $(DMG)_2Co(NCO)(OH_2)$ and $(DMG)_2Co(NCO)_2^-$. These were observed to hydrolyze in aqueous acid to give $(DMG)_2Co(NH_3)(OH_2)^+$ and $(DMG)_2Co(NH_3)_2^+$.

This note reports the preparation of N-bonded

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[1] M. Linhard and H. Flygare, *Z. Anorg. Allgem. Chem.*, **251**, 25 (1943).

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[3] A. V. Ablov, A. A. Popova, and N. M. Samus, *Zh. Neorgan. Khim.*, **14**, 994 (1969); *Chem. Abstr.*, **7**, 18421 (1969).